Surface modification of Pigment Blue 15:3 with aminosilsesquioxane oligomers for enhanced textile printing

H.A. Diab[a], S. A. Rashed [a] and O.A. Hakeim[b]

aTextile Research Division, National Research Centre, Dokki, Cairo, Egypt
bBeni-suef University, Faculty of Industrial Education, Textile Technology Department, Beni-suef, Egypt

Abstract:

Aminopropylsilsesquioxane oligomers (APS) encapsulated PB15:3 are formulated for *in situ* printing of cellulosic fabric and its blend. The encapsulation was developed by using various APS terminated groups; vinyl-sesquioxane (APSV) and methylsilsesquioxane (APSM) using the liquid-phase separation method. The characters of APSV-encapsulated pigments were examined by using thermal gravimetric analysis (TGA), Atomic force microscopy and electron microscope (SEM/TEM), Fourier transform infrared spectroscopy (FTIR) , dynamic light scattering (DLS), X-ray photoelectron (XPS). The characterization confirmed the successful encapsulation of PB15:3 into APSV. The vinyl terminated group in APSV provide a silicone formulations can be rabidly cured and crosslinked by UV or low thermal initiation to accelerate the driving force of the pigment printing process on cotton and polyester\cotton blend fabrics.The results showed that the encapsulated pigments improved the pigment print fixation on cellulosic fabric and its blend and decreased the requested amount of the binder and fixation temperature relative to the control sample. The colour strength and light fastness were greatly influenced by the mode of fixation and APS type.

Keywords: Aminopropylsilsesquioxane oligomers (APS); Vinyl terminated group; Cellulosic fabrics; UV irradiation and Pigment fixation.

1. Introduction

Pigment colorants have received much attention in different potential application; coating, printing and paint industries due to their excellent properties; photosensitivity, colour strength and transparency (1). Pigment coatings for textiles in dyeing and printing

have many advantages (2)., such as a simple and short product process, littlewastewater,

and low production cost.Howeverthe obvious drawbacks as the poor dispersion ability,

weather durability and the limited hiding powerare obviously the drawbacks for using organic pigments in manyapplications and conventional printing.Besides, the absence of their affinity for fibres necessitates the use of resinous binderto fix pigment particles on the fibre surface to acquire colourfastness (3,4).Pigment-based inks can be used to print most of fabric types, especially blend fabrics. They have many benefits with respect to dye-based inks such as simplicity of process, lower production costs, better productivity, improved color prediction, better water fastness and light fastness of the fabrics and reproducibility. Here too, the aforementioned problems as well as the coarse particles aggregates and clogging of head nozzles restrict their application (5-7).The pigment particles are easyto aggregate to form larger particles, due to the Van Der Waalsattractive forces, which represent a big disadvantage of pigments compared with dyes (8). Pigment agglomeration, thus significantly reduces the pigment efficiency, resulting in a lower quality. So, the feasible methods to overcome these drawbacks become the popular subject for study.Polymeric dispersantsduring the last years have proven good properties in stabilizing pigments in coating system (9, 10). However, the limitation related to the use of low molecular dispersants which can desorbed from the surface of the pigments at elevated temperature. As well as, the polymeric dispersants are easily getting tangled together after storing for a long time; have to be solved to avoid the poor stability (3). In recent years, more and morecopolymers have been synthesized and applied in pigment dispersions.Nano-scale organic pigments can be generated through ball milling or grinding pigments inthe presence of dispersing agent (11). Numerous studies on thepreparation, stabilization, and characterization of aqueous, well-dispersed pigment nanoparticle systems have been reported (12). Encapsulation of pigments with various polymers is the most prominent emerging application to enhance the pigment processing and prevent pigment agglomerations.Encapsulating the primary pigment particles with a layer of binder polymer, creating polymer shellsthat ensure the pigment particles remain separated during filmformation. It must be noted that a successful encapsulation technique should not impair the original color appearance of pigments but enhance their

dispersion. Many approaches of encapsulating organic pigments have been recently proposed, such as emulsion or miniemulsion polymerization, phase separation, layer-by-layerassembly, sol-gel and free radical precipitation polymerization. Moreover, some living materials such as macro-RAFT copolymer and polymerizable dispersant were also reported for pigment encapsulation (3, 13-15). The encapsulation of organic pigment into UV-curable resins using miniemulsion technique has been also studied by Hakeim and his co-workers (15-17). Liquid phase separation is a common encapsulation method for organic pigments and while often carried out in an aqueous medium. It wasachieved as follows: (1) the shell material was dissolved in solvent (A); (2) pigment powder, the core was well dispersed into the above solution; and (3) solvent (B), called a coacervation agent, which dissolves solvent (A) to partially desolvate but does not dissolve the shell material, is added to the dispersion.In this method, the pigment particles aregradually coated by partial desolvated molecular aggregates or the coacervates formed (14). The ink manufacturers are regularly used copper phthalocyanine pigment colours which are the universally organic pigments in textile industry, because they are coloristically very strong, extremely lightfast and weatherable (3). Water-borne silsesquioxane oligomers act as primers for metals, additives for acrylic latex sealants and as coupling agents for siliceous surfaces.They offer both organic group and silanol functionality. These amphoteric materials are stable in water solutions and unlike conventional coupling agents, have very low Volatile organic compounds (VOCs).Aminopropylsilsesquioxane oligomer-vinyl-sesquioxane copolymer (APSV) and Aminopropylsilsesquioxane-methylsilsesquioxane (APSM) oligomers are high molecular weight amino functional silicones with reactive silanol and amino functional group. They can readily form a stable polymer network because of its high aqueous solubility in addition to the presence of amino group. It shows a very unique combination of properties, unmatched by other polymeric systems because they form a very important bridge between organic and inorganic polymer chemistry (18).
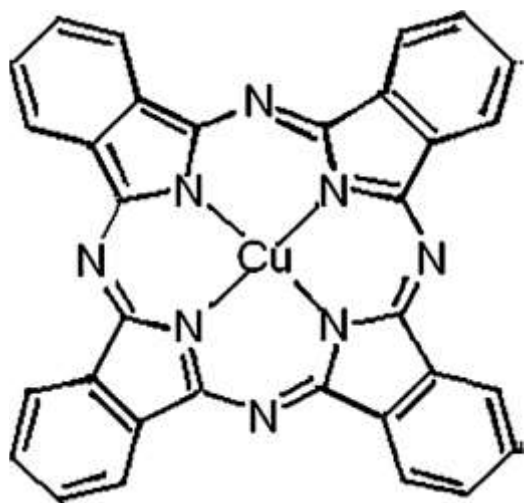
The current study aimed to develop a multifunctional and enhanced pigment prints on the cotton fabrics and polyester/cotton blend by encapsulation of pigment into Aminopropylsilsesquioxane oligomers. In this approach, C.I. Pigment Blue 15:3 (PB15:3) is encapsulated *via* phase separation method into aminopropylsilsesquioxane oligomers,

APSV and APSM using the liquid phase method.The assessment of encapsulation will be carried out using morphological observation, FT-IR and TGA and XPS. The influence of encapsulation as well as the functional hydroxyl and amino end groups of asminosilsesquioxane on the printing process of the printed fabrics will be determined. The main other concern is to find whether the presence of vinyl terminated groups in APSV could provide a silicone formulations which are capable of being rapidly cured and crosslinked by UV and low thermal initiation to accelerate the driving force of the pigment printing process on cotton and polyester\cotton blend fabrics.
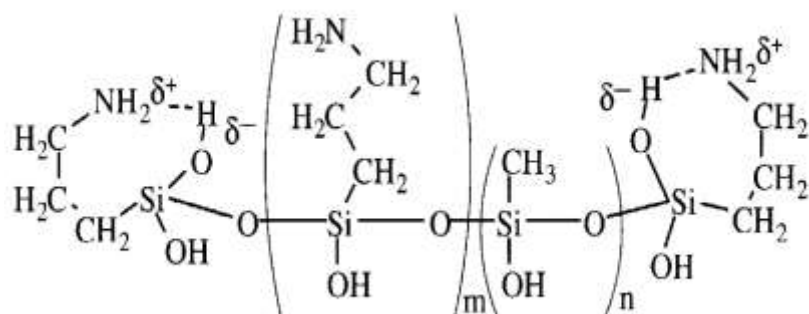
2. Experimental

2.1. Materials

Cotton and polyester/cotton50/50fabrics were supplied by Misr El Mahalla Co., Egypt. They were scoured by soaping with (2 g/l) nonionic detergent solution (Hocstapal CV from Clariant, Egypt) with a liquor ratio1:25, at $60\circ$C, for 45 min, followed by washing, and air dried.C.I. (Scheme 1) was supplied from Dye Star, Egypt. Water-borne silsesquioxane oligomers (Scheme 2),Aminopropylsilsesquioxane-vinyl-sesquioxane copolymer oligomer (APSV); 25-28% in water, viscosity 3-10 cP. And Aminopropylsilsesquioxane-Methylsilsesquioxane oligomer (APSM), 22-25% in water, viscosity 5-15 cP., were chosen in this work for encapsulation of pigment and purchased from ABCR Germany and, used without additional purification. Synthetic thickener Alcoprint (PTP) supplied by Clarient and Imperon Binder MTB (density ca. 1.03 g/cm3 and viscosity 35–70 MPas), acrylate based copolymer dispersion was supplied by Hoechst, Germany, are used in pigment printing. Firstcure DEAP Photoinitiator,2,2-Diethoxyacetophenone, available in liquid form and was supplied by Aldrich for UV Curing. Sodium persulphate, $Na_2S_2O_8$, was used as a radical initiator (Merck KGaA, Germany).Marlipal 13/80, non-ionic surfactant, C13-alcohol polyethylene glycol ether (8EO) was produced by SASOL Germany GmbH.All other chemicals and reagents usedwere of the laboratory grade.

Scheme1. C.I. pigment blue 15:3.   **Scheme2**. Water-borne silsesquioxane oligomers.

2.2. Methods

2.2.1. Preparation of Nano-scale pigment dispersion

Nano-scale PB15:3 dispersions were prepared according to Hakeim et al (14-17) by mixing 20 g of pigment with 200 ml distilled water and 2 g of Sodium dodecyl sulphate (SDS).This mixture was vigorously stirred, with a magnetic stirrer for30 min. The resulting mixture was then ball milled using Pascall Engineering (LQFS, UK) with 3-mm glass balls with ball: pigment ratio 100:1 for 48 h. The ball milled dispersion was then ultrasonicated using ultrasonic processor Vibra-Cell VCX500for 30 min at 65% amplitude.

2.2.2. Encapsulation of PB15:3 into aminosilsesquioxane oligomers

The encapsulation of pigment was carried out on the basis of aminosilsesquioxane oligomers /pigment weight ratio, 1:4. APSV or APSM (0.5 g) were dissolved in 40 ml of water; 2 g of PB15:3 was added to the above solution under stirring. The mixture was dispersed at 10000 rpm for 20 min with an Ultra-Turrax IKA T18 Basic instrument (IKA Instruments, Ltd.,

Staufen, Germany). Ethanol (40 ml) was mixed with the mixture at the rate of 5 ml/min. The resulting dispersion was centrifuged to produce slurry. Finally, the slurry was filtered, washed three times with distilled water; it was then dried at 60°C to obtain APS-encapsulated pigment powder.

2.2.3. Alkaline Pre-treatment of Polyester Prior to pigment printing

The adhesion improvement of APS-encapsulated pigment to polyester/cotton is performed by an alkaline pre-treatment of polyester/cottonin water solution containing 5 g/L of KOH for 30 min at 90°C with a liquor ratio 1:25. Subsequently, the samples were rinsed twice in cold tape water and then dried at room temperature.

2.2.4. Pigment printing

The paste formulations for pigment printing of cellulosic fabrics and its blend were prepared by adding the synthetic thickener (PTP, 25 g/kg) stepwise to water with stirring then the desired amounts of binder (MTB); 100 g/kg for conventional organic pigment and (25,50 or 100) g/kg for APSV or APSM-encapsulated pigment was then added followed by addition of acid catalyst, diammonium phosphate (5 g/kg) in case of conventional or APSM-encapsulated pigment printing. Finally 25 g/kg of pigment was added to the stock thickening. A water-soluble thermal or photo initiator, (5 per cent on weight of APSV-encapsulated pigment composition) was added in case APSV-encapsulated pigment.The printing pastes were applied to fabrics through a flat silk screen. After printing, the printed fabrics with conventional pigment were subjected for drying followed by thermal curing at 150°C for 5 min. One series of APSV-encapsulated pigment prints weredried at RT, and finally cured at temperatures of 80 °C for 5 min in an automatic thermostatic oven, produced by Warner Mathis, Switzerland. Another series of APSV-encapsulated pigment prints were air dried in a dark place at RT, and then one side of samples UV irradiated (UVATEC, Honle UV technology, Germany) using a KrCl excimer lamp (Heraeus, Germany).The printed samples were then washed with aqueous solution containing (2 g/L) non-ionic detergent at 60°C for 15 min.

2.2.5. Method for preparation of thermal and UV cured of APSV-encapsulated pigment film

APSV-encapsulated pigment powder, a water-soluble thermal or UV initiator (5 per cent on weight of APSV-encapsulated pigment) were mixed with 1 g/l Maripal, and then homogenized. It was drawn on aluminium foil with abar coater of 50mm wet film thickness. The wet film was dried at reduced pressure in a vacuum oven at 608C for 3 h. The APSV-encapsulated pigmentthermal cured filmwasdried at RT, and finally cured at temperatures of 80 °C for 5 min in an automatic thermostatic oven. The UV cured filmwasair dried in a dark place at RT, and then UV irradiated.

2.2.6. Color strength

Spectral reflection measurements of the dyed fabrics were carried out using a recording filter spectrophotometer. The color intensity expressed as K/S values of the printed samples were determined by applying the Kubleka-Munk equationat λ max 580 nm for pigment blue color and 625 nm for pigment green:

$$K/S = (1 - R)^2 / 2R \quad - \quad (1 - R_0)^2 / 2R_0$$

Where R is the decimal fraction of the reflectance of the dyed substrate, R_0 is the decimal fraction of the reflectance of the unprinted substrate, S is the scatteringcoefficient, and K is the absorption coefficient (19).

2.2.7. Fastness properties

Washing fastness tests were conducted according to the specified method, BS1006:C02 (20) Test 2 with a soap solution (5 g/l, liquor ratio = 50:1) for 45 min at 48–50◦C. The light fastness test was carried out according to the standard methods for determination of colorfastness of textiles using carbon-arc lamp, continuous (21).

2.2.8. Method of ultracentrifuge sedimentation velocity runs

Ultracentrifuge sedimentation velocity run was done bydispersion of 0.25 g APSV-encapsulated pigmentfilm in 25 ml of acetone as a solvent for pigment. This run was carried out for 30 min at room temperature.This test was adopted to give a supporting evidencefor encapsulation of Pigment Blue 15:3.

2.2.9. Characterization

Morphologies of original and encapsulated pigment werecharacterized by Atomic force microscopy (MMAFM-2; Digital Instruments, USA).They are exposed for plasma etching (plasma cleaner) for 60s before AFM observation to increase the clarityof morphological view. Transmission electron microscope (TEMJoel-JEM-1200, Japan) was also used for characterization of encapsulated pigment. One drop of pigment dispersion was diluted with distilled water and placed on 400-mesh carbon-coater copper grid, and dried in air. The particle size and droplet size as well as polydispersion index (PDI) were determined bylaser diffraction technique, DLS using ALV/CGS-3 goniometer with ALV/LSE-5003 auto correlator; ALV, Germany. Digital photographs were taken using digital camera (Sony DSC-V1).Thermogravimetric analyses (TGA) were performed using TGA 7 series (Perkin Elmar, USA), with a heatingrate of $5 \circ$C/min under air atmosphere. Fourier transform infraredspectra (FTIR) of were recorded on a Nicolet Nexus 560 FTIR spectrometer. X-Ray photoelectron spectroscopy (XPS) measurements were carried out using ultra Axis TM Spectrometer (Kratos Analytical). Spectra were collected with 144 W. Reference line: aliphatic/aromatic carbon (C-C, C-H or Carbon) of C 1s photo line by 285 e V. The elementary concentration is given in atomic%. The information depth for amino silicones using this analytical method is approximately 10 nm.

3. Results and discussions

Pigment surface modification provides a way to impart new and diverse properties to pigment printing while saving time; energy and auxiliaries. This work is designed to be focused on developing multifunctional encapsulated phthalocyanin pigment blue onto Aminopropylsilsesquioxane oligomer for in situ fabrication printing using thermal and UV curing.In practice, amino functional silicones are widely used in the textile industry for functionalization of cotton. Because of the interaction of amino groups with textile materials, amino functional siloxanes, the wall shell materials encapsulating the pigment are physically adsorbed onto fibre surfaces. This adsorption feature improves their durability during the washing process and the ionization of amino group provides strong attraction to the fabric.The crosslinking rate of a silicone polymer network formulation and its extent of reaction are important factors that determine its performance in a coating. The presence of vinyl terminated

groups in APSV have been developed a silicone formulations which are capable of being rapidly cured by thermal or UV irradiation in an attempt to decrease the curing temperature and exploring the rate of crosslinking and its effect on the printing with encapsulated pigment. This could be accelerated the pigment fixation on the cellulosic fabrics and its blend, reduces the amount of the binder and eliminating the high temperature cure and the acid catalyst. This opens up possibilities to solve the problems of the high temperature process, energy waste, material cost and avoiding the risk of destroying substrates at a high temperature.

3.1. Morphology and size distribution of encapsulated pigment particles

The influence of encapsulating agents, aminosilsesquioxane oligomers on the dispersion stability level of pigment plays an important role in the application of pigments. The ability of shell material to prevent pigment aggregation both during milling and long time storage is critical in preparation of pigment dispersions. The stability of original and APSV or APSM encapsulated phthalocyanine blue pigment before curing and fixation on textile fabrics were estimated by observing the color sedimentation with time. The more stable the dispersion, the lower the height of settled phase.Photographs taken of the color formulation after 15 days of storage at room temperature (RT), Fig. 1. It was shown from the results that APSV as encapsulating agent is of practical importance because it has the ability to achieve a high degree of dispersion and provided excellent stability for color formulation in storage and no significant pigment sedimentation was occurred during storing.

Fig.1. Photograph of shelf life stability of (a) APSV encapsulated pigment; (b APSM encapsulated pigment and (c) Nanoscle C.I. Pigment blue 15:3, after 15 days of storage at RT.

On the other hand, the APSM -encapsulated pigment blue was less uniformly dispersed with soft aggregation. On the contrary, the unencapsulated pigments showed pigment particle that are highly agglomerated in storage. This may be due to the characteristic feature of pigment which tend to coagulate or flocculate in storage due to the attractive pigment–pigment interaction. The results revealed that the encapsulation of pigment improves the pigment dispersion stability. The good stability arisen from the voluminous shells or intensified charges around pigment surface relied to the encapsulating agents, thus preventing flocculation and coagulation of the pigments.

In Fig. 2, three AFM photographs show the surface microstructure of nano-sized PB15:3 (Fig. 2(a)), APSV encapsulated pigment dispersion (Fig. 2(b)) and APSM encapsulated pigment dispersion (Fig. 2(c))
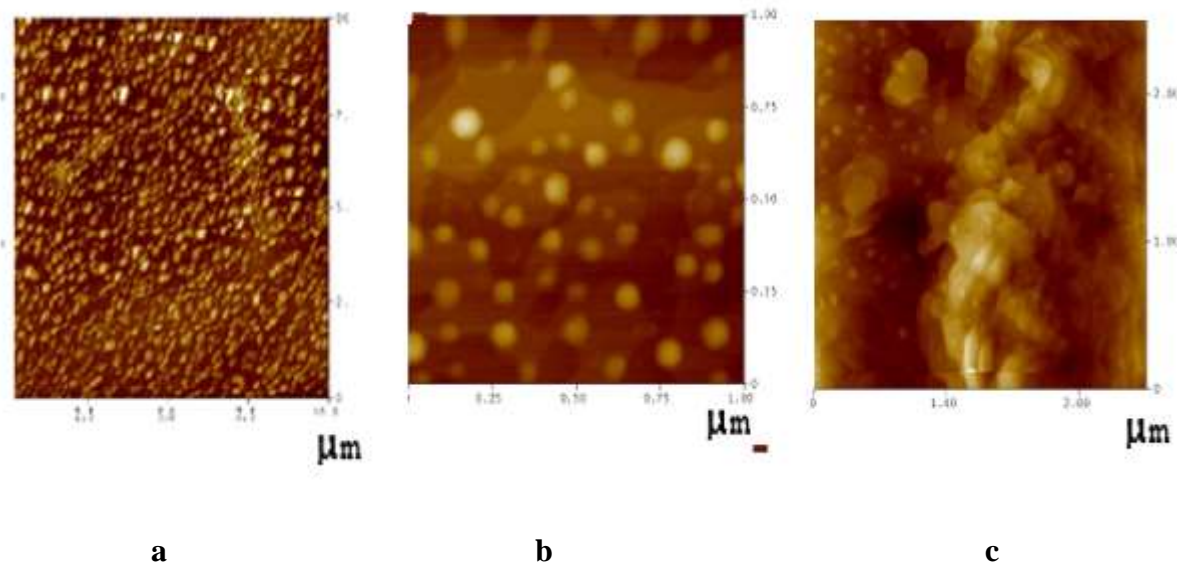

| a | b | c |

Fig. 2. Topography AFM images: (a) Nano-scale C.I. PB15:3 dispersions; (b APSV encapsulated pigment dispersion and (c) APSM encapsulated pigment dispersion.

The Topography AFM shows that, the morphologies of the encapsulated pigment obtained here are spherical, which somewhat different from the nano-sized pigment. As shown in Fig. 2b the height between the edge and interior part of the capsule are different and the presence of voids in the center of some encapsulated pigments. Here too, The AFM results were matched with shelf life stability in Fig. 1.It can be seen that the particles of APSV- encapsulated pigment dispersion were uniformly dispersed with negligible aggregation compared with Nano-scale C.I. PB15:3 dispersions and APSM encapsulated pigment dispersion. Morphological observation original and encapsulated pigment particles were also investigated using TEM images in Fig. 3. It can be seen that APSV- encapsulated pigment particles (Fig. 3(b)) were dispersed in a core–shell structure with negligible agglomeration. It is also seen in Figs. 3(c) that, soft agglomerates, assemblies of APSM- encapsulated particles held together by weak interactions was observed.
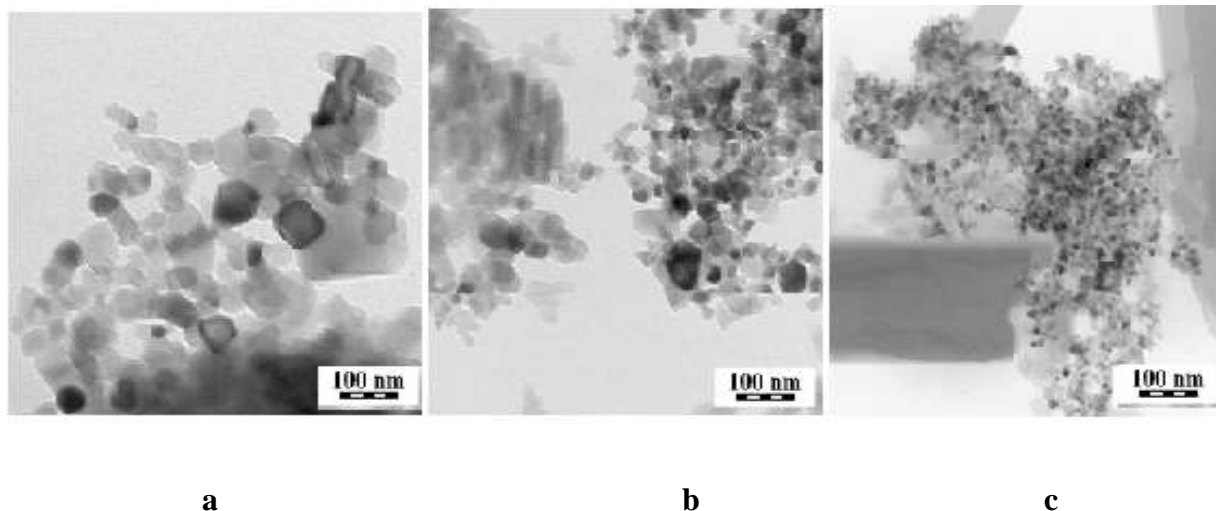
a   **b**   **c**

Fig.3.TEM photographs of (a) Nanoscle C.I. Pigment blue 15:3; (b APSV
encapsulated pigment dispersion and (c) APSM encapsulated pigment dispersion.

Generally speaking, APSV encapsulated pigment dispersion is electrically more stable than APSM encapsulated pigment dispersion. This may be due to that the molecular structure including the methyl groups in APSM may affect the colloidal stability of the latex and can also influence the morphology of encapsulated pigment produced, as in so-called core-shell particle. This led to the formation of inhomogeneous hybrid composite particles. This induction period was eliminated when APSV was utilized.
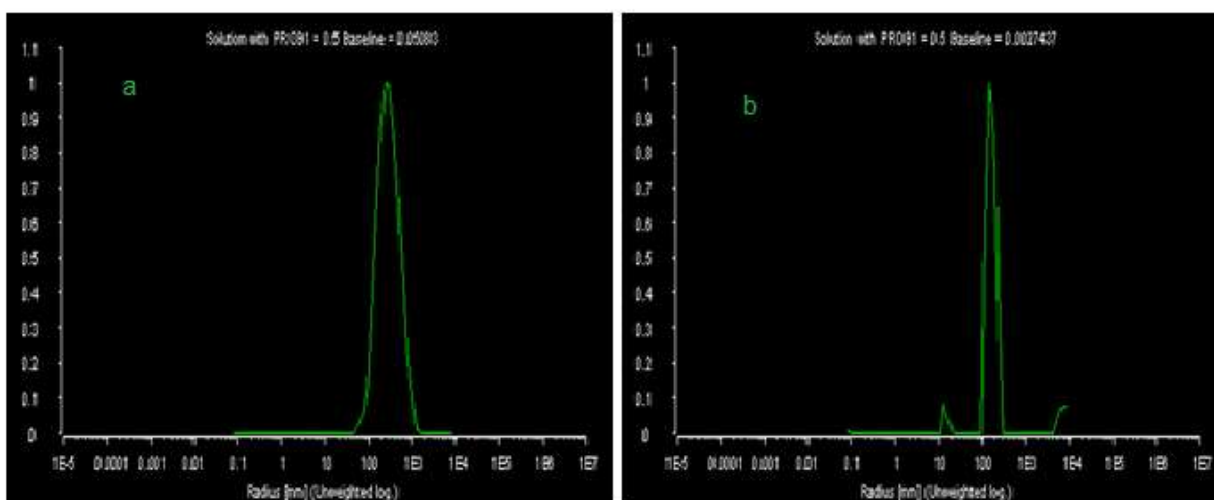

Fig. 4.particle size distribution for: (a) APSV encapsulated pigment and b) APSM encapsulated pigment.

The particle size distribution (PSD) in Fig 4 clarifies the effect of molecular structure of aminosilsesquioxane oligomers on particle size. It is obvious that PSD of APSM encapsulated pigment dispersion is bi-modal and consists of a minor fraction in the size range (< 100 nm) and a major fraction in the size range (> 300 nm). It is worthwhile to notice here that a hard agglomeration and the broad particle size of APSM encapsulated pigment dispersion were indicated from the high polydispersity indexes (PDI) values (~0.5). The results revealed that APSV encapsulated pigment had a single modal distribution of particles (Fig.4 a), which in turn, enhances the dispersibility of pigment particles. Moreover, the results of PDI for APSV encapsulated pigment (~0.2) clearly demonstrated that the high dispersion stability of APSV encapsulated pigment. This reflects the uniformly dispersed with soft aggregation of APSV encapsulated pigment compared with APSM encapsulated pigment which were matched with TEM images. It is clearly seen that the results of particle size of DLS are bigger and not consistent with TEM results. It was assumed that the TEM gives the size of nanoparticles in dried form where the hydration layer is not present while DLS tells the hydrodynamic diameter that includes core plus any molecule attached or adsorbed on surface as the liquid layer or any coating material is attached to the surface. Besides, TEM is a count based technique, and will thus show stronger confirmation of the smallest components in the size distribution, however DLS is intensity based technique, and this puts higher emphasis on the larger particle sizes.

3.2. Pigment printing

Pigment printing is one of the most common printing methods for many uses and for the easiest and simple method of application. They have no affinity for any fiber, used in a finely dispersed form and the film forming binders are used to fix these pigments to the surface through crosslinking reactions. The high molecular weight binders, based on acrylates, vinyl acetate, etc., are essential components for printing by thermal curing and are responsible for the harsh felling effect and lower crockfastness of the pigment prints. Moreover, the necessary high curing temperature, about 150∘C is a common risk for destroying some of the fabrics which may be deteriorated and cannot tolerate under the high temperature. The pigment printing on cotton and polyester/cotton (PES/CO) blend fabrics using APSV or APSM encapsulated pigments was compared with the pigment printing using the original color, to evaluate the difference of coloration performance of encapsulated and conventionally pigment color. The pastes for printing of cotton and its blend with encapsulated and original pigments were prepared by blending the pigment colors, with

binder (25, 50 and 100 g/Kg) and the synthetic thickener at the same color ratio. The printed conventional or APSM encapsulated pigments were fixed at 150◦C for 5 min. The prints of APSV- encapsulated pigment were subjected for drying at RT and finally cured at temperatures of 80 °C for 5 min in presence of thermal initiator or UV irradiated in presence of photoinitiator. The presence of vinyl terminated groups in APSV has prompted us to explore the development of silicone formulations which are capable of being rapidly cured and crosslinked on the surface of the fabrics by thermal or UV irradiation. This could be used to overcome the drawbacks of the pigment printing process by lowering the high curing temperature and the amount of binder used. Furthermore, the acid catalyst could be eliminated in this study without any side effect on cellulosic fabrics. The earlier alkaline pretreatment of (PES/CO) increase the adhesion of APSV to the surface of PES/CO, because of the absence of active group in polyester. The pretreatment in an alkaline solution containing 5 g/l KOH is permitted

Table 1

      K/S, washing and light fastness properties of original and APSV or APSM encapsulated pigments

printed cotton and polyester/cotton fabrics

Pigment color			K/S	Washing[a] fastness (Rating)			Light Fastness[b]	Handle
				Alt.	SC.	SW.		
Original	Co		7	4-5	4-5	4-5	5	H
	PES/CO		8	4-5	4-5	4-5	5	H
APSM 25	Co		8	4	4	4	6	S
	PES/CO		9	4	4	4	6	S
APSM 50	Co		9.5	4-5	4-5	4-5	6	S
	PES/CO		10	4-5	4-5	4-5	7	S
APSM 100	Co		10	4-5	4-5	4-5	6	S
	PES/CO		10.4	4-5	4-5	4-5	7	S
APSV 25	Th.	Co	12	5	5	5	7	S
		PES/CO	12.6	5	5	5	7	S
	UV	Co	11.3	5	5	5	7	S
		PES/CO	11.5	5	5	5	7	S
APSV 50	Th.	Co	12.8	5	5	5	7	S
		PES/CO	13	5	5	5	7	S
	UV	Co	11.9	5	5	5	7	S
		PES/CO	12.5	5	5	5	7	S
APSV 100	Th.	Co	12	5	5	5	7	S
		PES/CO	12.6	5	5	5	7	S
	UV	Co	11.2	5	5	5	7	S
		PES/CO	12.3	5	5	5	7	S

.

Alt. is the alteration, Sc is the staining on cotton, Sw is the staining on wool.

APSM 25 , APSM 50 and APSM100, printing using 25, 50 and 100g /Kg of binder respectively

APSV 25, APSV 50 and APSV100, printing using 25, 50 and 100g /Kg of binder respectively

Th. is the printing with APSM-encapsulated pigment under the thermal initiation

 UV is the printing with APSV-encapsulated pigment under UV initiation

aWashing fastness rating 1–5.

bLight fastness rating 1–8.

Table 1 shows the effect of encapsulation as well as the mode of print fixation on the color performance of printed cotton and polyester/cotton fabrics under the effect of energy, time and auxiliaries. Tables 1 clearly demonstrates that encapsulation of pigment using APSV or APSM enhances the colour strength of pigment prints regardless the type of fibre. It seems that the unfavourable amount of binder; 50 g/Kg, the half of the conventional amounts was adequate for conventional printed samples with APSM-encapsulated pigment to accomplish the required print

fixation that can bring about reasonable color strength. Besides, the APSM encapsulated pigment samples attained higher color strength than the original samples under these conditions. On the other hand the unfavourable printing conditions are not adequate for conventional unencapsulated samples to achieve the printing fixation balance for printed samples. The results revealed that the curing temperature of APSV-encapsulated pigment prints can be decreased in presence of thermal initiator from 150 to 80 °C. Furthermore, the required printing balance and color strength on cotton and PES/CO fabrics printed with APSV-encapsulated pigments was attained at low thermal fixation temperature and reduced amount of the binder (25 g/Kg) , compared to the conventional amount 100 g/Kg as well as elimination of acid catalyst. The un-encapsulated pigment looks to need conventional conditions of temperature, time and auxiliaries to reach equilibrium printing compared to the APSV-encapsulated pigment. Thermal initiator is used as a crosslinking initiator in presence of vinyl groups in APSV. Without thermal initiator additives; APSV incorporated the pigment is solidified on the surface of the fabrics via a reaction between the vinyl groups and C–H bonds of fabrics which occurred at higher temperatures (conventional thermal curing). When a thermal initiator is added, the solidification of APSV is via a crosslinking, in which the initiator is first broken into free radicals by thermal energy; the radicals then attack the double bonds of the vinyl groups of APSV to start a chain reaction of crosslinking between the APSV molecules and fabrics. In such radical-induced crosslinking which can occur at lower temperature. This could be the driving force for acceleration of APSV-encapsulated pigment printing under the unfavourable conditions of time, energy and auxiliaries. The presence of APSV crosslinking shell around the pigment surface decreased the inquiries of self crooslinker binder. It is worthy to mention that the thermal energy for curing of APSV-encapsulated pigment prints at 80 °C supplied for 5 min in presence of thermal initiator and less amount of binder is adequate to accomplish the required printing balance that can bring about reasonable colour strength. It was appeared that the increase of binder would be accompanied by generation of free radicals simultaneously, which may lead to the formation of short carbon chains. The efficiency of crosslinking is relatively difficult to grow from such short carbon chains. This can be reflecting on the reason for the sudden decreases of the colour strength of printed fabrics upon the increase of binder beyond 25%. It was therefore necessary to understand the possibility of UV curing for formulations containing APSV-encapsulated pigment, DEAP photoinitiator and less amount of binder.

Scheme3. Mechanism of photoinitator formulation

The photopolymerization of APSV-encapsulated pigment induced by UV- irradiation in presence of photoinitiator (Scheme 2) will increases the crosslinking of encapsulated pigment on the surface of the fabrics which in turn increases the color strength. Here too, a maximum radical concentration was reached with photoinitiator in presence of 25 g/Kg of binder without the need of acid catalyst, while higher concentrations of binder became less effective, due to radical– radical encounters which could give rise to various other secondary reactions. And presumably lead to the occurrence of lower level of effective cross linking between different polymer chains of APSV on the surfaces of fabrics; as a result, the colour strength will be decreased. Generally speaking, the result also reveals some variation between the different kinds of fabrics in the colour strength value acquired. This may be attributed to the variation between them in their weight and fibre physical properties.

Table 1 shows the light and washing fastness of the printed cotton and PES/CO samples with original and encapsulated pigment. It is clear that the printed samples had an excellent washing fastness within the range of 4-5, irrespective of the type of APS and fabric. Furthermore, APSV-encapsulated pigment prints displayed higher light fastness (7) than that in case of APSM-encapsulated pigment prints (ranged, 5-6). This may be due to that the increase of the crystalinity which generated from the thermal or UV radicals' initiation could resist the photo phading of the colors on the surface of cellulosic fabrics. It is also observed that the overall encapsulated pigment exhibited a soft handle compared to the original ones has a harsh feeling. It could be concluded that APSV-encapsulated pigment can accelerate the pigment printing process at low fixation temperature and reduced the amount of binder as well as eliminating the acid catalyst. For this in mind, the characterization of APSV-encapsulated pigment is the best of choice in the next studies.

3.3. Characterization of APSV-encapsulated pigment

In this context the UV-cured of APSV-encapsulated pigment film was subjected for characterization. Encapsulation of PB15:3 with APSV produces a core/shell structure and the impeded pigment should be successfully incorporated into the APSV shell. Otherwise, the unincorporated pigment would be either flocculated and sediment or adsorbed onto the surface of APSV as a result of the high hydrophobicity of the organic pigments. A film of APSV-encapsulated pigment, UV irradiated was assessed by the ultracentrifuge sedimentation test and compared with original pigment. Acetone; a solvent of the core pigment, PB15:3 and non-solvent of the APSV, was added to a film of encapsulated pigment or the original one and left to run in ultracentrifuge for 30 min. The supernatant after the ultracentrifugation was found to be colorless (Fig. 5b); while the unencapsulated pigment dissolved in acetone (Fig. 5a). This proved that PB15:3was completely encapsulated into APSV, and not physically adsorbed to its surface. It is also found that the colors of the encapsulated pigments are not impaired by the APSM, which indicating the retain of color performance under the encapsulation process.

Fig. 5. Digital photograph of: (a) original PB15:3 and (b) encapsulated PB15:3 ultra-centrifuged with acetone for 30 min.

FTIR spectra of original and UV-cured of APSV-encapsulated pigment film are shown in Figure 6. The FTIR spectrum of encapsulated pigment indicated the presence of wide peak at 3200 cm-1, is attributed to 1 are characteristics of the C=C bonds from the vinyl group of the APSV. The peak at 1124 cm− the characteristic absorption −NH2 groups in APSV. The peaks located at 1606 and 1410 cm–1 illustrates the presence of Si–O–Si bonds. An additional peak is also observed at 667 cm–1 and is attributed to Si–O–Si symmetric stretch. The band at 1273 cm- is the typical signal of Si-C bond in Si-CH2 of long chain bridges of propyl- silicone. The results also revealed that the most of characteristic band in FTIR spectra of original pigment are suppressed from the spectra of the encapsulated pigments. This is attributed to the shielding effect arising from the APSV shell.

Thermal stability of original pigment particles and APSV encapsulated pigments was followed by TGA within the range from 50 to 800∘C in Fig.7. It is clearly seen that the thermal decomposition of composites in APSV encapsulated pigments was shifted towards higher temperature range than that of the original pigments. This reflects the increase of thermal stability for organic pigments after encapsulation onto APSV. Besides, the APSV encapsulated pigment is thermally stable up to 200 ∘C. which is very similar to the thermogram of APSV that fit the complete coverage of pigments. This may be attributed to the much higher resistance to thromolysis for the crosslionked and UV cured APSV-encapsulated pigment structures shell around the pigment. It is clear that the original pigment contain higher water content than APSV

encapsulated pigments, where it has a distinctive decomposition below 200∘C This distinct mass losses could be corresponding to the loss of physically adsorbed water (moisture), or the loss of some volatile moiety (or moieties).
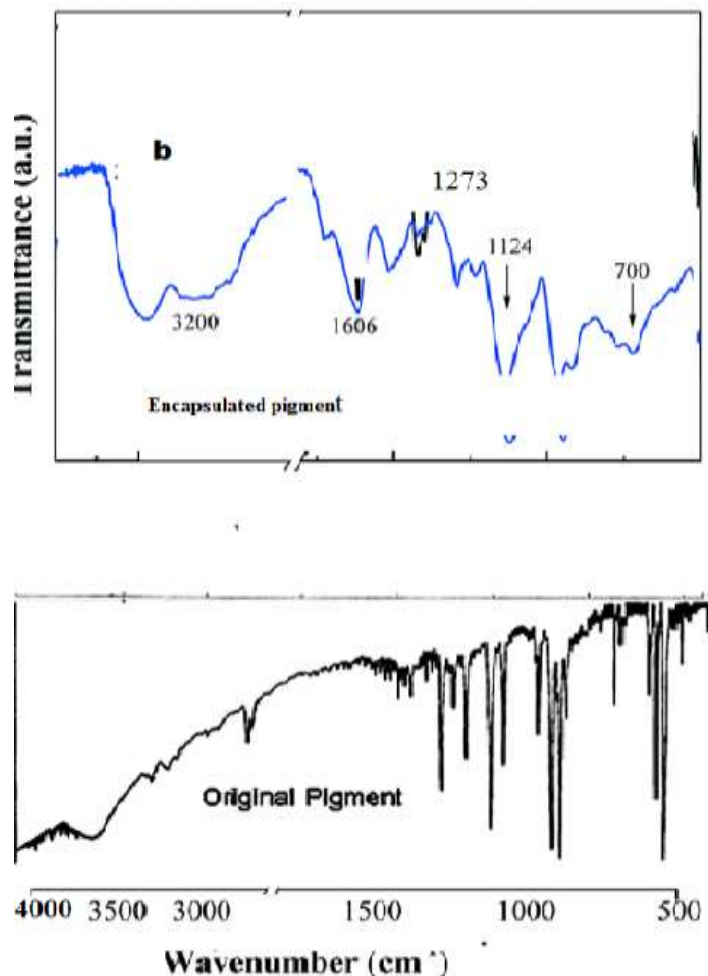

Fig. 6. FTIR spectra of PB15:3 and APSV-encapsulated pigment.

Besides, the first weight loss of~ 20% in the encapsulated pigments was observed in the temperature range of 300–450∘C that was attributed to the decomposition of APSV in the composite. It is worthy to mention that the onset temperature of thermal decomposition of PB15:3 after the removal of physically adsorbed water start at temperature of 450∘C to ~650∘C, which is the second weight loss ~80% in the themogram of encapsulated pigments. Therefore, it can be concluded that the pigments were successfully encapsulated onto APSV and consistent with the weight ratio of pigment to APSV, 4:1 as was cited in the experimental section.
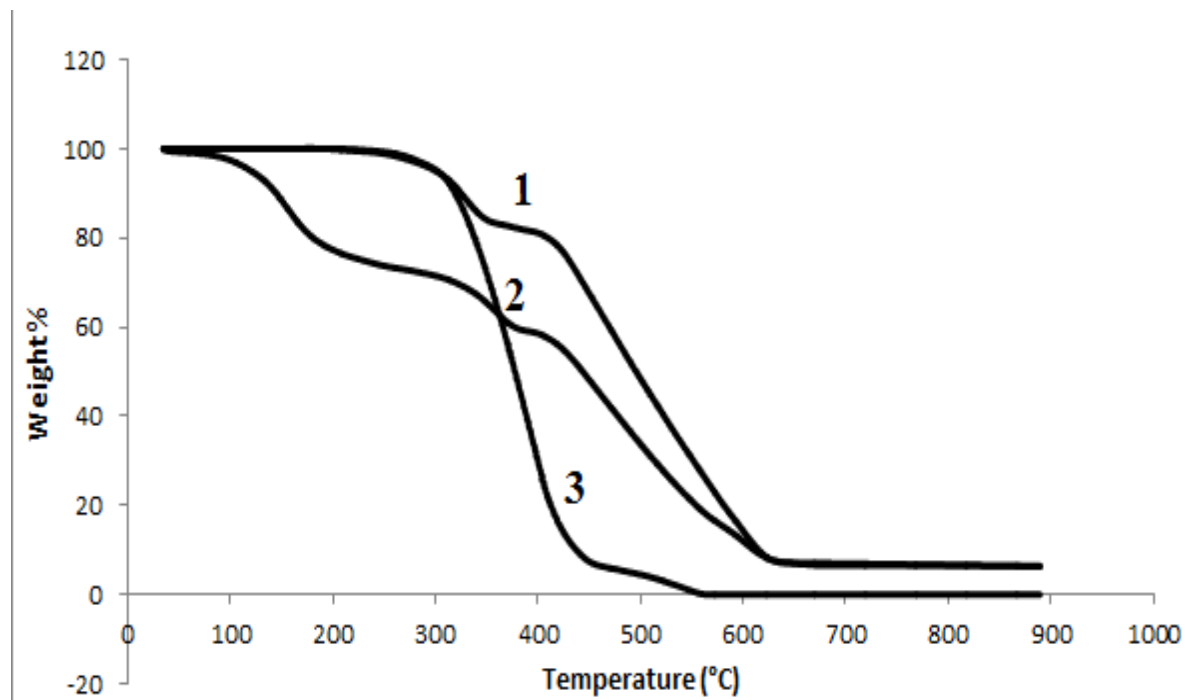
Fig.7. TGA thermographs of: (1) APSV-encapsulated pigment, (2) original PB15:3 and (3) APSV.

3.4. XPS characterization

The XRS spectrum was served for UV cured film of APSV-encapsulated pigment to confirm the effective encapsulation of pigment. Fig. 8 clearly proved the coverage of pigment with APSV shell. The surface sensitive technique detects the elementary composition of APSV in the encapsulated pigment. The results showed a significant increase of silicone and nitrogen content about 13% and 1.5% respectively in the encapsulated pigment attributed to the APSV shell. Besides the appearance of the elemental oxygen compositions in the encapsulated pigment can be relied to hydroxyl groups in the APSV shell. The absence of elemental composition of copper in original pigment, may be due to the chelation of copper with the hydroxyl groups in APSV. This result gave a supporting evidence for encapsulation of PB15:3 onto APSV.
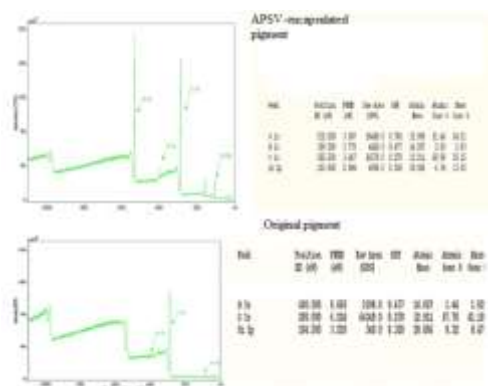
Fig.8. XPS spectra of original and APSV-encapsulated pigment

4. Conclusions

PB15:3 was encapsulated onto aminopropylsilsesquioxane oligomers, APSV and APSM with using a liquid-phase separation method. The APSV-encapsulated pigments were subjected for thermal and UV initiation without the need of acid catalyst in an attempt to accelerate the pigment printing on cellulosic fabrics and its blend. The characterization using different analytical tools gave supporting evidences for the successful encapsulation of pigments. APSV-encapsulated pigment dispersion were uniformly dispersed with negligible aggregation compared to APSM-encapsulated pigments. The results showed that the APSV encapsulation of pigment under the thermal or UV irradiation is a driving force for enhancement of pigment printing process in absence of conventional conditions. The presence of crosslinking shell, APSV around the pigment surface decreased the requirement of self crooslinker binder and the fixation temperature. Cotton and polyester/cotton blend can be printed with thermally or UV initiated APSV-encapsulated pigment at low fixation temperature and used a reduced amount of binder, 25 g/Kg without the use of acid catalyst. It can be concluded that the un-encapsulated pigments seemed to need a conventional condition of time, temperature and auxiliaries in order to get reasonable color strength. The crosslinked pigment color on the surface of the fabrics increased the color strength and light fastness.

References

1-Yuan, J. J., Zhou, S. X., You, B., & Wu, L. M. (2005). *Chemistry of Materials, 17*, 3587–3594.
2- Fang , K.J., Wang C.X., Zhang X. and Xu Y., , ColorationTechnology. 121 (2005) 325–329.
3- Haroun ,A. A., Diab, H.A. & Hakeim, O.A. (2016).C. *Carbohydrate* Polymers,146, 102–108.

4- Xue, C. H., Shi, M. M., Chen, H. Z., Wu, G., & Wang, M. (2006). *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 287*, 147–152.

5-Abdou, L. A. W., Hakeim, O. A., El-Gammal, M. S., & El-Naggar, A. M. (2009).. Journal of Applied *Polymer Science, 111*, 1892–1899.

6- Yuen, C. W. M., Ku, S. K. A., Kan, C. W. & Choi, P. S. R. (2007).. .*Fibers and Polymers*, *8*, 625-628.

7- Herbst, W., & Hunger, K. (2004). *Industrial organic pigments*. Germany: Wiley–VCH,Verlag GmbH.

8- Tiarks, et al. (2002) , Macro-mol. Symp. 187 739–752.

9- Fujitani, T. (1996), Progr.Org. Coating., 29, 97–105.

10- Khan ,A.U., Briscoe, B.J., Luckham, P.F. (2000), Colloids Surf. A: Physicochem. Eng. Aspects, 161, 243–257.

11- Cheng, W.T., Hsu, C.W., Chih, Y.W. (2004), J. Colloid Interface Sci., 270 ,106–112.

12- Sun, D. Li, G. (2007), Dyes Pigments, 72, 144–149.

13- Fu, Ѕ., Xub, C., Duc, C., Tiana ,A. & Zhanga, M. (2011). *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *384*, 68–74.

14- Hakeim, O. A, Arafa, A.A. & Abdou, L.A.W. (2015). *World Journal of Textile Engineering and Technology, 1*, 1–22.

15-Hakeim, O. A., Diab, H. A., & Adams, J. (2015). *Progress in Organic Coatings, 84*, 70–78.

16- Hakeim, O. A, Fan, Q. & Kim Y. K. (2010). *Pigment &Resin Technology, 39*, 3-8.

17- Hakeim, O. A., Arafa, A. A., Zahran, M.K. & Abdou, L. A. W. (2014). *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 447,* 172–182.

18- Hakeim, O. A., El Zawahry, M.M., Nermin M. Aly, El-Hawary, N.S., Diab ,H.A. and Ali Marwa (2015), Journal of textile Association , July-August,76,2, 90-101.

19-Judd, D., & Wyszecki, G. (1975). *Colour in business, science, and industry*. NY, USA:Wiley.

20-Achwall, W. B. (1985). . pp. 185–189. *Man-made text India* (28) Pigment printing.

21-AATCC. (1993). . pp. 3348. *Technical manual, method 16 A* (1988) (68) NC, USA:AATCC.

الملخص العربى

تتم عملية كبسلة ملونات البجمنت الزرقاء من خلال استخدام مركبات السيلكون الامينية بطريقة الفصل السائل وفى هذا البحث تم استخدام نوعين من مركبات السيلكون من حيث المجموعات الوظيفية سواء من وجود مجموعات الميثل او مجموعات الفنيل. وفى ضوء هذه الدراسة تم اجراء بعض التحاليل على الملونات المكبسلة بمركبات السيلكون الامنية والتى تحتوى على مجموعات وطيفية من الفنيل لها القدرة على التبلورباستخدام الاشعة الفوق بنفسجية وكذلك المحفز الحرارى.

وقد اثبت تحاليل الاشعة تحت الحمراء والميكروسكوب الالكترونى و كذلك التحليل الكمى الحرارى على نجاح عملية الكبسلة من خلاك استخدام مركبات السيلكون الامنية التى تحتوى على مجموعات الفنيل فقط ومن هذا المنطلق تم استخدام ملونات البجمنت المكبسلة فى طباعة القطن والبولى استر قطن والتى ادت بدورها الى تحفيز عملية الطباعة فى ظروف تحتوى على درجات حرارة منخفضة وكمية اقل من البندر المستخدم فى الحالة العادية حيث تصل الى ربع الكمية تقريبا .

وقد اوضحت النتائج زيادة شدة اللون وكذلك خواص الثبات للضوء والتى تعتمد بطريقة مباشرة على نوع التثبيت وكذلك مواد السيلكون المستخدمة.