



Synthetic Thickener in Textile Printing

Menna M. Ragab ^a, Ahmed G. Hassabo ^{b*} and Hanan A. Othman ^a

^a Textile Printing, Dyeing and Finishing Department, Faculty of Applied Arts, Benha University, Benha, Egypt.

^b National Research Centre (Scopus affiliation ID 60014618), Textile Industries Research Division, Pre-treatment, and Finishing of Cellulose-based Textiles Department, 33 El-Behouth St. (former El-Tahrir str.), Dokki, P.O. 12622, Giza, Egypt.

METHACRYLIC acid (MAA) - ethyl acrylate (EA) - ethylene glycol dimethacrylate (EGDM)/N, N'-methylene bisacrylamide (MBAM) polymers of different compositions were used as synthetic thickeners in pigment printing of cotton. Crosslinked polymers with different feed ratios were synthesized and their printing behavior was compared with the conventional kerosene emulsion thickener and a commercial synthetic thickener Alcoprint PTF in terms of color value, back penetration, wash, rub (dry and wet) and scrub fastness, and handle of the fabric. Methacrylic acid-based thickeners (solid content 4%), when used as a substitute for kerosene emulsion, produced prints with a harsh feel. Therefore, partial substitution of kerosene emulsion (60-80%) was tried and a significant improvement in the handle of fabric was observed.

Introduction

For many years the thickener requirements of textile printers have been met by naturally occurring gums such as guar, alginate, locust bean, starch, and cellulose derivatives. These thickeners require very long hydration times, have poor thermal stability, and a low degree of purity. They have therefore been modified chemically or by physical blending to produce products with suitable properties for a thickener. However, these products still have limitations in terms of availability, cost, purity, consistency, storage, etc. Natural thickeners used for pigment printing do not give satisfactory results in terms of depth of color, the brilliance of shade, wash fastness, and handle of the fabric. With the introduction of emulsion thickening, pigment printing has been successfully carried out for many years. In this type of thickener, kerosene or white spirit and water are stirred together at high speed in the presence of an emulsifier. Although oil-in-water emulsion gives excellent prints in terms of color yield, brilliance, and the feel of the fabric, the

use of such a large amount (50-80%) of solvent can create some problems, White spirit in the presence of air can form very explosive mixtures, Use of volatile solvents leads to pollution of the atmosphere by discharge of vapors into the air or of effluent into rivers, Increases in the prices of all petrochemical products make pigment printing very costly, Due to the above-mentioned limitations of natural as well as kerosene-based emulsion thickeners, there was a need for some safer and easily available synthetic substitutes at reasonable prices. [1, 2]

Synthetic thickener and its advantages

These aqueous-based synthetic thickeners are high molecular weight polymers containing an acidic monomer as an essential component (e.g., acrylic acid, methacrylic acid, maleic acid). These monomers ionize on the addition of a base to develop the desired viscosity. acrylamide is also widely used in synthetic thickening compositions because its copolymers are soluble in water. Synthetic thickener becomes more effective in textile printing (especially pigment

printing and printing of pet with disperse dye). The performance of a thickener depends on its advantage such as:

- a) A high degree of purity.
- b) High ability to penetrate the printing paste.
- c) Good depth and coloration for prints.
- d) Excellent dough stability.
- e) A print paste has a good shelf life.
- f) A thickener is pseudoplastic.
- g) A thickener should not undergo any chemical reaction, agglomeration, and/or dissociation with the dyes or pigment particles. [3]

Synthesis Techniques of synthetic thickener

Polymers used in the synthesis

The most commonly used monomers in synthetic thickenings are acid comonomer that has an important role to play because it is responsible for the thickening action through the development of viscosity on partial neutralization with a base. Neutralization converts the acid groups into carboxylate anions which repel each other, resulting in uncoiling and extension of the polymer chains. These extended polymer chains cannot freely slip past each other, thereby developing the viscosity. Table 1 clarifies the Most Commonly Used Monomers for Synthetic Thickeners

The cross-linking agent used in the synthesis

In addition, to the bifunctional vinyl monomers, cross-linkable monomers such as divinylbenzene, methylene bisacrylamide, and ethylene glycol dimethacrylate have also been used as one of the components for producing synthetic thickeners. In loosely crosslinked polymers, a printable viscosity can be accomplished at a much lower solids content compared to linear copolymers. [3, 4] This is very important because a higher solids content affects the feel of the fabric as well as its wash fastness properties. It is evident from the foregoing discussion that with the introduction of crosslinking agents in acrylic copolymers, very high viscosities can be attained at low solids contents, and this enables them to be used as substitutes for kerosene in pigment printing and printing with reactive, acid, and direct dyes also. Depending on the presence or absence of a crosslinking agent, it has divided these acrylic thickeners into two categories: alkali soluble and alkali swellable. It was found that the degree of fixation of the dye on the fabric is dependent on the extent of crosslinking. Transfer of the dye from the film of thickener to the substrate was increased by decreasing the extent of crosslinking. And the most commonly used crosslinking agent

for synthetic thickeners is followed in Table 2.

Polymerization procedure for the synthesis

The graft polymerization reaction was carried out in flasks containing an aqueous solution of monomer. The flasks were stoppered and placed in a thermostatic water-bath until the required temperature was reached. Nitrogen gas was purged through this solution to remove the dissolved oxygen. The pre-gelled starch and calculated amounts of sulphuric acid and ferrous sulfate were added and the reaction mixture was mixed thoroughly. To initiate the reaction a known amount of potassium monopersulphate solution was added. The contents were shaken occasionally during polymerization. After the desired reaction time, the flask contents were poured ethyl alcohol where a precipitate was formed that consisted of pre-gelled starch graft copolymer and the homopolymer. The homopolymer (poly methacrylonitrile) was removed from the reaction mixture by Soxhlet extraction using dimethylformamide for 12 h. It was found experimentally that, Soxhlet extraction using dimethylformamide as an efficient solvent is quite enough to remove polymethacrylonitrile (homopolymer) from its physical mixture via measuring the nitrogen content after each Soxhlet extraction. Finally, washed with pure ethanol and air-dried. [3, 5]

Mechanism of Viscosity Development

Knowledge of the flow behavior and mechanism of viscosity development is of fundamental importance in creating printing thickeners. In the aqueous solution of these synthetic thickeners, viscosity develops immediately after the addition of bases by the neutralization of polycarboxylic acid and/or maleic anhydride groups as shown below:

Earlier studies on polyacrylic acid showed that the neutralization of these polymers is not as straightforward as might be imagined. Studies using polyacrylic acid solutions of appreciably lower molecular weight indicate that the maximum viscosity is obtained at the neutral point and is lowered by an excess of alkali (see Fig. 1). [6]

Effect of pH on Viscosity

The viscosity of the synthetic thickeners is not only shear-dependent but also pH-dependent. As stated earlier, the viscosity increases up to a pH range of 7-8, and after that range, the addition of more alkali makes the solution less viscous. It was observed that the viscosity decreased from pH 7.6 to pH 9.4. and the viscosity of MMA IS at pH=3.

Effect of Electrolytes on Viscosity

The addition of base beyond the neutralization

TABLE 1. Most Commonly Used Monomers for Synthetic Thickeners.

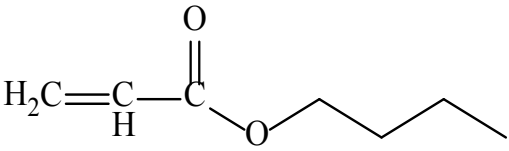
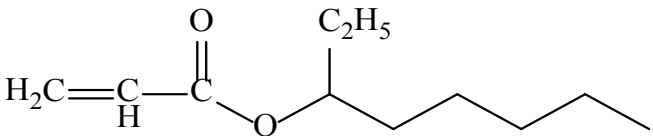
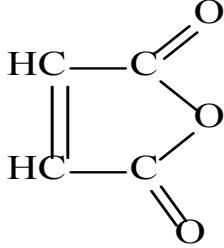
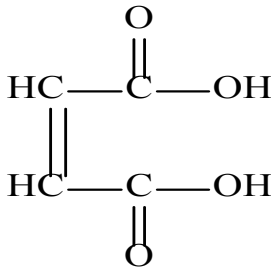
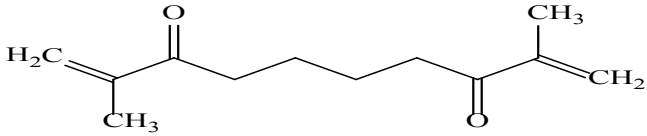
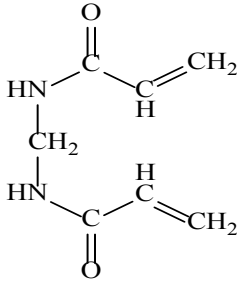
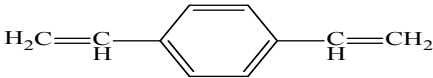
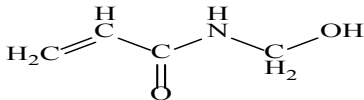
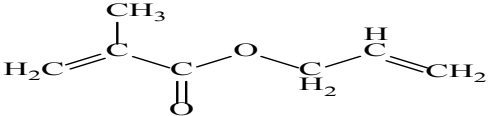
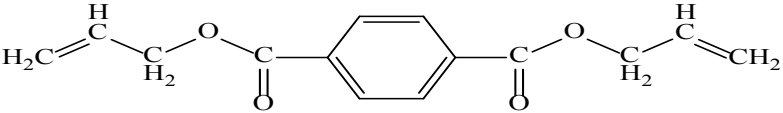
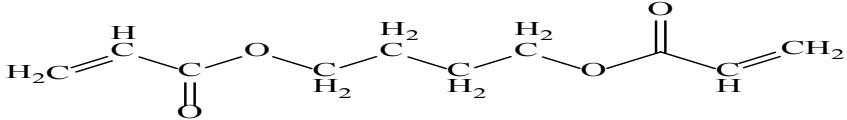
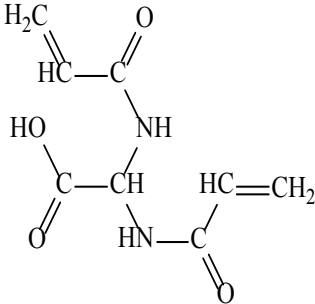
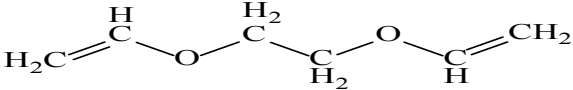
Name of monomer	Chemical Structure
Acrylic acid	$\text{H}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{COOH}$
Methacrylic acid	$\text{H}_2\text{C}=\underset{\text{CH}_3}{\text{C}}-\text{COOH}$
Ethyl acrylate	$\text{H}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{COOC}_2\text{H}_5$
Butyl acrylate	
2-ethyl hexyl acrylate	
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	

TABLE 2. 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	

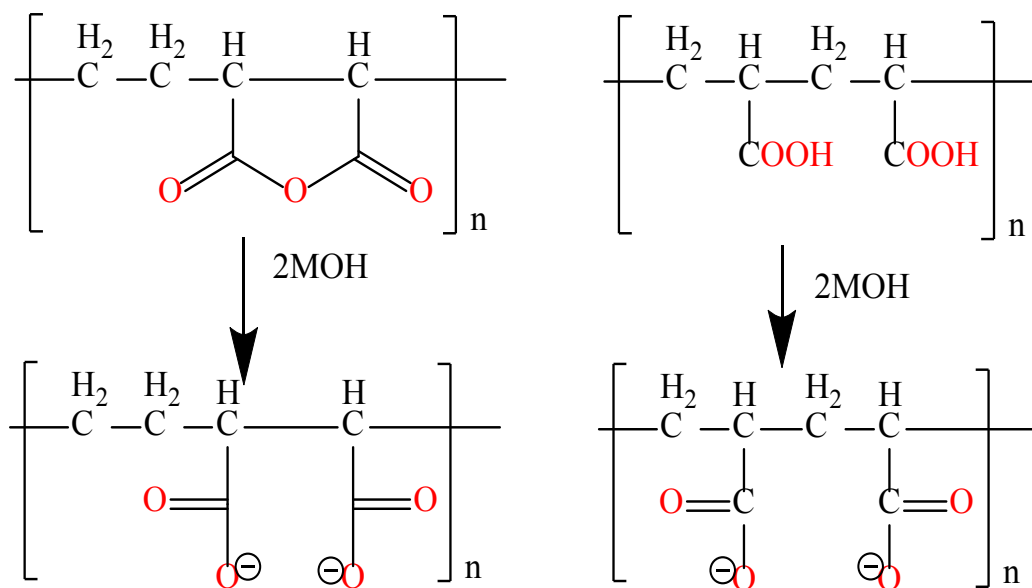


Fig. 1. mechanism of viscosity development.

point leads to viscosity reduction through an effect of the law of mass action, similar to the drop in viscosity observed when ions are added in the form of a salt, e.g., ammonium sulfate. Upon the addition of 1 % NaCl in a 4% solution of saponified polyacrylonitrile, the viscosity was reduced. Upon further addition of NaCl (4%), this viscosity was reduced. This is the biggest disadvantage of synthetic thickeners, and it makes them less suitable for printing with dye formulations containing salts. There is no salt content in pigment printing, so these thickeners are widely accepted. [7]

Performance of Synthetic Thickeners Acrylic copolymer

The discovery of acrylic polymers led to the use of polyacrylic acid in synthetic thickeners. later produced a series of acrylic-based synthetic products under the name Lutexal. and the common formula for acrylic acid is presented in Figure 1.

The use and performance of $\text{MAA}_{(68)}\text{EA}_{(5)}\text{BA}_{(15)}$ polymer crosslinked with butanediol acrylate in a printed cotton fabric with 5 % reactive dye Turquoise Blue. The printed fabric was cured, and the prints obtained had good colorfastness and handle. Another polymer having the same comonomers but a different composition can be also used. [1]

$\text{MAA}_{(4)}\text{EA}_{(18)}\text{BA}_{(18)}$ and N-methylol acrylamide as the crosslinking agent have been successfully used in pigment printing of PET-cotton blend. The prints showed good color yield and wash fastness.

Methacrylic acid-butyl acrylate compositions in a loose three-dimensional network using ethylene glycol as the crosslinking agent have found effective use in print paste formulations containing reactive, acid, and metal dyes and also with pigments. The uncross-linked copolymer has been used for the printing of nonwoven napped polyamide carpeting with acid dye. The paste gave a well-colored saturated clean print with a uniformly dyed nap and increased dye fixation. [8]

(Methacrylic acid -divinyl benzene- N-methylol acrylamide) polymers have also been successfully used with dyes and pigments for partial replacement of kerosene. When used with C.I. red dye, the paste did not dry on the printing stencil and exhibited good stability of the print during the washing step at 60°C.

Methacrylic acid-butyl acrylate-methyl methacrylate terpolymers also have been used in pigment printing for partial substitution of solvents. These terpolymers have good electrolyte resistance.

Methyl methacrylate polymers are also used as thickeners, and fabrics printed with them have a good handle, wash fastness, and color yield. It was investigated that the performance of polyacrylamide thickeners in reactive printing. The samples were comparable in the depth of shade, wash, light, and rubbing fastness with sodium alginate printed samples, but the stiffness was higher.

Polyacrylonitrile based on copolymers and a third component has also been used for the printing

of cotton fabric with vat and reactive dyes. The color value was 15-20% higher than the alginate printed samples and had equally good fastness properties. The feel of the fabric was soft. [3, 9]

Polyacrylic-based thickeners are commercialized under the name of Lutexal, Alcoprint, and Acrysol. Lutexal thickeners of various grades are available. Lutexal is reported to be outstanding in its suitability for solvent-free or low solvent pigment printing. Acrysol has been reported to be highly resistant to electrolytes. Alcoprint is a modified polyacrylic thickener that overcomes most of the problems associated with the gelling of black pigment [8]. Figure 1 illustrate the chemical structure of some Acrylic copolymer

Ethylene-MaleicAnhydride Copolymer

A considerable amount of work on ethylene-maleic anhydride copolymers (see Figure 3) cross-linked with divinylbenzene, allyl methacrylate, or ethylene glycol dimethacrylate has also been carried out, and the products have been used as thickeners in disperse dye pastes for polyester fabrics. An effort to further improve the performance of these thickeners in printing was made by adding a 2% sodium salt of carboxymethyl cellulose, and it was found

that these printing pastes are more resistant to a loss of viscosity upon the addition of electrolyte than paste not containing NaCMC. The addition also reduced the high shear thinning behavior, thus making it more like a natural gum. It was investigated that the mechanism and use of ethylene-maleic anhydride copolymers in the printing of cotton fabrics with acid dyes. For a linear polymer, the concentration required to achieve a printable viscosity is 10-18%, while for a crosslinked polymer it is 7-8%, depending on the molecular weight. The performance of these thickeners was found to be comparable with that of sodium alginate. [10]

Potassium acrylate-maleic anhydride acid copolymer

for the printing of cellulosic textiles with reactive dyes. Strongly colored prints with sharp pattern edges, good penetration, and a high degree of levelness and brilliance were obtained. The thickener was found to be compatible with alginate thickeners. The synthesis of maleic anhydride-alkyl vinyl ether copolymer with an amine. It is suitable for printing with vat, disperse, metal complex dyes, and pigments. [11, 12]

A copolymer of isobutene and maleic anhydride has been reported to be useful as a synthetic thickener

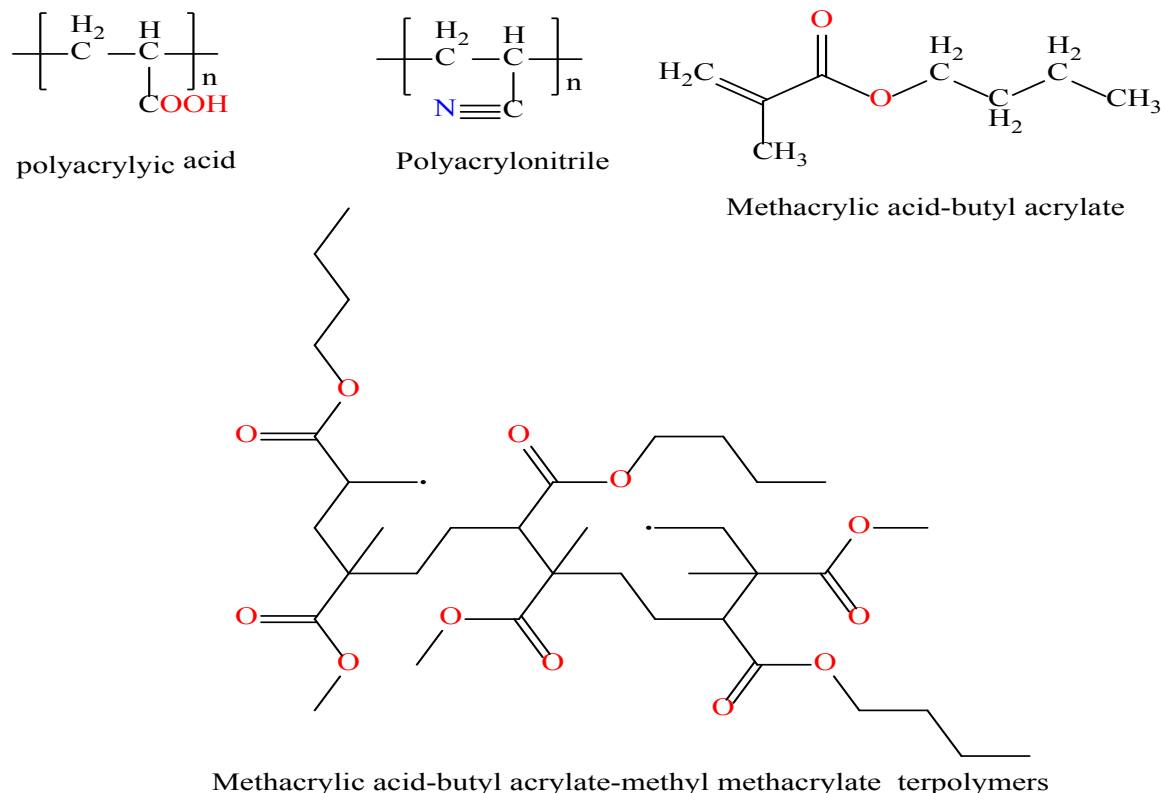


Fig. 1. chemical structure of Acrylic copolymer.

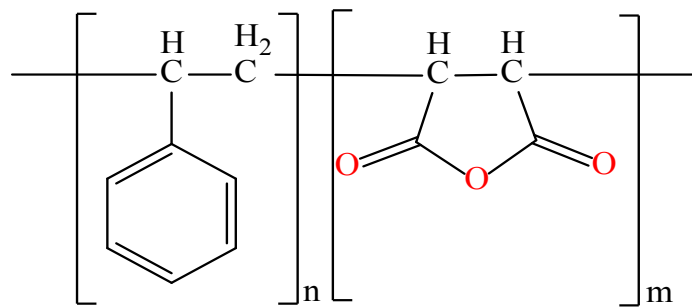


Fig. 2. chemical structure of Ethylene-Maleic Anhydride Copolymer.

for textile printing. (maleic anhydride) and the sodium salt of polymethacrylic acid has also been used as improved thickeners in textile printing. These synthetic thickeners are supplied in different forms (powders, dispersions, emulsions, etc.). In earlier days the synthetic thickening agents made up of high molecular weight polymers were delivered in powder form, which has many disadvantages. The inconvenience of dusting during weighing, the requirement of very high-speed stirring, and lump formation during paste preparation are some of the problems arising from the use of powdered polymers. Thus the use of a not-too-dilute pourable liquid was preferred. [3, 13]

Styrene (St) and butyl acrylate (BA) in both core and shell layers copolymer

They have been synthesized and employed in pigment printing pastes which were applied on 100% cotton and 65% cotton/35% polyester (PET) fabrics. The aim was to reduce the NMA content and the formation of free formaldehyde from pigment printing pastes by employing newly synthesized core-/shell-type polymers.

The synthesis of the core/shell latex has been completed in two steps, first of which is the synthesis of core and the second is the formation of shell over the core polymer.

The required amounts of anionic surfactant to

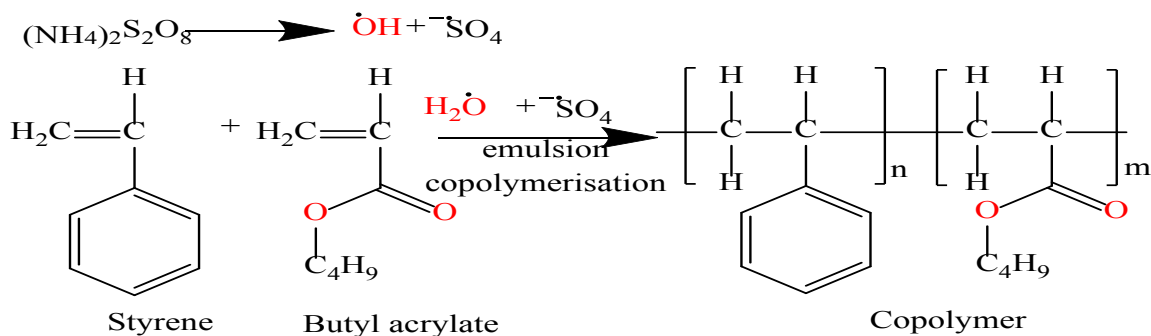


Fig. 3. chemical structure styrene (St) and butyl acrylate (BA) Copolymer.

form micelles and nonionic surfactant to increase the stability of the emulsions against freeze. and the crosslinking agents DAP and NMA, which contained AA, MAA and anionic and nonionic surfactants, and deionized water. The AA and MAA contributed to emulsion stability, DAP provided the crosslinking of the core, and NMA provided the crosslinking between binder and fabric during the printing process. [14]

Subsequently, 25% of the initiator solution and 5% of core pre-emulsion were introduced into the reactor and The remaining core pre-emulsion and initiator solutions were fed into the reactor at a constant flow rate.

The dry and wet rubbing fastness of printed fabrics has been tested with a crock meter according to The grayscale assessment. [15]

Before washing, spectrophotometric measurements were performed. The color penetration of the pastes has been calculated according to the literature procedure. The color penetration (P%) is the percent ratio of the color strength measured from the back of the fabric (K/S(back)) to the color strength measured from the front (K/S(front)). To determine the performance of the binders in the pastes, the printed fabrics were washed in a washing machine 5 times without drying. and this Table 3 clarifies the pigment printing paste.

TABLE 3. Recipe for pigment printing paste.

Ingredients	Weight percent
Binder	16
Defoaming agent	0.15
Amonia	0.35
Synthetic thickener	2.5
pigment	3
Water	Up to 100

Summary

Acrylic- or methacrylic-acid-based thickeners are the most commonly used synthetic thickeners. A bifunctional cross-linkable monomer is an essential component of synthetic thickening compositions to have a crosslinked polymer with a printable viscosity with a very low solids content (1-2%).

The emulsion polymerization technique is the most widely used synthesis technique for creating synthetic thickeners. Synthetic thickeners can replace natural as well as kerosene-based emulsion thickeners partially or completely with a minimum effect on the feel of the fabric. Most synthetic thickeners are highly sensitive to electrolytes, which makes them less suitable for printing formulations containing dyes with electrolytes.

Even though N-methylol acrylamide (NMA) improves the performance of the pigment printing paste, as mentioned earlier, it undergoes self-crosslinking reactions and evolves free formaldehyde. Therefore, the use of NMA in textile products is limited by standards. In this work, the aim was to decrease the NMA content and the development of free formaldehyde from pigment printing pastes with the help of newly synthesized core-/shell-type polymers. According to the experimental results, comparing with a single-phase commercial polymer which includes 4% NMA, it has been verified that employing a 30/70% (w/w) styrene acrylic polymer described here succeeds in decreasing the total NMA content without sacrificing the performance of the final product. [5, 16]

Acknowledgments

The authors are gratefully grateful to acknowledge to faculty of Applied Arts, Benha University. Thankful are also acknowledge to National Research Centre (NRC).

J. Text. Color. Polym. Sci. **Vol. 18**, No. 1 (2021)

References

1. El-Sherbiny, S. and Xiao, H., "Surface Characteristics of Coated Paper Improved by Plastic Pigments and Synthetic Thickeners". *MATERIALS AND INTERFACES*, **44**(26) 9875-9883 (2005).
2. Sinha, P., Datar, A., Jeong, C., Deng, X., Chung, Y.G. and Lin, L.-C., "Surface Area Determination of Porous Materials Using the Brunauer–Emmett–Teller (Bet) Method: Limitations and Improvements". *The Journal of Physical Chemistry C*, **123**(33) 20195-20209 (2019).
3. Bajaj, P., Goyal, M. and Chavan, R., "Synthetic Thickeners in Textile Printing: A Critique". *Journal of Macromolecular Science, Part C: Polymer Reviews*, **33**(3) 321-348 (1993).
4. Clarke, W. and Miles, L.W.C., "Synthetic Thickening Agents for Textile Printing. ". *Review of Progress in Coloration and Related Topics*, **13**(1) 27-31 (2008).
5. Solangi, W.H., Noonari, Z.A., Channa, A.A., Khan, M.Q. and Siyal, A.B., "Influence of Binders and Thickeners of Pigment Printing Paste on Light Fastness and Crocking Fastness of the Fabric". *International Journal of Science and Research (IJSR)*, **3**(5) 1024-1033 (2014).
6. Hussien, A., Abdelrahman, M., Wahab, S., Mashaly, H., Ali, s., Maamoun, D. and Khattab, T., "Review in Textile Printing Technology". *Egyptian Journal of Chemistry*, **63**(9) 3465- 3479 (2020).
7. Wetzel, W.H., Chen, M. and Glass, J.E., "Associative Thickeners". **248**, 163-179 (1996).
8. Iqbal, M., Mughal, J., Sohail, M., Moiz, A., Ahmed, K. and Ahmed, K., "Comparison between Pigment Printing Systems with Acrylate and Butadiene Based Binders". *Journal of Analytical Sciences, Methods and Instrumentation*, **02**(02) 87-91 (2012).

9. Kaczmarek, J.P. and Glass, J.E., "Synthesis and Characterization of Step Growth Hydrophobically-Modified Ethoxylated Urethane Associative Thickeners". *Langmuir*, **10**(9) 3035-3042 (1994).
10. EL-SHERBINY, S. and XIAO, H., "Effect of Polymeric Thickeners on Pigment Coatings: Adsorption, Rheological Behaviour and Surface Structures". *Journal of Materials Science*, **39**, 4487-4493 (2004).
11. Abdel-Halim, E.S., Emam, H.E. and El-Rafie, M.H., "Utilization of Hydroxypropyl Cellulose and Poly(Acrylic Acid)-Hydroxypropyl Cellulose Composite as Thickeners for Textile Printing". *Carbohydrate Polymers*, **74**(4) 938-941 (2008).
12. Abdel-Halim, E.S. and Al-Deyab, S.S., "Utilization of Hydroxypropyl Cellulose for Green and Efficient Synthesis of Silver Nanoparticles". *Carbohydrate Polymers*, **86**(4) 1615-1622 (2011).
13. Jassal, M. and Sajaj, P., "Developments in Acrylic - Based Thickeners as Substitute of Emulsion Thickeners for Pigment Printing". *Indian Journal of Fibre & Textile Research*, **26**, 143-155 (2001).
14. Gouveia, T.H.N., Públis, J.d.C., Ambrosano, G.M.B., Paulillo, L.A.M.S., Aguiar, F.H.B. and Lima, D.A.N.L., "Effect of at-Home Bleaching with Different Thickeners and Aging on Physical Properties of a Nanocomposite". *European Journal of Dentistry*, **10**(1) 082-091 (2019).
15. Eren, M., Akbulut, G., Senler, S. and Kayaoğlu, B.K., "Synthesis of Core-Shell-Type Styrene Acrylic Latexes with Low NMA Content and Their Application in Pigment Printing Pastes". *Journal of Coatings Technology and Research*, **15**(1) 121-129 (2017).
16. Dennis, F.J., "Evaluation of Sodium Polyacrylate Thickeners in Styrene-Butadiene Latices". *Journal of Industrial Textiles*, **7**(127) 85 (1977).

المثخنات الصناعية في طباعة المنسوجات

منه الله محمد رجب^١، احمد جمعه حسبو^٢، حنان علي عثمان^١

^١ قسم طباعة المنسوجات والصبغة والتجهيز، كلية الفنون التطبيقية، جامعة بنها، بنها، مصر
^٢ المركز القومي للبحوث، شعبة بحوث الصناعات النسيجية، قسم التحضيرات والتجهيزات للألياف السليلوزية،
٣٣ شارع البحوث (شارع التحرير سابقاً)، الدقي، ص. ١٢٦٢٢، الجيزة، مصر

تم استخدام بوليمرات حمض الميثاكريليك (*MAA*) - إيثيل أكريلات (*EA*) - إيثيلين جليكول ثنائي ميثاكريلات (*EGDM*) / *N*، *N*-ميثيلين بيساكرلاميد (*MBAM*) كمثخنات تركيبية في طباعة الصبغة على القطن. تم تصنيع البوليمرات المتشابكة بنسب تغذية مختلفة وتمت مقارنة سلوكها في الطباعة مع مثخن مستحلب الكيروسين التقليدي ومكثف صناعي تجاري *Alcoprint PTF* من حيث قيمة اللون، والاختراق الخلفي، والغسيل، والفرك (الجاف والرطب) وثبات الفرك، والمقبض. من القماش. مثخنات أساسها حمض الميثاكريليك (محتوى صلب ٤٪)، عند استخدامها كبديل لمستحلب الكيروسين، تنتج مطبوعات ذات ملمس قاس. لذلك، تمت تجربة الاستبدال الجزئي لمستحلب الكيروسين (٦٠-٨٠٪) ولوحظ تحسن كبير في التعامل مع القماش.