

E. Matyjas-Zgondek,
A. Bacciarelli,
E. Rybicki,
M.I. Szykowska*,
M. Kołodziejczyk**

Institute of Architecture of Textile,
Technical University of Lodz,
ul. Zeromskiego 116, 90-543 Łódź

* Institute of General and Ecological Chemistry,
Technical University of Lodz,
ul. Zeromskiego 116, 90-543 Łódź

** Institute of Technical Biochemistry,
Technical University of Lodz,
ul. B. Stefanowskiego 4/10, 90-924 Łódź

Antibacterial Properties of Silver-Finished Textiles

Abstract

In this paper, the results of research on the bacteriostatic efficacy of selected silver particles: nano-Ag, sub-micro-Ag, AgCl in the finishing of textiles are presented. The shape and size of the silver compounds used were estimated by analysis of SEM images. The size and size distribution of the silver compounds were also approximated by the Dynamic Light Scattering method (DLS). The experiments prove that the antibacterial treatment of textile fabrics by the padding-squeezing technique using silver compounds in the resin matrix can be easily achieved. SEM images of the silver-finished fabrics indicated that, generally, silver compounds were well dispersed on the fabric surface, but in some cases they form agglomerates of single particles. The Agar Diffusion Test was used to estimate the biological activity of the treated fabrics. Two strains of bacteria: Gram-positive (*Bacillus subtilis*) and Gram-negative (*Escherichia coli*) were used for this purpose. The washing fastness of Ag-finished textiles was monitored using two modern instrumental methods: ICP-OES and LA-ICP-TOF-MS. The results obtained proved the good and long-lasting bacteriostatic efficacy of silver nanoparticles applied during the finishing of cotton.

Key words: silver nano-particles silver submicro-particles, silver-finished textiles, antimicrobial activity, ICP-OES, LA-ICP-TOF-MS, finish durability.

Over the past decade, there has been a strong push towards the development of silver-containing materials for commercial use that exhibit antimicrobial and bactericidal properties.

Silver, in its many oxidation states (Ag^0 , Ag^+ , Ag^{2+} , and Ag^{3+}) has long been recognised as having an inhibitory effect towards many bacterial strains and microorganisms commonly present in nature [1-2].

Studies have also demonstrated the antiviral activities of various metal nanoparticles against the human immunodeficiency virus (HIV-1) [3].

However, the exact mechanism by which silver inhibits microbial growth is not entirely understood. Several investigations have suggested possible mechanisms involving the interaction of silver ions with biological macromolecules. Generally, it is believed that heavy metals release ions, which react with the thiol groups (-SH) of surface proteins. Such proteins protrude through the bacterial cell membrane, allowing the transport of nutrition through the cell wall.

Monovalent silver ions (Ag^+) are believed to replace the hydrogen cation (H^+) of sulphhydryl or thiol groups, inactivating the protein, decreasing membrane permeability, and eventually causing cellular death [1, 4].

Recently, a great many antimicrobial-finished textiles have been accepted for use in clinical settings to block the transmis-

sion of pathogens. These products contain antimicrobial agents such as silver, quaternary ammonium chloride, and chitosan, and show antibacterial activity against a wide range of microorganisms [5].

Nano-silver particles have an extremely large specific surface area, thus increasing their contact with bacteria or fungi and vastly improving their bactericidal and fungicidal effectiveness [6].

Silver chloride is a well-known antimicrobial agent that is commonly used in hospitals as a catheter coating for wound dressing applications, and when mixed with poly(methyl methacrylate) is also used in bone cement application [7].

However, it is difficult to compare their effectiveness because different methods have been used for evaluation.

In this study, cotton fabrics were treated with the proposed antimicrobial formulations based on commercial Ag-nanoparticles, submicro- (Ag)- particles obtained by the chemical reduction of silver nitrate with L-ascorbic acid, and on silver chloride obtained by the chemical reaction of silver nitrate with hydrochloric acid and the Helizarin Binder ET95 as a self-crosslinking agent.

The effect of this treatment on the growth of certain bacteria (*Escherichia coli*) and *Bacillus subtilis* was studied using the Agar Diffusion Test. The size and particle size distribution of silver particles themselves as well as silver particles on cotton fabric were estimated by the scanning

electron microscopy (SEM) method and Dynamic Light Scattering method (DLS).

The durability of antimicrobial finishing against washing was assessed using quantitative (ICP-OES) and semi-quantitative (LA-ICP-TOF-MS) methods. It made it possible to determine the silver content on the fibre before and after several washings and to compare those results with the change in antimicrobial activity observed.

Experimental

Materials and Methods

Woven cotton fabric of plain weave with a surface mass of 100 g/m² was desized and chemically bleached before silver finishing.

Helizarin Binder ET95 – a BASF product: anionic water dispersion of mixed acrylic polymers, self-crosslinking binding agent of density ca. 1.03 g/cm³ and pH ca. 7-9 was used after suitable dilution to fix the silver particles to the cotton fabric surface.

The product was diluted to the proper concentration (10%) using double-distilled water at ambient temperature. The concentration of the binder in the finishing bath was estimated on the basis of preliminary experiments to get the proper ratio of resin content to the quantity of silver particles, thus ensuring effective antimicrobial performance.

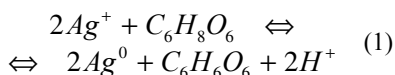
Nanoparticles Ag, a Sigma Aldrich product (No. 576832-5G), were used as

supplied. According to Sigma Aldrich specifications, the particle size was below 100 nm, with a thermal resistance of 1.59 Wm/cm at 20 °C and a specific surface area of 5.0 m²/g.

Silver nitrate, L-ascorbic acid and hydrochloric acid (35-38%), products of ChemPur and POCH, respectively, were of a high purity grade.

Submicro – Ag particles were synthesised using the modified method, proposed earlier by Suber et al. [8]. To obtain the nano- silver particles, we carried out the chemical reduction of an aqueous solution of silver nitrate (0.1 M/dm³) with an aqueous solution of L-ascorbic acid (0.1 M/dm³) in the presence of PVP using (polyvinylpyrrolidone) – Kollidon 90F, a BASF product, as a stabilising agent.

L – ascorbic acid has the ability to precipitate the metallic silver in acidic solutions according to the following reaction:



After the precipitation process had been completed (nano-particles' formation), the sediment was repeatedly rinsed with double-distilled water, followed by methanol and next dried at 80 °C.

Silver chloride particles were synthesised by precipitation from an aqueous solution of 0.1 M/dm³ silver nitrate with a drop wise addition of an aqueous solution of pure hydrochloric acid (0.1 M/dm³), which was then vigorously stirred. The sediment was repeatedly rinsed with double-distilled water, followed by methanol and next dried at 80 °C at dark conditions.

Antibacterial finishing of textiles – Cotton samples were triple padded in the dispersion of nanosilver particles (with silver concentration of 1 g/dm³, 2 g/dm³, and 5 g/dm³) in the Helizarin Binder ET95 finishing bath using a laboratory padding-squeezing machine, a product of E. Benz, Switzerland; the pressure of the padding – squeezing shafts was 40 kG/cm. Then the cotton samples were dried at 90-100 °C for 3-4 min and cured at 130 °C for 2 min.

Washing fastness of the silver-finished textiles was estimated according to Standard PN-EN ISO 105-C06:1996/ Ap1:1999 ; the AIS method without metal balls, where ECE Standard Detergent of SDC Enterprises Ltd. was applied.

After each laundering the samples were rinsed twice in double-distilled water and next dried at 80 °C. The durability of antimicrobial finishing of the cotton samples was assessed after 5 washings.

Scanning electron microscopy (SEM) – the size and shape of the nano- and submicro-particles was examined with a JSM-5200LV scanning electron microscope, made by JEOL (Japan). SEM images were observed with a magnification of 100x to 20000x with an accelerating voltage of 20kV and registered by a SemAfore slow-scan digital image recording system. The size of the silver particles studied was determined from the SEM images using the UTHSCSA Image Tool version 3.0.

The **Agar Diffusion Test**, according to Standard PN-EN ISO 20645:2007, was used for the evaluation of antimicrobial properties against *Escherichia coli* (Gram-negative bacterium-internal name: LOCK 0836 1998) and *Bacillus subtilis* (Gram-positive bacterium, internal name – LOCK 0816 1975, IBPRS, AATCC 6633). The Agar diffusion test is a method of testing the effectiveness of antimicrobial agents by measuring their inhibition zones.

Quantitative determination of the silver content in silver-finished cotton before and after washing was carried out using the **ICP-OES** (Inductively Coupled Plasma-Optical Emission Spectrometer) method. Nano-Ag – the finished cotton samples were homogenised with an agate mortar and mineralised (approximately 200 mg of material) with 5 cm³ of concentrated nitric acid, a J. T. Baker product, using a microwave oven made by Milestone MLS-1200 MEGA., USA. An analysis of the Ag content of the fabric was performed with inductively coupled plasma optical emission spectrometry IRIS-AP, a product of Thermo Jarrel Ash, USA, at the emission line of 328.068 nm.

Semi-quantitative determination of the silver content in the silver-finished cotton before and after multiple washings was carried out using the **LA-ICP-TOF-MS** (Laser Ablation-Inductively Coupled Plasma-Time of Flight-Mass Spectrometry) non-destructive method to compare the results obtained with those of the ICP-OES method. The details of the method used were described earlier [9].

An Optimass 8000 ICP-TOF-MS instrument, produced by GBC (Australia),

coupled with a laser ablation unit (LA), a product of CETAC Laser Ablation System (USA), was used. The action of a high-energy laser beam on a solid results in the evaporation and removal of material in the form of neutral atoms and molecules as well as positive and negative ions from the surface of the solid exposed to this radiation.

To determine the silver content, the nano-Ag-finished sample of cotton fabric, finished in the bath comprising 5 g/dm³ of nano-particles, was tested for the durability of the antibacterial effect after 5 washing cycles and then subjected to LA-ICP-TOF-MS determination.

The silver-finished samples (before and after 5 washings) were placed inside an ablation cell, and a laser beam was focused on the surface of the samples. The set of parameters for the LA-ICP-TOF-MS system is shown in **Table 1**. When the laser was fired, a cloud of particles was produced. These particles were removed from the sampling cell by argon carrier gas and then transferred through an ICP plasma torch, a TOF analyser and an MS interface to a mass detector. The time needed to reach the detector is strictly linked to the value of the mass-to-charge ratio (m/z) [9].

From the data of the quantitative and semi-quantitative determination of the silver content before and after washing, the washing fastness indicator (WFI) was calculated:

$$WFI_{\%} = \frac{NoC_{aw}}{NoC_{bw}} \cdot 100 \quad (2)$$

where:

NoC_{aw} – content of silver or number of counts in the sample, after washing,

NoC_{bw} – content of silver or number of counts in the sample, before washing.

The proposed indicator describes the percentage of silver content in the fabric after multiple washing and manifests the durability of silver-finished textiles against washing [10].

DLS – Dynamic light scattering was used to determine the size distribution profile of small particles in solution. DLS, which has many variations, does not by itself identify the chemical nature of a nanoparticle. The Particle Sizing System NICOMP 380, a product of Nicomp,

Santa Barbara, California, uses Dynamic Light Scattering (DLS) to obtain the particle size distribution for samples with particles ranging from 2 nm to 10 microns. Through the use of the proprietary Nicomp analysis algorithm, the 380 is able to analyse complex multi-modal distributions with the highest resolution and reproducibility available.

A simplified schematic diagram of the DLS module is shown in **Figure 1**. Light from a laser is focused into a glass tube containing a dilute suspension of particles. The temperature of this scattering cell is held constant, for reasons which will soon become apparent. Each of the particles illuminated by the incident laser beam scatters light in all directions. The intensity of light scattered by a single, isolated particle depends on its molecular weight, overall size and shape, as well as on the difference in refractive indices of the particle and surrounding solvent. The incident light wave can be thought of as consisting of a very rapidly oscillating electric field, of amplitude E_0 (frequency approx. 10^{15} Hz).

Results and discussion

Figure 2 shows an example of SEM images of silver particles used as a starting material for preparing the silver-finished antimicrobial cotton. As can be seen, the nano Ag particles by Sigma Aldrich (**Figure 2a**) are spheroid in shape, with an average diameter of 20-90 nm. The silver particles, synthesised according to [8], have entirely different morphologies due to the synthesis conditions, as was observed in the paper mentioned earlier (**Figure 2b**). The average sub-micro Ag particle size is in the range of about 0.47 μm to 2.28 μm , with a majority of particles having an average diameter of 0.73-0.98 μm and 1.77-2.02 μm with rather narrow size distribution; as can be seen from the particles' size distribution histogram (**Figure 3**, see page 104).

Table 1. Set of parameters for the LA-ICP-TOF-MS system for testing nano-Ag finished textiles.

Laser Parameters		TOF-MS		ICP	
Laser power, mJ	9 per shot	Skimmer, V	1,500	X position, mm	11.2
Pulse rate, Hz	20	Extraction, V	1,100	Y position, mm	-1.1
Spot size, μm	150	Z1, V	770	Z position, mm	-0.1
Rate of scan, $\mu\text{m/s}$	100	Y Mean, V	-160	Nebulizer flow, L/min	0.79
–	–	Y Deflection, V	2	Plasma flow, L/min	10
–	–	Z Lens mean, V	-1,030	Auxiliary flow, L/min	1
–	–	Z Lens deflection, V	-2	Power, W	800
–	–	Lens body, V	-130	–	–
–	–	Fill, V	-38	–	–
–	–	Fill bias, V	0	–	–
–	–	Fill grid, V	-18	–	–
–	–	Pushout plate, V	720	–	–
–	–	Pushout grid, V	-580	–	–
–	–	Multiplier gain, V	2,850	–	–
–	–	Reflectron, V	699	–	–

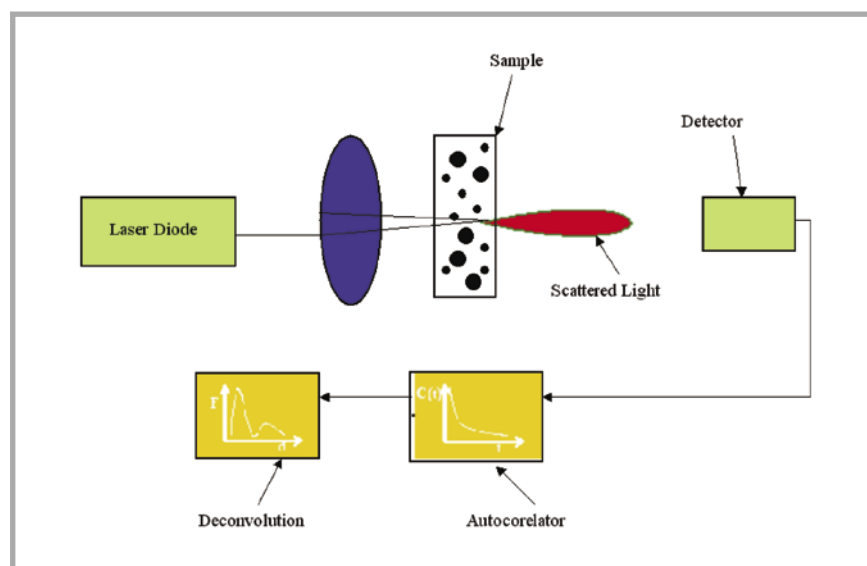


Figure 1. Simplified block diagram of – NICOMP DLS Instrument [NICOMP 380 User Manual].

In the case of silver chloride particles, the SEM image reveals (**Figure 2c**) that AgCl particles also have a different morphology and a rather flat-like structure, with an average diameter of particles clearly exceeding 10 μm . It is commonly known from literature that the particle

size of silver nanoparticles is strongly dependent on, and influenced by the molar ratio of reducing agent to the silver salt, temperature and pH value [11].

The morphology of the silver finished cotton sample was examined with the

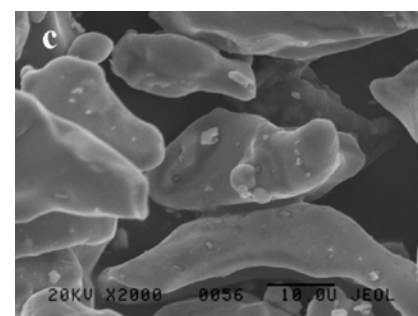
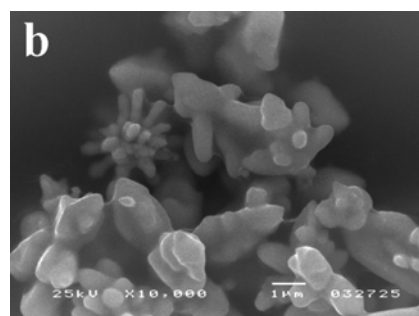
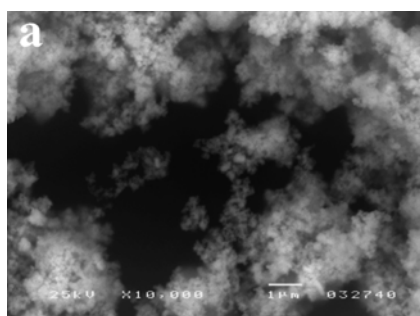


Figure 2. SEM images of the silver compound particles: a) nano-Ag (Sigma Aldrich), b) sub-micro-Ag (this work), c) AgCl (this work).

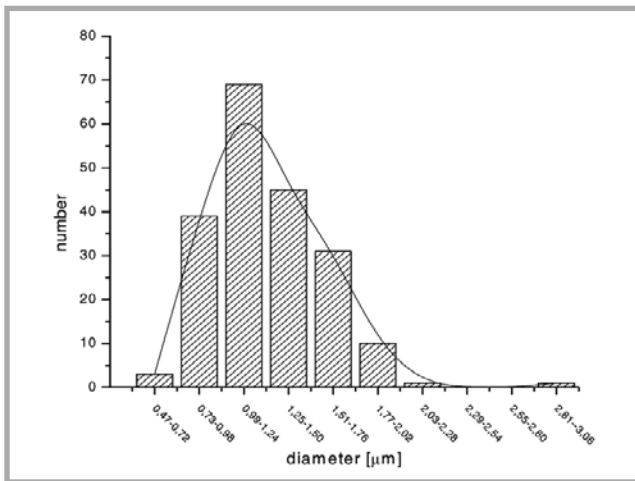


Figure 3. Particle size distribution histogram of the sub-micro-Ag particles.

scanning electron microscopy technique. **Figure 4** shows SEM images of the silver finished-samples using both the Sigma Aldrich nano-Ag particles and sub-micro Ag-particles, synthesised in this work, in the Helizarin Binder ET95 matrix. A comparison of the SEM images obtained at a magnification of 100x allows to draw the conclusion that an application of both the silver particles for the silver finishing of textiles leads to the uniform distribution of aggregate silver particles on the fibre surface. A more detailed analysis of the SEM images of the silver-finished cotton at magnifications of 20,000x and 10,000x proved that the silver particles were partly uniformly distributed on the fibre surface, but several hundred nano-

silver particles aggregated into a cluster, as shown in **Figure 5**, irrespective of the type of silver particles used. A similar observation, using the transmission electron microscopy (TEM), was recently published in literature [12].

Size distribution profiles of the silver particles were also determined with the use of the DLS method. Nanosilver particles (Sigma Aldrich), sub-micro Ag particles and AgCl particles were dispersed in 2 ml of double-distilled water. DLS measurements were carried out using a NICOMP 380 instrument, Particle Sizing Systems. Particle sizes were measured at 23 °C. Data were acquired and processed by accompanying CW388 software. The Gaussian size distributions

and Nicomp size distributions of nano-Ag particles (Sigma Aldrich), sub-micro Ag particles and AgCl particles in the water solution are shown in **Figures 6, 7** and **8**. **Table 2** (see page 106) shows the intensity weight, volume weight and number weight of Ag-nanoparticles sub-micro Ag particles and AgCl particles as obtained by the DLS method.

Based on DLS analysis (**Table 2**), the size range of nanosilver particles (Sigma Aldrich) is 19-124 nm, sub-micro silver particles 0.29-2.1 μm and for silver chloride particles it is from 0.96 to 11.45 μm. It can be seen that the results obtained from SEM analysis and the DLS method are comparable.

Figure 9 (see page 106) shows, as an example the Agar Diffusion Test results for the nano-Ag –finished cotton (Sigma Aldrich), sub-micro-Ag finished cotton (this work) and AgCl- finished textiles (this work) for two kinds of bacteria strains *Bacillus subtilis* and *Escherichia coli*, respectively. The antibacterial activity is estimated on the absence or presence of bacterial growth in the contact zone between the agar and the sample, as well as on the appearance of an inhibition zone. It can be seen that a strong antimicrobial effect towards the Gram (-) and Gram (+) bacteria is manifested, proving that all the silver compounds can be used for the antimicrobial finishing of cotton fabric.

Table 3 (see page 106) shows changes in the inhibition zones of the silver-finished textiles for both of the bacteria strains applied, using various concentrations of silver particles in the finishing bath before washing and after five washings. It can be seen that antimicrobial effectiveness is strongly dependent on the silver concentration used in the finishing bath. The biggest effectiveness in antimicrobial performance of silver-finished cotton was observed for nano-Ag particles supplied by Sigma Aldrich. Much smaller inhibition zones, but still satisfactory from a microbiological point of view, were observed for sub-micro-Ag particles. Practically the lowest antimicrobial action of the AgCl particles used for fabric finishing was observed.

The washing performance of the silver-finished textiles reveals that in the case of nano-Ag-particle-finished fabric, the bacteria inhibition zones remain practically unchanged after 5 washing cycles. Almost the same concerns the sub-micro-Ag particles synthesised in this work. In the case of AgCl particles, satisfactory

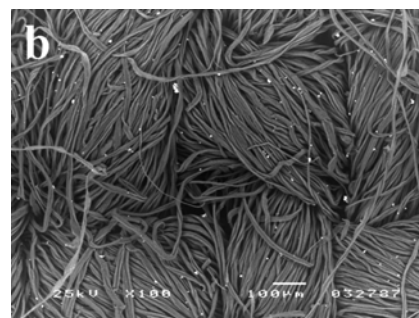
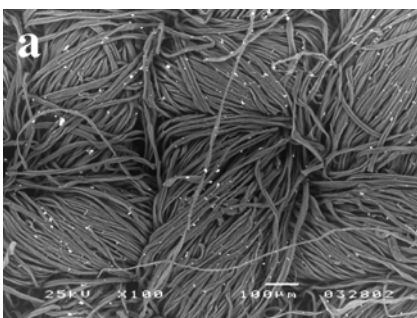


Figure 4. SEM images of the fabric treated with a composition of Ag and polymeric resin: a) nano-Ag (Sigma-Aldrich) finished textiles, b) sub-micro-Ag (this work) finished textiles.

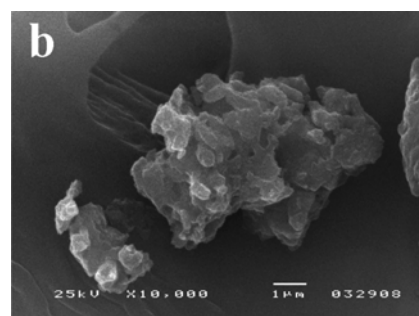
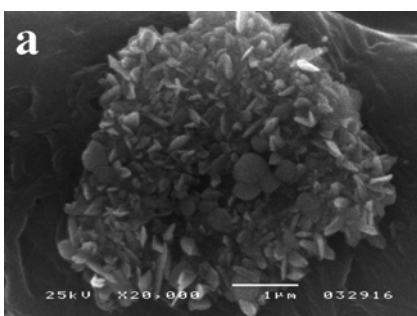


Figure 5. SEM images of the agglomeration of silver in the fabric: a) nano-Ag (Sigma-Aldrich) finished textiles, b) sub-micro-Ag (this work) finished textiles.

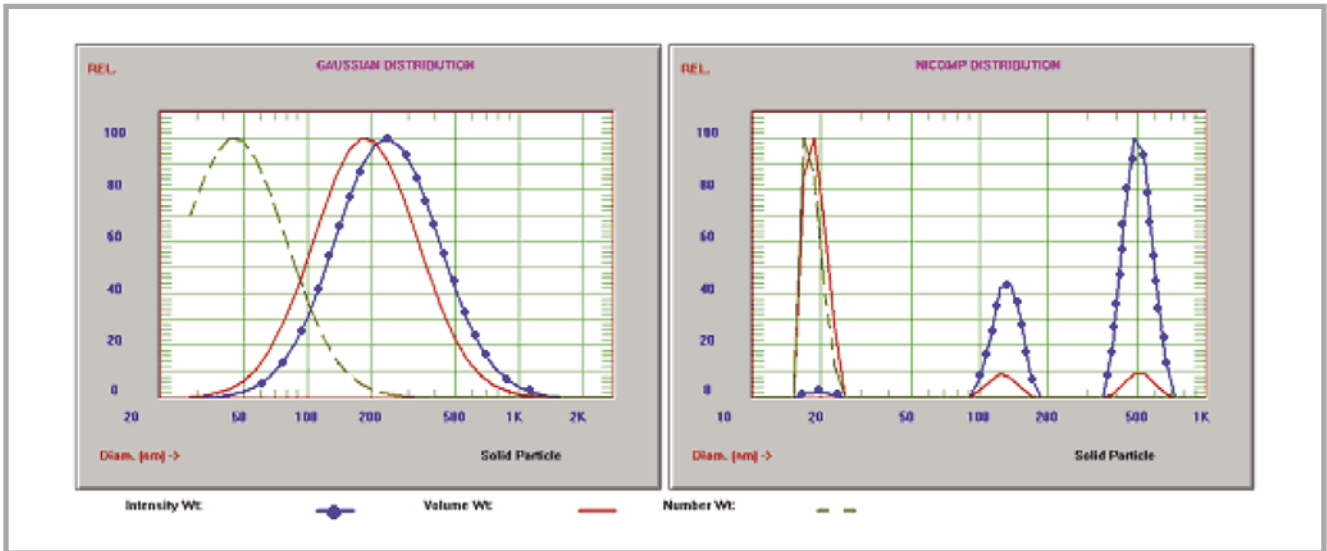


Figure 6. Gaussian distribution and Nicomp distribution of nano-Ag particles in the water dispersion as obtained by the Dynamic Light Scattering Method (DLS).

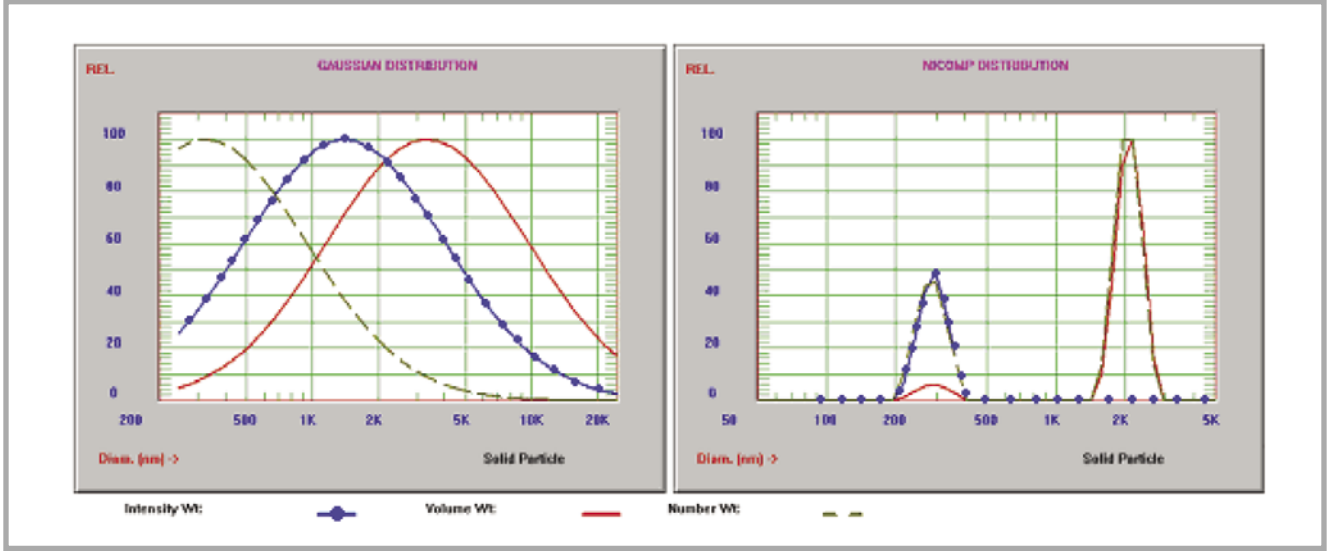


Figure 7. Gaussian distribution and Nicomp distribution of sub-micro Ag particles in the water dispersion, as obtained by the Dynamic Light Scattering Method (DLS).

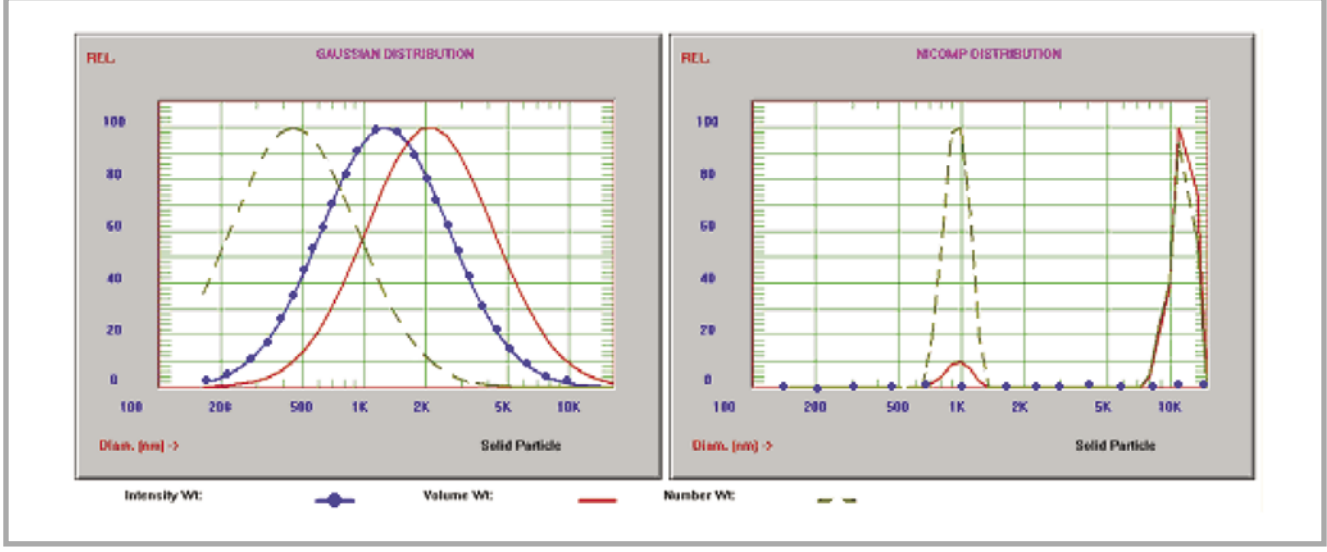


Figure 8. Gaussian distribution and Nicomp distribution of sub-micro AgCl particles in the water dispersion, as obtained by the Dynamic Light Scattering Method (DLS).

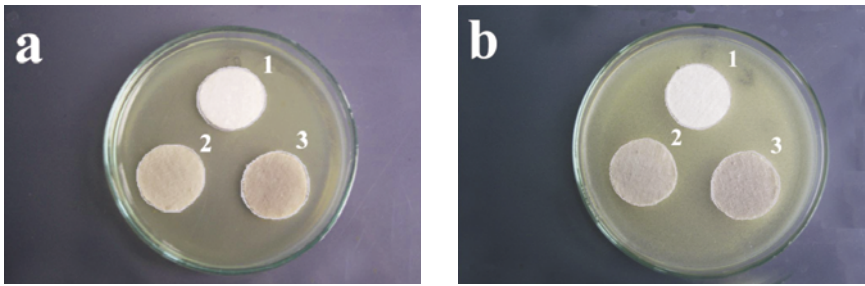


Figure 9. The agar diffusion test for a) *Escherichia coli* b) *Bacillus Subtilis 1* – nano-Ag (Sigma-Aldrich) finished textiles, 2 – sub-micro-Ag (this work) finished textiles, 3 – AgCl (this work) finished textiles; the antibacterial activity is estimated on the absence or presence of bacterial growth in the contact zone between the agar and the sample, as well as on the appearance of an inhibition zone.

Table 2. Intensity, volume and number weights of Ag-compounds dispersed in the distilled water.

Ag compounds	Intensity weight		Volume weight		Number weight	
	Mean diameter, nm	Percent, %	Mean diameter, nm	Percent, %	Mean Diameter, nm	Percent, %
Nano Ag (Sigma Aldrich)	19.1	1.3	19.6	92.6	291.0	99.3
	124.5	23.9	125.8	4.1	124.0	0.6
	421.4	74.8	427.7	3.2	421.4	0.1
Sub-micro Ag	294.3	32.9	295.7	5.9	19.6	31.2
	2,094.1	67.1	2,121.9	94.1	2,094.1	68.8
AgCl	964.7	51.5	978.2	8.7	964.7	51.5
	11,450.1	48.5	11,618.5	91.3	1,1450.1	48.5

Table 3. Bacteria inhibition zones of Ag-finished cotton fabrics.

Composition of x,g/l Ag compounds and polymeric resin			Bacteria's inhibition zones, mm			
nano-Ag (Sigma Aldrich)	sub-micro-Ag (this work)	AgCl (this work)	<i>Escherichia coli</i> (G-)		<i>Bacillus Subtilis</i> (G+)	
			before washing	after 5 washings	before washing	after 5 washings
1	–	–	0.5	0.5	0.5	0.5
2	–	–	0.5	0.5	1.0	0.5
5	–	–	1.0	0.5	2.0	1.0
–	1	–	below sample	below sample	below sample	below sample
–	2	–	0.5	below sample	0.5	below sample
–	5	–	1.0	1.0	1.0	1.0
–	–	1	0.0	0.0	0.0	0.0
–	–	2	1.0	0.0	1.0	0.0
–	–	5	1.5	0.5	3.5	0.5

Table 4. Changes in the Ag average content of the 5 g/l nano-Ag (Sigma-Aldrich) finished fabric before and after 5 washing.

Composition of x, g/l nano-Ag and polymeric resin	Content of Ag, mg/kg		Content of Ag, mg/m ²		WFI, %
	before washing ± %RSD	after 5 washings ± % RSD	before washing	after 5 washings	
1	1,505 ± 0.7	257.8 ± 0.5	150.5	25.78	17.13
2	3,697 ± 0.7	734.7 ± 0.6	369.7	73.47	19.87
5	11,030 ± 0.2	5,523 ± 0.2	1103	552.3	50.07

Table 5. Number of counts of different Ag isotopes from the nano-Ag finished fabric before and after washing (5g/l nano-Ag).

Ag isotopes	Number of counts		WFI, %
	before washing	after 5 washings	
¹⁰⁷ Ag	166 307 920	86 474 512	52.0
¹⁰⁹ Ag	161 142 384	83 673 296	51.9

results were obtained only at the highest concentration of those particles (5 g/dm³) in the finishing bath.

The results obtained distinctly confirm that the application of nano-silver particles for antibacterial finishing of textiles is more beneficial than using the other silver particles in this work.

Changes in the average silver content of cotton fabric finished in 10% water dispersion of nano-Ag particles (Sigma Aldrich) in the Helizarin Binder ET95 before and after several washings, as obtained by the ICP-OES method, are shown in **Table 4**. The data obtained are expressed in ppm (mg/kg) of the cotton fabric and in mg/m², taking into account the surface mass of cotton fabric, which is 100 g/m².

It can be observed that the average content of nano-Ag particles on fabric is in good relation to the silver particle content in the finishing bath. Depending on the nano-Ag particle content in the finishing bath, in the range of 1g/dm³ – 5 g/dm³, the average silver content on the fabric, ranging from 1,505 to 11,030 ppm, was estimated, respectively. After five washings, a sudden decrease in silver content on the fabric was observed. The change in the WFI-factor proves that after multiple washing, ca 17% – 50% of the initial silver content is still present on the finished fabric. A comparison of the results obtained with those shown in **Table 3** allows to draw the conclusion that a very low amount of silver (ca 26 mg/m²) in the form of nanoparticles is needed to finish fabric cotton bactericidal. One can almost conclude that this amount of silver, acting as a bactericide, may be smaller by a factor 2 taking into account that the finishing process of the cotton fabric was carried out on both sides, but the microbiological determination was done using one side of the silver-finished textile only. This observation strongly proves that the application of nanotechnology should be preferred over sub-microparticles application for the powerful finishing of textiles.

The nano-Ag particle content on the cotton fabric before and after 5 washing cycles can be estimated using the LA-ICP-TOFMS method. **Figure 10** shows changes in the mass spectrum of the nanosilver amount in the finished cotton fabric before (red line) and after 5 washing cycles (green line). The data obtained reveal that

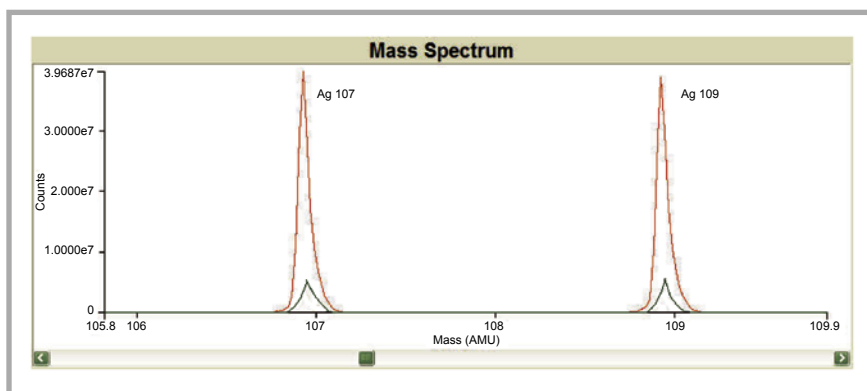


Figure 10. Results of semi-quantity assessment of the nano-Ag content in cotton fabric using the LA-ICP-TOF-MS method, red line – results before washing, green line – results after washing.

the mass spectrum consists of the characteristic two peaks for the two different Ag isotopes: Ag¹⁰⁷ and Ag¹⁰⁹. The calculated data taken from the mass spectrum using the specially designed computer programme are presented in **Table 5**.

The data shown in **Table 5** prove that the number of counts for certain silver isotopes, expressed as the *WFI* indicator, decreased insignificantly after 5 washing cycles – ca 52% of the nano-Ag is still present on the fabric. It is shown the data obtained by this semi-quantitative method coincide well with those obtained using the ICP-OES destructive method, ensuring the comparable results.

Conclusions

As was shown by the analysis of the SEM images, the synthesis of silver particles using L-ascorbic acid as a reducing agent caused that the larger size of silver particle was of a different morphological structure to those supplied by Sigma Aldrich.

The results of the DLS analysis of all the particles examined are compared with the ones obtained from the SEM images.

The silver particles used in this work were well dispersed in the finishing bath containing Helizarin Binder ET95. The SEM images confirmed that the morphological structure of the cotton fabric during finishing was almost uniformly covered by aggregates of silver particles, but in some cases the formation of agglomerates of silver particles on the textile surface was observed.

The application of silver-containing dispersions in the resin matrix for the antibacterial finishing of cotton fabric showed the efficient bacteriostatic efficiency of such finishes.

Nanoparticles, even in very small amounts, can provide the final product with bacteriostatic properties due to the fact that nano-scaled materials have a high ratio of surface area to volume.

To ensure comparable results in the bactericidal activity of the other silver particles used with those obtained while using nanoparticles, a bigger concentration of these compounds has to be used.

The results of both of the instrumental methods applied in this work, namely ICP-OES and LA-ICP-TOF-MS, for the determination of the silver content on cotton fabric, in relation to those obtained for microbiological estimation of bactericidal efficacy, indicate that silver particles are couple well with the fabric proving the long-lasting durability of such a finish against washing.

Both of the ICP techniques in this work (destructive and non-destructive) can be applied as suitable and sensitive methods for determination of the relative silver content on textiles, and washing fastness. It is noteworthy that the application of the LA-ICP-TOF-MS method in this study allows to detect silver isotopes without any destruction of the sample being investigated.

Acknowledgments

The authors would like to express their gratitude to Henryk Wrzosek of the Department of Fibre Physics and Textile Metrology, Technical University of Lodz, for taking the SEM photographs of nano-Ag and sub-micro-Ag particles, as well as the SEM photographs of the nano-Ag and sub-micro-Ag finished textiles.

This work was supported by the 6th Framework EU Integrated Project DIGITEX, IP 026740-2, "Digital Fast Patterned Microdisposal of Fluids for Multifunctional Protective Textiles."

References

- Clement J. L., Jarret P. S., "Antibacterial Silver", *Metal-Based Drugs*, 1, 467-482 (1994).
- Jiang H.Q., Manolache S., Wong A.C.L., Denes, F. S. "Plasma-enhanced deposition of silver nanoparticles onto polymer and metal surfaces for the generation of antimicrobial characteristics", *Journal of Applied Polymer Sci.*, 93(3), 1411-1422 (2004).
- Sun R. W.-Y., Chen R., Chung N., P.-Y. Ho C.-M., Lin C.-L. S. Che, "Silver nanoparticles fabricated in Hepes buffer exhibit cytoprotective activities toward HIV-1 infected cells", *Chemical Communications*, 5059-5061 (2005).
- Feng Q.L., Wu J., Chen G.Q., Cui F.Z., Kim T.N., Kim J.O., "A mechanistic study of antibacterial effect of silver ions on *Escherichia coli* and *Staphylococcus aureus*", *Journal of Biomedical Materials Research*, 52(4), 662-668 (2000).
- Takai K., Ohtsuka T., Senda Y., Nakao M., Yamamoto K., Matsuoka J. and Hirai Y., "Antibacterial Properties of Antimicrobial-Finished Textile Products", *Microbiol. Immunol.*, 46(2), 75-81 (2002).
- Lee H. J., Yeo S. Y., Jeong S. H., "Bacteriostasis and skin innocuousness of nanosilver colloids on textile fibre", *Textile Research Journal*, 75(7), 551-556 (2005).
- Potiyaraj P., Kumlangdudsan P., and Dubas S.T., "Synthesis of silver chloride nanocrystal on silk fibers", *Materials Letters*, 61, 2464-2466 (2007).
- Suber L., Sondi I., Matijevic E., "Preparation and the mechanism of the formation of silver particles of different morphologies in homogeneous solutions", *Journal of Colloid Interface Sci.* 288(4), 489-495 (2005).
- Szynkowska M.I., Czernski K., Paryjczak T., Rybicki E., Włochowicz A., "Testing Textile Using LA-ICP-MS-TOF Method", *Fibres & Textiles in Eastern Europe*, 58(4), 87-90 (2006).
- Bacciarelli A., Rybicki F.E., Matyjasz-Zgondek E., Kołodziejczyk M., "Antibacterial properties of nano silver finished textiles". X Conference of Faculty of Engineering and Marketing of Textile; Lodz, March 2007.
- Wanzhong Z., Xueliang Q., Jianguo C., "Synthesis of silver nanoparticles – Effect of concerned parameters in water/oil microemulsion", *Materials Science and Engineering B*, 142, 1-15 (2007).
- Chen W., Wu W., Chen H., Shen Z., "Preparation and characterization of noble metal nanocolloids by silk fibroin in situ reduction" *Science in China – Series B Chemistry*, 46(4), 330-338 (2003), <http://219.238.6.20/>

Received 20.01.2008 Reviewed 18.06.2008