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A Valuable Observation on Thickeners for Valuable Utilisation in the Printing of Different Textile Fabrics



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Abstract

Thickeners are high molecular weight polymers used to impart viscosity and plasticity to the printing paste. Thickeners play an essential role in any printing process. Their main purpose is to hold dyestuffs, chemicals, and other printing auxiliaries to the fabrics during the method of printing. The goodness of the resulting print depends on the chemical and physical properties of the thickeners applied. The depth, the brightness of the colours, and particularly the sharpness and smoothness of the print are influenced or even determined by them.

Keywords: Thickeners, gum, Rheological properties, textile material.

1. Fabrics

1.1. Cotton

Cotton is very popular in textile industry since the beginning of industrial revolution. Cotton is the purest form of cellulose found in nature. It is the seed hair of plants of the genus Gossypium. [1]

Cotton is very popular in textile industry since the beginning of industrial revolution. Cotton is the purest form of cellulose found in nature. It is the seed hair of plants of the genus Gossypium.[1] Raw cotton fiber contains on dry basis 90-95% cellulose, 1-2% protein material 0.3-1% waxes, 0.7-1.2% pectin's and small amounts of organic acids and ash-producing inorganic substances. Variations in these values will arise from differences in soil, climate, weather, variety of cotton and other related factors that influence plant growth and development. Purification of raw fiber by any of several chemical processes results in a material that is at least 99% cellulose. [2-5]

Cellulose means a linear polysaccharide built up of a hydro glucose unit which are connected with **Table 1. [9, 10]**

1.2. **Wool**

The wool fiber is composed of a particular protein known as "keratin". This keratin consists of long each other by β - $(1\rightarrow 4)$ glycosidic linkages and possess an orderly structure (**Figure 13**) the cellulose chain therefore consists of several hundred glucose units. [6]

The degree of polymerization (DP) depends on the origin and state of cellulose fiber. Natural cellulose fibers have an average DP from 2000 to 3000, whereby the generated fibers show a DP between 250 to 750.one in position 6 is a primary hydroxyl group the reactivity of primary alcoholic groups seems to be related to isomerization.[7] Chemical reaction with cellulose molecule will take place in the amorphous regions and on the crystallite surfaces, but not within the crystalline regions. [8]

1.1.1. Physical and Chemical Properties

Cotton is characterized by abundance, fine crosssection, low cost, high strength and durability, ability to absorb moisture, coloration ability, etc. However, cotton has certain drawbacks such as little resistance to heat, weathering effects, fungi, bacteria and low wrinkle resistance polypeptide polypeptide chains. The chains have eighteen different amino acids. The most of these amino acids have the general formula H₂N.CHR.COOH In this formula R is a side chain of varying character. [11]

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Table 1: General Properties of cotton

Macroscopic feature		
Length	0.3–5.5 cm	
Cross-section	Kidney-shaped	
Colour	Generally white, may be cream-coloured or brown	
Light-reflection	Low luster, dull appearance	
Physical properties		
Tenacity (cN/dtex)	2.6 to 4.4 (dry), 3.2 to 5.3 (wet)	
Stretch and elasticity	3–7% elongation at break. At 2% elongation, recovery is 70%	
Resiliency	Low	
Abrasion resistance	Fair to good	
Dimensional stability	Fabrics may shrink during laundering	
Moisture regain	8.5%	
Specific gravity	1.54 g/cm ³	
Chemical properties		
Effects of bleaches	Highly resistant to all bleaches	
Acids and alkalies	Highly resistant to alkalies. Strong acids and hot dilute acids will cause disintegration	
Organic solvents	Resistant to most organic solvents	
Sunlight and heat	Withstands high temperatures well. Prolonged exposure to light will cause yellowing due to oxidation	
Resistance to stains	Poor resistance to water-born stains	
Dyeability	Good affinity for dyes. Dyed with direct, vat, and basic dyes Vat dyeing produces excellent wash and light fastness	

Polypeptides are composed by multiple concentrations of □-amino acids by their amino and carboxyl groups to compose secondary amide (peptide) bonds (¬CONH¬). The common structure of all proteins or polypeptides may be main chain (¬NH-CH-CO-NH-CH-CO-ETC¬) of the long-chain molecules and other have is in side chains (R1, R2, R3, ETC). These side groups vary in size and chemical nature, some may be hydrophilic, some hydrophobic, some basic and others are acidic [12].

The different types of covalent cross-link and noncovalent interaction hold the individual peptide chains in wool together (Figure 1).

In addition to their occurrence between separate polypeptide chains (interchain), these bonds can also occur between different parts of the same chain (intrachain) (Figure 2). With respect to the properties and performance of wool, inter chain bonds are the more important of the two. [13]

1.2.1. Physical and Chemical Properties

Wool fiber is soft, durable, safe in nature, and has high wear and tear resistance. It has good characteristics such as elasticity, resilience, poor resistance to alkalis with good resistance to acids, and good insulation property. [14] (**Table 2**)

1.3. polyester fiber

Polyester has rapidly grown to become the most

widely used man-made fiber in the world fiber in the world, since its commercial introduction in 1953. [15] A polyester fiber is manufactured fiber in which the fiber-forming substance is any long-chain synthetic polymer composed of at least 85% by weight of ester of a dihydric alcohol and terephthalic acid the most widely used polyester fiber is made from the linear polymer polyethylene terephthalate (PET), and therefore polyester has become synonymous with PET (see **Figure 4**)

Polyester is made by reacting an acid with an alcohol. Terephthalic acid or dimethyl terephthalate and ethylene glycol polymerize by condensation reaction to form the polyester polymer. [17]

The polymer is melted and extracted through a spinneret, forming filaments that are solidified by cooling in a current of air. Heating and stretching the filaments to several times their original length, forming an oriented semi-crystalline structure and imparting the desired physical properties, draw the spun fiber. The fiber structure has strong influence on the applicability of the fibers and depends heavily on the process parameters. [18]

Figure 1: Covalent cross-link and non-covalent interaction in wool

Figure 2: Example of an intrachain crosslink in wool

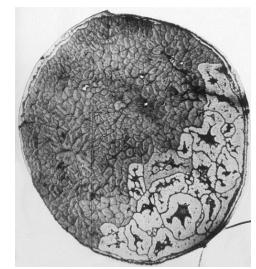


Figure 3: The cross-sectional View of wool Fibers

$$- \begin{bmatrix} O \\ C \end{bmatrix} - C \begin{bmatrix} O \\ O \end{bmatrix} - CH_2 - CH_2 - O \end{bmatrix}$$

Figure 4: Chemical structure of (PET)

1.3.1. Physical and Chemical Properties

Polyester fibers have very high dry and wet tensile strength, and high initial modules of elasticity. Polyester also characterized by low moisture regains. This is due to its compact, well ordered physical structure. Garments made from polyester fiber are also quick-dried, don't swell in water and have a high resistance to deformation. (

 Table 3: General properties of polyester [22]

Properties of polyester

Macroscopic feature

Polyester can be made in any length or diameter required by the fiber producer and the yarn and fabric manufacturer.	
Oval to circular with variation in diameter medulla is concentric and variable in size (see Error! Reference source not found.).	
The fiber is partially transparent and white or slightly off white	
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2.5 to 9.5 (dry), there is no loss of strength when polyester is wet	
The amount of elongation possible for polyester varies inversely with	
tenacity. Stronger fibers have a lower degree of elongation.	
Elastic recovery of high-tenacity fibers is good regular tenacity polyester	
exhibits some variation in elastic recovery.	
1.38 or 1.22 g/cm ³ depending on the type of polyester fibers.	
The melting point of polyester is close to that of polyamide, ranging from 250 to 300°C.	
the moisture regain of polyester is	
Low, ranges between 0.2 to 0.8 percent	
•	
Polyester has to excellent to good resistance to mineral and organic acids.	
Highly concentration of mineral acid at high temperatures will result in	
degradation.	
Polyester has good resistance to weak alkalis and fair resistance to strong	
alkalis at room temperature. This resistance is reduced with increased	
temperature.	
Polyester fibers are generally resistant to organic solvents.	
Polyesters can be dyed with dispersing, azoic, and developed dyes at high	
temperatures.	

2. Thickener

2.2. The essential properties of the Thickener

As printing paste should contain a thickener to improve their properties, therefore thickeners should have characteristic properties such as: [23]

- 1. Soluble in water and easily prepared with suitable rheological properties.
- Suitable for mixing with other thickeners and compatible with other ingredient in printing paste.
- 3. It should be cheap and easily available
- 4. Stability to storage, pressure and temperature during printing
- 5. It should not retain the colour or keep away the colour from the fabric
- 6. The thickener should have poor affinity for dyes and other chemicals

Table 4)

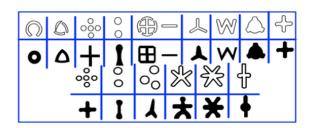
- a) Natural thickeners
- b) Modified natural thickeners
- c) Synthetic thickeners

) [19-21]

- The thickener should produce a solid film that does not stick and that has good mechanical and elastic properties and good adhesion.
- 8. Chemical stability in the drying process.
- 9. The thickener should produce good color intensity, brilliance, and uniformity.
- 10. It should not retain the colour or keep away the colour from the fabric
- 11. Easily to be removed and after the washing process, the fabric should be soft and feel must not be adversely affected. [24]

2.3. Classification of Thickeners

Thickeners can be divided into three categories depending on their origin (



A VALUABLE OBSERVATION ON THICKENERS FOR VALUABLE UTILISATION.....

Figure 5: The cross-sectional View of polyester Fibers

Table 2: General properties of wool [16]

Macroscopic feature		
Length	Wool fiber length range roughly from 5 to 50cm.	
Cross-section	Oval to circular with variation in diameter medulla is concentric and variable in size (see Figure 3).	
Colour	White, off-white, yellow, brown and black	
Physical properties		
Tenacity (cN/dtex)	Wool fibers possess low to moderate strength with tenacities of 1-2 g/d (9-18 g/tex) dry and 0.8-1.8 g/d (7-16 g/tex) wet.	
Elongation and elasticity	Elongations at break vary from 25% to 40% dry and 25% to 60% wet. Wool shows 99% recovery at 2% extension, and even at 20% extension, a recovery as high as 65% is observed. Wool fibers have excellent resiliency and recover readily from deformation except under high humidity.	
The stiffness of wool	The stiffness of wool varies according to the source and the diameter of the individual fibers. The moisture regain of wool is very high and varies between 13% and 18% under standard conditions.	
Specific gravity	Wool fibers have specific gravities of 1.28-1.32.	
Heat effect	Wool is little affected by heat up to I50aC and is a good heat insulator due to its low heat conductivity and bulkiness, which permits air entrapment in wool textile structures.	
moisture regain	The moisture regain of wool is very high and varies between 13% and 18% under standard conditions.	
Chemical properties		
Effect of acids	Wool is resistant to attack by acids	
Effect of alkalies	Wool is extremely vulnerable to attack by weak bases even at low dilutions.	
Effect of solvents	Wool is insoluble in all solvents except those capable of breaking the disulfide cross-links, but it does tend to swell in polar solvents.	
Effects of oxidizing bleaches	Wool is irreversibly damaged and colored by dilute oxidizing bleaches such as hypochlorite.	
Effects of Reducing agents	Reducing agents cause reductive scission of disulfide bonds within the wool, eventually causing the wool to dissolve. Under controlled conditions, reducing agents can be used to partially reduce the wool and flat set or set permanent pleats in the wool.	

Table 3: General properties of polyester [22]

	Table 5. General properties of polyester [22]	
Properties of polyester		
Macroscopic feature		
Length	Polyester can be made in any length or diameter required by the fiber producer and the yarn and fabric manufacturer.	
Cross-section	Oval to circular with variation in diameter medulla is concentric and variable in size (see Error! Reference source not found.).	
Colour	The fiber is partially transparent and white or slightly off white	
Physical properties		
Tenacity (cN/dtex)	2.5 to 9.5 (dry), there is no loss of strength when polyester is wet	
Elongation and elasticity	The amount of elongation possible for polyester varies inversely with tenacity. Stronger fibers have a lower degree of elongation. Elastic recovery of high-tenacity fibers is good regular tenacity polyester exhibits some variation in elastic recovery.	
Specific gravity	1.38 or 1.22 g/cm ³ depending on the type of polyester fibers.	

Heat effect	The melting point of polyester is close to that of polyamide, ranging from 250 to 300°C.	
Moisture regain	the moisture regain of polyester is	
Chemical properties	Low, ranges between 0.2 to 0.8 percent	
Effect of acids	Polyester has to excellent to good resistance to mineral and organic acids. Highly concentration of mineral acid at high temperatures will result in degradation.	
Effect of alkalies	Polyester has good resistance to weak alkalis and fair resistance to strong alkalis at room temperature. This resistance is reduced with increased temperature.	
Effect of solvents	Polyester fibers are generally resistant to organic solvents.	
Dyeability	Polyesters can be dyed with dispersing, azoic, and developed dyes at high temperatures.	

3. Thickener

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 - Table 4)
 - d) Natural thickeners
 - Modified natural thickeners

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3.3. Classification of Thickeners

Thickeners can be divided into three categories depending their origin

Synthetic thickeners

Table 4: Classification of Thickeners

Tuble 1. Classification of Thickeners		
Thickeners		
i.Natural	ii.Modified natural	ii.Synthetic
A. Plant exudates	A. Starch derivatives	A. Vinyl polymers
Karaya gum	1. British gum	1. Polyvinyl Alcohol (PVA)
2. Tragacanth gum	2. Dextrin	2. Polyvinylpyrrolidone (PVP)
3. Arabic gum	3. Carboxymethyl Starch (CMS)	
		B. Acrylic polymers
B. Plant Seeds	B. Cellulose derivatives	1. Polyacrylamide
1. Locust bean gum	1. Carboxymethyl Cellulose (CMC)	2. Polyacrylic acid
2. Tamarind seed gum	2. Methyl cellulose	
3. Guar gum	3. Hydroxyethyl- cellulose	
C. Seaweed extracts		
1. Alginates		
D. Starch		

3.3.1. Natural Thickeners

Natural thickeners can be defined as products obtained from natural sources such as plants, seeds, seaweeds and microorganisms. The natural thickening agents used in printing process are mostly polysaccharides with plenty of hydroxyl groups derived from plant exudates, sea weeds, seeds and roots. Some of them are suitable for printing with

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certain class of dyes, but many times they have to be

modified to suit the requirements of printing. [25-31]

Polysaccharides are natural biopolymers isolated from renewable sources such as animals, plants, fungi, bacteria and seaweeds. [32] the main characteristic of polysaccharide is their ability to modify the properties of aqueous mediums because of their capacity to thicken, chelate, emulsify, stabilize, flocculate, swell and suspend, or to form gels, films and membranes. [33]

3.3.1.1. Plant exudates

Most plant families include types that exude gums in some extent. Exudate gums are among the oldest natural gums being known .The three major exudate gums Karaya gum, Tragacanth gum and Arabic gum have a unique range of functionalities. [34-39]

Gums are biopolymers which mainly consist of carbohydrates sometimes with small amounts of proteins and minerals. [40]

a) Karaya gum

Karaya gum an acetylated polysaccharide exudate of Sterculia urens trees. It is a branched anionic polysaccharide used as a thickener. Gum karaya is a highly charged (ionic) hydrocolloid. It contains about 37% galacturonic acid. It is partly acetylated (about 8% acetyl groups by weight). [41]

To be used as a thickener in printing process, Karaya gum is modified for increasing its solubility because its Particles do not dissolve in water but swell extensively. This is done by cooking a water suspension of gum karaya under pressure or oxidizing it with some oxidizing agents such as persulfale or persilicate.

Modified gum karaya is suitable for the direct printing of colors on cotton fabrics. It produces smooth prints, and the printing film can be easily to be removed from the fabric after fixation of the dye. [42]

b) <u>Tragacanth gum</u>

Tragacanth gum is an exudation from the stems and branches of Asiatic species of Astragalus. It looks dull or milky white to brown depending on its quality. It is so complex, extremely branched, hydrophilic, and heterogeneous anionic polysaccharide. It is naturally found as a slightly acidic calcium, magnesium, and potassium salt. [43]

In textile printing, Tragacanth gum is now less popular than other thickening agents which can be processed more easily. It has 6-7% solids content. It can be used successfully for printing cotton with pigment. It is combined with British gum for wool printing. It is also used in artificial silk staple printing and in direct, acid, basic, and azoic color printing on cellulose. [44]

c) Arabic gum

Arabic gum is a complex, branched, natural polysaccharide, extracted from the stems and

branches of Acacia trees manly Acacia Senegal and Acacia Seyal. It is a highly neutral or slightly acidic in nature, and it contains calcium, magnesium, and potassium salts. [45]

Arabic gum as a Thickener is prepared with 50% solid content. Their viscosity is very good. They have high ability of adhesion and pigment binding capacity. Thickeners made from gum Arabic used in block printing on wool and silk. Arabic gum is used in acid, direct, basic, and azoic color printing on cellulose fabrics and disperses dyes on polyester fabrics. [44]

3.3.1.2. Plant Seeds

Plant seeds produce seed galactomannans commonly known as seed gums located mainly in the endosperm particularly in Leguminosae. Seed galactomannans are neutral, water-soluble, and heterogeneous polysaccharides. In general, they are consisted of β -(1 \rightarrow 4)- linked D- mannopyranose main chains to which are attached α -(1 \rightarrow 6)- linked D- galactopyranosyl units (**Figure 6**). [46, 47]

Figure 6: General Molecular structure of galactomannan

a) Locust bean gum

Locust bean gum (carob gum) is a white to yellowish white powder obtained by crushing the endosperm of the seeds from the fruit pod of the carob tree. It is mainly comprised of the high molecular weight polysaccharides composed of galactomannans consisting of a linear chain of $(1\rightarrow4)$ -linked β -D mannopyranosyl units with $(1\rightarrow6)$ -linked α -Dgalactopyranosyl residues as side chains (**Figure 7**). Locust bean gum swells in cold water, but it does not completely dissolve. It dissolves in high temperature and its viscosity increases after cooling. [48]

Figure 7: Structure of locust bean gum

Locust bean gum Used as a Thickener can be used

in alkali-resistant printing pastes and is suitable for preparing printing pastes with all kinds of dyes. It is removed easily after washing process and the printed fabric has soft tough. [44, 49]

b) Tamarind seed gum

Tamarind seed gum is seed polysaccharide obtained from the endosperm of the tamarind tree seeds. It is a high molecular weight, nonionic carbohydrate polymer consisting of a main chain or β (1-4)-D- glucopyranosly units with a side chain consisting of a single xylopyranosyl unit attached to every second, third and fourth D-glucopyranosly unit through and an α -D-(1-6) linkage (**Figure 8**). [50]

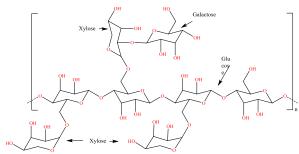


Figure 8: Structure of Tamarind seed gum

Tamarind gum polysaccharide is a monomer of glucose, galactose and xylose in molar ratio of 3:1:2. It is easily hydrating in cold water but required viscosity is achieved by boiling. Its rheological properties are non-Newtonian thixotropic solutions like most natural polysaccharides. [51]

c) Guar gum

Guar gum is extracted from the seed of the legume Cyamopsis tetragonolobus. It is a non-ionic, hydrophilic polysaccharide composed of linear chain of D-mannopyranose units joined by β -(1 \rightarrow 4) linkage with a side-branching unit of a single D-galactopyranosyl unit joined to every other mannose unit by α -(1 \rightarrow 6) linkages (**Figure 9**). [52]

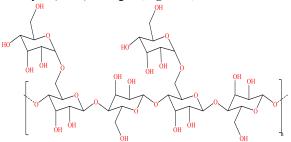


Figure 9: Chemical structure of guar gum

Guar gum contains higher galactose content than Locust bean gum. It is insoluble in most organic solvents but it swells and disperses in cold and hot water. Even at low concentrations, guar gum produces highly viscous and it is influenced by temperature, pH, presence of salts and other solids. Gradually, by increasing the concentration of Guar Gum in water the viscosity of Guar Gum solution increases. Its rheological properties are non-

Newtonian pseudoplastic solutions related to its high molecular weight and the existence of hydrogen bonds. [53]

3.3.1.3. Seaweed extracts

Seaweeds contain high molecular weight polysaccharides known as phycocolloids. The principal extracts that could be obtained from seaweeds are agars, alginates and carrageenan (**Figure 10**). Phycocolloids can be dissolved in water to thicken solutions and form gels. Among the Phycocolloids, alginate is widely used in textile industry as thickener, stabilizer, and gel and film former.[54]

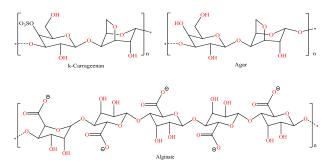


Figure 10: Molecular structures of agar, κ-carrageenan and alginate polysaccharides

d) Alginates

Alginates are derived from brown seaweeds. They are salts of alginic acid which consist of two monomers, D-mannuronic acid (M) and L-guluronic acid (G). [55]

Alginates consist of 1, 4- β -D-mannuronic acid (M) and 1, 4 α -L-guluronic acid (G) monomers, with a homogeneous (poly-G, poly-M) or heterogeneous (MG) block composition (**Figure 11**). [**56**]

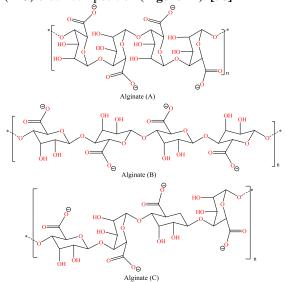


Figure 11: Chemical structures of the various blocks in the alginates

Sodium alginate is produced by treating alginate with aqueous alkali solutions, usually with NaOH. It is widely used in printing cellulose fabrics with

reactive dyes because there isn't any interaction between sodium alginate and the reactive dyes .It hasn't primary hydroxyl groups so that there isn't any competition between with cotton for the dye. [57] Alginates have a unique position in reactive printing because they give brilliant and soft prints with good color intensity.[58]

e) Starch

The main stored carbohydrate in plants is starch. Starch is extracted from seeds especially corn, wheat, and rice, and from tubers or roots especially potato, sweet potato and tapioca. The different in appearance, properties and particle size distribution of the starches depend on various plant sources and species. [59] Starch is consisted of α-d-glucose repeated units attached together by α -(1, 4)glycosidic bonds and to some extent by α -(1, 6)glycosidic bonds. It is a mixture of linear and branched polysaccharides, amylose and amylopectin. [60] Amylose consists of glucose units linked by α glycosidic bonds a (1, 4), mainly forming a linear chain. Amylopectin composes of glucose units attached in α (1, 4) and α (1,6) links, fundamentally yielding a branched structure. (Figure 12) [61, 62]

Both of these ingredients starch is insoluble in water. When the starch is boiled in water, these grains swell and explode forming a smooth and homogeneous gelatin. [62] Starch as printing textile thickener is difficult to wash out and imparts a harsh feeling and a stiff handle to a printed fabric with uneven blotches. [27]

3.3.2. Modified natural thickeners

These are obtained by the modification of cellulose, starch and gums by chemical, physical and thermal means. Since they are more suitable when compared to natural thickeners, their use in textile industry is increasing.

3.3.2.1. Starch derivatives

a) British gum

British gum is formed by roasting unmodified starch. British gums are prepared by heating starch at a high temperature without added acid but in some cases some acids or alkalis are added.

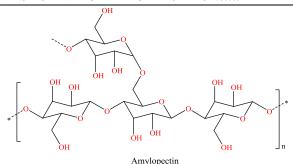


Figure 12: Structure of starch amylose (A) and amylopectin (B)

b) Dextrin

Dextrin is produced by heating dry starch in the presence of an acid with or without small amounts of moisture. There are categorized as white dextrin, yellow (or canary) dextrin.

British gum and dextrin are more water-soluble and form less viscous solutions or dispersions than its main starch. [63]

c) Carboxymethyl Starch (CMS)

Carboxymethyl Starch (CMS) is acquired by etherification of native starches. The properties of starch are significantly changed. Carboxymethylation reaction was happened between starch and chloroacetic acid (MCA) in the presence of alkali. **164.651**

CMS has been evaluated as a thickener in polyester printing with disperses dyes and it has also been used for reactive printing. This thickener gives as good a color yield as sodium alginate. CMS gives very bright and soft prints. CMS is suitable for use in alkaline or acidic printing pastes. In roller printing, a higher color yield can be obtained using CMS. In the field of textile printing, CMC is worse than CMS because it gives lower colour yield. [66, 67]

3.3.2.2. Cellulose derivatives

Cellulose is the most numerous biopolymers found in the nature, and is especially substantial polysaccharides because of its wide diversity of applications in industry, (e.g., paper, textiles etc).

Cellulose is a linear and completely solid homopolymer containing D-glucose repeating anhydroglucose units. These units are attached together by $\beta\text{-}(1{\longrightarrow}4)$ glycosidic bonds created between C-1 and C-4 of adjacent glucose unites (Figure8). **[68, 69]**

Figure 13: Chemical structure of cellulose

Cellulose derivatives were prepared and finetuned to get certain wanted properties. Cellulosic ethers with good water solubility have been intensively studied, to identify new thickening products for textile printing.

a) Carboxymethyl Cellulose (CMC)

Carboxymethyl cellulose (CMC) which is mostly used as sodium salt NaCMC is one of the most widely applied polyelectrolyte cellulose derivatives. NaCMC is an anionic substance, water-soluble and polyelectrolyte. CMC has huge applications in the food, industry, personal care/cosmetic, paper and textile. For example, it is used a thickener in textile printing industry and to prevent the redeposition of soil removed by detergents during the fabric washing process. CMC contains a hydrophobic polysaccharide backbone and many hydrophilic carboxyl groups, and hence shows amphiphilic properties **Figure 14**. [70]

CMC as a thickener in textile printing can be applied based on the high-viscosity and film-forming characteristics of sodium carboxymethyl cellulose have been proposed. It is utilized in the printing of vat dyes, and it is a good exchange for gum tragacanth. It is coagulated by metal salts and hence cannot be used for basic or chrome dyes. It is also applied in polyester printing with disperse dyes, but is not used in reactive printing because it combines with reactive dyes under printing conditions which results in poor color yield and formed an insoluble carboxymethyl cellulose which cannot easily wash off, thereby generating prints with a harsh feel. [71]

b) Methyl cellulose

Methylcellulose is one of cellulose derivatives. It can be made ready for use from the reaction of alkalicellulose with dimethyl sulfate (DMS) or methyl chloride. Several products of great commercial prominence can be advanced from methylcellulose. For instance, it may be used as thickener in the textile printing industry. MC is the simplest cellulose derivative, where methyl groups (-CH₃) replace the hydroxyls at C-2, C-3 and/or C-6 positions of anhydro-D-glucose units (**Figure 15**). [72]

Figure 14: Chemical structure of Na salt of carboxymethyl cellulose

Figure 15: Chemical structure of repeating unit of methylcellulose

c) Hydroxyethyl- cellulose

Hydroxyethyl cellulose is one of cellulose derivatives. It can be made ready for use from the reaction of alkali-cellulose with dimethyl sulfate (DMS) or methyl chloride. Several products of great commercial prominence can be advanced from hydroxyethyl cellulose. For instance, it may be used as thickener in the textile printing industry. hydroxyethyl cellulose is one of the simplest cellulose derivative, where hydroxyethyl groups (– CH₂CH₂OH) replace the hydroxyls at C-2, C-3 and/or C-6 positions of anhydro-D-glucose units (**Figure 15**). [72]

Figure 16: Chemical structure of repeating unit of hydroxyethyl cellulose

3.3.3. Synthetic Thickeners

The use of polyacrylic acid in synthetic thickeners because of the discovery of acrylic polymers. The aqueous-based synthetic thickeners are high molecular weight polymers including an acidic monomer as fundamental component (acrylic acid, methacrylic acid, maleic acid). These monomers ionize by adding a base to improve the desirable viscosity. [73, 74]

3.3.3.1. Vinyl polymers

a) Polyvinyl alcohol (PVA)

Polyvinyl alcohol (PVA), which is basically made from polyvinyl acetate through hydrolysis, is readily degradable by biological organisms and in water is a solubilized crystalline structure polymer. Polyvinyl alcohol polymers are uncommon crystalline water-soluble polymers and contain a hydrophilic group and a hydrophobic group. There by showing a superior surface activity. [75] PVA as thickener, PVA has extremely harmonized enough water solubility, thickening characteristic and covering film strength, and having excellent storage stabilization in terms of the viscosity in an aqueous solution. [76] Chemical structure of polyvinyl alcohol was illustrated in Figure 17.

b) Polyvinyl pyrrolidone (PVP)

Polyvinylpyrrolidone (PVP) is a water-soluble, non-toxic and non-ionic amorphous polymer with high solubility in polar solvents. It has been widely used in textile field. PVP is also known as polyvidone or povidone. It is a synthetic polymer including linear

1-vinyl-2-pyrrolidone groups. This polymer has a carbon chain consisting of an amide group in the side substituent and owning a poly-N-vinyl amide structure. [77] Chemical structure polyvinylpyrrolidone was illustrated in Figure 17.

Figure 17: Chemical structure of polyvinyl alcohol and polyvinylpyrrolidone

3.3.3.2. Acrylic polymers

a) Polyacrylamide

Polyacrylamides are high molecular weight watersoluble made from acrylamide or the combination of acrylamide and acrylic acid. Polyacrylamide has many applications because of its water solubility and versatile chemical and physical properties. It is used as thickener in printing textiles. [78]

Polyacrylamides are generated by the polymerization of acrylamide (C₃H₅NO), component acquired by the hydration of acrylonitrile. The dissolved monomers (single-unit molecules) are motivated to polymerize through the action of freeradical initiators. In the consequent polymer, the acrylamide recurring unit has the following structure: [79, 80] Chemical structure of Polyacrylamide was illustrated in Figure 18.

b) Polyacrylic acid

Acrylic polymers are generally known as acrylics. The monomers are esters of acrylic and methacrylic acid. Acrylic acid polymers and copolymers cover a very huge range of applications, such as

- 1. Hydrosoluble agents for dispersing agents
- 2. Thickeners
- 3. Flocculating and super-absorbent agents
- Detergent auxiliaries
- 5. Organic synthesis
- Copolymer emulsion for paints 6.
- Cosmetics, papers, varnishes and inks

In dispersions for leather, textiles, non-woven fabrics, glues and adhesives, cleaning and waxing products. Besides, plastics, synthetic resins, synthetic rubbers and lattices. [81]

Polyacrylic acid as thickener, it has been used successfully in many aqueous systems for years. this thickener has been successfully used in the printing of cotton fabrics with vat and reactive dyes and printing polyester with disperse dye stuff. It is used for pigment printing. [82] Chemical structure of polyacrylic acid was illustrated in Figure 18.

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Figure 18: Chemical structure of polyacrylamide and polyacrylic acid

4. Rheology of printing paste

Rheology is defined as the study of the flow and deformation of matter which describes the interrelation between forces, Deformation, and time. The term rheology originates from the Greek words 'rheo' translating as 'flow' and 'logia' meaning 'the study of', although as from the definition above, rheology is as much about the deformation of solidlike materials as it is about the flow of liquid-like materials and in particular deals with the behavior of complex viscoelastic materials that show properties of both solids and liquids in response to force, deformation and time. Rheology deals more specifically with the relationship between shear stress, shear rate and time. [83]

4.2. Viscosity

There are two basic types of flow, these being shear flow and extensional flow. In shear flow, fluid components shear past one another while in extensional flow fluid components flowing away or towards one other. The most common flow behavior and one that is most easily measured on a rotational rheometer or viscometer is shear flow and this viscosity introduction will focus on this behavior and how to measure it. [84]

4.3. Shear Flow

To understand rheology better, it is important to consider the effect of a simple shear on a deformable material to define the laminar shear flow, shear stress, and shear rate. When a material is subjected to external forces, it is deformed depending on the stress distribution all over the material. A particular type of stress field results in a laminar shear flow. For example, let us consider a liquid contained between two parallel plates at a distance of y apart. The top plate slides in the x-direction, while the bottom plate does not move. Material deformation occurs by the relative deformation (i.e. slipping) of the different layers without any transfer of material from one layer to the other. As can be seen in **Figure 19**, the velocity varies only in the y-direction and not at all in the two directions perpendicular to y. [85]

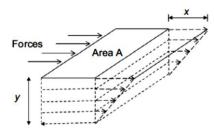


Figure 19: Schematic illustration of shear flow

4.4. Shear stress

During a laminar flow, two layers move along each other. This relative displacement results in



friction forces acting tangentially to the layers, and these are called shear forces (F). Let us consider two consecutive layers, 1 and 2, moving at parallel speeds, V1 and V2 (**Figure 20**). Assuming that layer 1 is moving faster than layer 2 (i.e.V1> V2), it is evident that layer 1 exerts on layer 2 a shear force that accelerates layer 2. Reciprocally, layer 2 exerts on layer 1 a shearing force that tends to slow down layer 1. When reported to the unit areas (S) on which they are acting, these forces result in a physical quantity of great importance in rheology, namely shear stress. Shear stress (s) is defined by the following relationship:

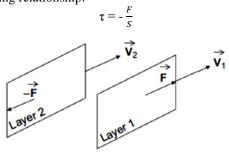


Figure 20: Relative movements between two successive layers

The shear stress τ is a force per unit area and is expressed in Pascal in the International System of Units. It is a function defined at each point of the material and varies from one layer to another. Due to symmetry, τ is usually considered constant at all points of the same layer. [86]

4.5. Shear rate

Let us consider the particular case of a laminar shear flow with a planar symmetry, as in the previous example where the material is sheared between two parallel planes, with one moving while the other is fixed to define the shear deformation.

Let us also consider particles that at time t=0 belong to cross-sections located at distances x+dx from the fixed plane (**Figure 21**). At a later time t, the particles of the cross-sections located at x and x b dx have traveled the distances u(x, t) and u(x+dx, t), respectively, where x is the location of the particle relative to the lower (fixed) plane. The shear deformation can be defined by the following relationship:

$$\gamma_{(x,t)} \frac{u_{(x+d_{x,t})} - u_{(x,t)}}{d_x} = \frac{du_{(x,t)}}{d_x}$$

It is noted that the shear deformation does not depend on the displacement $u_{(x,\ t)}$ itself, but on its variation when passing from one layer to another infinitely close layer. This relates to the shear rate, which is the derivative concerning the time of the shear strain γ

$$\gamma = \frac{d_{\gamma}}{d_t}$$

The shear rate, therefore, has an inverse dimension of time and is expressed in s-1 [87]

4.6. Different rheological behaviors

several rheological models have been proposed to describe the flow curve of materials. These models are identified according to the macroscopic response of the material subjected to various shear rates. The most common models are shown in **Figure 22**. [88]

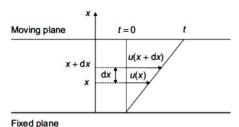


Figure 21: Definition of shear rate

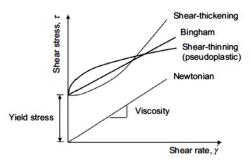


Figure 22: Illustration of different rheological behaviors the cases of shear thinning and shear thickening shown include yield stress, which is not necessarily always the case

4.6.1. Newtonian fluids

Viscosity is a "measure" of the resistance posed by the material (liquid or gas) during flow. Between two parallel planes of area A, one is stationary and the other moves under force, F, with velocity, v, and the intervening space is filled with sheared fluid (see **Figure 23**) consequently; there is a velocity gradient in the direction of the distance between the planes, $\frac{dv}{dy}$, between the stationary and the moving planes:

$$\frac{dv}{dy} = \gamma$$

Where γ is the shear rate.

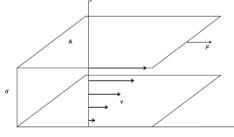


Figure 23: Schematic of simple shear flow

Newtonian fluids exhibit ideal viscous flow behavior. According to Newton's postulate, the shear stress, τ , was related to the velocity gradient, shear rate, γ :

τ= ηγ

Where n is a constant for the liquid under examination and it is known as a coefficient of viscosity or dynamic viscosity. Flow curves of Newtonian fluids are shown in Figure 24. Fluid a is more viscous than fluid b. The flow curve of a Newtonian fluid is always a straight line passing through the origin, and the viscosity of a Newtonian fluid is constant and proportional to the slope. The measurement of the shear rate and shear stress at a single point on the flow curve is sufficient to define the viscosity at all shear rates and shear stresses. A linear relationship between shear rate and shear stress is obligatory for most of the fluids, for example, air, water, gasoline, molten metal, and honey. It can be concluded that this relationship is correct for all of the gases and liquids of low molecular weight. [89-91]

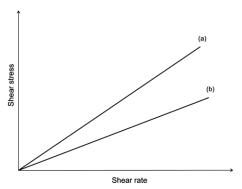


Figure 24: Flow curves of Newtonian fluids

4.6.2. Non-Newtonian Fluids

Fluids, where the flow curve is not linear or does not pass through the origin, are non-Newtonian fluids. Many fluids do not demonstrate a simple relationship between shear rate and shear stress, for example, molten polymers, paints and varnishes, buildings materials, and food. The non-Newtonian fluids can be divided into two groups: (1) fluids without yield stress τ 0 and the flow curve passes through the origin and (2) fluids that exhibit yield stress τ 0 and flows when the shear rate exceeds a value τ 0. In this section, the non-Newtonian flow behavior without yield stress is presented. [92, 93]

4.6.3. Pseudoplastic flow

The largest and probably most important class of non - Newtonian fluids are those which exhibit pseudoplastic flow. Which show a decrease in viscosity with increasing rate of shear. Familiar examples are found in paint systems, printing inks, and disperse systems generally. In such systems

The viscosity/shear relationship has an important bearing on technological requirements, and in general, a high degree of pseudo-plasticity is undesirable since this implies poor flow at low rates of shear. A precise knowledge of the viscosity/shear relationship is also important both as a practical basis for rheological characterization and a fundamental

understanding of non - Newtonian behavior. [94]

Most thickeners products including natural and synthetic thickeners exhibit pseudoplastic flow. Unlike pseudoplastic flow is exhibited by polymers in solution, the plastic system is composed of flocculated particles in suspension. The diagram of the velocity of deformation versus shearing stress can exhibit various other shapes. In this case, the mentioned relationship as seen in **Figure 25** is nonlinear, the viscosity decreases as the shearing stress increases.

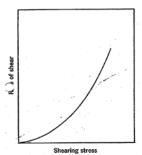


Figure 25: Flow curves of pseudoplastic flow

4.6.4. Bingham flow

Bingham flows are fluids that show Newtonian behavior above a certain minimum shear force

$$\tau = \eta \frac{du_x}{d_z} + \tau_o$$

If shear forces below this threshold are applied, the fluid will behave like a solid. Above this threshold, the fluid will behave like a Newtonian fluid. Typical examples of Bingham fluids are gels and thick solutions, *e.g.*, ketchup, dough, tough paste, and blood. [95]

It can be seen from **Figure 26** that the curve does not pass through there is an elastic one up to τ_f . The flow begins. The viscosity $d\tau/dD$ decreases until it reaches a constant value at the value τ m from this value onwards, the curve is linear. [96]

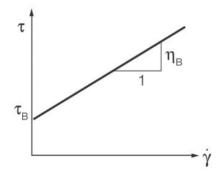


Figure 26: Bingham model for the calculation of the yield point

4.6.5. Plastic flow

Plastic fluids behave similarly to pseudo-plastic fluids, but they have an initial threshold shear force τ_0 similar to Bingham fluids. Below this threshold value, they will behave like a solid. Above this threshold, they will behave like a pseudo-plastic

fluid. [97]

Plastic flow curves do not pass through the origin but rather intersect the shearing stress axis (or will if the straight part of the curve is extrapolated to the axis) at a particular point referred to as the yield value. A Bingham body does not begin to flow until shearing stress corresponding to the yield value is exceeded. At stresses below the yield value, the substance acts as an elastic material. The slope of the rheogram is termed the mobility, analogous to fluidity in Newtonian systems, and its reciprocal is known as the plastic viscosity, U. The equation describing plastic flow is $U = \frac{F - f}{G}$ Where f is the yield value, or intercept on the shear stress axis in dynes/cm²- [98]



Figure 27: Flow curves of plastic flow

Plastic flow is associated with the presence of flocculated particles in concentrated suspensions. As a result, a continuous structure is set up throughout the system. A yield value exists because of the contacts between adjacent particles (brought about by van der Waals forces), which must be broken down before flow can occur. Consequently, the yield value is an indication of the force of flocculation: The more flocculated the suspension, the higher will be the yield value. Frictional forces between moving particles can also contribute to yield value. Once the yield value has been exceeded, any further increase in shearing stress (F - f) brings about a directly proportional increase in G, rate of shear. In effect, a plastic system resembles a Newtonian system at shear stresses above the yield value. [99]

4.6.6. Dilatant Flow

Certain suspensions with a high percentage of dispersed solids exhibit an increase in resistance to flow with increasing rates of shear. Such systems increase in volume when sheared and are hence termed dilatants. This type of flow is the inverse of that possessed by pseudoplastic systems. Whereas pseudoplastic materials are frequently referred to as "shear-thinning systems,"

Dilatant materials are often termed "shear-

thickening systems." When stress is removed, a dilatant system returns to its original state of fluidity. Substances possessing dilatant flow properties are invariably suspensions containing a high concentration (about 50% or greater) of small, deflocculated particles. [100]

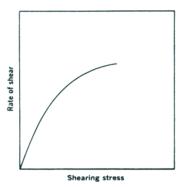


Figure 28: Flow curves of dilatant flow

Dilatant behavior can be explained as follows (see **Figure 29**). At rest, the particles are closely packed with minimal inter-particle volume (voids). The amount of vehicle in the suspension is sufficient, however, to fill voids and permits particles to move relative to one another at low rates of shear. Thus, a dilatant suspension can be poured from a bottle because under these conditions it is reasonably fluid. **[101]**

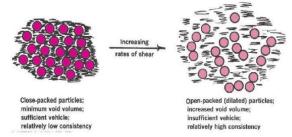


Figure 29: Dilatant behavior

As shear stress is increased, the bulk of the system expands or dilates; hence the term dilatant. The particles, in an attempt to move quickly past each other, take on an open form of packing, as depicted in the above figure. Such an arrangement leads to a significant increase in the inter-particle void volume. The number of vehicles remains constant and, at some point, becomes insufficient to fill the increased voids between particles. Because the particles are no longer completely wetted or lubricated by the vehicle, the resistance to flow increases. Eventually, the suspension will be set up as a firm paste. [102]

4.6.7. Thixotropic flows

Thixotropy is defined as the progressive decrease in viscosity with time for constant applied shear stress followed by a gradual recovery when the stress is removed. Thixotropy is a time-dependent shear thinning property. [103]

Thixotropy can be defined as an isothermal and slow recovery of material consistency, lost through shearing. If the rate of shear is reduced once the desired maximum is reached, the down curve would be superimposable on the up curve. This is true for Newtonian systems. In the case of non-Newtonian systems, the down-curve can be displaced relative to the up-curve. With shear-thinning systems (i.e., pseudoplastic), the down-curve is frequently displaced to the left of the up curve, showing that the material has a lower consistency at any one rate of shear on the down-curve than it had on the up curve. This indicates a breakdown of structure (and hence shear thinning) that does not reform immediately when stress is removed or reduced. [104]

This phenomenon is known as thixotropy. Typical rheograms for plastic and pseudoplastic systems exhibiting this behavior are shown below. Thixotropic systems usually contain asymmetric particles. These particles set up a loose three-dimensional network in the sample through numerous points of contact. At rest, this structure confers some degree of rigidity on the system, and it resembles a gel. As shear is applied and flow starts, this structure begins to break down as points of contact are disrupted and particles become aligned. [105]

The material undergoes a gel-to-sol transformation and exhibits shear thinning. On removal of stress, the structure starts to reform. This process is not instantaneous. Rather, it is a progressive restoration of consistency as asymmetric particles come into contact with one another by undergoing random Brownian movement. The most apparent characteristic of a thixotropic system is the hysteresis loop formed by the up curves and down curves of the rheogram. The area enclosed between the "up" and "down" curves (the hysteresis loop) is an indication of the extent of thixotropy of the material. This relates to the energy needed to break down the reversible microstructure of tested material. Thus, a highly thixotropic material is characterized by having a large area within the loop. If up- and down curves coincide perfectly, the material is non-thixotropic. In a thixotropic system, the nature of rheogram largely depends on the rate at which shear is increased or decreased. Typically, the period over which the shear rate is increased (up-curve) is equal to the period over which it is decreased (down curve). The response in terms of material shear stress is recorded and plotted against time. [106] Thixotropy can be measured by two methods: (a) At the constant shear rate and (b) At a variable shear rate

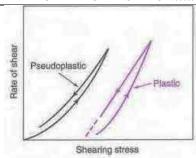


Figure 30: Flow curves of Thixotropic flows

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