

## Novel Starch Based Thickeners for Cotton Printing Using Vat Dyes

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**F**ORMIC acid was reacted with different kinds of starch to yield O-Formate derivatives. Starches used included corn starch, rice starch and oxidized corn starch. Thus obtained O-formates derivatives were submitted to assessment for acyl content, degree of substitution (D.S), solubility and rheological characteristics. The highest % acyl and DS value were obtained with corn starch and the least values with rice starch while oxidized corn starch stood in Mid-way position. All these starch formate derivatives displayed non-Newtonian thixotropy. Nevertheless, the degree of thixotropy and situation of the rheogram with respect to the rate of shear axis were determined by both natures of the starch before derivatization and storing time of the paste. The degree of derivatization of starch via O-Formylation, expressed as D.S., was a governing factor for apparent viscosity of the pastes. Color strength (K/S) and fastness of cottons printed using the starch derivatives in question were very comparable, if not higher than those obtained with the conventional British gum thickener. This was observed irrespective of the D.S. of the formate derivatives of starch and time of printing paste storing and advocated current thickeners as good substitutes for conventional printing thickeners.

**Keywords:** Starch, o-formylation, Vat dye, and Printing.

### Introduction

Huge quantities of starches find wide-spread application in various industries. Among this mention is made of the following. Starches are employed to provide body and consistency to solutions, as vehicle for transferring colours, as adhesives for paper products, as a sizing agent in textiles, and as a source of energy in human and animal diets[1].

In the field of coloration as per vat printing, starch is advocated as printing thickeners. Vat dyes offer a wide range of bright colours that are resistant to wet treatment and weather conditions. This places the vat dyes in prominent places among the other classes of dyes. They are used for printing cotton and other cellulosic fabrics in addition to wool fabrics. Although this group of dyes involves a wide range of types of molecular structure which are often complex yet all Vat dyes contain one or more carbonyl ( $=C=O$ ) groups. [2,3]. Treatment of vat dyes with reducing agents results in combination of the carbonyl groups with

hydrogen to bring about the leuco compounds, which contain secondary hydroxyl group. Such leuco compounds do not undergo dissolution in water but form soluble sodium derivatives in the presence of alkalis. When cotton fabrics are printed using vat dyes, this dye is fixed in an alkaline medium in presence of a strong reducing agent. The so obtained prints are then subjected to oxidation whereby the solution compounds are converted to the insoluble coloured derivatives[4].

Starch is one of these thickeners which can be mixed with alkali and used in direct printing of vat dyes. The higher amount of starch in thickening, yields richer prints (high colour yield). However the levelness of the color yield is diminished correspondingly. That is why printers are looking for alternative thickeners and better substitutes that can function better in the printing paste along with improving the overall fastness properties of the printed fabrics[4,5].

From the academic point of view emphasis was placed on chemical modification and derivatization

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of starches and other polysaccharide thickeners in order to improve their technical performance and promote their utilization[6-13]. Literature reviews on starch esters have extensively been published[1,14-18]. Starch esters which provide salt stability and functional properties such as hydrophobic, cationic or anionic character at relatively low cost are those of commercial value. Among the possible treatments, O-formylation has already been proposed. Nevertheless literature concerned lacked information on the resulting degradation products of O-formylation of starch because of its heterogeneity. Studies[19]related to starch modification, disruption and hydrolysis during O-formylation showed that formic acid acts both as an efficient reactant and as a powerful degrading agent.

Previous reports[20,21], have shown that the highly active formic acid leads to a disruption of the semi-crystalline starch granule and dispersion of amylose and amylopectin macromolecules meanwhile it reacts with some of the hydroxyl groups of these two polymers to produce their "formate esters". This O-formylation reaction causes gelatinization of starch and allows further esterification of free hydroxyl groups[22,23]. Other Studies[24,25]exhibited that esterification takes place essentially on C-6 of the glucose unit, forming to a monoformic ester with a degree of substitution (DS) equal to 1. These results are in conformation with other studies reported elsewhere[26].

The present work is targeted to synthesize novel thickening agents and to study their technical feasibility in printing fabrics with vat dyes. O-formylation of different types of starch is carried out and the obtained starch formate derivatives is submitted to acyl, D.S and rheological measurements and printing application.

## **Experimental**

### *Materials and reagents*

#### *Fabric*

Mill desized, Kier boiled and bleached poplin cotton fabric (140 g/m<sup>2</sup>) produced by Misr/Helwan for Spinning and Weaving Company. This fabric was used throughout the current work.

#### *Starches*

-Egyptian corn starch was kindly supplied by Misr Co. for Starch and Glucose, Cairo. Chemical analysis showed that this starch acquired a moisture content of 11.90, and nitrogen content of 0.06%.

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- Egyptian rice starch was kindly supplied by Misr Co. for Starch and Yeast, Alexandria. Chemical analysis showed that this starch acquired a moisture content of 9.52% and nitrogen content of 0.125%.
- Oxidized starch and British gum were also kindly supplied by Misr Co. for Starch and Yeast, Alexandria.

#### *Chemicals*

Vat dye used was indanthrene vat dye (C.I. Vat Orange 1) under the commercial name Cibanone Golden Yellow RK (Scheme 1).

- Sodium sulphoxalate formaldehyde (Rongalite C) was used as a reducing agent.
- Hostapal was used as CV-ET non -ionic detergent.
- Formic acid, Methyl alcohol, Ethyl alcohol, Glycerin, Sodium perborate, Potassium hydroxide, Sodium hydroxide Hydrochloric acid, and phenol phthaline indicator were of laboratory grade chemicals.

#### *Methods*

##### *Starch esterification*

Formic acid solution, (FA) 99%, was used to chemically modify corn starch, rice starch & oxidized starch as follows (Divers *et al.*, 2007) : 50 g (0.31 mol) of dry starch were introduced in a flask containing 250 mL of 99% formic acid (FA), which corresponds to 305 g (6.62 mol) of FA. The mixture was stirred at 20 °C for 6 h. At the end of the reaction, the solution was gently poured into methanol (1 L) and the precipitated polymer was filtered off and washed three times with methanol (3 x 300 mL) to remove FA in excess until a neutral pH was obtained. The samples were then dried in an oven at 50 °C for 24 h under vacuum. The yield of the reaction was 85%.

##### *Preparation of the printing paste*

This was done according to the popular potash / Rongalite process. The following is the recipe which has been employed:

Preparation of stock thickener:

Thickening agent*	600 g
Glycerine	80 g
Potassium carbonate	150 g
Rongalite C	150 g
Water	20 g

Total 1000 g

\*The thickening agent used was either starch formate (15%) or British gum (40%).

Preparation of the printing paste:

Dye -----	30 g
Water -----	70 g
Stock thickener -----	800 g
<hr/>	
Total -----	1000 g

The required amount of dyestuff was pasted with warm water and stirred well to make homogenous suspension paste. The previously prepared stock thickening was added into the paste and mixed thoroughly.

#### Printing technique

All the printing pastes were applied to cotton fabric as per flat screen printing.

#### Fixation, and after printing treatments

After printing and drying, the printed goods were subjected to steaming at 120°C for 15 minutes. Then the printed fabrics were rinsed and oxidized using 2g/L sodium perborate and 10 g/L acetic acid (30%). After oxidation the fabrics were boiled for 5 minutes in an aqueous solution containing 2 g/l non-ionic detergent namely, Hostapal CV, rinsed with cold water and air dried then assessed for K/S and overall fastness properties measurements.

#### Analysis and measurements

##### Determination of the degree of substitution

Before analysis, the prepared starch formates were dried at 70 °C for 24 h. About 1 g of formate was introduced into a flask containing 100 mL of an ethanol–water solution (75/25 v/v). The suspension was stirred at 50 °C for 30 min, cooled at room temperature and 50 mL of a 0.5 mol/ L KOH solution was added. After 72 h of stirring, the base excess was titrated with hydrochloric acid (0.5 mol/ L) using phenolphthalein as indicator[27]. A blank analysis was carried out on native dried sample. The DS was calculated from the following equations (1-3):

$$\text{acyl \%} = \frac{m_a}{m_e} \times 100 \dots\dots\dots(1)$$

$$\text{acyl \%} = \frac{(V_b \times V_a)}{m_e} \times 100 \dots\dots\dots(2)$$

$$\text{DS} = \frac{162 \times \text{acyl \%}}{[(m_e \times 100)(\text{acyl \%}(m_e \times 1))]} \dots\dots\dots(3)$$

where  $m_a$  is the ester weight in formate (g),  $m_e$  is the sample weight,  $V_b$  is the HCl solution volume (L) for native sample,  $V_a$  is the HCl solution

volume (L) for ester,  $M_e$  is the molecular weight of grafted ester group (g mol<sup>-1</sup>) ( $M_{CHO} = 29.04$  g mol<sup>-1</sup>) and  $m_e$  is dried formate weight[26].

#### Determination of the rheological properties

The rheological properties of the printing pastes were measured using Rheomat-15 at 25°C and the apparent viscosity ( $\eta$ ) at various rates of shear was calculated from the shearing stress ( $\tau$ ) and rates of shear ( $d$ ) as follows(equ.4):

$$\eta = \frac{\tau}{d} \dots\dots\dots(4)$$

#### Colour measurements

The colour strength (K/S) was measured by reflection spectroscopy with a Hunter Lab Ultra Scan PRO spectrophotometer according to a standard method[28].

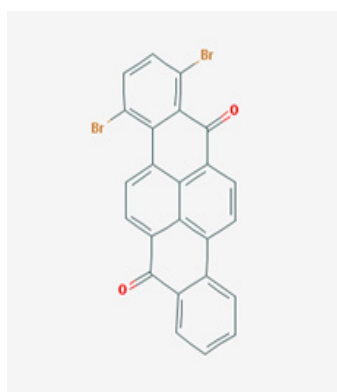
### Results and Discussion

Starch is a biopolymer, specifically a polysaccharide, found in numerous plants to store energy. Its composition speaks of linear amylose and branched amylopectin[29]. These two macromolecular polymers arrange themselves into a complex structure including different levels of organization with alternating crystalline and amorphous regions[30], thereby leading to the well-known 10–100  $\mu\text{m}$  granule structure, being dependent on the starch origin[31].

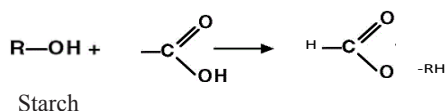
In order to improve the properties of starch and make it feasible for certain performance, it is a must to submit starch for modification and/or derivatization treatment. The latter involves oxidation, hydrolysis, esterification, etherification, grafting and crosslinking. For instance, oxidation of starch with sodium hypochlorite (NaOCl) results in conversion of the hydroxyl groups to carbonyl groups and then to carboxyl groups. The said oxidation was also reported to highly influence the extent of oxidation reaction[32-34]. More amorphous starch structures, or more loosely packed crystalline structures, may provide more accessible reaction site for oxidizing agent in comparison with crystalline starch. Furthermore, the high amylose corn starches may affect the extent of oxidation, by changing the packing of amylopectin double helices. According to previous report[35] the amylose might disrupt amylopectin double helical packing by both a mechanism of co-crystallization between amylose and penetration of amylose macromolecules into the amorphous region of the cluster. As a consequence, the crystalline lamellar

size increases. On the other hand treatments were based on acidic reaction (hydrochloric acid hydrolysis) caused a degradation of the starch granules through the preferential hydrolysis of the amorphous regions[36, 37].

In this context mention should be made of formic acid as interesting reactant among the chemically modifying agents for starch. Chemical modification of starch with formic acid promotes starch compatibility with synthetic polymers by decreasing its hydrophilic character. The O-formylation reaction leads to the incorporation of the hydrophobic formate group in the molecular structure of starch (Scheme 2)[19].



**Scheme 1. Chemical structure of Vat Orange 1.**



**Scheme 2. O- Formylation of Starch**

Current research is undertaken with a view to shed more insight on the chemical modification of starch through its reaction with formic acid. Dependence of O-formylation of starch on type and molecular structure of starch is studied. Also studied is the rheology of starch formate derivatives, their stability and suitability as thickeners for printing cotton fabric with vat dyes. Thus formate derivatives of rice, corn and oxidized corn starches were prepared, purified and analysed for the degree of substitution (DS) and results obtained for the DS are shown in Table 1. As is evident the D.S. display values of 0.81, 0.96 and 1.15 for the formate derivatives of corn-, rice- and oxidized starches respectively.

Such differences may be attributed to the differences in molecular weight, the ratio between amylose and amylopectin, and also the ratio between amorphous and crystalline regions of starch architecture, as compared to oxidized starch architecture, which limited an effective reaction of formic acid on the hydroxyl groups due to steric effect. However, the adverse effect of prior creation of carbonyl and/or carboxyl groups due to oxidation on the charge of the starch hydroxyls can't be ruled out.

#### *Rheology*

The term rheology refers to studying the mechanical properties of concentrated colloidal system such as flow, ductility and plasticity. There is also empirical relationship between flow properties characterising various thickeners and their use and suitability for printing a variety of designs[4].

Rheological properties of pastes prepared from starch formate derivatives are shown in figures 1,2 and 3. Aqueous pastes were prepared using concentration of 15% at pH 10. The rheological properties were measured using Rheomat-15 immediately after preparation as well as after storing the pastes for 48 hours and for 7 days.

Figures 1,2 and 3 depict the experimental rheograms for starch formates derived from corn starch, rice starch and oxidized corn starch for the freshly prepared pastes, and after storing these for 48 hrs and for 7 days respectively.

By and large, Fig. 1 shows that all the pastes under investigation display a non-Newtonian thixotropic behaviour, because the relation between the shearing stress and the rate of shear is not linear and the up and down flow curves are not coincident. That is, when the viscosity (resistance to flow) of these pastes is measured using a large applied force (shearing stress) which, in turn generates a high velocity of flow (shear rate), the apparent viscosity is less than that of the same paste determined using smaller force and at lower rate of flow. When the paste is submitted to a force which causes deformation, on removal of the applied force (i.e. structural break down), the system needs time to rebuild itself and retains its original viscosity.

Figure 1 makes it evident that, the type of starch used for preparation of starch formate and consequently the degree of o-formylation, (i.e. D.S.) play a dominant role on the viscometric properties of the pastes in question. As the degree

of formylation increases, the rheogram is shifted far from the rate of shear axis indicating an increment in the apparent viscosity at a constant rate of shear. This will be discussed later.

Figures 2 and 3 illustrate the effect of storing of starch formate pastes on their rheological properties. A comparison between Fig. 2 and 3 in one side with Fig. 1 on the other side, would indicate that storing of these pastes for 48 hours and for 7 days highly affect the rheological

properties of these pastes. As is obvious the degree of thixotropy (i.e.: the area between the up and down flow curves) changes and the oxidized starch formate pastes change into non Newtonian pseudoplastic behavior, since its up and down flow curves are non-linear and curves are not coincident. This implies that the system rebuilds itself immediately after removal of the applied force and the paste retains its original viscosity immediately.

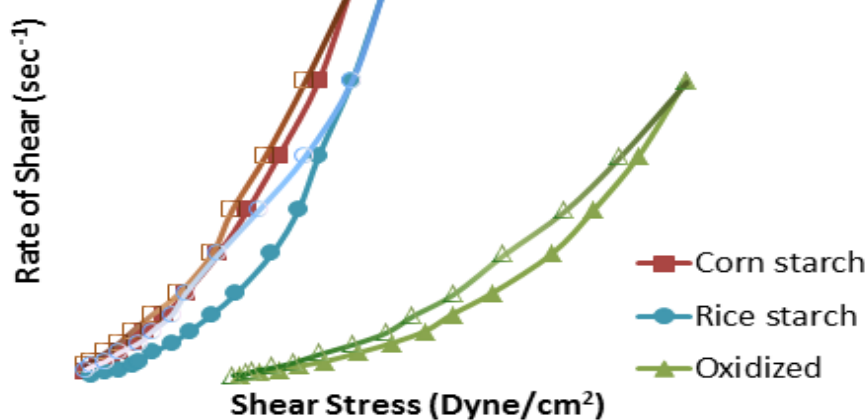


Fig. 1. Rheograms of freshly prepared starch formate derivatives

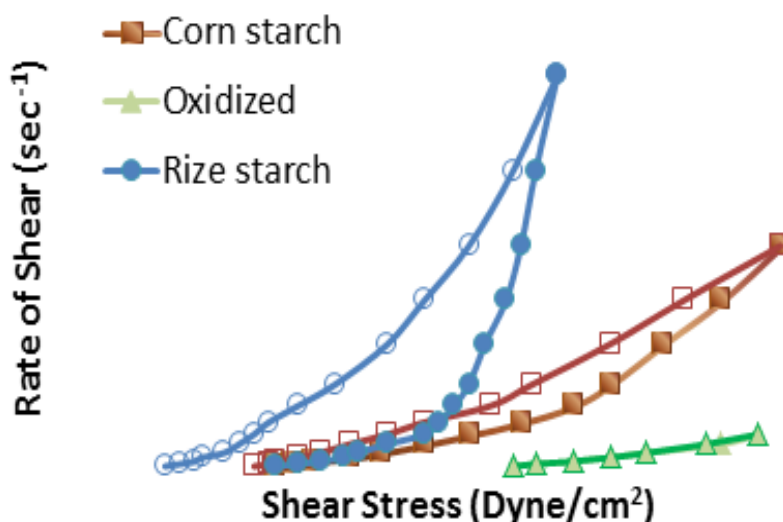


Fig. 2. Rheograms of freshly prepared starch formate derivatives after storing for 48 hours.

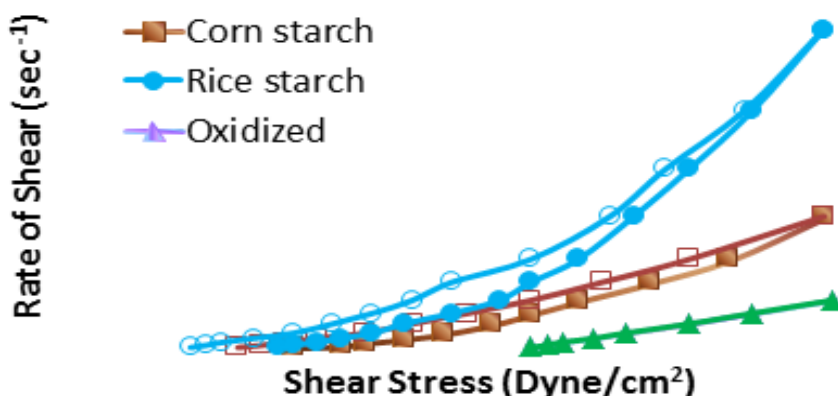


Fig. 3. Rheograms of freshly prepared starch formate derivatives after storing for 7 days.

Reduction in the degree of thixotropy by storing could be associated with the formation of hydrogen bonding and /or Van der Waals forces during storing. When these were subjected to an applied Force, the bonds between starch formate chains were deformed. Rebuilding of these bonds doesn't occur immediately by removing the applied force because the system needs time to rebuild itself and retain its original viscosity.

It is as well to have a further look at Fig. 1,2 and 3. It is seen that the location of the rheogram with respect to the rate of shear axis varies with the variation of the type of starch used for modification. Differences in rheological properties and apparent viscosity of the three different types of starch formate may be a manifestation of differences in molecular weight, the ratio between amylose and amylopectin, and amorphous and crystalline ratios.

A close examination of the rheograms under study would indicate that, the location of the rheogram with respect to the rate of shear relies on the time of storing. As the storing time increases the location of the rheogram is shifted far from the rate of shear axis implying an increase in apparent viscosity by storing at a constant rate of shear. This state of affairs is more clarified in Tables 2, 3 and 4.

Table 2 shows that for a given rate of shear increasing the degree of o-formylation (expressed as D.S.) of starch is accompanied by increment in

apparent viscosity. For example at a rate of shear 9.77 sec<sup>-1</sup>, the apparent viscosity of the three types of starch formate derivatives exhibit values of 28.03, 42.04 to 128.91 poise for the derivatives having D.S values of 0.81, 0.96 and 1.15 respectively. Besides the extra weight conferred on starch by the incorporated acyl groups, the effect of a formylation reaction and its impact on morphology and fine physical structure of starch may in combination account for this.

In order to verify the effect of storing of the pastes under investigation on their apparent viscosity at specific rate of shear, comparison was made among Tables 2,3 and 4. Obviously, at a rate of shear of 9.771 sec<sup>-1</sup>, freshly prepared paste exhibits apparent viscosity value of 28.03 poise. This value increases to 140.12 poise and 154.13 poise after storing the paste for 48 hours and for 7 days respectively. This situation is encountered irrespective of the extent of formylation.

Increment in viscosity of starch formate derivatives under the effect of storing is indicative of crosslinks occurring between adjacent chains. It is also likely that, storing favors inducing higher swellability of the derivative thereby leading ultimately to higher viscosity.

#### Printing

Vat dyes are among the oldest natural colouring materials used for textiles [36]. They encompass a wide range of structural types with often complex molecules. However, all vat dyes

TABLE 1. Effect of type of starch used on the % acyl, D.S. and solubility of the O- formylated product.

Sample	Type of starch	Starch formate		Solubility in		
		% acyl	D.S.	Water*	Ethanol	DMSO
I	Corn	12.725	0.81	soluble	insoluble	soluble
II	Rice	14.73	0.96	soluble	insoluble	soluble
III	Oxidized	17.26	1.15	soluble	insoluble	soluble

TABLE 2. Effect of D.S. of starch formate derivatives on the apparent viscosity of their pastes for freshly prepared pastes\*.

Rate of Shear (Sec <sup>-1</sup> )	Apparent viscosity in poise for o-formylated starch acquire:		
	D.S.= 0.81 (Formylated corn starch)	D.S.= 0.96 (Formylated Rice starch)	D.S.= 1.15 (Formylated oxidized starch)
2.18	-----	75.36	351.67
2.93	46.72	74.76	289.69
3.85	42.67	71.12	241.79
5.14	37.29	63.92	197.09
6.78	36.35	52.49	165.57
9.77	28.03	42.04	128.91
13.12	25.04	37.56	106.43
17.26	22.20	31.73	88.83
23.03	20.21	28.53	71.33
30.38	18.02	24.33	59.48
44.1	15.52	20.49	46.56
59.22	13.41	16.18	36.99
77.92	11.95	14.05	30.92
103.9	10.54	-----	25.03
137.1	8.98	-----	-----

\* The concentration of the pastes was 15%, pH. 10.

**TABLE 3.** Effect of D.S. of starch formate derivatives on the apparent viscosity of their pastes for pastes after storing for 48 hours\*.

Rate of Shear (Sec <sup>-1</sup> )	Apparent viscosity in poise for o-formylated starch acquire:		
	D.S.= 0.81 (Formylated corn starch)	D.S.= 0.96 (Formylated Rice starch)	D.S.= 1.15 (Formylated oxidized starch)
2.18	376.78	376.78	778.69
2.93	299.03	308.37	607.41
3.85	248.91	256.02	497.82
5.14	213.07	207.75	399.51
6.78	177.69	165.57	323.06
9.77	140.12	126.11	252.22
13.12	116.86	104.34	198.25
17.26	99.94	82.49	-----
23.03	83.22	64.19	-----
30.38	67.59	50.47	-----
44.1	50.91	37.25	-----
59.22	41.61	28.20	-----
77.92	34.43	22.14	-----
103.9	-----	17.13	-----
137.1	-----	13.58	-----

\* The concentration of the pastes was 15%, pH. 10.

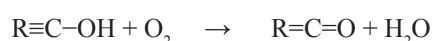
**TABLE 4.** Effect of D.S. of starch formate derivatives on the apparent viscosity of their pastes for pastes after storing for 7 days\*.

Rate of Shear (Sec <sup>-1</sup> )	Apparent viscosity in poise for o-formylated starch acquire:		
	D.S.= 0.81 (Formylated corn starch)	D.S.= 0.96 (Formylated Rice starch)	D.S.= 1.15 (Formylated oxidized starch)
2.18	376.78	351.67	753.58
2.93	336.41	280.34	579.37
3.85	277.35	234.68	455.15
5.14	234.38	191.76	362.22
6.78	197.87	161.53	290.76
9.77	154.13	123.31	224.19
13.12	125.21	104.34	183.64
17.26	104.69	88.83	155.46
23.03	89.16	71.33	-----
30.38	76.61	59.48	-----
44.1	60.22	45.32	-----
59.22	-----	36.98	-----
77.92	-----	30.92	-----
103.9	-----	25.56	-----
137.1	-----	-----	-----

\* The concentration of the pastes was 15%, pH. 10.



contain one or more carbonyl groups ( $=C=O$ ), which, are converted to form leuco compound containing ( $=C-OH$ ) through combination with hydrogen upon treatment with reducing agents. The as formed secondary alcohols do not dissolve in water but form soluble sodium derivatives ( $\equiv C-ONa$ ) in the presence of alkalis as mentioned in the introductory section of the present work. When subjected to air or oxidized with a suitable oxidizing agent, the sodium compound undergoes conversion to the insoluble coloured derivatives as expressed by the reactions shown under:



Hence printing with vat dye needs a thickener which is not affected by the reducing agent and alkali that are inevitably added as auxiliaries to the vat dye printing paste. Achieving this is rather the essential goal of the present work as already stated. The goal is to pursue starch formate derivative as a new thickener for printing cotton fabrics with vat dyes [37].

Different printing pastes thickened by starch formate derivatives and containing Cibanon G. Yellow RK (C.I. Vat orange 1) were prepared as described in the experimental section. Starch formate derivatives from different starch sources having different D.S values These embrace corn starch formate, rice starch formate and

oxidized starch formate having DS values of 0.81, 0.96 and 1.15 respectively. For the sake of comparison, a printing paste containing the same vat dye and thickened by British gum as a conventional, commercial thickener was also prepared. In practice, the British gum thickener is recommended for vat dye printing.

The as prepared pastes were used for screen printing of cotton fabrics. Printing was carried out immediately after preparation of the printing paste or after storing of the pastes for 48 hours or 7 days before the start of printing. After printing and drying the printed fabrics, were exposed to steaming then to oxidation with sodium perborate solution then to washing and finally to drying at room temperature. After being conditioned, the printed fabrics were evaluated for measuring K/S and overall fastness properties. The results obtained with Cibanon Yellow RK are set out in Table 5.

Results of Table 5 show that all printed fabric samples acquire soft handle except that the sample printed using freshly prepared corn starch formate of DS 0.81 as a thickener. This peculiar situation could be ascribed to the lower solubility of the freshly prepared corn starch formate printing paste. Once this is the case, the latter will be strongly sticking to the fabric sample and prevent creation of the soft handle to the printed fabric. That is, washing could not remove residual

**TABLE 5. Colour strength, expressed as K/S of cotton fabric samples printed using pastes thickened by the prepared starch formate derivatives or British Gum when printing was performed using freshly prepared pastes, 48 hours and 7 days stored pastes containing Vat dye namely Cibanon Golden Yellow RK.**

Thickener used	Printing paste	K/S	Washing fastness		Rubbing fastness		Perspiration fastness				Handle
			Alt.	St.	Dry	Wett	Alt.	St.	Alt.	St.	
British Gum	Fresh	6.97	4-5	4	4	3-4	4	4-5	4	4	S
	48h.	5.79	4-5	4-5	4	3	4-5	4-5	4-5	4-5	S
	7 days	4.98	4-5	4-5	4	3	4-5	4-5	4-5	4	S
I D.S.= 0.81 (Formylated Corn starch)	Fresh	5.50	4-5	4	3	2-3	4-5	4-5	4	4-5	H
	48h.	5.77	4-5	4-5	2-3	2	4-5	4-5	4-5	4-5	S
	7 days	5.78	4-5	4-5	3	2-3	4-5	4-5	4-5	4-5	S
II D.S.= 0.96 (Formylated Rice starch)	Fresh	6.28	4-5	4-5	3-4	2-3	4	4-5	4-5	4	S
	48h.	6.79	4-5	4-5	3	2	4	4-5	4-5	4-5	S
	7 days	7.19	4-5	4	3-4	2-3	4-5	4-5	4	4-5	S
III D.S.= 1.15 (Formylated oxidized starch)	Fresh	7.65	4-5	4-5	4	2-3	4-5	4-5	4-5	4-5	S
	48h.	7.64	4-5	4-5	4	3	4	4-5	4-5	4-5	S
	7 days	7.96	4-5	4-5	4	3	4-5	4-5	4-5	4	S

thickener from the prints only with this freshly prepared paste of corn starch formate.

Table 5 contains the K/S as well as the overall fastness properties of the printed fabrics including fastness to rubbing, to washing, and to perspiration. As is evident the K/S and fastness properties of cotton fabrics printed using printing pastes based on starch formate derivatives before and after storing these pastes for two or seven days are nearly identical to those obtained using British Gum as a thickener.

Results of Table 5 imply that formylation of starch converts it into a stable thickener with high ability to transfer the dye from the printing paste to the fabric. Starch macromolecules seem to undergo changes in their chemical and physical structure during treatment with formic acid. The ultimate results are possible products which are capable of swelling, dispersing, and jumping in aqueous medium without elimination of intermolecular forces between themselves and water.

The colour strength (K/S) of fabric samples printed using the pastes after being stored for 48 hours and for 7 days before commencing printing are shown respectively in Table 5. It is observed that storing of the printing paste thickened with British Gum decreases the K/S values and, the longer the duration of storing the higher is the decrease in K/S. This could be associated with partial decomposition of the reducing agent under the influence of alkali and long storing. In contrast pastes thickened by starch formate derivatives are more stable to storing as the K/S values of the printed fabrics do not nearly change through storing of the printing pastes for 2 or 7 days. This may be attributed to the stability of the starch formate derivatives under alkaline conditions. This suggests that starch formate can be used safely in printing cotton fabrics with vat dyes.

### **Conclusion**

Different types of starch, namely Corn, Rice, and Oxidized starch were modified via o-formylation using formic acid (99%). Derivatives obtained were purified and the degree of substitution by the formate ester groups (D.S.) was determined. Also, determined were the rheological properties of the pastes of the prepared derivatives. In addition suitability of the latter as thickeners in printing of cotton fabrics with vat dyes were examined. Conclusion arrived at from these studied may be presented as given below

1. The D.S. display values of 0.81 for starch formate from corn starch; 0.96 for rice starch formate and; 1.15 for oxidized starch formate.
2. The starch formate samples are soluble in water, and dimethyl sulphoxide, but insoluble in ethanol. This is observed despite the different sources of the parent starches used for the preparation of starch formate derivatives.
3. Rheological properties of all the prepared starch formate samples were characterized by non-Newtonian thixotropic characteristics.
4. Storing of the pastes in question for 48 hours and for 7 days exert a remarkable effect on the rheological properties of these pastes. Apparently the degree of thixotropy changes and the oxidized starch formate pastes change into non Newtonian pseudoplastic.
5. As the degree of o-formylation (expressed as D.S.) of starch increases, the apparent viscosity of the paste of the prepared derivative increases.
6. The apparent viscosity of the prepared pastes also increases by storing for 48 hours and for 7 days.
7. Starch formate can be used safely in printing cotton fabrics with vat dyes.
8. The K/S and overall fastness properties of cotton fabrics printed using starch formate derivatives before and after storing of the pastes for two or seven days are nearly identical to those obtained using the British gum as thickener.
9. All the printed samples acquire soft handle except that sample printed using freshly prepared corn starch formate of D.S. 0.81.

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## أستحداث نشا جديد معتمداً علي المتخنات لطباعة الأقمشه القطنيه بأستخدام صبغات الأحواض

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يتفاعل حمض الفورميك مع الأنواع المختلفة من النشا لإنتاج مشتقات (O-Formate)، وقد أشتملت الدراسة علي بعض النشويات المختلفة مثل نشا الذرة، نشا الأرز، بالإضافة الي نشا الذرة المؤكسد. هذا وقد خضعت مشتقات (O-Formate) التي تم الحصول عليها لتقييم كلاً من محتوى الأسيل، درجة الاستبدال (D.S)، الذوبان، والصفات الريولوجية. وقد اثبتت النتائج ان أعلى قيمة لكلاً من (cyl & DS%) تم الحصول عليها مع نشا الذرة وأقل قيم مع نشا الأرز بينما نشا الذرة المؤكسد وقفت في منتصف الطريق. كل هذه المشتقات فورمات النشا كانت (non-Newtonian thixotropy). ومع ذلك، تم تحديد درجة (thixotropy) وحالة (rheogram) فيما يتعلق بمعدل محور القص من كلا طبائع النشا قبل اشتقاق وزمن تخزين العجينة. كانت درجة اشتقاق النشا عن طريق O-Formylation معبرا عنها D.S. هي عامل حاكم لدرجة لزوجة عجائن الطباعة. كانت قوة اللون (K / S) وخواص الثبات المختلفه للأقمشه القطنيه المطبوعه باستخدام المشتقات النشوية موضوعاً للمقارنة، إن لم يكن أعلى من تلك التي تم الحصول عليها باستخدام مثخن البريطاني التقليدي. وقد لوحظ هذا بغض النظر D.S مشتقات فورمات النشا ووقت التخزين معجون الطباعة يمكن استخدامه كبديل جيد لمخنات الطباعة التقليدية.