



## A Critique on Synthetic Thickeners in Textile Printing

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**T**HICKENERS are high molecular weight chemicals that give thick pastes in water and are utilized in textile printing. These give the printing paste stickiness and plasticity, allowing it to be applied to a fabric surface without spreading and keep the pattern outlines even under strong pressure. Their primary role is to keep or adhere dye particles in the desired location on the fabric until the dye transfer and fixing are complete. Because the printing paste is applied by squeegee pressure to a roller or a screen, its viscosity must be high enough to avoid quick diffusion or flushing of the colour through the fabric, which would result in the poor print definition. Or mark.

**Keywords:** Thickeners; Natural; synthetic; performance.

### Introduction

Thickeners are high molecular weight chemicals that give thick pastes in water and are utilised in textile printing. These give the printing paste stickiness and plasticity, allowing it to be applied to a fabric surface without spreading and keep the pattern outlines even under strong pressure. Their primary role is to keep or adhere dye particles in the desired location on the fabric until the dye transfer and fixing are complete. Because the printing paste is applied by squeegee pressure to a roller or a screen, its viscosity must be high enough to avoid quick diffusion or flushing of the colour through the fabric, which would result in the poor print definition. Or mark. Furthermore, the thickener should provide a consistent paste viscosity, allowing for a uniform and controlled flow across the screen. The shade (depth) of the printed cloth changes if the viscosity changes during the run. The viscosity stability must not only be stable at the time the printed fabric is on the machine, but it must also be stable throughout weeks or months of storage. [1, 2]

*Characteristics of thickeners [3, 4]*

a) simplicity and ease of preparation.

b) Detachment from the fabric's surface.

c) Low cost and easy to obtain.

d) Easy to remove after drying by washing.

e) Printing paste distribution is homogeneous.

f) suitable for Printing styles and techniques.

g) The type of fabric that was used.

h) Printing ingredient compatibility and stability, including dyes and auxiliaries.

i) Create sharp outlines that don't bleed or spread.

j) Good mechanical qualities to keep the dry film from dusting.

k) Good colour yield due to good diffusion.

l) Absorption of condensed water is good, ensuring that dye and water have enough space.

#### *The different kinds of thickeners*

The main types of thickeners based on the natural and synthetic polymers used are: (Natural thickeners, Modified natural thickeners, Synthetic thickeners). [5-7] The main types of thickeners are listed in Table 1.

**TABLE 1. The main types of thickeners**

Natural	Modified natural	synthetic
A. Plant exudates	A. Starch derivatives	A. Vinyl polymers
1. Gum karaya Gum tragacanth Gum arabic	British gum CMS Saponified starch	PVA PVP
B. Seed or root	B. Cellulose derivatives	B. Acrylic polymers
Locust bean gum Tamarind seed gum Guar gum	CMC Methylcellulose Hydroxyethylcellulose	Polyacrylamide Polyacrylic acid
C. Seaweed extracts	C. Gum derivatives	C. Other synthetic copolymers
Alginates	Meyopro gum	
D. Others		
Starch Crystal gum Pectin		

*Natural Thickeners*

Textile printers have often depended on natural gums like guar, alginate, locust bean, starch, and cellulose derivatives to thicken their prints. These thickeners are low in purity, require long hydration times, and have poor thermal stability. As a result, they've been chemically or physically combined to create thickener-like substances. These, however, have limitations in terms of availability, price, purity, consistency, and storage. Colour depth, shade brightness, wash fastness because even after fixing the thickener remains its water-soluble properties, and fabric handle are all negatively impacted by natural thickeners used in pigment printing. [2, 3, 8-13]

Natural thickeners are recommended over synthetic thickeners because they are less expensive, more readily available, and environmentally friendly. Natural thickeners are generally non-polluting, renewable substances that can be used indefinitely. Natural thickeners, on the other hand, have several drawbacks, including:

- Microbial pollution: Gums have a moisture balance of 10% or more and structurally contain carbohydrates; yet, they are exposed to the external environment during production, thus microbial contamination is a possibility.
- Uncontrolled dehydration rate: The species and climate conditions contained in a given resource may vary due to variances in the collecting of natural materials during different

seasons and different areas. Appropriate monographs on available gum should be promoted.

- Low viscosity storage: This occurs when the gum has dissolved the paste's viscosity increases when it comes into contact with water. Because of the complicated nature of the chemical structure of the gum, it has been discovered that the viscosity decreases during storage. [14]

Thickeners derived from nature, such as Starch is a low-cost, commonly available polysaccharide that has a long history in the textile printing industry. It has a variety of drawbacks, and to address them, it may be subjected to chemical alteration. Modifications that offer anionic character are of interest, and the carboxymethyl ether, among the numerous starch ethers that have been developed, could be advantageous to the reactive dye printer. They've been suggested for usage in alginate-alginate mixes to boost colour yield. Modified starch, on the other hand, still contains groups that can react with reactive dyes, particularly those with a high reactivity or a large molecular size. As a result, alginates, polyacrylic acids, and carboxymethyl starches all have advantages and disadvantages when it comes to reactive dye printing. [15]

*Modified natural thickeners*

Natural thickeners that have been changed are known as semi-synthetic thickening agents. These are made by altering cellulosic materials, starch,

and gums using chemical, physical, and thermal processes. Modified polylactic acid has recently been employed as a thickening agent. One of the most important topics in materials research is biodegradable materials. Biodegradable polymers include polylactic acid, polyglycolic acid, and polycaprolactone, to name a few. This is due to their inherent and important renewable properties, such as transparency, good film-forming properties, high-quality thermal stability, good mechanical and processing properties, and other important properties such as biocompatibility and biodegradability. [8, 11, 12]

#### *Emulsion Thickeners*

The emulsion is used to describe a distribution of two immiscible liquids within one another. One liquid (the inner phase) is suspended in the form of very fine droplets in the other liquid (the outer phase). Essentially these are dispersions of inner hydrocarbon oil (white spirit, mineral spirits) in a continuous phase oil-in-water (o/w) emulsion, or dispersion of an aqueous phase in hydrocarbon oil-in-water (w/o) emulsion. A stable emulsion is formed in the presence of an emulsifying agent. The viscosity of the emulsion is determined with prescribed limits by the relative volume of the inner and outer phases. The o/w emulsion can be thinned by the addition of water and thickened by the addition of a white spirit. Conversely, w/o emulsions are thickened with water and thinned with white spirit. The role of emulsion thickenings is to wet the surface of the textile material very rapidly. They have good running properties, short dyeing times and because of their low solid content a readily washed out spirit of white. Emulsion thickenings' job is to quickly wet the surface of the textile material. They have good flowing qualities, quick dyeing periods, and are easily rinsed out due to their minimal solid content. [14]

Kerosene Emulsion Thickeners have disadvantages like The risk of an explosion in the dryer, air pollution, the loss of valuable Emulsion Thickeners during the drying and curing process, and the scarcity of Emulsion Thickeners for household use are all factors to consider. [16, 17]

Many nations have strict restrictions controlling the amount of white spirit that printworks can dump into the atmosphere or in the effluent to rivers and these laws have been tightened in recent years as public concern for the environment has increased. Many difficulties could be solved by reducing the amount of white

spirit required or eliminating it. White spirit was quite inexpensive when emulsion systems were first introduced. However, the sharp rise in oil costs, notably in the early 1970s, had a significant impact as a result of this, the price of white spirit has skyrocketed. [18]

#### *Synthetic thickeners*

Synthetic thickeners are long-chain polymers with partially cross-linked carboxylic groups. The compounds can expand significantly in water and generate high viscosity gels when neutralized. Polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylic acid, and polyacrylamide are examples of synthetic polymers. [8]

Synthetic thickening agents have recently become popular in polyester printing. They have a low electrolyte finish, especially with disperse dyes. [1, 19]

#### *Thickener performance*

The performance of a thickener depends on its advantage such as:

- a) An extremely high level of purity.
- b) Excellent ability to pierce the printing paste
- c) Prints with good depth and colouring.
- d) Outstanding dough stability.
- e) A print paste lasts a long time.
- f) A thickener has the property of being pseudo-plastic.
- g) A thickener should not react chemically with the dyes or pigment particles, causing aggregation, dissociation, or agglomeration. [3]

#### *Viscosity*

Viscosity may be defined in two ways (a) Viscosity is the ratio of shearing stress to the rate of shearing, or (b) Viscosity is the measure of the resistance of a liquid to flow:

$$\text{Viscosity} = \text{Shear stress} / \text{Shear rate}$$

Shear stress is the resistance of the liquid to flow under the influence of an applied force:

$$\text{Shear stress} = \text{Force} / \text{Area Sheared}$$

$$\text{Shear rate} = \text{Velocity} / \text{Clearance}$$

The layers of a liquid move at various rates when it is sheared in a laminar flow. The rate of shear is influenced by several factors, including the relative rate of motion of the layers. The distance between the shearing planes is the other. [1]

*Different synthetic thickeners in textile printing*  
*Vinyl Polymers*  
*Polyvinyl alcohol (PVA)*

The most important qualities include easy film formation, grease, oil, and solvent resistance, high tensile strength, great adhesive and binder capabilities, and the ability to function as a dispersion stabilizer. It's used as a thickener and for sizing artificial fibres in printing. [20]

PVA produces high-quality films with good tensile strength and flexibility, and it has a wide range of applications in several sectors. For diverse applications, PVA blends with various biomaterials are employed. PVA, starch, and LDPE, for example, are utilized in food packaging as moisture transitions. Chitosan-PVA blended films are utilized as a medical tool and for drug delivery. PVA has been used to chemically modify other polymers for biomedical applications. [21]

PVA is made by polymerizing vinyl acetate monomer to form PVAc, then hydrolyzing the acetate groups to produce PVA. Three hydrolysis processes are relevant in the manufacturing of PVA, depending on the catalyst used. Acidolysis, aminolysis, and alkaline hydrolysis are some of them. Alkaline alcohol is commonly used to convert PVAc to PVA on a big scale. To hydrolyze the acetate groups, the ester was replaced with methanol in the presence of sodium hydroxide in this hydrolysis process. Fig. 1 and Fig. 1 shows the PVA manufacturing process and the mechanism of the synthesis of poly(vinyl alcohol). PVA is a semi-crystalline hydrophilic synthetic polymer having a great mechanical property and a planar zigzag structure. PVA is a polymer that is chemically and thermally stable. [22]

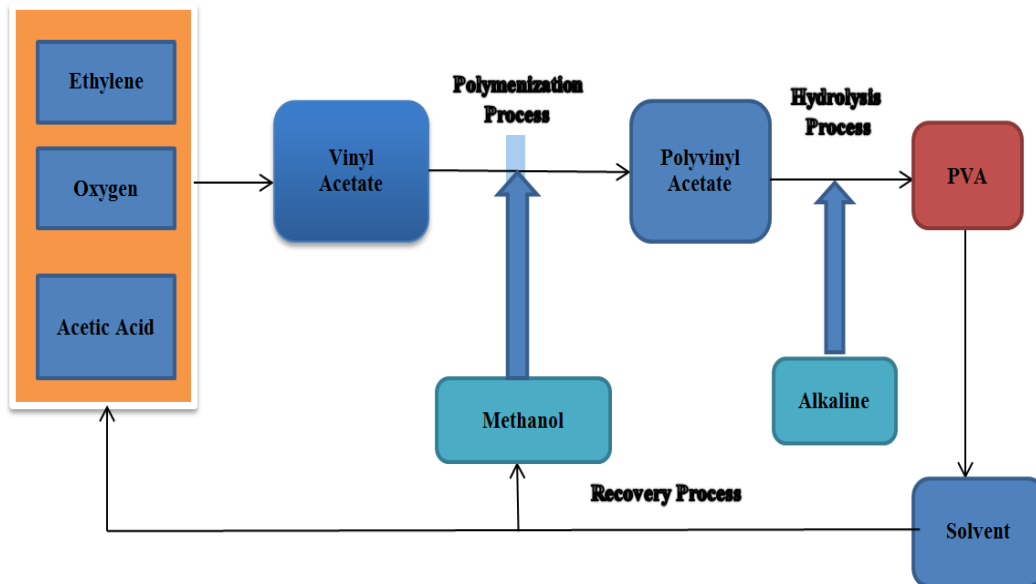


Fig. 1. PVA manufacturing process

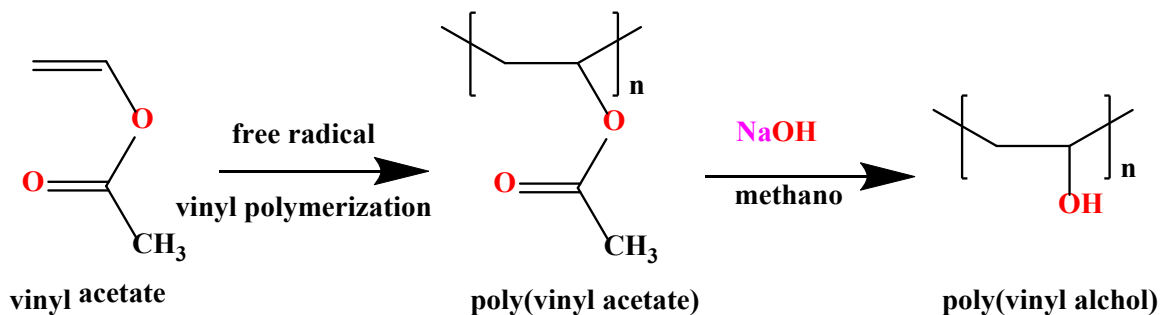


Fig. 1. Mechanism of the Synthesis of poly(vinylalcohol)

*Polyvinylpyrrolidone*

Polyvinylpyrrolidone (PVP) stands for polyvinylpyrrolidone, which is an N-vinylpyrrolidone homopolymer. Plasdone, Polyclar, and Pregel ST are sold by General Aniline and Film Corp. (USA), while Albigen A, Kolliden, Luviskol, and Igecol are sold by BASF (Germany). Because the product is readily soluble in rapidly agitated water, heat speeds up the process. The pH of the paste determines its viscosity. In concentrated HCl, the viscosity increases, but PVP precipitates out in strong caustic. It is stable for a long time if 0.1 to 0.2 percent chlorophenols are added. To manufacture cellulose acetate, it's mixed with sodium alginate, CMC, and cellulose acetate. [3]

*Polyacrylamide*

Polyacrylamide is easily dissolved in water. Because polyacrylamide is nonionic, changes in viscosity with pH between 1 and 10 are minor. When stored at a pH level above 10, the polymer

is susceptible to hydrolysis and a rapid increase in viscosity. Electrolytes such as ammonium chloride, calcium sulphate, sodium bicarbonate, and sodium nitrate are readily tolerated by it. [20]

*Polyacrylic*

These aqueous-based synthetic thickeners are made up of high molecular weight polymers with an acidic monomer as the main component (e.g., acrylic acid, methacrylic acid, maleic acid). When a base is present, these monomers ionize, resulting in the desired viscosity.

Preparation of eco-friendly synthetic thickener from acrylic acid, methacrylic acid and hexadecanol called CP by putting Methacrylic acid, hexadecanol and H2SO4 into a flask hexadecyl methyl acrylate was created by heating to 90°C and reacting for 3 hours. The oil phase was made up of Span-80 as an emulsifier, azobisisobutyronitrile as an initiator, hexadecyl

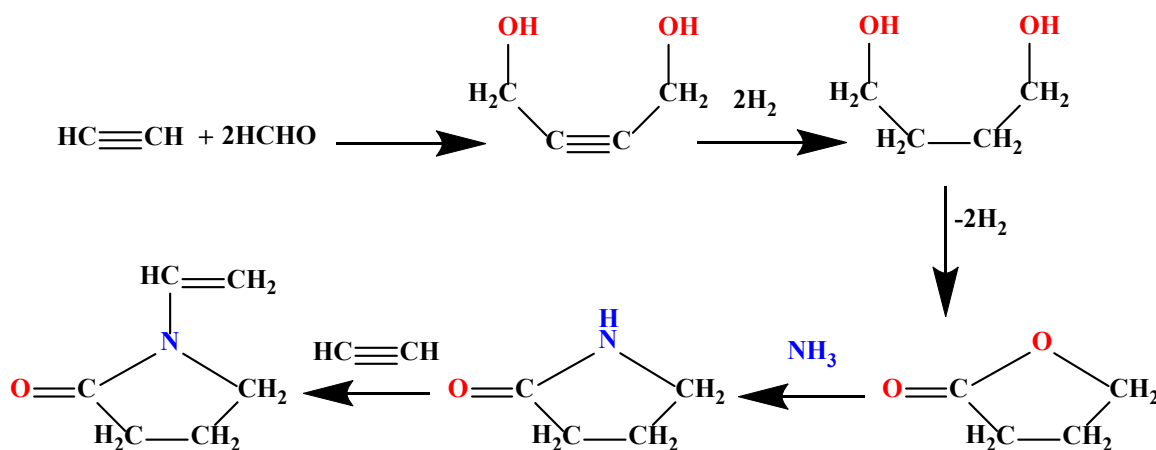


Fig. 1. Mechanism of the Synthesis of Polyvinylpyrrolidone

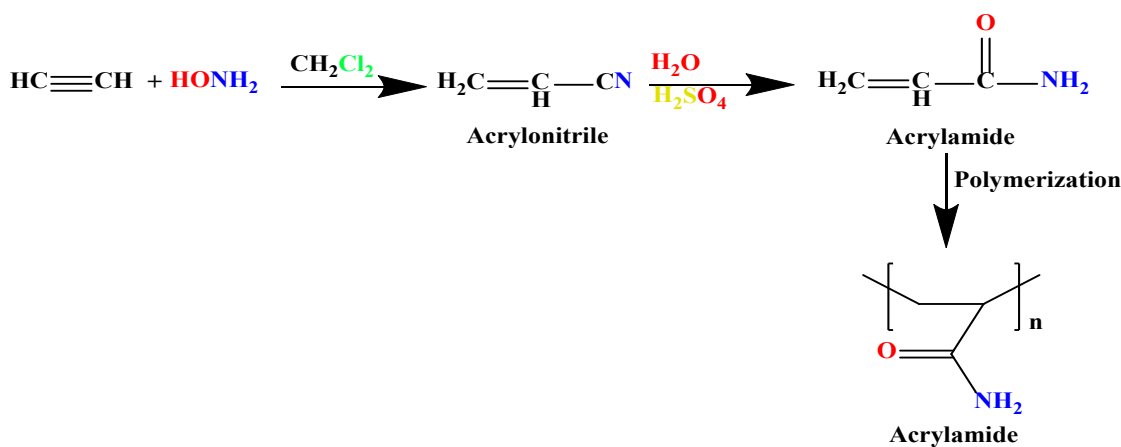
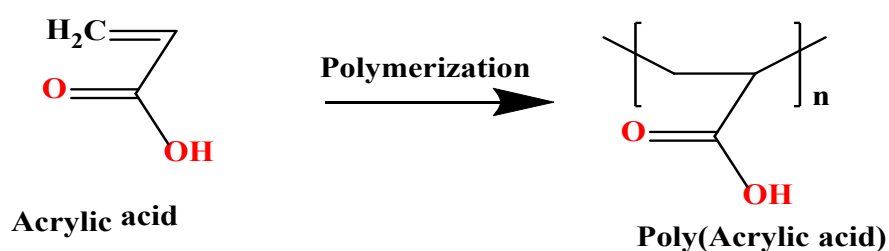


Fig. 1. Mechanism of the Synthesis of Polyacrylamide





**Fig. 1. Mechanism of the Synthesis of Polyacrylic.**

methyl acrylate, xylene, and white mineral oil in a moderate amount. Acrylic acid neutralised with ammonia and a crosslinker (MBAM) were dissolved in distilled water to make up the water phase. The water phase went into the emulsion kettle first, followed by the oil phase. After 30 minutes of emulsification, they were poured into the reactor. The mixing speed was set to 110 revolutions per minute. When heated to 60°C in a nitrogen-free environment, polymerization begins. After vacuum pumping separated the water and xylene, thickener CP was produced. CP thickener has a high ability to thicken with a modest amount of water. It works well as a thickening in the preparation of pigment printing paste. It can be used for both flat and rotary screen printing and can be used on a range of materials. The stability of modulated colour paste with thickening CP is excellent. The printed product features a crisp outline, vibrant colour, and excellent colour yield. It outperforms similar imported products in terms of performance. Thickener CP has a superior ability to hold water and is electrolyte resistant. It's also easy to work with when it comes to printing binder and pigment colour paste. (16)

*The advantages of synthetic thickeners:*

- The amount of solids required to create a printed viscosity is insignificant (0.5-2 percent).
- The nature of a thickening must be pseudo-plastic.
- The shelf life of a print paste should be long.
- Because most dyes contain electrolytes, a thickener must not undergo any chemical reactions, agglomeration, or dissociation with the dyes or pigment particles, and it must not be electrolyte sensitive.

Synthetic thickeners can be customized to have all these qualities, making them ideal alternatives for natural and emulsion thickeners. Acrylic or methacrylic copolymers with their esters or

acrylamide, ethylene, and maleic anhydride have traditionally been employed as thickeners in textile printing. After partial neutralization with a base, the acid comonomer is responsible for the production of viscosity, which is vital in the thickening process. The acid groups are transformed into carboxylate anions, which react with one another and cause the polymer chains to uncoil and lengthen. Viscosity arises as a result of the enlarged polymer chains being unable to readily slip over one another. [3]

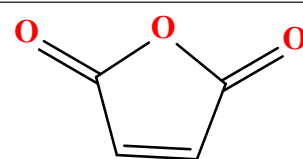
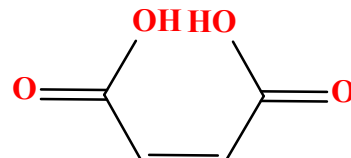
In addition to bifunctional vinyl monomers, cross-linkable monomers such as divinylbenzene, methylene bisacrylamide, and ethylene glycol dimethacrylate were used as one of the components in the manufacture of synthetic thickeners. In loosely crosslinked polymers, a printed viscosity can be reached with a far lower solids content than in linear copolymers. [5, 14]

This is important since a higher solids content affects the fabric's feel and washability. As previously stated, adding crosslinking agents to acrylic copolymers allows for extremely high viscosities at low solids contents, allowing them to be used as kerosene substitutes in pigment printing as well as printing with reactive, acid, and direct dyes. The presence or absence of a crosslinking agent has been used to divide these acrylic thickeners into two categories: soluble in alkali and swellable in alkali. It was revealed that the degree of dye-fixing on the fabric is dependent on the degree of crosslinking. Dye transmission from the thickening film to the substrate is improved by lowering the degree of crosslinking. Improved dye transfer from the thickening film to the substrate

*Uses of Synthetic thickeners in textile printing*

polyacrylic acid (PAA), polyacrylic acid/polyethylene glycol (PAA/PEG), polyacrylic acid/polyethylene glycol (PAA/PEG), and polyacrylic acid/ polymethacrylic acid (PAA/PMA) are used

TABLE 2. lists the most often utilized monomers in synthetic thickenings.

Name	Chemical structure
Acrylic acid	$\text{H}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{COOH}$
Methacrylic acid	$\text{H}_2\text{C}=\underset{\text{CH}_3}{\text{C}}-\text{COOH}$
Ethyl acrylate	$\text{H}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{COOC}_2\text{H}_5$
Butyl acrylate	$\text{H}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{COOC}_4\text{H}_9$
2-Ethyl hexyl acrylate	$\text{H}_2\text{C}=\underset{\text{H}_2\text{C}-\text{CH}_3}{\text{C}}-\text{COOC}_6\text{H}_{13}$
Acrylamide	$\text{H}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{CONH}_2$
Ethylene	$\text{H}_2\text{C}=\text{CH}_2$
Maleic anhydride	
Maleic acid	

with reactive dyes for printing cotton fabrics and when compared with a natural thickener such as sodium alginate show increasing in viscosity values and the K/S values. [23, 24]

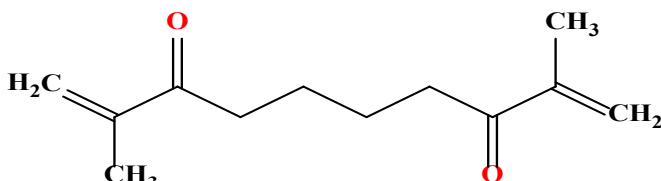
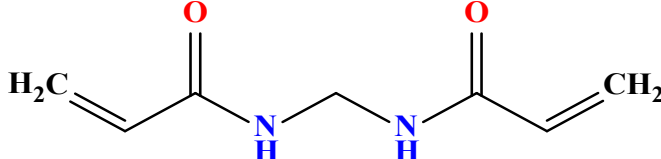
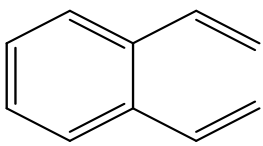
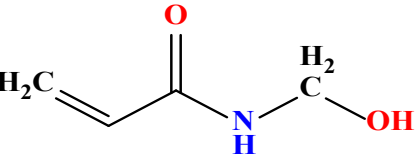
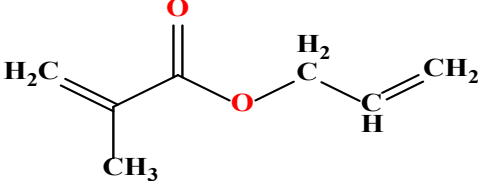
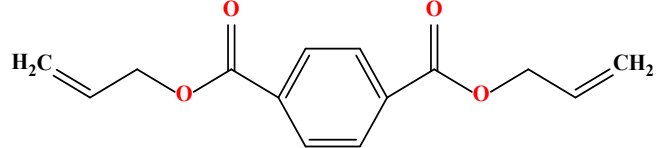
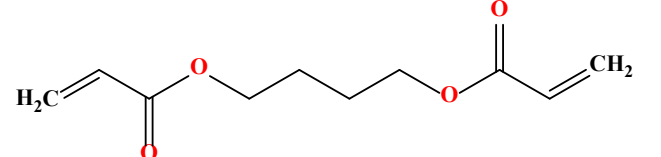
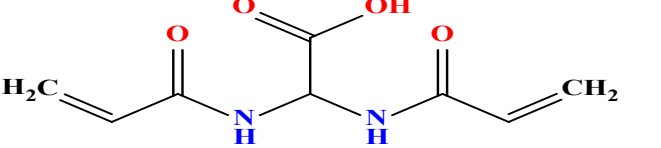
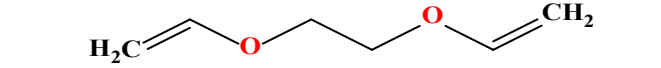
Kerosene Emulsion Thickener has been replaced with copolymers of acrylic or methacrylic acid with their esters or acrylamide and maleic anhydride and their crosslinked polymers using ethyleneglycol dimethacrylate, N, N-methylene bisacrylamide, divinylbenzene, methylol acrylamide as cross-linking agents to print cotton fabrics. The synthesized thickeners gave good results in colour value, print sharpness and wash and rub fastness. [16, 17]

Polyacrylic acid was used to print regenerated cellulosic fibre and given higher K/S values than sodium alginate. [25]

Styrene acrylate can be safely used to make printing paste for screen printing cotton and polyester textile fabrics with pigment colours. For samples printing with methyl methacrylate styrene (MMA)-based materials, the maximum K/S is achieved, and the fastness qualities vary from acceptable to excellent. [26]

The viscosity of polyacrylate thickener is affected by shear stress, although it recovers fast once the tension is removed. Meanwhile, its drooping property and weak capillary action, as well as its weak filament dragging ability and outstanding thickening ability, can balance its permeability on hydrophobic carpets and gravity. make it acceptable for printing on a digital printer as a result, it's ideal for digital nylon carpet printing. [27, 28]

**TABLE 3. Most Commonly crosslinking for Synthetic Thickeners**

crosslinking	Chemical structure
Ethylene glycol dimethacrylate	
N,N-methylenebisacrylamide	
Divinyl benzen	
N-methylol acylamide	
Allylmethacrylate	
Diallyl phthalate	
Butanediol diacrylate	
Bisacrylamido acetic acid	
Divinyl glycol	



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*Conflict of interest*

The authors declare that there is no conflict of interest

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## نظرة على المثخنات الصناعية في طباعة المنسوجات

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المثخنات عبارة عن مواد كيميائية ذات وزن جزيئي مرتفع تعطي معاجين سميكة في الماء وتستخدم في طباعة المنسوجات. هذه تعطي معجون الطباعة الالتصاق واللدونة ، مما يسمح بتطبيقه على سطح القماش دون أن ينتشر ويحافظ على الخطوط العريضة للنمط حتى تحت ضغط قوي. يتمثل دورهم الأساسي في الاحتفاظ بجزيئات الصبغة أو لصقها في المكان المطلوب على القماش حتى اكتمال نقل الصبغة وتثبيتها. نظرًا لأن معجون الطباعة يتم تطبيقه عن طريق ضغط الممسحة على بكرة أو شاشة ، يجب أن تكون لزجته عالية بما يكفي لتجنب الانتشار السريع أو تدفق اللون عبر القماش ، مما قد يؤدي إلى ضعف تعريف الطباعة. أو مارك.

**الكلمات الرئيسية:** مثخنات ، طبيعي ، صفة ، اصطناعي.