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INFLUENCE OF ADDITIVES ON THE CHARACTERISTICS OF NANOPARTICLES

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Abstract: *Here the influence of additives on NPs in spray formulation used for textiles treatement is assessed. After oleofobization with Tubiguard textile materials from 100% cotton were spray-treated in a specialized chamber with Ag NP and CeO_2 NP in 3 sizes ranges (<100nm, <200nm, 2-3μm) in a water – ethanol - based dispersions containing aditional additives. Electron microscopy analyzes by light field, high resolution and electron diffraction on selected area analyses highlighted the spherical and polyhedral form of the nanoparticle the homogeneitiy of the nanoparticles dispersion. Analysis of the uniformity, morphology and distribution of the nanoparticles on textile matrices were performed by using: the SEM (Scanning electron microscope) made on Quanta 200 FEY, the TEM (Transmission electron microscopy) and EDS (Energy-dispersive X-ray spectroscopy), IPC-MS Analyses (Inductively coupled plasma mass spectrometry). Analysis of the influence of the chemical auxiliaries on the shape and dimension of the nanoparticles were made for: solution of CeO_2 and Tubiguard VCN-5g/l, Solution of nanoCeO_2 and RucoDry(5 g/l) and RukoLink (1 g/l), solution of Ag NPs and Tubiguard VCN(5g/l), solution of nanoAg and RucoDry (5 g/l) and RukoLink (1 g/l).The TEM analysis reveals that dimensions and shape of the NPs did not change under the action of the chemical auxiliaries.*

Key words*:* textiles, nanoparticles, additives, microscopy

1. INTRODUCTION

In the early 2000s, a series of national and international reports highlighted the importance of nanotechnology, but also acknowledged the potential risks. These reports led to an increased interest in nanoparticles toxicology, accompanied by a change in terminology. Several preclinical and clinical studies have approached short-term inhalation and the respiratory effects of nanoparticles. For example, studies in the field noticed associations for nanoparticles and carbon with reductions of the pulmonary function in asthmatic patients, and healthy adolescents and adolescents suffering from asthma in New York showed an increase in the inflammation indices [1]. Most preclinical and clinical studies on UFPs (ultrafine particles) were conducted with diesel exhaust gases and diesel exhaust gases particles (DEP), a particularly rich source of UFPs. These studies revealed a respiratory tract inflammation in healthy individuals, including elevated levels of inflammatory cells and mediators (fig.1,2).

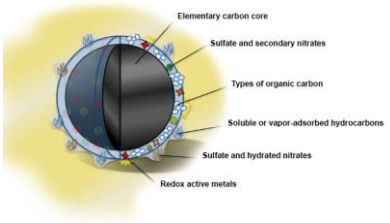

***Fig. 1**: Complex Composition of UFP*

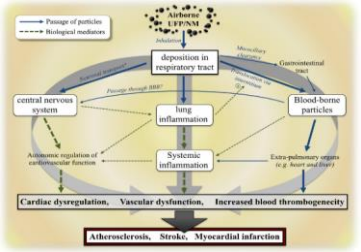

***Fig. 2**: Action Mechanisms of UPF*

2. CHARACTERIZATION OF AG NPS

The Ag nanoparticles from SIGMA-ALDRICH are part of the materials category from the NM series destined only for testing in the research activity, being also included in the international testing program OECD WPMN (OECD Paris 2009-ENV-JM-MONO-2009-20 ENG Manual [3].

By the analyses [4-5] of **differential calorimetry (DSC**) the DSC thermogram was obtained which highlighted for Ag NPs, the apparition of 4 peaks corresponding to some values of the onset of: 51,54ºC, 124,97ºC, 202,26ºC and 353,63ºC determined by the degradation of the stabilization agents at the melting temperature of Ag (961,8^{0}C). The nanoAg **FT-IR-ATR analysis** of the Ag NPs highlighted the peaks corresponding to the absorbtion maxima attributed to the stabilization agents (Polyoxyethylene glycerol trioleate and Polyoxyethylene Sorbitan mono laurate), these absorbing radiation in the range of 4000-600 cm^{-1};. The TEM images in light field obtained on AG NPs (fig. 3) reveal that they are spherical and polyhedral, with a mean particle dimension of 50,55 nm ± 1.97 nm and a very uniform dispersion (fig.4). The regular sequence of the crystalline planes indicated that the nanocrystallites are uniform from a crystalline viewpoint, without having the amorphous phase and the only phase formed is the Ag.

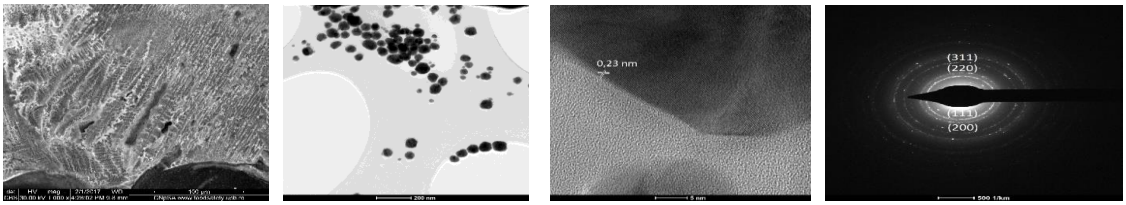

***Fig. 3**: SEM Image a) TEM images in light field b) HR-TEM and SAED images -nanoAg*

The *dynamic light scattering* (DLS) characterization was performed using an electronic scanning microscope for high-resolution imaging, HR-SEM (FEI Inspect F50), which revealed the bimodal granulometric distribution of the nanoAg, identifying a 46% mass fraction of particles with an average diameter of 6.4 nm, respectively a mass fraction of 54% of particles with an average diameter of 172 nm (fig. 5).

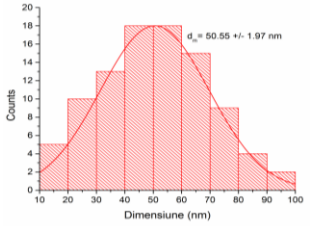

***Fig. 4**: Dimension Distribution of Ag* NPs

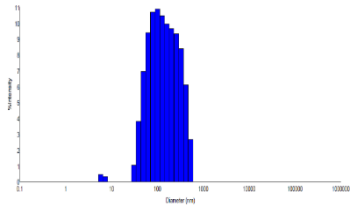

***Fig. 5**: Bimodal Distribution of Ag NPs*

3. CeO_2 NPs CHARACTERIZATION

The CeO_2 nanoparticles were delivered by Sigma Aldrich under similar conditions to the Ag NPs. **The FT-IR analyzes** of the CeO_2 NPs revealed the small number of characteristic peaks specific to a high purity degree of the cerium oxide. **The SEM and TEM characterization** of the CeO_2 NPs revealed their polyhedral form. A very large variation in dimension and shape was remarked. The crystalline planes with a distance of 3.1 Å corresponding to the families of crystalline planes (311) were observed. The nanocrystallites are uniform from a crystalline viewpoint without having the amorphous phase, the only phase being that of polycrystalline cerium. The CeO_2 NPs showed a peak at the level of 357nm.

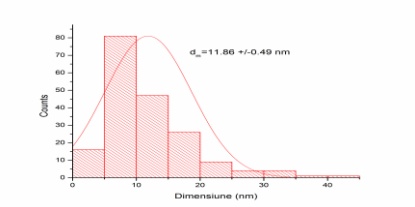

***Fig. 6**: Distribution Diagram of CeO_2 NPs*

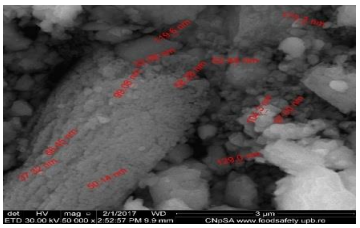

***Fig. 7**: SEM Images - CeO2 NPs*

4. FUNCTIONALIZATION EXPERIMENTATIONS

The woven fabrics made from 100% cotton were dyed and oleophobized by applying the technological flow [6]: desizing, boiling, bleaching/dyeing, oleophobization with: Rucostar EEE6 (70g/l) and acetic acid (1ml/l) with a takeover degree of 80%, drying: T=120^{0}C, condensation: 150^{0}C for 2 min.

The degree of oleophobization of the white woven fabric was at a good level, grade 5, compared to the dyed fabric, of average level – grade 2-3. The superficial wetting resistance recorded good values for both fabric variants (grade 5). For all the woven fabric variants, very good values were obtained for the parameter: color change (4-5) and color yield (4-5 and 5). The SEM images evaluation of the oleophobized woven fabrics after the washing resistance test revealed that it is *resistant* for fabrics from 100% white cotton and *partially resistant* for dyed fabrics from 100% cotton.

In order to study the uniformity, morphology and distribution of the nanoparticles on the woven fabrics surface of 100% cotton, the NPs were used in three dispersion formulas: F1 with UPW, ultra pure water, F2 with UPW and 57% ethanol and F3-1% Tween -20 + UPW and a formula for Ag NPs-F1-UPW-ultra-pure water).

5. RESULTS AND DISCUSSIONS

5.1 Analysis of the uniformity, morphology and distribution of the nanoparticles on textile matrices

5.1.1 The SEM (Scanning electron microscope) **analyses** made on Quanta 200 FEY equipment reveal the following aspects:

- the woven fabrics variants of 100% cotton oleophobized with **Rukostar EEEF 6** and treated with **CeO_2 NPs** show a very low loading degree and the CeO_2 NPs are dispersed on the surface of the fibers at large distances both in the case of using the F1 and F2 dispersion;
- the woven fabrics of 100% cotton oleophobized with **Rukostar EEEF 6** and treated with **Ag NPs** reveal that the degree of loading is relatively higher in the variant treated with F2 compared to the

F1. Ag NPs are dispersed on the surface of the fibers at large distances, exhibiting a slight tendency to agglomerate in the F2 - treated variant (57% ethanol) (fig.8);
- the variants oleophobized with **NUVA 2114** and treated with **CeO_2 NPs** show a high loading degree and the **CeO_2 NPs** are concentrated in some areas with uneven distribution and in the form of agglomerations, more accentuated in the F1 (UPW);
- the woven fabrics variants oleophobized with **NUVA 2114** and treated with **Ag NPs** show a relatively higher degree of loading than in the case of the variant oleophobized with Rukostar EEF6. The Ag NPs are distributed unevenly in the form of agglomerations.

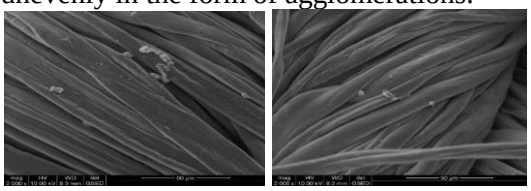

***Fig. 8**: SEM Images -CeO2 NPs*

5.1.2 The TEM (Transmission electron microscopy) ***and EDS*** **(**Energy-dispersive X-ray spectroscopy) ***analyzes*** were made on the Titan Themis 200 equipment for the woven fabrics variants treated with CeO_2 NPs oleophobized with NUVA 2114 (5g/l) (fig 9).

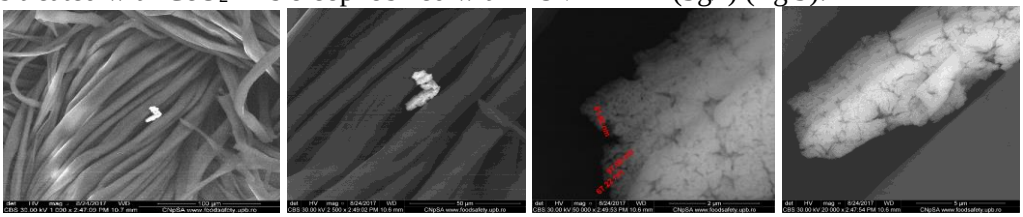

***Fig. 9:** SEM-TEM Images*

- *the variant oleophobized* with NUVA 2214 and sprayed with CeO_2 NPs in dispersion with UPW (ultra-pure water) shows NPs deposited on the surface of the fabric and among the yarns. The EDS spectrum indicates the presence of the CeO_2, as an element present in the nanoparticles deposited; *in the woven fabric variant oleophobized* with *NUVA2114* and sprayed with CeO_2 NPs in dispersion of UPW and 57% ethanol, the images did not identify the CeO_2 on the surface of the fabric; for the *woven fabric variant* sprayed with CeO_2 (F3-15 Tween-20) and oleophobized with NUVA 2114 it is revealed that the arrangement of the nanoparticles is in the form of agglomerations; the nanoCeO_2 dimensions are of 60 and 70 nm.

5.1.3 IPC-MS Analyses (*Inductively coupled plasma mass spectrometry)*

The inductively coupled plasma mass spectrometry or ICP-MS is an analytical technique used for elemental determinations.

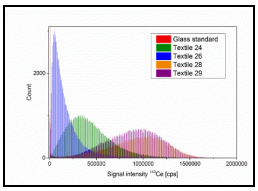

***Fig. 10**: NanoCeO2 Hystogra*

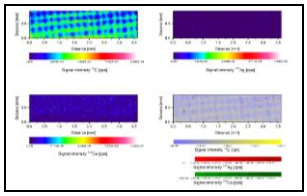

***Fig. 11**: LA-ICP-MS Results*

***Fig. 12**: NPs Dispersion*

The samples were fixed with resin on a glass slide and were ablated consecutively. ^{13}C, ^{107}Ag, ^{137}Ba și ^{140}Ce were detected, but Barium was used as control. ^{13}C was used to locate the

fabrics. The data confirmed the first optical impression from the contour signals. For the ^{107}Ag signals we noticed that the glass standard ablation or that of the resin leads to similar distributions of decreasing intensity, which indicates a low background. The signal's distribution and intensity are different in the four variants (fig.10,11). The depth of NPs integration in the fabric was identified and that was at max. 1 μm (fig12).

5.2 Analysis of the influence of the chemical auxiliaries on the shape and dimension of the nanoparticles

In order to evaluate the influence of the chemical auxiliaries used in the oleophobization formulas of the textile materials on the form and dimension of the Ag and CeO2 NPs, the TEM electronic transmission microscopy (UPB-Bucharest) was employed for the treatment formulas with CeO2 (0,5 g/l)/ Ag (0,5 g/l NPs, Tubiguard VCN - 5 g/l respectively RucoDry (5 g/l) and RukoLink (1 g/l) used to treat 100% cotton woven fabrics.

5.2.1 Solution of CeO_2 and Tubiguard VCN-5g/l. The TEM images in light field reveal that the sample is composed of predominantly polyhedral form particles, which are arranged in the form of agglomerations of 200-300 nm. The high-resolution transmission electronic microscopy image reveals crystallographic planes with a distance of 2.70 Å corresponding to the families of crystalline planes (200). The regular succession of the crystallographic planes indicated that the nanocrystallites crystals are uniform from a crystalline viewpoint without having the non-crystalline phase. From the electron diffraction image on the selected area obtained on the cerium oxide nanopowder we can deduce that the only phase formed is the cubic cerium one.

5.2.2 Solution of nanoCeO_2 and RucoDry(5 g/l) and RukoLink (1 g/l). From the high-resolution transmission electronic microscopy image obtained on the CeO2 sample from the solution with RucoDry (5 g/l) and RukoLink (1 g/l): crystallographic planes with a distance of 3.12 Å corresponding to the families of crystalline planes were observed (1 1 1). Also, the regular succession of the crystallographic planes indicated that the nanocrystallites are uniform from a crystalline viewpoint without having the non-crystalline phase. From the electron diffraction image on the selected area obtained on the cerium oxide nanopowder presented in Figure 5 we can deduce that the only phase formed is the cubic cerium one.

5.2.3 Solution of Ag NPs and Tubiguard VCN(5g/l): the images revealed that the nanoparticles form is spherical, these being dispersed very uniformly. From the high-resolution transmission electronic microscopy image obtained on the nanoAg sample from the solution with Tubiguard VCN crystallographic planes with an interplanar distance of 2.04 Å corresponding to the families of crystalline planes (200) specific to the silver nanoparticles were observed. Also, the regular succession of the crystalline planes indicated that the nanocrystallites crystals are uniform from a crystalline viewpoint without having the non-crystalline phase. From the electron diffraction image on the selected area obtained on the Ag NPs we deduced that the only phase formed is the cubic silver one(fig.13,14,15).

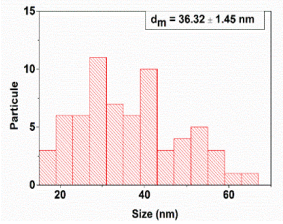

***Fig.13**: Dimensions Diagram of Ag NPs*

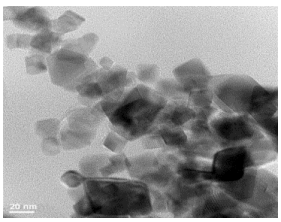

***Fig.14**: CeO_2 NPs*

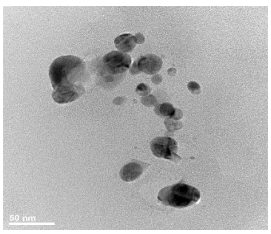

***Fig.15**: Ag NPs*

5.2.4 Solution of nanoAg and RucoDry (5 g/l) and RukoLink (1 g/l)*:* the TEM analysis reveals that the nanoparticles form is spherical, these being in the same time very well dispersed. From the high-resolution transmission electronic microscopy image obtained on the nanoAg sample from the solution with *RucoDry(5 g/l) and RukoLink (1 g/l)* cristaline planes with an interplanar distance of 2.35 Å corresponding to the families of crystalline planes (1 1 1) specific to the nanoAg were observed. Also, the regular succession of the crystallographic planes indicated that the nanocrystallites are uniform from a crystalline viewpoint without having the non-crystalline phase. The electron diffraction image on the selected area obtained on the nano Ag highlighted that the only phase formed is the cubic silver one.

6. CONCLUSIONS

The dimension and shape analysis of the Ag and CeO_2 NPs was made by means of the SEM scanning electronic microscopy, TEM transmission and dinamic light scatering (DLS).

The influence of the chemical auxiliaries on the shape and dimension of the Ag and CeO2 NPs was determined by SEM, TEM and DLS analyzes that revealed that they maintain their shapes, dimensions and initial crystalline state.

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