TOWARDS WASHABLE SMART TEXTILES: INVESTIGATING THE IMPACT OF OXIDIZING BLEACHING AGENTS ON SILVER-PLATED TEXTILE ELECTRODES

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ABSTRACT

Although textile-based skin electrodes are promising for comfortable long-term monitoring, their washability remains an issue. In this study the impact of oxidizing bleaching agents, contained in commercially available detergents, on electrical properties of silver-plated textile electrodes is analyzed and discussed. To determine the best care instructions to maintain textile electrodes' reliability, silver-plated knitted conductive fabrics have been washed 30 times using powder and liquid detergents (with and without bleaching agents, respectively). Results show that liquid detergents should be preferred to powder ones as those agents oxidize the silver layer, reducing its conductivity and making it more vulnerable to mechanical stress.

Keywords: bleaching agents, e-textile, smart textile, silver yarn, , oxidation, washability

1. INTRODUCTION

Even though a great market success has been announced since many years, no smart garment has been a great mass market success yet. In fact, even if a lot of e-textiles prototypes have been developed in laboratories since 2000 [1], only few smart garments have already hit the market [2]. One of the main reasons is the fact that wearable textronic prototypes suffer from poor washability and reliability [3]. The need to study the impact of the washing process on textronics was underlined back in 2004 [4]. However, few research papers have tackled this particular issue until now, although it can be noted that the washability aspect of recent developments is more clearly taken into account [5],[6],[7]. As noted by Zaman et al. [8] there is a lack of standardizations on the washing process to be followed, the detergent used and the number of washing cycles required to claim that a smart textile is washable. As a results, among the few studies that can be found on the subject, smart garment prototypes are claimed washable according to ISO 6330:2000[9] [10], ISO 105-C01 standard [11] or ISO15797 [10], method 61-2010 of the American Association of Textile Chemists and Colorists (AATCC, Table 1)[5]. Nevertheless, it is important to point out that all of them differ from household laundering at the customers' home which is of prime interest for the present study. There is a global consensus on the impact of washings which is the loss of conductivity of the conductive materials no matter their nature (conductive yarns [12], inks [13] or polymers like PEDOT [6], [7], [14]). In most of the studies only the mechanical stress of the washing process was taken into account and made responsible for this loss of conductivity. However, as electronic parts are mostly made of metal, the chemical aspect should not be forgotten. Kellomäki et al. [9] reported the color change (from silvery to darker grey) of their silver based antenna and explained it by the oxidation of silver. This phenomenon has not been much reported in the literature as the few studies on the washability of a silver material (conductive past, silver coated yarn, silver nano-particles) used bleach free detergents. Only Slade et al. [12] were found to use a detergent with bleaching agents and concluded that metal-coated fabrics performed poorly after washing cycles. The specific responsibility of the bleaching agents, accounting for such results, was not highlighted. In this study the impact of oxidizing bleaching agents on a silver-plated-nylon fabric used as a sensing skin electrode in a smart garment is investigated. To this purpose, the fabric was washed 30 times with (powder detergent) and without (liquid detergent) the bleaching agents. Then the evolution of the conductivity, the silver content, the surface aspect and the color of the fabrics were analyzed and compared throughout the washing cycles.

2. MATERIALS AND METHODS

2.1 Realization of textile Electrodes

Silver plated nylon yarns were purchased from three different suppliers. They will be referred to as yarn A, B and C. Double jersey fabrics (back side in cotton) were produced with each yarn on an industrial circular knitting machine (CMO4A, Orizio).

2.2 Washing Conditions

As this study is done for a garment manufacturer, the washing conditions should be those of its customers at their homes. Samples of 60x60cm^2 of each fabric were washed in a domestic washing machine (ENF 1486 EHW, Electrolux) with the delicate cycle (30°C washing for an hour with a wringing at 400rpm) using different detergents. The lot n°1 was washed with a powder detergent (Omo Concentrated Professional from Diversey S.A) which contains bleaching agents. The lot n°2 was washed with a liquid detergent (Eco bulle Bio from Bulle Verte) which does not contain any bleaching agents. Square samples of 10x10cm^2 were cut out of the big sample and withdrawn after every cycle until 30 cycles, then line dried. For both lots, random everyday clothes were put inside the machine with the samples to simulate a real household washing. As a results 30 washed samples were obtained for each lot.

2.3 Color Evaluation

As silver oxides and silver sulfides tend to be darker than pure silver, the lightness of the samples through washings has been measured to reveal the potential presence of those silver oxides. Assessing the color change of textile has already been used to determine the remaining coating material on the textile [15]. In this study this method has been used to estimate the potential surface oxidation of the conductive layer of the fabric. Color change of the silver-plated-nylon electrodes throughout the washing cycles was measured by using spectrophotometer (CM-3610A, KONIC MINOLTA). The measurement conditions were set up with an illuminant D65 and 10° standard observer. The CIELAB (International Commission on Illumination) color space coordinates (L*: measurement of electrode lightness, a*: measurement of greenness to redness, b*: measurement for blueness to yellowness) were measured. Nevertheless, only the L* value (lightness) was taken into account for the discussion as it can be directly related to the surface oxidation. For each sample, several measurements of L* were done to have a low standard deviation (SD<1) before taking the mean L*. In fact, 10 measurements were done on each sample.

2.4 Electrical Characterization

The electrical characterization of the samples consisted in measuring the surface resistivity of the samples and the linear resistance of the yarn. Surface resistivity is defined as the electrical resistance of the surface of the material. This measurement was carried out by a KEITHLEY 8009 resistivity test fixture according to ASTM D 257-99 [12]. The linear resistance of the yarn is calculated as the resistance per unit length (measured in $\Omega.m^{-1}$). To this purpose 1 cm of a conductive yarn taken from the electrode was measured by a multimeter (2461 Sourcemeter, Keithley) then multiply by 100 to obtain linear resistance of the yarn in $\Omega.m^{-1}$ Five yarns were measured from each electrodes then the mean resistance was taken.

2.5 Scanning Electron Microscope (SEM) Observation

In order to observe the damages of the silver layer on the conductive yarn, a scanning electron microscope (Phenom ProX, ThermoFischer Scientific, US) was used. The identification of different chemical elements in our samples was accomplished with the Element Identification (EID) software package and a specially designed and fully integrated Energy Dispersive Spectrometer (EDS). The identification aimed at determining the percentage of silver still present on the washed samples and the potential silver oxide that could have been formed during washing cycles. Reference sample (without washing) and samples washed respectively 10, 20 and 30 times have been observed and compared.

3. RESULTS AND DISCUSSION

After 30 washing cycles, a major color difference can be noticed between the samples washed with (lot n°1) and without bleaching agents (lot n°2). Indeed, the samples washed with the powder detergent are visually much darker than the ones washed with the liquid detergent. This visual difference was quantified by the spectrometer (Figure 1). Electrodes' lightness tends to decrease significantly throughout washing cycles with bleach whereas it is steadier with a bleach free detergent. As silver oxide and sulfide are darker than pure silver, the oxidation of the pure silver layer can account for the observed color change.

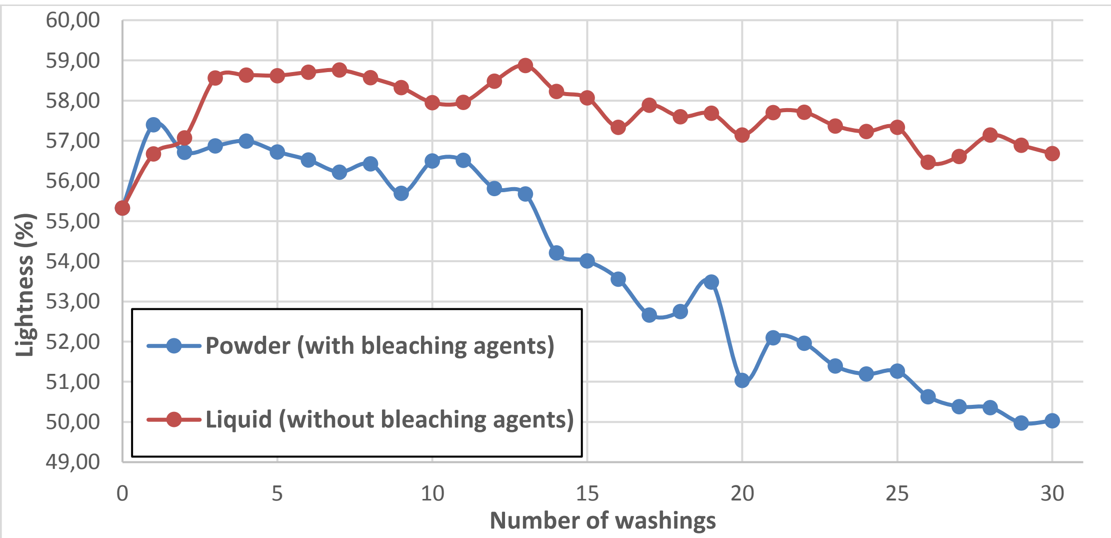


Figure 1. Evolution of lightness with the washings

Moreover, as these products of oxidation are less conductive than pure silver, their presence could be highlighted by the electrical characterization of the samples. Undeniably, whereas after 30 washings with a powder detergent none of the yarns remains conductive, those from lot n°2 present still a high conductivity after 30 washings. Similarly, the surface resistivity of the electrodes has skyrocketed with powder detergents but have barely changed with liquid ones.

Table 1. Electrical characterization of the electrodes

		Yarn A		Yarn B		Yarn C	
		Lot n°1 R ($\Omega.m^{-1}$)	Lot n°2 R ($\Omega.m^{-1}$)	Lot n°1 R ($\Omega.m^{-1}$)	Lot n°2 R ($\Omega.m^{-1}$)	Lot n°1 R ($\Omega.m^{-1}$)	Lot n°2 R ($\Omega.m^{-1}$)
Yarn Linear Resistance	Reference R_0	551,1		580,0		309,9	
	10 washings R_{10}	6,9E+02	5,7E+02	8,4E+02	7,2E+02	9,6E+02	6,7E+02
	20 washings R_{20}	5,6E+03	5,9E+02	1,3E+04	7,9E+02	4,8E+05	8,7E+02
	30 washings R_{30}	1,1E+07	9,2E+02	3,8E+06	1,1E+03	5,8E+09	1,1E+03
	R_{30}/R_0	1,98E+04	1,7	6,53E+03	2,0	1,87E+07	3,7
		R (kΩ)	R (kΩ)	R (kΩ)	R (kΩ)	R (kΩ)	R (kΩ)
Electrode Surface Resistivity	Reference R_0	9,8	9,8	9,4	9,4	9,4	9,4
	10 washings R_{10}	10,6	9,7	9,6	9,7	10,3	9,9
	20 washings R_{20}	10,9	9,5	11,2	9,5	123,9	9,8
	30 washings R_{30}	149,5	9,5	3,2E+03	9,5	>10E+06	9,9
	R_{30}/R_0	15	1	341	1	>10E+06	1

To determine which yarn was more damaged by washing cycles, the ratio between the linear resistance after 30 washings (R_{30}) versus before being washed (R_0) has been calculated. It turns out that even if yarn B has the highest linear resistance before washing, its resistance after 30 washings is the lowest of the three and has only doubled. In the meantime, the resistance of yarn A and C has been multiplied by 6 and 8, respectively. Since the lightness of the washed samples is quite similar to the reference sample for the lot n°2, oxidation can't be the only explanation of the observed rise in linear resistance. SEM observation revealed that no matter the detergent used, the silver layer on the nylon is damaged, even if no bleaching agents is used. These damages result from the mechanical stress on the fabric in the machine during washing cycles. According to Lee al., [16] the mechanical actions during washing cycles can be classified into three types: the hydrodynamic flow action, the flexing and the abrasion action. As illustrated in Figure 2, the silver layer tends to scratch and crack after washing. This can account for the loss of conductivity of the yarn even if they are not oxidized. Nevertheless, it can be noted that much more silver has been rubbed from the conductive layer when the sample was washed in oxidizing condition (lot n°1). It implies that oxidizing conditions make the silver layer more vulnerable to mechanical stress. Most probably silver oxides are less bonded to the nylon and tends to be easily removed under mechanical stress. At the filament level the more silver particles are rubbed, the less conductive is the yarn. At the fabric scale the less probable is the contact between two conducting parts so it reduces even more the fabric's conductivity.

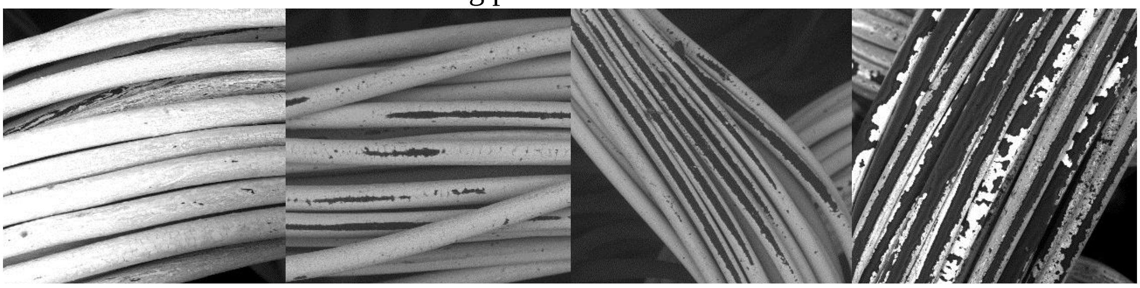
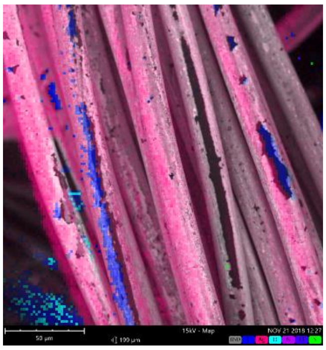
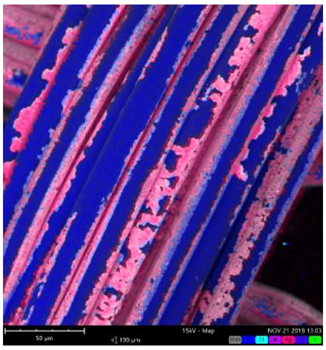


Figure 2.SEM observation of the silver layer after 0,10,20 and 30 washings



Element Symbol	Atomic Conc.	Weight Conc.
C	53.83	20.67
Ag	19.11	65.92
O	17.82	9.12
N	9.00	4.03
Cl	0.13	0.15
S	0.11	0.12

Figure 4. Silver layer (observation and compostion) after 30 washings (lot n°1)



Element Symbol	Atomic Conc.	Weight Conc.
C	64.59	43.48
O	15.76	14.13
N	14.39	11.29
Ag	5.09	30.75
Cl	0.13	0.26
S	0.05	0.10

Figure 3. Silver layer (observation and compostion) after 30 washings (lot n°2)

The loss of silver in weight can be roughly determine by the Element Identification of the EDS. Indeed, as the observed areas of the yarn can't be strictly the same, a comparison between the two compositions can't be drawn directly. To precisely quantified this, a further study supported by thermogravimetric analysis will be carried out. According to those results, about four times more silver seems to remain on the washed samples with a bleach free detergent. This difference can explain why the conductivity of samples from lot n°2 is so much higher. Furthermore, regarding the insignificant presence of sulfur, the dark color observed cannot be explained by the presence of silver sulfide. Since nylon is made of oxygen, the presence of silver oxides is difficult to highlight with this method.

4. CONCLUSION

Knitted fabrics made from three different silver-plated-nylon yarns have been washed 30 times with two different detergents (with and without bleaching agents). It turns out that all of the yarns present similar results. On the one hand, when washed with bleaching agents (powder detergent) they tarnish, their conductivity decreases dramatically and the silver layer is severely damaged. On the other hand, when washed without bleaching agents (liquid bio detergent), no color change can be visually noticed, their conductivity slightly decreases resulting from a smaller damaging of the silver layer. It can then be concluded that bleaching agents, contained in powder detergents, tend to oxidize the silver layer on the yarn's filaments. As a result, the yarn's conductivity diminishes dramatically or is even lost after few washings cycles. But as these fabrics are meant to become sensing skin electrodes of smart garments, their conductivity is a necessity unless the garment would not be "smart" anymore. That's why smart garments, incorporating silver-plated-nylon electrodes, must be washed only with liquid detergents as those detergents do not contain any bleaching agents.
A further study will quantify more precisely, with a thermogravimetric analysis, the loss in silver throughout the washing cycles. It will also go deeper into the characterization of the products of oxidation. Furthermore, as evidenced by SEM observations, even with liquid detergent the mechanical stress has damaged the silver layer in only 30 washings. That's why method to protect the silver layer from mechanical stress should be further explored.

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