



Advancements in Thickening Agents Used in Textile Printing

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Abstract

A thickening agent that's particularly suitable for printing pastes is, water-insoluble, water-swellable, or water-swollen polymer made by reverse phase polymerization of a mix of water-soluble. Where there are three basic styles of thickeners: a) polysaccharide thickener, b) synthetic thickener, c) emulsion thickener, all of them may be used as a thickening agent alone or a combination of them. Synthetic products, particularly, have come under severe criticism for his or her high environmental pollution at the manufacturing stages and applications. However, auxiliaries derived from natural resources, especially from plants, are considered biodegradable, non-toxic, and non-allergenic than their synthetic counterparts. The most goal of this review is to administer an summary of educational study within the field of thickening agents supported thickener and also the potential application in textile printing.

Key words: Thickening agent, Textile, pigment printing, Thickener.

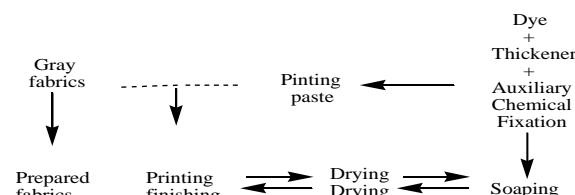
1. Note

Textile printing can be defined as localized dyeing. Unlike dyeing, in printing the dye penetrates into the selected area of the fabric surface. The coloring matter is restricted in the design area by means of a thickening agent, which provides stickiness and plasticity to the printing paste which, in turn, prevents the dye from spreading outside the design outlines even under high pressure^{1,2}. A distinction is usually made between printing methods and printing styles. The commonly known printing styles are^{2,3}:

- 1) Direct printing: where printing pastes interact with the surface of the fabric without subsequent processing modifications⁴,
- 2) Discharge printing: in which subsequent processing of printed fabrics is accomplished to bleach or destroy certain colors in printing design.
- 3) Resist printing: where a specific part of the fabric is protected, by wax or other preventing materials, to prevent color penetration into the fabric surfaces by print paste.
- 4) Burn-out printing: where the burn-out style of printing is completed by using a paste containing

chemicals, these chemicals are able to dissolve or destroy one of the fiber components of blend fabric.

At the end of the printing process, the color is fixed on the printed fabric by two methods, heat treatment alone and/or with steam as the dye and fabric used. After fixation, the printed fabric is soaping where the thickener is dissolved out in the water leaving the selective dyed portion⁵. A line diagram is illustrated in the following scheme 1 to describe the overall printing technique:



Scheme 1: Printing technique

Textile Printing is carried out by using thickening agents with the *acceptable* dye and required chemicals. Thickeners are usually, high

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relative molecular mass, water-soluble, able to swell substances with colloidal character which are *employed* in their thickened state as thickeners for printing with an solution of pigments, and/or dyes^{6,7}. Thickening agents form an *important a part of* any printing process. Thickener could be a heavy mass that imparts flexibility, stickiness, and plasticity to the printing paste, so it should be utilized for the fabric printing without color bleeding or their distinct boundaries being disturbed and be eligible for maintaining the look outlines⁸⁻¹⁰. A thickener must be a colorless, viscous paste that's made from one or more thickening agents^{9,10}. The thickener must be stable, doesn't react or chemically combine with dyes and it should be compatible with the dyes and dyeing auxiliaries used.

Function of Thickener^{11,12}:

The thickening agent has the following functions during printing of textiles:

- Give the required viscosity to the printing paste.
- Maintaining the presence of chemicals contained in the printing paste and preventing it from decomposition.
- Convey the print components in the print paste on the surface of the printed fabrics.

Factors to be considered when selecting a thickener¹³:

There are many factors that should be taken into consideration during selection of the proper thickener. These include:

- Type and quality of the fabric surface to be printed.
- Compatibility between it and the dye used in printing.
- Degree of stability of the printing paste.
- Styles and printing methods.
- Effect on color depth, such as penetration as well as fixation.
- Preparation and elimination of the thickener.
- Cost.
- Demand of Biotic oxygen

The basic characteristics to be available in printing thickener:

The basic requirements of the practical colorant when selecting the thickening agent can be summarized to^{14,15}:

- Stability to storage should be good.
- It must have physical and chemical features such as viscosity, desired flow properties, ability to wet and adhere to the internal surface of the print fabrics. It should be consistent with the other printing paste components^{16,17,18}
- The thickener should dry properly to prevent color from spreading
- It should have good adhesion to the fibers to avoid loss of colorant during mechanical handling.
- It must have a minimum effect on color yield and ease of removal.
- It should not clog the print screen.
- Should be ensured that there is proper steaming to provide free space for the dye molecules to move towards the fabric
- Thickener must be available at an acceptable price, reproducible in quality, and easy to obtain.

Classification of thickeners^{5,19}:

There are three major types of thickeners that are available nowadays in the market:

- 1- Polysaccharide thickener
- 2- Synthetic thickener
- 3- Emulsion thickener

The thickeners that are produced from plants are attractive alternatives to synthetic thickeners. This is because of their biocompatibility and low toxicity. Natural thickeners are preferred to synthetic thickeners because they are relatively cheap, easily available, and in harmony with nature. Natural thickeners are generally eco-friendly (non-polluting) renewable resources for sustainable supply, on the contrary, synthetic thickeners have many disadvantages such as high cost, high toxicity, and high environmental pollution. It is obtained from non-renewable sources and may lead to harmful side effects. In recent years, interest in the environment has started to increase in interest²⁰⁻²³.

Polysaccharide thickener:

Nature has always fascinated the humanness with brilliant and healthy products. For the time being, the world has become increasingly knowing the environmental issues. Synthetic products, in

particular, have come under severe criticism for their high environmental pollution at the manufacturing stages and applications^{23, 24}. On the other side, auxiliaries derived from natural resources, especially from plants are considered to be biodegradable, non-toxic as well as non-allergenic than their synthetic counterparts. Although there is a limited study on natural materials toxicity for textile applications, many researchers have informed that there is no adverse reaction to humans^{22, 25-28}.

Thickening agents are considered an essential part of applying dyes and/or pigment to fabric's indefinite design. Generally, the function of the textile thickening agent is to carry dyestuffs, chemicals, and any other printing assistants to the textile surface during the printing process. To achieve this function, gums produced from seeds or roots of the plant, starch, and its derivatives, methyl, and carboxymethyl cellulose, xanthan gum, and some plant exudate gum are excellent candidates, since they can supply high viscosity at low concentrations and possess the advocate rheological behavior^{29, 30}. The chemical structure of some of these polysaccharides are shown in figure 1:

Classification of plant seed gum:

Plants are considering as a source that provides the largest amount of gum in higher quantities in varieties of plants, seaweeds, fungi, and other microbial sources where they perform a number of structural and metabolic functions¹⁵. The different gums can be classified as follows³¹:

- 1) According to charges: can be classified as Non-ionic seed gums such as guar gum, locust bean gum, xanthan gum, tamarind gum, galactomannan, etc. Anionic gums such as Arabic gum, karaya gum, tragacanthin gum, gellan, cashew gum, etc.
- 2) According to the source: can be classified as
 - Shrubs/tree exudates as:
 - plant origin: such as Arabic gum, ghatti gum, Karaya gum, Boswellia gum, Neem gum, Khaya gum, Albiza gum, and Tara Gum,
 - Seed gum: as Guar gum, Tamarind gum, Locust bean gum, larch gum, etc.
 - Microbial origin (Bacterial and Fungi): Xanxan gum, Dextran gum, Letinan gum, Guardian, Cretine and Sclerigulucan, pullulan, zanflo, schizophyllan, Baker's yeast glycan, emulsan. etc.

- Animal origin: Natural gums have also been obtained from animal sources, such as include chitin, chitosan, chondroitin sulfate, and hyaluronic acid.

3) Classification based on shape: According to the shape can be classified as

- Short branched e.g. xanxan gum and guar gum.
- Branch e.g Arabic gum, karaya gum, Boswellia gum, cashew gum, hakea gum.

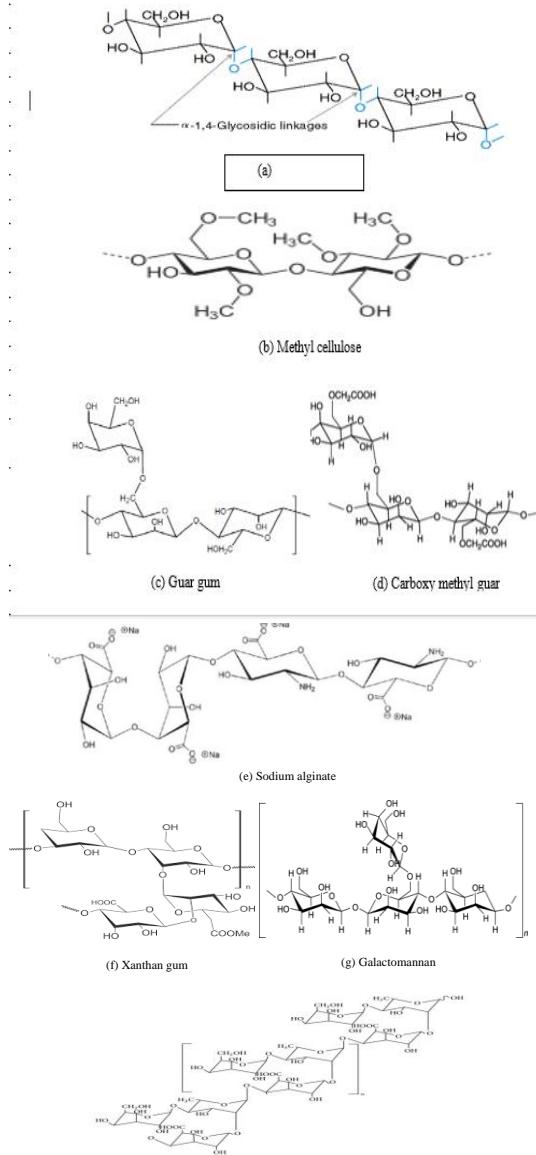


Fig 1: The chemical structure of some polysaccharides used in thickeners

Advantages of natural gum³²:

There are many advantages of natural gum as:

- Biodegradable: All living organisms produced biodegradable polymers. They progress a renewable resource and they have no adverse impact on humans and/or environmental health
- Biocompatible: almost all plant material, chemically, are carbohydrates composed of repeating monosaccharide units.
- Non-toxic: because the repeating unit in plant structure is monosaccharide units, hence they are non-toxic.
- Low cost: It must be cheaper to use natural resources, also the production cost must be lower if compared with synthetic materials.
- Eco-friendly treatment: gum from different resources must be easily collected in large quantities due to the simple production processes.
- Local accessibility: governments in developing countries encourage plant production for wide application.

Disadvantages of gum^{33,34}:

On the other side there are many disadvantages of natural gum as:

- Microbial pollution: The moisture balance content of the gums is usually 10% or more and structurally contain carbohydrate, during production, they are exposed to the external environment, so there is an opportunity for microbial contamination
- Uncontrolled dehydration rate: Due to differences in the collection of natural materials at different seasons and different regions, species, and climate conditions present in a given material may vary. There is a need to promote appropriate monographs on available gum.
- Reduced viscosity storage: Usually when the gum dissolved in water, there is an increase in the viscosity of the paste. It has been found that after storage the viscosity is reduced, this is because of the complex nature of the chemical structure of the gum.

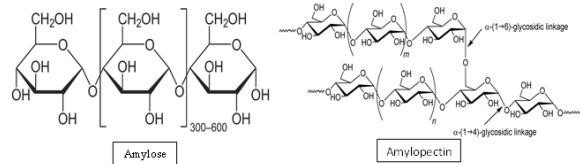
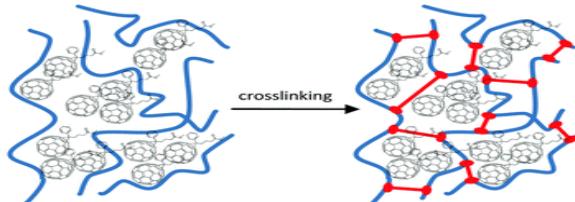


Fig 2: Constituent of starch



- Fig. 3 Crosslinking polymer



Fig.4: Mango Kermel (FeSO_4 and CUSO_4) Cassia seed gum (FeSO_4 and CUSO_4)

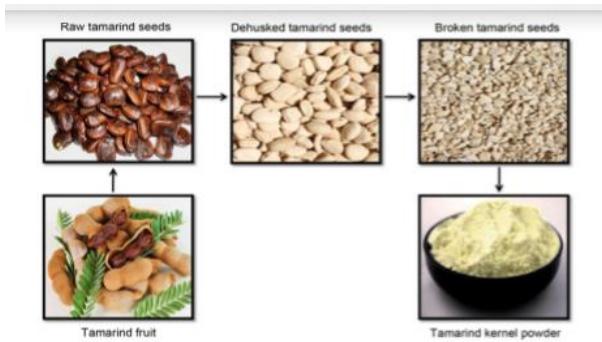


Fig. 5. Production of tamarind kernel powder.

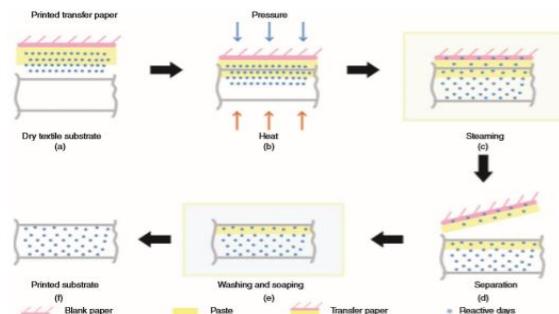


Fig. 6: Steps included in the dry transfer printing

Starch:

Starch is a homopolymer of D-glucopyranose (glucose) units, with most of the jointed units by α 1:4

glucoside linkages. Most starches contain 20-30% of the linear chain polymer, known as amylose, together with an irregularly branched material, amylopectin. Amylopectin has an α (1:6) glucoside linked branch for each 15-30 glucose unit. Separation of these products can be achieved by fractional dissolution or precipitation. In the natural state, starch is always found in a strongly aggregated form. It is necessary to break down the starch granules to obtain smooth, viscous paste³⁵.

Amylose is not stable and forms gels and precipitates of amylose aggregates, this phenomenon is known as retro gradation and is undesirable in printing paste during printing processes (are not easily re-dissolve). While amylopectin forms clear, stable, not retro gradation due to chain branching^{35,36}

Fig 2: Constituent of starch

Starch should be modified to provide the desirable properties for specific uses by improving its solubility, viscosity, and resistance to aging. There are several steps needed to modify starch^{36,37}:

- 1) Pre swelling
- 2) Gelatinization
- 3) Controlled degradation
- 4) Starch decomposition products

Starch derivatives³⁸:

Starch derivatives contain the modified starch which changes the chemical structure of some D-glucopyranose units' molecules. The most important in textile printing are starch ester, starch ether, and grafted starch. Modified starch properties by derivatization is an important operator to the continued and increased use of starch to provide thickening agents and other useful products. The important example of starch derivatives is:

- a) Starch ethers as (methyl starch, carboxymethyl starch, hydroxyethyl starch, cyanethyl starch, carbamoylethylation /carboxyethylation).
- b) Starch graft copolymers and starch composite
- c) Starch esters, as (starch acetate, starch phosphate)

Cellulose derivatives-based thickeners³⁵:

Water-soluble cellulose ethers are usually used as thickeners in printing of textiles. The most popular cellulose ethers are:

- i) Water-soluble methyl cellulose
- ii) Hydroxyethyl cellulose
- iii) Water-soluble ethyl cellulose
- iv) Carboxymethyl cellulose

Synthetic thickeners³⁹:

Successful utilize of the aqueous system into textile pigment printing and its useful effect on integrity, ecological pollution as well as the economy of the procedure has given impetus to the use of synthetic thickener. Synthetic thickeners are high molecular weight polymer (300,000-500,00) containing an acidic monomer as an essential component, such as acrylic, methacrylic, or maleic acid⁴⁰. The acid comonomer appears to be the main constituent of synthetic thickeners, it is responsible for building viscosity when neutralized with a base which is necessary thickening action. Neutralization convert acid groups into carboxylate anion which repel each other, which lead to break of the polymer chain and developing the viscosity.

Crosslinking agents have been primarily used as a thickener in textile pigment printing, such as copolymers of acrylic or methacrylic acid with their ester or acrylamide, ethylene, and maleic anhydride, and their crosslinked polymers using ethylene glycol dimethacrylate, N, N methylene bisacrylamide, divinylbenzene, methylool acrylamide, etc. Many researchers have been studied the different system for replacing kerosene, partially or completely, based on this chemical composition.

The small degree of transverse cross-linked bind the polymer chain together. In acidic conditions, polymer chains stay in a normal coiled shape. On neutralization using a base, the chains become polyanion, and under the action of strong repulsive force, straightening and chain separation occurs to the maximum possible extent. Because of crosslinking, they act as hydrated particles with more than a hundred-fold expansion of their original size but are held in a tightly packed condition. This change leads to very high viscosity of the printing paste⁴¹. These different states of the thickening polymer are illustrated in fig 3.

Fig. 3 Crosslinking polymer

There are mainly two methods of polymerization available for the synthetic thickener preparation⁴²:

- 1- *Solution polymerization*: monomers are soluble in organic solvents (alone and/or a suitable mixture) are used as the medium for polymerization with free radical initiation. The solvent medium is such that the polymer after its

formation becomes insoluble in this solvent and stays as a suspension at the end of the polymerization step. These suspended polymers are separated as fine solid powder.

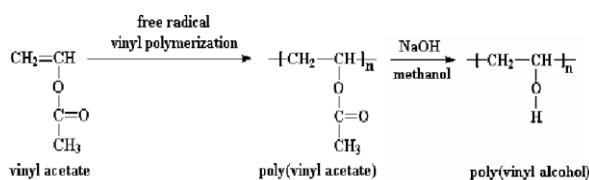
- 2- *Emulsion polymerization:* it is the most commonly used synthesis technique for producing pigment printing paste, it has many advantage as
 - a) The obtained emulsion can be directly converted to the printing paste after neutralization with base.
 - b) Since the medium elaborated is water, the use of expensive solvents and the recovery problem are removed.
 - c) Relatively low polymerization temperature $\approx 80^{\circ}\text{C}$.
 - d) Higher molecular weight polymer can be obtained if compared to other polymerization processes.
 - e) High rates of polymerization occurred simultaneously with a high degree of polymerization (reducing reaction time).

The discovery of acrylic polymers leads to the use of polyacrylic acid in synthetic thickeners. These aqueous-based synthetic thickeners are of high molecular weight containing an acidic monomer as an essential component. The advantages of thickener depend on⁴¹⁻⁴³:

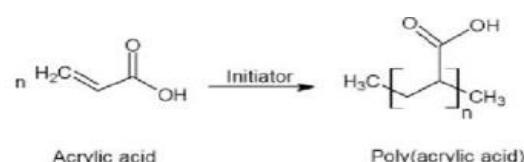
- i) The solid content required to achieve a printable viscosity should be very low.
- ii) The thickener should be pseudoplastic in nature.
- iii) It must have a good shelf life.
- iv) Thickener must not undergo any chemical reaction, agglomeration, or dissociation with dye molecules.

Examples of synthetic thickeners⁴⁴:

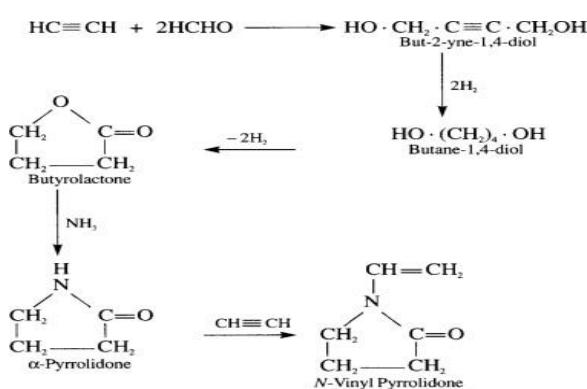
1) Polyvinyl alcohol



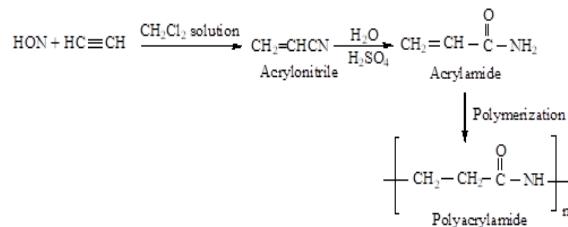
2) Polyacrylic acid



3) Polyvinyl pyrrolidine (PVP):



4) Polyacrylamide:



Emulsion thickener:

The emulsion is a system resulting from the presence of one liquid suspended in another liquid that does not mix with each other. The following factors help to configure emulsifier:

- 1- A substance has a surface activity that helps in the formation of the emulsion and affects the surface tension of the molecules of both liquids, weakening them and giving the opportunity to the molecules of the two-fluid to mix together forming one surface.
- 2- Strong electric sterile helps to break down the two liquids molecules which allow them to adhesive to each other's.

More specifically, emulsions can be used as oil in water (O/W) emulsifying agents and/or Kerosene in water. The last emulsions are most widely used in textile wet processing as the prevailing part of pigment printing pastes. Pigment prints form about half% of the total prints on fabric substrates all over the world⁴³; at least 50% of which are performed by using kerosene

emulsions, without the addition of any other polymeric thickenings' agents.

The main function of kerosene emulsions is to carry other printing paste components such as the pigments, binder, crosslinking agent, and catalyst. They work as carriage, for these components, allowing them to penetrate easily to the suitable places on the fabric surface according to the printing styling⁴⁵. When printed fabric drying the both (kerosene and water) evaporate, leaving other components in direct contact with the fabric. When curing takes place, the binder forms a film on the fabric surface, where the pigment particles are embedded. Kerosene emulsion printing pastes are characterized by pseudoplastic flow properties.

This is useful when applying the printing paste onto the fabric as the viscosity of the paste is reduced upon shearing which facilitates its movement onto the fabric through the screen holes or cylinder engravings. After repose, the paste recapture its original viscosity, which leads to sharp prints as a result of retardation the paste diffusion through the internal and external space of the fabric^{46,47}.

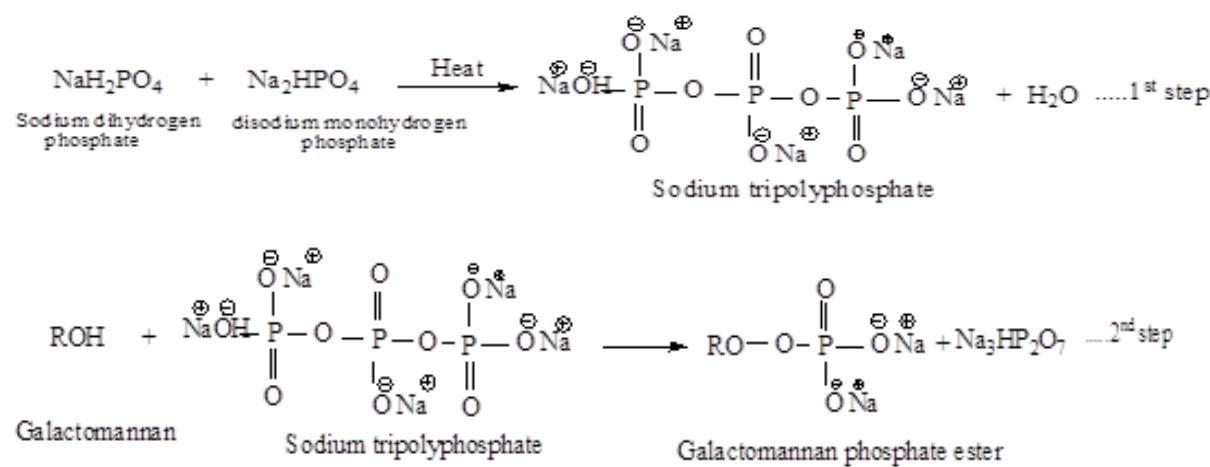
Application of thickening agent on textile printing:

Galactomannan gum can be extracted from locally obtainable sesbania seeds and submitted to chemical modification via carboxymethylation with monochloroacetic acid under the catalytic reaction of NaOH (sodium hydroxide) to improve its properties was investigated⁴⁷. The carboxymethylation was done in a non-aqueous medium using different

concentrations of the etherifying agent to realize carboxymethylation sesbania galactomannan gum (CMSG) derivatives with different degrees of substitution (D.S). It was found that:

- The amplitude of carboxymethylation increased as the etherifying agent concentration increase.
- Local sesbania seeds gum swells in cold water, but when used in printing paste is not stable for storing (fermentation takes place). Modification of sesbania galactomannan gum via carboxymethylation changes it into water-soluble and increase its paste stability to storing.
- Carboxymethylation CMSG gum paste is characterized by non-Newtonian pseudoplastic behavior. Storage has no significant effect on the rheological properties of these pasteS
- Obtained CMSG gum could be used successfully as a thickening agent in printing cotton fabric using reactive dyes.

Synthesis of some eco-friendly water-soluble carbohydrate derivatives extracted from Egyptian locally available sesbania plant seeds was represented⁴⁸, and their appropriateness as thickening agents in textile printing paste was investigated. This was done via subjecting sesbania seed galactomannan gum to chemical modification (phosphorylation) through heating of the moistened blends of the gum with a mixture of orthophosphate salts as dihydrogen and hydrogen sodium phosphate. Three different phosphate ester derivatives are prepared for different reaction times (30, 60, 90 min) at two steps:



The obtained results can be summarized as follow:

- Reaction time plays an important role in the extent of the phosphorylation reaction expressed as P%,
- The stability of printing pastes to storing increases when added modified sesbania seed gum via phosphorylation, storing has no effect on the rheological characteristics of these pastes and it characterized by a non-Newtonian pseudoplastic behavior
- Apparent viscosity of the paste of the derivatives, at a constant rate of shear, decreases, as the extent of the reaction (P%) increases,
- The obtained derivatives can be used successfully as thickening agents in printing wool fabrics with acid dye,
- The highest K/S is obtained by using Meypro gum (commercial thickening agents). Moreover, the (K/S) values of the printed fabrics increases by increasing the P% of the prepared derivatives, and the highest (K/S) is obtained by using the derivative which acquires 0.61 P%
- The phosphate derivative of sesbania seeds of the highest P% (0.61), could be used successfully as a thickening agent in printing wool fabrics with acid dyes, where the (K/S) value is slightly decreased if compared to the Meypro gum and the overall dye fastness properties remain almost remaining the same.

Chemical modification of galactomannan gum extracted from fenugreek seeds via oxidation with different concentrations of sodium chlorite was investigated. The different factors which effect on the oxidation processes such as pH, reaction time, as well as liquor ratio was studied⁴⁹. The obtained gum was analyzed for the acidic and reducing properties expressed as carboxyl and carbonyl contents, respectively. The result illustrated that oxidized galactomannan gum extracted from fenugreek seed using 1g /100g paste of 3% galactomannan gum at pH 4, liquor ratio 1:30 at 60°C temperature for 30 minutes, could be used successfully as a thickening agent in printing cotton, linen and viscose fabrics with reactive dyes. The K/S (color strength) values and colorfastness properties for these fabrics printed using this prepared thickener is either higher or equal if compared with samples printed using commercial sodium alginate.

Polysaccharide gum such as guar gum, obtained from the seeds of the shrub *Cyamopsis tetragonolobus* can be used in different applications as well as several forms (native or chemically modified form)⁵⁰. In textile printing, guar gum can also be partially depolymerized to promote dye penetration, improve swelling in water and realize the desired rheological properties. Guar gum is extracted from guar seeds by a thermo-mechanical process that leaves ca. 3% of largely insoluble proteins in the gum, produced from the endosperms aleurone layer. When printing silk fabrics with acid or metalized dyes, guar endogenous insoluble proteins connect tightly to anionic dyes, causing sedimentation of colored aggregates on the printed fabric. This causes failure on the printed fabric in the form of tiny visible dots, which lowers the quality of the final products. In order to remove these dotting, an innovative printing thickener composed of depolymerized guar gum mixed with a bioengineered subtilizing protease has been developed. To solubilization the gum, and thorough the preparation mixture of the printing paste, the protease hydrolyzes the insoluble proteins guar gum, producing soluble peptides that are washed off by the post-printing treatments of the printing fabric. This enzymatic treatment prohibits dotting and significantly enhances the quality of the silk print, without any loss on the tensile strength of the treated fabric.

Chitosan was used as a functional finishing on textile treatment to impart antimicrobial advantage and increase dye uptake of fabrics was mixed with different ratios of gelatinized starch³. The extracted chitosan was analyzed by 1H-NMR, IR, and X-ray diffraction pattern. These blends were investigated as a thickening agent in textile printing by using *Curcuma tentoria* as a natural dye. The authors have measured the rheological properties and the viscosity of the printing paste. In addition, they study the effect of chitosan on the printing properties of different fabrics (natural, blends, and synthetic fabrics) expressed on the color strength (K/S) value and related color parameters of the printed fabrics, and they assessed the antimicrobial properties of printed fabrics. The aim of this review was to approach the most recent scientific literature dealing with textile thickening agents, their chemical structure, classification, functional properties, and their application in textiles printing, in addition to their biotechnological applications. From the fundamental point of view, it was remarkable to note the preference of textile printing applications for natural thickener when compared with synthetic one due to their non-toxicity, low

cost, availability, biodegradability, and biosafety. The use of bio-degradable to process natural thickener and their derivatives or blends, is gaining prominence in the textiles industrial field due to the advantages in the use of natural materials sourced from natural origin, since the use of these materials is likely to cause less environmental pollution.

Obtained results established that: i) the printed fabrics using these new thickeners showed an increase in the (K/S) value and related parameters of the printed fabrics giving darker color, ii) chitosan increased the dye uptake into the fabrics, iii) the new blends have definite rheological properties under different shear stress during the entire printing process, iv) improved of fastness properties of the printed fabrics to washing, rubbing, perspiration, as well as light fastness, v) the treated fabrics were found to be antimicrobial. So, a non-toxic, eco-friendly, multifunctional finish has been developed for using natural dye in printing all fabrics.

El-Thalouth et al. (2013) were evaluated enzymatically hydrolyzed starches in discharge, discharge-resist, and burn-out technique. The author subjected maize starch to gelatinization at 70°C then treated it by using different amount of -amylase enzyme (0.025-0.1 ml/50 gm starch) and added it to the printing paste as a thickening agent for the above-mentioned printing technique on cotton fabrics, and wool/polyester as well as viscose/polyester/lurec blend fabrics. The obtained data illustrated that: 1) the enzymatic treatment of maize starch changes the rheological properties from thixotropic into pseudo-plastic, 2) apparent viscosity decrease as the concentration of amylase enzyme increase, 3) enzyme-treated starches achieve a better result when it used as a thickening agent when to apply a discharge-resist printing technique if compared with the commercial sodium alginate, vis-a-vis in case of discharge printing, 4) the enzyme that prepared using 0.1 ml/50 gm starches could successfully use as a thickening agent in the burn-out technique of both wool/polyester and viscose/polyester/lurec blend fabrics³.

A simple and efficient method for the preparation of carboxymethyl starch (CMS) using the combined effect of insoluble wheat starch and microwave irradiation was described⁵¹. The reaction of starch and monochloro acetic acid and/or its sodium salt in the presence of NaOH (sodium hydroxide) in isopropanol or isopropanol: water (80: 0 v/v) gives CMS.

The different parameters that affect the reaction such as, degree of substitution (D.S.), active content (A.C.), and alkaline fluidity (A.F.) of the CMS with consideration of the reaction time and concentration of reactants was studied. The result showed that the microwave irradiation technique is an efficient and rapid technique for the synthesis of carboxymethyl starch in IPA: water mixture.

Screen-print silk fabric by using Butea monosperma flower dye extract using natural thickening against (cassia seed gum and mango kernel gum) was studied⁵¹. Two mordant (Copper Sulphate and/or Ferrous Sulphate) was selected for this study. Colorfastness properties and CIE LAB values of the screen-printed samples were evaluated. The results revealed that silk fabric can successfully screen printed with extracted natural dye (Butea monosperma) and natural thickening agents (Mango kernel and Cassia seed gum) with Ferrous Sulphate and Copper Sulphate. Printed samples with both the mordant exhibited very good to excellent fastness towards sunlight, washing, rubbing, and perspirations. Hence, the study of a natural thickening agent with natural dye using screen printing is very much possible, giving all-round performance properties.

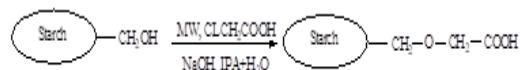


Fig.4: Mango Kermel (FeSO₄ and CuSO₄) Cassia seed gum (FeSO₄ and CuSO₄)

The print cotton fabric with pigments using a new thickening agent extracted from Aloe Vera gel in combination with sodium alginate was the axis of attention⁵². The obtained results were compared with the standard printing recipe containing synthetic thickener, and it was found that a favorable effect of Aloe Vera was achieved. According to the obtained data, the results show that the printed fabric characterized by sharpness, color yield, overall fastness properties, softness, and water vapor transmission, is dependent on the percentage of Aloe Vera gel in the thickener combination, printing auxiliary's concentration, and the curing conditions. Favorable printing properties were carried out by using a printing paste containing 80% Aloe Vera/20% sodium alginate (700 g kg⁻¹), pigment (50 g kg⁻¹), binder (145 g kg⁻¹), fixer (10 g kg⁻¹), and ammonium sulfate (5 g kg⁻¹), then drying at 85 °C for 5 min and curing at 150 °C for 3 min. The sample printed with

the new recipe illustrated excellent rubbing fastness and handle properties, with a slightly lower color yield, when compared with the sample printed with a synthetic thickener. According to all these results, we can say that Aloe Vera gel-based thickener can be used as a new alternative thickening agent for pigment printing with better print properties.

The tamarind kernel thickener can be used as a textile printing thickener was approved⁹. Because it is biodegradable, non-toxic, and biocompatible with nature, so it can be used successfully as an alternative to synthetic thickeners. Besides that, the unique properties of tamarind kernel thickener, such as high viscosity at low concentration, soluble in cold water, low price, high solid content, and low molecular weight if compared with other polysaccharides qualify it to be considered as a functional thickener in textile printing. Tamarind kernel thickener has all the main advantages of a textile thickener. It adhered the print paste well to the fabric forming an elastic film with no cracking and shattering. It was observed to be compatible with other components of the printing paste and no coagulation occurred. It also observed that it exhibited in an acidic medium, which makes it appropriate for printing with disperse dyes, and it was easily removable from the fabric surface after treatment. According to the qualitative and quantitative results, it was observed that the printed samples in presence of carrier gave better results if compared with the samples printed without the use of the carrier. The best results were obtained at 25 % tamarind kernel thickener concentration with 30 min steaming at 130 °C. Printed samples by using tamarind kernel print paste exhibited excellent fastness to washing and rubbing (dry and wet).

Cao, H. et al.⁵³ reported that the pre-treatment of polyester fabric using xanthan gum and salt can enhance the color penetration and printing clarity of inkjet printing, and the divalent salt can give higher K/S values and printing clarity. The most preferable pretreatment condition was (0.3% xanthan gum paste and 0.1 mol/L calcium chloride). Dye diffusion and adsorption performance on pretreatment fabric using xanthan gum and salt can significantly affect the fabric surface, which affects the fabric and fiber surface of both isotropic and anisotropic surfaces. Using the five level system, the method of ink elliptical coefficient (T) and the ink ellipse area (S) to evaluate the

pretreatment of polyester fabric inkjet printing sharpness is feasible.

Dry transfer technology including adhesion and steaming prepared for the printing of untreated silk and cotton fabrics with reactive dyes was studied⁵⁴. The transfer paper was coating by mixed polysaccharide thickeners composed of adhesive high-substituted hydroxypropyl cellulose (H-HPC) and another thickener (such as sodium alginate (SA), carboxymethyl cellulose (CMC), hydroxyethylcellulose (HEC), guar gum (SG-9), or carboxymethyl starch (SG-24)). Design on the transfer paper was acquired by means of ink-jet. The thermal plasticity of H-HPC was observed and 120 °C was determined as the preferable adhesion temperature. Rheological examination of all the thickeners verified that their shear-thinning behavior preferable successful coating. By comparing the effects of different mixed thickeners on the prints' quality with respect to color depth, sharpness, colorfastness, and handle, it was concluded that the color depth depended on the adhesion extent and reactivity between the thickener and reactive dye using-HPC/SA produced the highest color depths while the use of H-HPC/HEC produced the lowest color depths. The sharpness was obviously influenced by the different mixed thickeners. A preferable design was accomplished when the other thickener was CMC, SG-9, or SG-24. The color fastness and handle were favorite, irrespective of the mixed thickeners used.

The possibility of modification of different starch types likely Corn, Rice, as well as Oxidized starch via o-formylation using formic acid (99%) was investigated⁵⁵. Obtained O-formates derivatives were purified and submitted to assessment for acyl content%, degree of substitution (D.S), solubility as well as rheological characteristics. In addition suitability of the prepared one use as a thickener in the printing of cotton fabrics with vat dyes was studied. The results arrived from these studies can be summarized as given below:

- ⊕ The highest acyl% and DS value were obtained for oxidized starch formate (1.15), and lowest D.S. values for starch formate from corn starch; while oxidized corn starch stood in Mid-way position.
- ⊕ Depending on the source of parent starches used for the preparation of starch formate derivatives, it was observed that the obtained

- starch formate samples are soluble in water, and dimethyl sulphoxide, but insoluble in ethanol
- All the prepared starch formate samples were characterized by non-Newtonian thixotropic characteristics for rheological properties.
- The obtained data illustrated that the storing of pastes in question for 48 hours and for 7 days exert a remarkable effect on the rheological properties of these pastes. The thixotropy degree changed and the oxidized starch formate pastes changed into non-Newtonian pseudoplastic.
- According to D.S., it was observed that as the degree of o-formylation of starch increases, the apparent viscosity of the prepared derivative paste increases. In addition, the apparent viscosity of the prepared pastes also increases by storing for 48 hours and for 7 days.
- The prepared starch formate can be successfully used safely in printing cotton fabrics with vat dyes.
- The color strength (K/S) and overall fastness properties of printed cotton fabrics using prepared starch formate derivatives either before or after storing of the pastes are nearly the same to those obtained when using the British gum as a thickener.
- All the printed samples using the prepared thickener acquire soft handle unless that sample printed using freshly prepared corn starch formate.

Some researcher established a benign technique for the synthesis of oxidized galactomannan fenugreek gum extracted from fenugreek seeds using sodium per-borate (SPB) via microwave irradiation as a heating source⁵⁶, under a variety of conditions encompassing SPB concentration, duration of oxidation, temperature, and pH of the oxidizing medium. The obtained oxidized galactomannan fenugreek gum was subjected to the quantitative determination of microstructural features, namely, carboxyl and carbonyl group as well as rheological properties, additionally to its application as a thickener in reactive printing. Formation of carbonyl and carboxyl groups in gum macromolecular structures under study besides the observed amendment in the rheological properties, and the success of its application in reactive printing, advocate current oxidized gum to substitute the commercial thickener (sodium alginate) which is universally accepted as a

thickener for printing cotton fabric with reactive dyes. Preferable condition to obtain oxidizing Galactomannan fenugreek gum is (0.75 g SPB/100, 5g/40ml H₂O of galactomannan gum, pH 7 at 60°C for 5 min). K/S values and the overall colorfastness properties for the fabrics printed using the prepared thickener, using microwave irradiation, and/or using conventional heating are either higher or equal to the identical samples printed using commercial sodium alginate. The scanning electron microscopy illustrated a slight difference between the two heating techniques with regard to the shape of the particles. FTIR describes the association interaction chemistry of the created Carboxyl and carbonyl group.

The same author developed a new technique oxidized galactomannan fenugreek gum (GMFG) under the combined effect of ultrasound waves and sodium metaperiodate (SMPI)⁵⁷. The oxidation process was done under consideration of different parameters that affect oxidation processes namely SMPI concentration, oxidation pH medium, oxidizing bath temperature and oxidation time. The obtained oxidized GMFG samples, along with the non-oxidized gum was subjected to the quantitative analysis namely, carboxyl and carbonyl group apparent viscosity as well as rheological properties to determine its microstructural. the results data can be summarized as:

- The above-mentioned factors affecting oxidation of GMFG using the ultrasonic-SMPI system, increasing the quantity of these factors is accompanied by a noteworthy increase in carbonyl content and residual of SMPI (NaIO₄).
- The oxidizing GMFG obtained by using the sonication-SMPI technique is more stable than the non-oxidizing one during storing for a long time
- From the obtained data It can be said that the most appropriate conditions for the oxidation processes are SMPI 0.5g/5g GMFG when used as an oxidizing agent in combination with sonication to produce oxidized GMFG, pH 3 for 30 min at 50°C.
- Musty has occurred after one day to non-oxidizing GMFG while the oxidized is not musty before two weeks.
- The cotton fabric sizing by using oxidized GMFG acquired antimicrobial activity which made it suitable for medical textiles purposes

- Oxidized GMFG show increased solubility vis-viz decreased in apparent viscosity by increasing the extent of oxidation if compared to the non-oxidized GMFG. This recommended employment of the currently developed sonication-SMPI system as a green oxidizing agent for the fabrication of water-soluble and easily removable GMFG with a wider field for application.

On the other side, acrylic acid to graft copolymerization of galactomannan gum extracted from Cassia Saligna seeds in the presence of potassium persulphate as an initiator was used⁵⁸. The researcher also studied the rheological property of the grafted gum and its viscosity at different rates of shear as well as its utilization as a thickening agent in printing cotton fabrics with reactive dyes. Furthermore, the obtained results elucidate that grafted gum could be used safely as a thickener in the printing of cotton fabric, instead of the commercial thickener of sodium alginate using silk screen printing. The K/S values, as well as the colorfastness properties for the printed fabrics using this prepared thickener, is either higher or equal to corresponding samples printed using commercial sodium alginate.

The possibility of the formulated of micro-encapsulated pigments into biodegradable printing pastes and their properties were analyzed has been investigated⁵⁹. The pigment was used as the core material and polylactic-based biodegradable thickener was used as the wall-former. Cotton/polyester blend fabric was printed with the prepared micro-encapsulated pigment without dispersing, penetrating,

and leveling agents or other auxiliaries. Average particle size and size distribution, morphological structure, and elemental composition using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were used to analyze the microencapsulated pigment. The difference in viscosity and paste stability was observed upon storing over 7 days at room temperature. The micro-encapsulation process gives better colorfastness properties.:.

The synthesis of novel biodegradable synthetic thickener capable to provide good quality prints with less wastewater pollution was successfully prepared⁶⁰. The synthesized biodegradable triglyceride polylactic acid (TGLA) star polymer hydrogel via one-pot reaction by direct polycondensation of lactic acid and glycerol was obtained. The chemical structure of the produced polymer was confirmed by Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (¹H-NMR), and gel permeation chromatography (GPC)., The rheological properties and biodegradation of the prepared thickener were also investigated. Furthermore, technical evaluation of TGLA as an environmentally friendly thickening agent able to apply in printing of different fabrics was studied, and the chemical oxygen demand (COD) and biological oxygen demand (BOD) were described. In addition, the use of such thickening composite in printing such different fabrics with pigment and different types of dyes (reactive, acid, metal complex, basic, and disperse dyes) was described. The obtained results showed that:

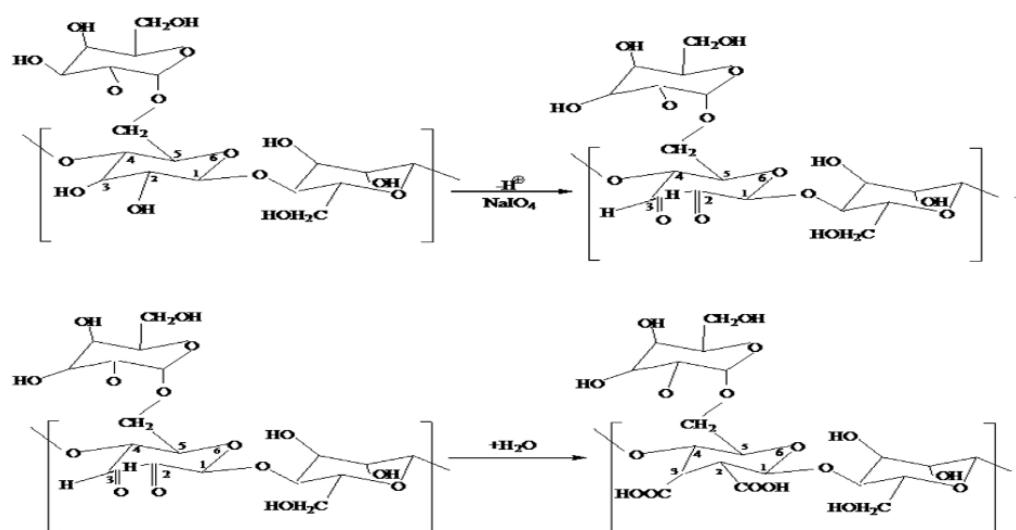


Fig. 7: Provisional Mechanism of the Synthesis of Oxidized GMFG

- When the lactic acid content increases, the print's quality of the prepared thickening hydrogels increased as well as the apparent viscosity and biodegradation rate.
- The TGPLA composite paste is characterized by a non-Newtonian pseudoplastic performance and their apparent viscosity increases upon neutralization.
- Printing pastes are very stable against storing if compared with mypro-gum as a natural thickener.
- The molecular weight and composition of the TGPLA polymers could be adapted by altering the molar ratio of lactic acid and glycerol
- Printing pastes thickened with TGPLA containing a ratio of 98% of lactic acid and 2% of glycerol; achieved similar color strength (K/S) values and colorfastness properties if compared to those prints from commercial synthetic thickeners.

Carboxymethyl cellulose samples with different degrees of substitution (D.S.) values from rice straw via pulping followed by etherification with monochloro acetic acid in the presence of sodium hydroxide as a catalyst was successfully prepared⁶¹. The D.S., rheological properties as well as suitability as thickening agents in different printing styles of the prepared derivatives were assessed. It was found that:

- The carboxymethyl cellulose derived from rice straw is characterized by a non-Newtonian pseudoplastic behavior. Apparent viscosity of prepared derivatives at any specific rate of shear depends on the D.S.
- All the prepared derivatives could be used successfully as a thickening agent in printing of cotton fabrics (discharge and/or discharge/resist printing style). Also, they could be used as thickening agents for burn-out of wool/polyester blended fabrics using sodium hydroxide. So, desirable printing samples could be obtained using these techniques.

Bains, S²⁹ reported that both natural dyes, as well as natural thickening agents, represented an ideal choice for the printing of fabric, this is due to natural dyes and natural thickening agents have better biodegradability and higher compatibility with nature. In addition, there is an interest in the use of natural dyes as well as a natural thickener that has been growing rapidly due to the result of urgent natural standards imposed by many countries in response to

toxic and allergic reactions associated with synthetic dyes and/or synthetic thickeners. So the author has been carried out to prepare eco-friendly natural dye printing paste from the Arjun dye Bark extract using natural thickening agent i.e. Cassia tora seed gum. The experiments were undertaken to block print desized cotton fabric with the prepared printing paste. The optimized factors were determined by using 2.5% and 5% of the concentration of the extracted gum. Two mordants, 5% Alum and 2% Ferrous Sulphate were selected for the improvement of colorfastness properties. Colorfastness properties and CIE Lab values for block printed samples were evaluated. Obtained results showed that the cotton block printed samples with both mordants exhibited excellent to very good fastness. Thus, it was concluded that cotton fabric can be successfully safely in block printed methods using a 5% of natural thickening agent.

The influences of microwave irradiation in absence of α -amylase enzyme on the properties of different kinds of starches (namely maize (MS), rice (RS), and wheat starch (WS) was investigated⁶². The different kind of starch was subjected to microwave irradiation in the presence and /or absence of α -amylase enzyme namely under different factor that effects on starch properties. The different kind of starch was subjected to microwave irradiation in the absence of α -amylase enzyme namely under different factor that effects on starch properties, such as starch enzyme concentration, time, temperature and power level (watt) of microwave irradiation. The authors have evaluated the influence of these treatments on the solubility and rheological properties of treated starches. Moreover, they investigated the visibility of using these treated starches as a thickening agent in the burn-out printing style in the printing paste. The results demonstrated that the optimum condition was (10g starch (irrespective of the starch nature) in 100 ml water at pH 7 then added 0.2 ml of the α -amylase enzyme). The mixture was subjected to cure at 55°C for 3 minutes at 30 watts under microwave irradiation. The obtained results also, illustrated that the apparent viscosity increases at a constant rate of shear by increasing the concentration of starch, temperature and treatment time, exposure of starch to microwave irradiation of in presence of enzyme convert the rheological properties of these starches from non-Newtonian thixotropic into non-Newtonian pseudoplastic. The prepared pastes using the modified starch were successfully used in printing wool/polyester (45/55) or wool/nylon (70/30). The

obtained illustrated that there is a loss in weight of the burn-out printed wool/polyester or wool/nylon is slightly higher when using modified starches if compared with the commercial one (mypro gum), while the overall colorfastness properties are nearly the same.

A novel approach toward the production of multifunctional printed technical textiles was introduced ⁶³. Three different metal oxides nanoparticles including titanium dioxide, magnesium oxide, and/or zinc oxide were prepared and characterized. Natural wool and synthetic acrylic fibers pretreated with the prepared metal oxide nanoparticles then followed by printing using a polylactic acid-based paste containing acid or basic dyes. Another route was applied via post-treatment of the fabrics under study with the metal oxide nanoparticles after running the printing process. The K/S and overall colorfastness properties of pre- and post-treated printed fabrics were evaluated and compared with untreated printed ones. It was found that the color strength value of the coated textile substrates significantly increase in the presence of nanoparticles on a fabric surface during the coating process. The K/S and overall colorfastness properties of pre- and post-treated printed fabrics were evaluated and compared with untreated printed ones. It was found that the color strength value of the coated textile substrates significantly increase in the presence of nanoparticles on a fabric surface during the coating process. These increased depending on the nature and concentration of the applied metal-oxide, as well as the nature of colorant and fabric. Furthermore, the applied metal-oxide nanoparticles acquire the printed fabrics with good antibacterial activity, high UV protection, photocatalytic self-cleaning, and enhanced overall the colorfastness properties. Those results indicate that the applied metal oxide-based nanoparticles could introduce ideal multifunctional prints for fabrics.

Conclusion:

The aim of this review was to approach the most recent scientific literature dealing with textile thickening agents, their chemical structure, classification, functional properties, and their application in textiles printing, in addition to their biotechnological applications. From the fundamental point of view, it was remarkable to note the preference of textile printing applications for natural thickener when compared with synthetic one due to their non-toxicity, low cost, availability, biodegradability, and

biosafety. The use of bio-degradable to process natural thickener and their derivatives or blends, is gaining prominence in the textiles industrial field due to the advantages in the use of natural materials sourced from natural origin, since the use of these materials is likely to cause less environmental pollution.

References

1. L. W. Miles, *Textile printing*, 1994, **240**.
2. H. Kipphan, *Handbook of print media: technologies and production methods*, Springer Science & Business Media, 2001.
3. A. El-Thalouth, A. Ragheb, S. Nassar, M. Ibrahim and A. Shahin, 2013.
4. K. Haggag, A. Ragheb, I. Abd EL-Thalouth, S. Nassar and H. El-Sayed, *Life Science Journal*, 2013, **10**, 1646-1654.
5. M. Rinaudo, *Polymer International*, 2008, **57**, 397-430.
6. E. Tavassoli-Kafrani, H. Shekarchizadeh and M. Masoudpour-Behabadi, *Carbohydrate polymers*, 2016, **137**, 360-374.
7. L. Dai, T. Cheng, C. Duan, W. Zhao, W. Zhang, X. Zou, J. Aspler and Y. Ni, *Carbohydrate polymers*, 2019, **203**, 71-86.
8. R. Whistler, *Industrial gums: polysaccharides and their derivatives*, Elsevier, 2012.
9. H. Chaudhary and V. Singh, *Fibers and Polymers*, 2018, **19**, 2514-2523.
10. R. Freitas, S. Martin, G. Santos, F. Valenga, M. Buckeridge, F. Reicher and M.-R. Sierakowski, *Carbohydrate Polymers*, 2005, **60**, 507-514.
11. Y. Uzuhashi and H. Miyashita, Google Patents, 2002.
12. R. Fijan, M. Basile, R. Lapasin and S. Šostar-Turk, *Carbohydrate polymers*, 2009, **78**, 25-35.
13. B. Gladman, S. Usher and P. Scales, Proceedings of the Ninth International Seminar on Paste and Thickened Tailings, 2006.
14. M. Teli, V. Shanbag, P. Kulkarni and R. Singhal, *Carbohydrate polymers*, 1996, **31**, 119-122.
15. S. Haruna, B. S. Aliyu and A. Bala, *Bayero Journal of Pure and Applied Sciences*, 2016, **9**, 159-165.
16. A. M. Hussien, *Egyptian Journal of Chemistry*, 2020, **63**, 5-9.
17. M. Abou Taleb, K. Haggag, T. B. Mostafa, A. Abou El-Kheir and H. El-Sayed, *Indian Journal of Fibre & Textile Research (IJFTR)*, 2018, **43**, 83-91.
18. N. El-Shemy, K. Haggag, E. El-Kharady and H. El-Sayed, *Journal of natural fibers*, 2017, **14**, 10-25.
19. F. Concha and R. Bürger, *KONA powder and particle Journal*, 2002, **20**, 38-70.
20. F. M. Tiller, C. S. Yeh and W. F. Leu, *Separation Science and Technology*, 1987, **22**, 1037-1063.
21. P. Albuquerque, L. C. Coelho, J. A. Teixeira and M. G. Carneiro-da-Cunha, 2016.
22. M. Shahid and F. Mohammad, *Journal of cleaner production*, 2013, **57**, 2-18.
23. U. Sewekow, *Melliand Textilberichte/International textile reports (German edition)*, 1988, **69**, 271-276 145-148.

24. M. V. Nsom, E. P. Etape, J. F. Tendo, B. V. Namond, P. T. Chongwain, M. D. Yufanyi and N. William, *Journal of Nanomaterials*, 2019, **2019**.
25. R. Schneider and S. Šostar-Turk, *Dyes and pigments*, 2003, **57**, 7-14.
26. A. Hebeish, A. Ragheb, S. Nassar, E. Allam and J. A. El Thalouth, *Journal of applied polymer science*, 2006, **101**, 931-943.
27. P. A. Sandford and J. Baird, in *The polysaccharides*, Elsevier, 1983, pp. 411-490.
28. R. Lapasin and S. Pricl, in *Rheology of industrial polysaccharides: Theory and applications*, Springer, 1995, pp. 250-494.
29. S. Bains and M. Sethi, *International Journal of Bio-resource and Stress Management*, 2017, **8**, 175-178.
30. L. Wang, R. Li, J. Shao and Z. Wang, *Journal of Applied Polymer Science*, 2017, **134**.
31. Y. Zhou, F. Pervin, V. K. Rangari and S. Jeelani, *Materials Science and Engineering: A*, 2006, **426**, 221-228.
32. R. Malviya, P. Srivastava and G. Kulkarni, *Advances in Biological Research*, 2011, **5**, 1-7.
33. R. R. Bhosale, R. A. M. Osmani and A. Moin, *International Journal of Pharmacognosy and Phytochemical Research*, 2014, **15**, 901-912.
34. V. D. Prajapati, G. K. Jani, N. G. Moradiya and N. P. Randeria, *Carbohydrate polymers*, 2013, **92**, 1685-1699.
35. B. Zhang, H. Gong, S. Lü, B. Ni, M. Liu, C. Gao, Y. Huang and F. Han, *International journal of biological macromolecules*, 2012, **51**, 668-674.
36. M. S. Quigley, P. H. Santschi, C.-C. Hung, L. Guo and B. D. Honeyman, *Limnology and Oceanography*, 2002, **47**, 367-377.
37. A. P. Díaz, D. Lourdin, G. Della Valle, A. F. Quintero, H. Ceballos, T. Tran and D. Dufour, *Carbohydrate polymers*, 2017, **157**, 1777-1784.
38. M. Witczak, R. Ziobro, L. Juszczak and J. Korus, *Journal of Cereal Science*, 2016, **67**, 46-57.
39. K. Chojnacka, *Chemical engineering and chemical process technology*, 2010, **12**.
40. P. Bajaj, M. Goyal and R. Chavan, *Journal of Macromolecular Science, Part C: Polymer Reviews*, 1993, **33**, 321-348.
41. P. A. Williams, *Handbook of industrial water soluble polymers*, John Wiley & Sons, 2008.
42. C. L. McCormick, A. B. Lowe and N. Ayres, *Encyclopedia of polymer science and technology*, 2002.
43. J. Nicholson, *The chemistry of polymers*, Royal Society of Chemistry, 2017.
44. A. H. Tabba and P. Hauser, *Textile Chemist & Colorist & American Dyestuff Reporter*, 2000, **32**.
45. M. Abo-Shosha, F. Nassar, Z. El-Sayed and A. Hassabo, *Research Journal of Textile and Apparel*, 2009.
46. M. Abo-Shosha, F. Nassar, K. Haggag, Z. El-Sayed and A. Hassabo, *Research Journal of Textile and Apparel*, 2009, **13**, 65.
47. M. Rekaby and A. Abdel-Rahman, *Research Journal of Textile and Apparel*, 2012.
48. M. El-Molla and A. Abd El-Rahman, *Man-Made Textiles in India*, 2011, **39**.
49. E. Baldaro, M. Gallucci, C. Formantici, L. Issi, S. Cheroni and Y. M. Galante, *Coloration Technology*, 2012, **128**, 315-322.
50. E. Abdou, H. El-Hennawi and K. Ahmed, *Journal of Chemistry*, 2013, **2013**.
51. S. Babel and R. Gupta, *Journal of Textile Science & engineering*, 2016, **6**, 1-3.
52. M. T. Islam, S. H. Khan and M. M. Hasan, *Coloration Technology*, 2016, **132**, 255-264.
53. H. Cao, L. Ai, Z. Yang and Y. Zhu, *Polymers*, 2019, **11**, 1504.
54. Q. Li, G. Chen, T. Xing and S. Miao, *Coloration Technology*, 2018, **134**, 222-229.
55. A. Hebesih, M. Rekaby and A. Abd El-Rahman, *J. Chem*, 2018, **61**, 813-824.
56. A. Hebesih, A. Abdelrahman, S. Nassar, H. Elsayad and N. Elshemy, *Egyptian Journal of Chemistry*, 2019, **62**, 1971-1986.
57. A. Hebeish, A. Abdelrahman, S. Nassar, H. Elsayad and N. Elshemy, *Egyptian Journal of Chemistry*, 2019, **62**, 627-644.
58. M. El-Molla and A. El-Rahman, *Egyptian Journal of Chemistry*, 2018, **61**, 329-336.
59. M. Abdelrahman, S. Wahab, H. Mashaly, D. Maamoun and T. A. Khattab, *Egyptian Journal of Chemistry*, 2020, **63**, 2-3.
60. M. S. Abdelrahman, H. Sahar, H. Mashaly, S. Mahmoud and D. Maamoun, *Appl. Ecol. Environ. Sci*, 2018, **6**, 35-47.
61. A. A. Ragheb, S. Nassar, I. Abd El-Thalouth, M. Ibrahim and A. Shahin, *Carbohydrate polymers*, 2012, **89**, 1044-1049.
62. S. Tawfik, S. H. Abd Elsalam, S. H. Nassar, I. A. Sehata, N. S. Elshemy and A. El-Thalouth.
63. M. S. Abdelrahman, S. H. Nassar, H. Mashaly, S. Mahmoud, D. Maamoun, M. El-Sakhawy, T. A. Khattab and S. Kamel, *Coatings*, 2020, **10**, 58.