Egypt. J. Chem. **56**, No. 1, pp. 49-59 (2013)

Electrocatalytically Oxidized Starch as Sizing and Finishing Agent

H.H. Shaarawy, S.M. El-Rafie[*], A.M. Abd El-Ghaffar[*] and M.H. El–Rafie[*]

Chemical Engineering Department and [*]Textile Research Division, National Research Centre, Giza, Egypt.

HEREIN an industrial innovation was presented, where it provides cleaner, safer, and cheaper practice for sizing of cotton and cotton/polyester blend warp yarns. The innovation based on the use of electrocatalytically prepared oxidized starch using mixed oxidant generated via brine electrolysis as sizing agent. At electrolysis conditions: current density 7.5mA/cm^2-12mA/cm^2, temperature 30°C, initial pH 3, duration of the electrolysis 1 hr supporting sodium chloride concentration 7.5g/l, and material to liquor ratio 1:10, via Rhodium –titanium thermally activated modified electrode. Good sizing agent with suitable viscosity which leads to both formation of a film and penetration of the yarn was obtained. The apparent viscosity (151mpa.s^{-1}/516) obtained at the above mentioned electrolysis conditions represents the proper oxidized starch used as sizing agent. This new formula leads to the reduction of the softener used with increasing sizing process efficiency.

Textile warps are usually subjected to sizing before weaving. Sizing makes yarn weavable by providing the individual yarn with some form of protection in order to enable it to withstand the action of healds, reed and the rubbing of chafing caused by adjacent yarns. Effectiveness of sizing process depends on the adhesion between size and fiber/yarn, the rheological properties of the size material and many other factors[1, 2].

After weaving, the loom state fabric is usually subjected to a Desizing process with a view to completely remove the sizing materials from the fabric before the latter is subjected to subsequent treatments such as scouring, bleaching, mercerizing, dyeing, printing and finishing. Desizing process depends upon the ease of removal of the size material from the fabric.

Starch is used in the final finishing of cellulosic based textiles by which the completed fabrics are given a finish which alters the handle of the fabric by binding, stiffening and weighting. Unmodified starches give surface covering with little penetration and produce stiff based like finish. Low viscosity starches are needed when high-solid starch dispersion with pumpable and workable viscosity is required.

Starch suffers from serious defects, the most outstanding of which are: (a) unstability of viscous solution of starch particularly when there is fluctuating of temperature during cooking and sizing operations, (b) the very high molecular size of starch limits the penetration in the bulk of the textile threads, (c) rigidity of the starch films particularly in absence of good lubricants, and (d) susceptibility of starch to rot and degradations by microorganisms. These defects detract from the properties of starch as sizing agent for textile. To eliminate or, at least, to minimize these shortcomings, chemical modification of starch has become a must.

Chemical modification of starch with a view of improving its properties has been the subject of several studies[3]. It can be effected via oxidation[4-11], hydrolysis[12-14], esterification[15-19], etherification[20-22], crosslinking[23-25], dextrinization[26], and grafting[27-32].

Such reaction process causes significant changes in the physical as well as chemical structure of starch which, in turn, are reflected in solubility, viscosity performance and resistance to ageing of native starch and solution or pastes prepared thereof. Oxidation of starch is one of the most promising techniques for modification of starch to achieve suitable sizing agent for textile industry. Oxidation of starch could be achieved via chemical oxidation in several mediums such as hypochlorite, chlorates, hydrogen peroxide,… etc [33,34] and air oxidation (35). On the industrial production of oxidized starch by chemical means acquire that the law reaction temperature is needed to inhibit cooking during the oxidation process. The chemical oxidation of starch has several disadvantages such as loss of catalytic activity, unstable concentration due to storage, unused residual oxidant at the end of the reaction and difficulty of handling and some of them are environmentally and healthy unsafe. Electrocatalytic oxidation is a new trend for oxidation of starch due to the ease of control of the electrochemical oxidation process, the high catalytic and chemical activity of the Electrogenerated species and Starch oxidation represents the most important and the cheapest technique of starch modification [36].

The present work is undertaken with a view to evaluate the oxidized starches having different apparent viscosities, which are prepared by electrochemical oxidation method. This evaluation could be carried out as follows: a) studying the feasibility of sizing and desizing of cotton textiles using the obtained oxidized starches as sizing agent and b) studying the performance properties of cotton fabrics finished with native and oxidized rice starch.

Experimental

Materials

Rice starch was supplied by the Egyptian Starch and Yeast Manufacturing Company, Alexandria, Egypt. Different kinds of cellulosic based fabrics and different kinds of nonionic softeners were kindly supplied from El-Nasr Spinning, Weaving and Dyeing Company, El-Mehalla EI-Kobra.

Oxidation procedures

Oxidized starches were prepared by the electrocatalytic technique as mentioned in our preparation studies, where Titanium/Rhodium thermally activated modified electrode prepared as mentioned [37] was used to oxidize starch via generation of mixed oxidant by brine electrolysis, Fig.1 represents the electrochemical setup used for preparation of oxidized starch. Different current densities were used to obtain oxidized starches having variable viscosities, Table 1 shows the relation between current density and the properties of the obtained oxidized starches, *e.g.* apparent viscosity measured at rate of share $516S^{-1}$, carbonyl and carboxyl content. The electrolysis conditions where current density (variable values), temperature 30°C, initial pH 3, duration of the electrolysis 1hr supporting sodium chloride concentration 7.5g/l, and material to liquor ratio 1:10.

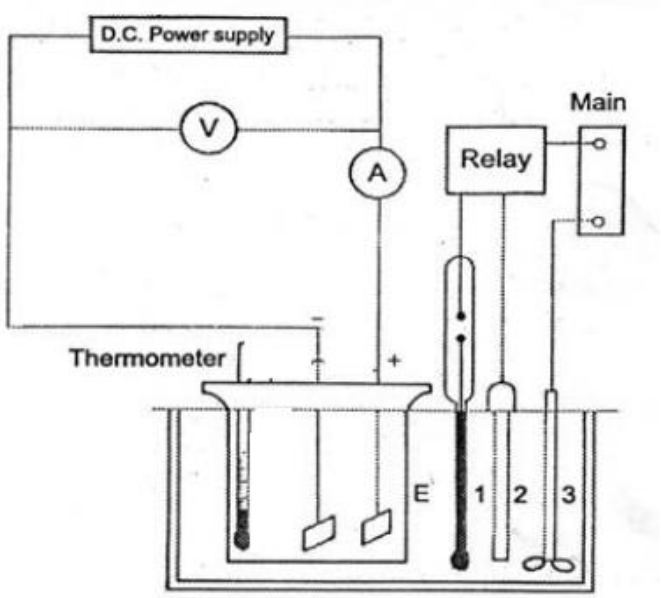

Fig. 1. Oxidized starch electrochemical preparation set up .

TABLE 1. Relation between current density and oxidized starch properties.

Variable current density (mAm/cm^2)	Apparent viscosity ($mpas^{-1}$/ 516)	Carbonyl content (meq/100gm starch)	Carboxyl content (meq/100gm starch)
Untreated Starch	350	1.77	5.91
7.5	151	6.02	19.34
8.4	72	4.8	28.36
12	20	20.52	32.7

Analysis

The carbonyl content of oxidized starch was determined according to the reported methods[38]. The carboxyl content of oxidized starch was determined according to the hydroxyl amine hydrochloride method[39]. The rheological properties were measured using co-axial rotary viscometer (Haake RV20) under the following experimental conditions: - range of rate of share between 258-1290 S^{-1}, temperature 80°C.

Sizing of cotton textiles

Aqueous slurry of native rice starch or oxidized rice starch derived thereof (10%) was cooked at 90°C for 20 min. Light cotton fabric samples (stripes, 5x30cm) were treated with the cooked solution via impregnation followed by squeezing to a wet pick up Ca.I00% then dried at temperature 100°C for 5 min. The sized samples were tested for warp tensile strength and warp elongation at break according to ASTM proceeds D-2256-66 T.4.

The % size add-on can be calculated according to the following formula:

$$\text{Size Add-on \%} = (W_1 - W_O)/ W_O \times 100$$

where:
W_0 = weight of sample before sizing.
W_1 = weight of sample after sizing.

Desizing

Desizing was carried out by washing the sized samples with hot water at different temperatures viz. 60^0C, 80°C and 95°C for 5 min. The loss in fabric weight by Desizing treatment is referred to as removal percentage which can be calculated according to the following formula:

$$\text{Size Removal \%} = (W_1 - W_2)/(W_1 - W_0) \times 100$$

where:
w_0 = weight of sample before sizing.
w_1 = weight of sample after sizing.
w_2 = weight of the sized sample after washing.

Final finishing treatment

The cotton fabric was padded twice in padding liquor containing the following ingredients, cooked starch, softener and optical brightener with known concentration which depend on the kind of the fabric to be treated; and then squeezed in a laboratory mangle to wet pick up of Ca.100% on weighing of fabric, The so-treated fabric was then stretched back to its original dimensions on a pin frame for drying at 120°C for 5 min. The finished fabrics were evaluated via determining Textile Tensile Strength Tester (ASANO Machine MFG.), Constant rate of traverse/speed 300mm/min and the stiffness via Surface Roughness Measuring instrument (Surfcorder) SE. 1700a, Kosaka Lab.

Results and Discussion

Utilization of the oxidized starch as sizing agent

Table 2 illustrates the effect of the sizing light cotton fabric, with native and oxidized rice starches having variable apparent viscosity, on the size add-on, tensile strength (T.S), elongation at break (E.A.B.) and abrasion resistance (A.R.). The data illustrate that (a) sized samples exhibit higher tensile strength, elongation at break and abrasion resistance than that of an unsized fabric, (b) size add-on decreases by decreasing the apparent viscosity of the starch used, taking in mind that the cotton fabric was padded under the same pressure and in a solution with the same solid content (10%), (C) sizing cotton fabric using starch having apparent viscosity. (151mpa.s^{-1}/516) gives values of T.S and A.R. slightly higher than using unoxidized starch (350 nma.s^{-1}/516) and significantly higher than that of oxidized starches having lower viscosities, (d) decreasing the viscosity of 'the oxidized starch is accompanied by a decrement in T.S. and A.R. of the treated fabrics, (e) regardless of the size used the E.A.B. of the sized samples is lower than that of unsized samples (f) the E.A.B. decreases by decreasing the apparent viscosity of the starch used. All the above findings may be attributed to that, the sizability depends on the viscosity of the starch. At higher viscosity the yarns are coated on the surface rather than penetrated by the sizing material, the reverse holds true in case of using low viscosity sizing material which leads to high penetration rather than forming a film on the yarn surface. Good sizing agent should have suitable viscosity which leads to both formation of a film and penetration of the yarn; thereby oxidized starch with apparent viscosities (151mpa.s^{-1}/516) represents the proper oxidized starch used as sizing agent.

Table 3 shows the effect of the apparent viscosity of starch used on the efficiency of size removal when the sized samples were washed with hot water at different temperatures 60°C, 80°C and 95°C for 5 min. The data indicate that, (a) decreasing the apparent viscosity is accompanied by significant enhancement in the percent size removal, (b) raising the washing temperature leads to higher extent of size removal. This behavior could be ascribed to the extent of degradation due to starch oxidation using the electrocatalytic means which liberates mixed oxidants with high oxidative efficiency. Formation of oxidized starch with lower viscosity reflects the formation of oxidized starch with lower molecular weight which is easy to be removed by hot water.

TABLE 2.Effect of the sizing light cotton fabric, with native and oxidized rice starches having variable apparent viscosity, on the size acid-on, tensile strength, elongation at break and abrasion.

Apparent viscosity ($mpas^{-1}$/ 516)	Size add on %	Tensile strength (kgm)	Elongation %	Abrasion (cycle)
Untreated Fabric	----	30	5	30
Native Starch 350	16.93	41	5.5	42
151	11.12	44	4.5	44
72	10.2	38	3.4	36
20	9.64	36	3.2	34

TABLE 3. Effect of the apparent viscosity of starch used on the efficiency of size removal.

Apparent viscosity ($mpas^{-1}$/ 516)	Size Removal %		
	Washing Temperature °C		
	60	80	95
350	20	56	60
151	32	44	50
72	47	74	81
20	90	95	100

Utilization of the oxidized starch as final finishing agent for cellulosic based textiles

Native starch (Unoxidized starch) is usually used as final finishing agent for cellulosic based fabrics to impart binding, stiffening and weighing for the finished fabrics. Using native starch for finishing is accompanied by several problems during processing and the performance properties of the finished fabrics which leads to addition of softeners in finishing formulations. It is understandable that cooked native starch has high viscosity and is not easily pumpable. The high viscosity cooked starch forms film on the surface rather than penetration inside the fabric. To eliminate or at least to minimize these defects, native starch was substituted by oxidized starches with different apparent viscosities. The roughness of the surface of the treated fabrics was taken as a measure for the softening properties. The treated fabrics were also evaluated via determining the stiffness properties.

Traditionally finishing recipes and fabrics specifications used in El-Nasr Spinning, Weaving and Dyeing Company, El-Mehalla El-Kobra are applied in this studies to compare the effect of incorporation of different viscosities oxidized starches instead of native starch. Upholstery fabrics with different specifications and finishing formulations are used as shown in Tables 4 and 5.

Table 5 shows the effect of using native and oxidized starches having different apparent viscosity on surface roughness of the treated fabrics. The roughness was taken as a measure of softness of the finished fabrics. The data indicate that, (a) regardless of the fabrics specifications and the finishing recipe

used the surface roughness decreases by decreasing the apparent viscosity of the starch used (*i.e*. the softness increases), (b) the softness of the fabrics finished with oxidized starch is better than that treated according to the traditional method used in the company using native starch, (c) fabrics finished according to modified finishing recipes; lower amount of softner added to the finishing formulation; have softness properties (values between brackets) comparable with those produced when traditional finishing recipe was used and the softeness is still better than that obtained on using native starch.

TABLE 4. Fabric specification and finishing formulations for the fabric used in finishing treatment. Different specifications (Kinds) of upholstery fabrics were used have plain weave (1×1) constriction.

Sample Number	Traditional finishing Recipes	Modified finishing Recipes	Fabric Specification					
			Raw Materials				Fabric Density	
			Fabric Weight (gm/m^2)	Fabric Width (cm)	Warp Yarn	Weft Yarn	Warp Thread/ cm	Weft Picks/cm
1	2% Starch + 7% Nasr soft	2% Starch + 5% Nasr soft	358	240	65% Cotton 35% polyester	100% Cotton	70	64
2	2% Starch + 5% Nasr soft	2% Starch + 3% Nasr soft	118	90	100% Cotton	100% Cotton	68	84
3	2% Starch + 7% Nasr soft	2% Starch + 5% Nasr soft	169	240	100% Cotton	100% Cotton	77	68
4	2% Starch + 5% Nasr soft	2% Starch + 3% Nasr soft	231	128	100% Cotton	100% Cotton	38	62
5	2% Starch + 5% Nasr soft + Adesesol (softener)	2% Starch + 5% Nasr soft + 0%Adesesol (softener)	318	240	100% polyester	100% Cotton	64	77

TABLE 5. Effect of apparent viscosity of starch used on the surface roughness of the treated fabric .

Apparent Viscosity ($mpas^{-1}$/ 516)	Roughness (µm)				
	1	2	3	4	5
Untreated Fabric	16.99	18.84	17.97	16.89	16.16
Untreated Starch 350	15.48	17.81	15.2	15.42	16
151	15.52	17	14.2	14.8	15
	(15.62)	(17.73)	(14.5)	(14.35)	(15.36)
72	15.34	17.00	13,81	14.21	15.20
	(15.50)	(17.31)	3.78	(14.23)	(15.26)
20	14.8	16.20	12.79	13,22	4.73
	(14,7)	(16.36)	(12,80	(13.25)	(14.72)

Table 6 shows the effect of using native and oxidized starches on the stiffness properties of the treated fabrics. It is clear from the data that (a) stiffness of the treated fabrics is higher than that of the untreated fabrics, (b) values of the stiffness of the treated fabrics depend on the fabric specification, (c) stiffness of fabrics treated with oxidized starch is lower than that of the fabrics treated with

native starch, (d) stiffness decreases by decreasing the apparent viscosity of the starch used and (e) applying the modified recipe leads to marginal decrement in the stiffness properties (values between brackets). The decrement in the stiffness reflects the lower add-on of the finishing material on the treated fabrics. It could be concluded from these. data that using oxidized starch as final finishing agent instead of native starch in El-Nasr Weaving, Spinning and Dyeing Company leads to a reduction in the amount of softener used, that means lower production cost.

Conclusion

Rice oxidized starch having different apparent viscosities, and prepared via electrochemical oxidation method using mixed oxidant resulted by the electrolysis of saline solution using the titanium/ rhodium thermally activated modified electrode was successfully used as sizing and finishing agent for cotton textile fabrics. The obtained oxidized starch was evaluated via determining the carbonyl and carboxyl contents. Results obtained indicate that the oxidized starch is suitable to be used as a sizing agent for textile fibers and it could be concluded that using oxidized starch as final finishing agent instead of native starch leads to a reduction in the amount of softener used in the finishing formulation, that means lower production cost.

TABLE 6. Effect of apparent viscosity of starch used on the stiffness of the fabric.

Apparent viscosity (mpa.s^{-1}/516)	Stiffness (gm.cm)				
	1	2	3	4	5
Untreated Fabric	124.10	26.20	62.81.	84.7	127.8 3--
Untreated Starch 350	174.22	29.5	91.5	108.95	156.8
151	152.15 (149.2)	27.14 (25)	71 (70.54)	93.55 (90.55)	146 (140.94)
72	127.92 (127,92)	23.6 (2().6)	63.09 (60.09)	103.71 (100.7)	134.2 (130.3)
20	125 (120.89)	11.8 (11.8.)	63.09 (60.03)	75.07 (70.06)	127.9 (125.28)

References

1. **Hari, P.K. and Behere, P.KP,** *10th, International Symposium. on Warp Sizing*, Doc, *9-10/199200 Denkeendrof*, Germany.

2. **Trauter, J.**: *3rd Annual Sizing Symposium II T Delhi, 1980. II Delhi* (1960).

3. **Rutenberg, M. W. and Solarek, D.,** Starch Derivatives: Production and Uses. (1984).

4. **Ali, S. Z. and Kempf, W.,** *Starch/Starke*, **38**, 83–86 (1986).

5. **Daris Kuakpetoon and Ya-Jane Wang,** Structural characteristics and physicochemical properties of oxidized corn starches varying in amylase content. *Carbohydrate Research*, **341**, 1896 –1915 (2006).

6. **Kawaljit, Singh Sandhu, Maninder, Kaur, Narpinder, Singh and Seung-Taik, Lim,** A comparison of native and oxidized normal and waxy corn starches: Physicochemical, thermal, morphological and pasting properties. *Food Science and Technology*. doi:**10**.1016/j.lwt.2007.07.012 (2007).

7. **Li, J.H. and Vasanthan, T.,** Hypochlorite oxidation of field pea starch and its suitability for noodle making using an extrusion cooker. *Food Research International*, **36**, 381–386 (2003).

8. **Muhrbeck, P., Eliasson, A.C. and Salomonsson, B.A.C.,** *Starch/Starke*, **42**, 418–420 (1990).

9. **Salomonsson, B.A.C., Anderson, R., Torneport, I.J. and Theander, O.**, *Carbohydrate Research*, **217**, 221–225 (1991).

10. **Salomonsson, B.A.C. and Theander, O.,** *Starch/Strake*, **44**, 260–263 (1992).

11. **Sa´nchez-Rivera, M.M., Garcı´a-Sua´ rez, F.J.L., del Valle, Vela´zquez M., Gutierrez-Meraz, F. and Bello-Pe´ rez, L.A.,** Partial characterization of banana starches oxidized by different levels of sodium hypochlorite. *Carbohydrate Polymers*, **62**, 50–56 (2005).

12. **Abraham, T.E., Krishnaswamy, C. and Ramakrishna, S.V.,** *Starch/Starke*, **40**, 387–392 (1988).

13. **Pessa, E., Suorit, T., Auto, K. and Poutanen, K.,** *Starch/Starke*, **44**, 64–69 (1992).

14. **Singh, V. and Ali, S. Z.,** *Starch/Starke*, **39**, 402–405 (1987).

15. **Agboola, S.O., Akingbala, J.O. and Oguntimein, G.B.,** *Starch/Starke*, **43**, 13–15 (1991).

16. **Jarowenko, W.,** In: O.B. Wurzburg (Ed.), *Modified Starches: Properties and Uses* (pp. 55–77). Fla: CRC Boca Raton (1987).

17. **Maroza, K. and Tomasik, P.,** *Starch/Starke*, **43**, 66–69 (1991).

18. **Muhrbeck, P., Svensoon, E. and Eliasson, A.C.,** *Starch/Starke*, **43**, 466–468 (1991)

19. **Muhrbeck, P. and Tellier, C.,** *Starch/Starke*, **43**, 25 (1991).

20. **Forrest, B.,** *Starch/Starke*, **44**, 179–183 (1992).

21. **Hellwlg, G., Bishoff, D. and Rubo, A.,** *Starch/Starke*, **44**, 69–74 (1992).

22. **Nachergaele, W.,** *Starch/Starke*, **41**, 27–31 (1989).

23. **Chaudhari, M.R., Kamath, N.D., Bhide, S.V. and Kale, N.R.,** *Starch/Starke*, **41**, 415–416 (1989).

24. **Hahn, D. E. and Hood, L.F.,** *Journal of Food Science*, **45**, 518–522 (1980).

25. **Kulicke, W.M., Aggour, Y.A. and Elsabee, M.Z.,** *Starch/Starke*, **42**, 134–141 (1990).

26. **Jones, E.I., Morgan, L.B., Robert, J.F.L. and Todd,** *Chemical Abstracts*, **49**, 2748 (1955).

27. **Chinnaswamy, R. and Hanna, M.A.,** *Starch/Starke*, **43**, 396–402 (1991).

28. **El-Rafie, M. H., Zahran, M. K., El- Tahlawy, Kh. F. and Hebeish, A.,** *Polymer & Polymer Stability*, **47**, 73–85 (1995).

29. **Fanta, G.F., Burr, R.C. and Doane, W.M.,** *Journal of Applied Polymer Science*, **29**, 4449–4453 (1984).

30. **Hebeish, A., El-Rafie, M.H., Higazy, A. and Ramadan, M.A.,** *Starch/Starke*, **44**, 101–107 (1992).

31. **Hebeish, A.M.H., Zahran, M.K., El- Rafie, M.H. and El-Tahlawy, Kh. F.,** *Polymer & Polymer Composites*, **4**, 129–141 (1996).

32. **Hong, D.H. and Carr, M.E.,** *Starch/Starke*, **44**, 268–271 (1992).

33. **Qin Zhua, Rainer Sjöholmb, Kari Nurmic, and Eric Bertoft,** Structural characterization of oxidized potato starch. *Carbohydrate Research*, **309** (2), 213–218 (1998).

34. **Ya-Jane Wang and Linfeng Wang,** Physicochemical properties of common and waxy corn starches oxidized by different levels of sodium hypochlorite. *Carbohydrate Polymers*, **52** (3), 207–217 (2003).

35. **Anna, Bala-Piasek and Piotr, Tomasik,** Air oxidation of potato starch over vanadium (V) catalyst. *Carbohydrate Polymers* , **38** (1), Elsevier – Jan 1, (1999).

36. **Shaarawy, H.H., El-Rafie, S.M., Abd El-Ghaffar, A.M. and El–Rafie, M.H.,** Electrocatalytic oxidation of rice starch using mixed oxidant generated via titanium/rhodium thermally activated modified electrode: Part (I). *Carbohydrate Polymers*, **75**, 208–213 (2009).

37. **Baraka, A.M., Shaarawy, H.H. and Hamed, H.A.,** Electrodeposition of rhodium metal on titanium substrates. *Anti-Corrosion Methods and Materials*, **49**(4), (2002).

38. **Daul, G.R., Rinhard, T. and Rcid, J.D.,** *Text. Res. J.* 23-719 (I953).

39. **Kalimova, V.A. and Zabrodina, K.S.,** *Zhakh*, **15**, 726 (1960).

(Received 8/4/2013;
accepted 29/5/2013)

تحضير نشا مؤكسد بطريقة الحفز الكهربى لاستخدامه كمادة مالئة ومجهزة

حسن شعراوى، صفاء محمد الرافعى* ، عبد الرحمن محمد عبد الغفار* و محمد حسين الرافعى*
قسم الهندسة الكيميائية و*شعبة بحوث النسيج – المركز القومى للبحوث – الجيزة – مصر .

يقدم هذا البحث ابتكارا جديدا حيث يعرض طريقة نظيفة وآمنة وغير مكلفة لملئ توليفات من خيوط القطن والبوليستر الملفوفة وتعتمد هذه الطريقة على استخدام عينة من النشا المؤكسد بطريقة الحفز الكهربائى كمادة مالئة وتم تحديد الظروف التى تتم من خلالهاعملية الأكسدة باستخدام قضيب مطور ومنشط حراريا ومكون من عنصرى الروديوم و التيتانيوم والنشا المتكون بهذه الطريقة ذو لزوجة مناسبة تهيئه لأن يكون فى صورة فيلم ينفذ بسهولة من خلال الخيوط المعالجة ويملؤها وهذه الطريقة تقلل ايضا من كمية المواد المنعمة المستخدمة فى هذه العملية.