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RESEARCH ARTICLE

THE FUNCTIONALIZATION TECHNOLOGIES WITH NANOPARTICLES

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ABSTRACT

CeO_2 nanoparticles were characterized by SEM and TM analyzes that showed a size of about 10 ± 0.46 nm and a ployed shape. By Differential Scanning Calorimetry (DSC) was obtained the thermograme that releved the absence of cerium oxide sample peaks due to the high melting point 2400°C, the temperature range in which the sample was analyzed being between 35°C and 500°C. Two ypes of CeO_2 dispersions were made, in ultra pure water (UPW) and solvent. The statistical indicators: average, coefficient of variation and standard deviation were calculated and they showed higher values in the case of dispersion with solvent then dispersion in UPW. The evolution study of the amount of CeO_2 on the surface of knits depending on the treatment of resistance to acid/alkaline perspiration and washing releved for all fibrous mixtures, white or dyed, a decrease of max.5% of the amount of NP on the surface of the knits after the tests of acid, alkaline and washing perspiration. Statistical indicators of dimensions and distances distribution of CeO_2 on the surface of knits depending on the nature of the oleophobic agent revealed the tendency to increase the average values of the agglomeration dimensions does not differ significantly from the oleophobic variant with Nuva N 2114 compared to the one with Rucostar EEE6 in all three categories of treatments: acid, alkaline and washing. The evolution of the statistical indicators of the distribution of the distances between CeO_2 on the surface of oleophobic knitwear with Nuva N2114 or Rucostar EEE6 and functionalized with CeO_2 in UPW dispersion shows that the average distance between CeO_2 agglomerations is significantly more balanced acid/alkaline and washing, compared to the oleophobic variant with Nuva N 2114. The friction test leads to an increase in the size and distances between the nanoparticles.

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INTRODUCTION

The marketing of products using nanotechnology could reach about a thousand billion dollars a year in 2015. Nanotechnology is developing at a fast pace globally, with a short duration between the effective date of an invention and its commercialization [Agency Toxic Subst, 2005]. According to the Nanotechnology Consumer Products Inventory, over 600 such products are currently produced by 322 companies in 20 countries […]. Ultra-fine particles (UFPs) are a category of particles that, when inhaled, can cause negative health effects. These particles have a diameter of up to 100 nm and are therefore true nanoparticles in terms of size. Their nanometre size differentiates them from large particles (with diameter of up to 10 μm, PM10) and fine particles that pollute the air (with diameter up to 2.5 μm, PM2.5). The most important properties of nanomaterials in nano-bio interactions are dimension, shape, purity, surface area, charge, hydrophobicity, aggregation state, crystallinity, electron energy level, and the potential to generate Reactive Oxygen Species (ROS)[…]. These properties can be correlated with the biological results according to a set of structure-activityflowdiagrams, an example being shown in fig. 1. The surface properties of the particles determine the cellular uptake pathways, the subcellular processing mechanisms and the cytotoxicity [Araujo, 2008]. The Fenton reaction is one of the mechanisms by which the metallic impurities on the Carbon Nanotubes (CNT) surface can induce ROS generation (fig. 2). Finally, (d) particle dissolution (e.g. ZnO, CdSe, Cu) can produce free ions capable of inducing ROS generation and toxic effects in cells. Fever of metal smoke may be an example of this type of toxicity [Araujo, 2008].

Areas of application in textiles: Nanotechnology has a large areas of application: medicine, food and agriculture, nanoelectronics, textiles etc.(fig.3)[3]. Enhancement of textile materials by nanotechnology is expected to become more than trillion-dollar industry in the next decade, with tremendous technological, economic and ecologic benefits [4].

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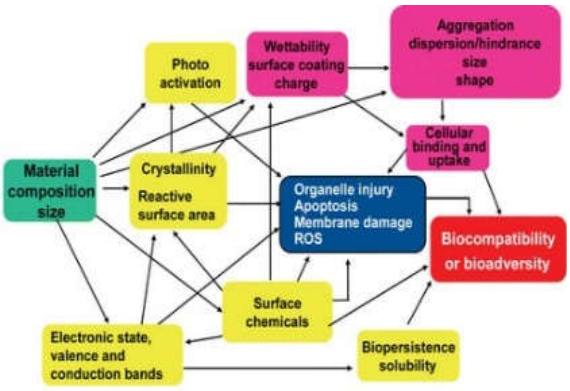

Fig. 1. Structure-activity flow diagram

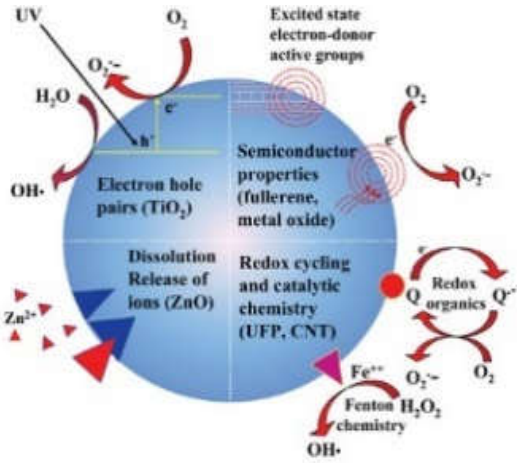

Fig. 2. Fenton reaction

Fig. 3. Areaof application

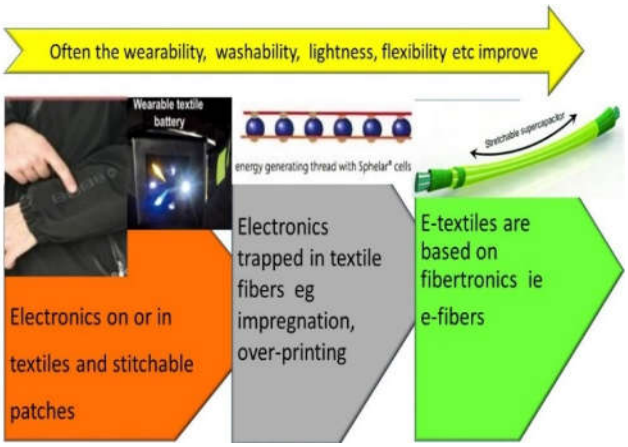

Fig. 4. Application in textiles

We can define nanotechnology in textile as the understanding, manipulation, and control of matter at the above-stated length, such that the physical, chemical, and biological properties of the materials (individual atoms, molecules, and bulk matter) can be engineered, synthesized, and altered to develop the next generation of improved materials, devices, structures, and systems [Brook, 2004].

Application of Nanotechnology can beexplain in three ways:

- Application in department wise
- Application in properties of textile material
- Application in apparel industry

Nanotechnology can be used in engineering desired textile attributes, such as fabric softness, durability, and breathability and in developing advanced performance characteristics, namely, water repellency, fire retardancy, antimicrobial resistance, etc., in fibers, yarns and fabrics (Fig.4) [Brown, 1988]. The Nanofibers are defined as fibers with diameters less than 100 nanometers. In the textile industry, this definition is often extended to include fibers as large as 1000 nm diameter. They can be produced by interfacial polymerization, electrospinning, and force spinning. Carbon nanofibers are graphitized fibers produced by catalytic synthesis.

The risk of nanotoxicity to human health: The toxicity of nanomaterials is often linked to their extremely small size. Smaller particles have a greater reactive surface area than larger particles, are more chemically reactive and produce greater numbers of reactive oxygen species that include free radicals. Reactive oxygen species production has been found in a diverse range of nanomaterials including carbon fullerenes, carbon nanotubes and metal oxides [Chen, 2006]. This is one of the primary mechanisms of nanoparticle toxicity; it may result in oxidative stress, inflammation, and consequent damage to proteins, membranes and DNA(fig.5).

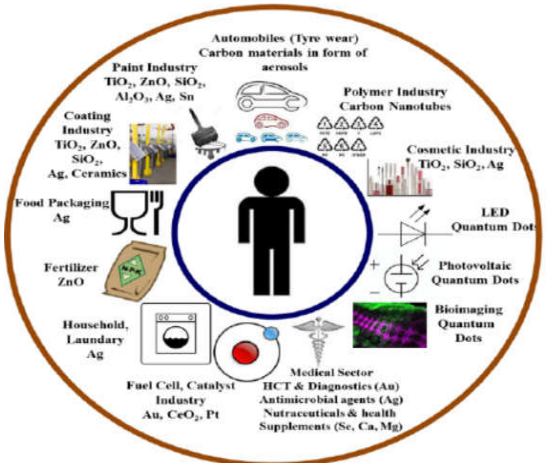

Fig. 5. Risk of nanoparticles

MATERIALS AND METHODS

Cerium was discovered in Sweden by Jöns J. Berzelius and Wilhelm von Hisinger and independently in Germany by Martin Heinrich Klaproth in 1803. The element's name comes from the asteroid Ceres, discovered two years earlier by Giuseppe Piazzi. Cerium is the most abundant of the lanthanides.

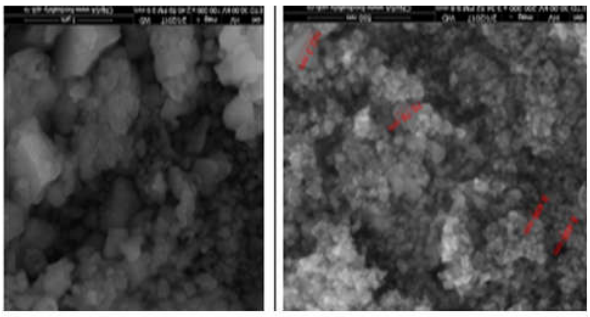

Fig.6. SEM images

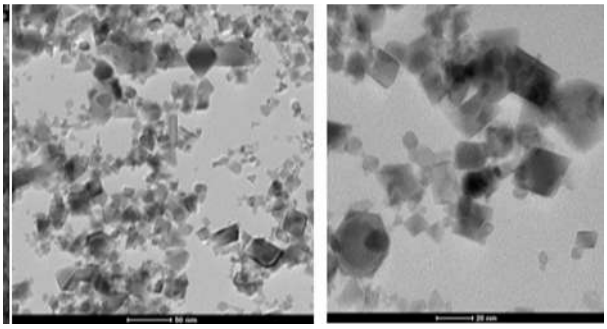

Fig. 7. TEM images in the light field

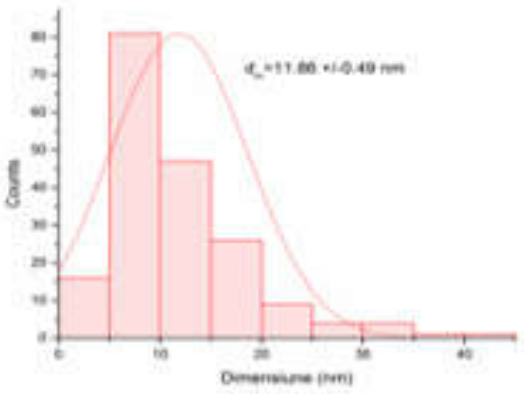

Fig. 8. Size distribution diagram

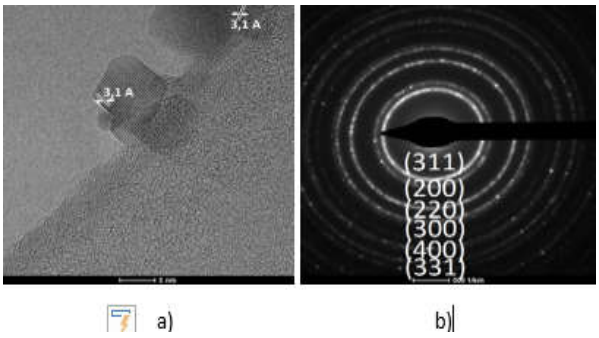

Fig.9. HR-TEM and SAED images

It is not found freely in nature, but it is found in a series of minerals, mainly alanine, bastnaesite, monazite. From a commercial point of view, cerium is prepared by chloride electrolysis or by melted fluoride reduction with calcium. Cerium has 30 of isotopes whose half-life is known, with mass numbers of 123 to 152. Of these, three are stable, 136Ce, 138Ce and 140Ce. The mostabundant isotope is 140Ce at 88,5%. SEM images of CeO_2 were obtained by using the FEI Quanta 200 scanning microscope (Fig.6).

The TEM images in the light field (fig. 7) and HR-TEM and SAED images(fig.8) on the CeO_2 NP reveal that the sample is made up of particles of a polyhedral shape withan average size of 11.86 nm ± 0.49 nm. The particles have a very large variation in size and shape (Fig. 8). From the high resolution SEM image obtained on CeO_2 and shown in fig.9,*a*, the crystalline planes with the 3.1 Å distance can be seen corresponding to the family of crystalline planes (311). At the same time, the regular succession of the crystalline planes indicates that the nano-crystallites are uniform from the crystalline point of view, without any amorphous stage. From the electron diffraction image on the selected area obtained on the cerium nano-powder shown in fig. 9,*b*, one may infer that the only stage formed is that of the polycrystalline cerium. By Differential scanning calorimetry (DSC) was obtained the thermogram from figure 10.

The absence of cerium oxide sample peaks is due to the high melting point 2400°C, the temperature range in which the sample was analyzed being between 35°C and 500°C. The functionalization of textile materials with dispersion formula composed of UPW and solvent the following were used: 742 g UPW (MilliPure)and 1026 g ethanol (w> 99.9%) in a glass flask of 2 l; there were added 14.40 g of2-butanone (MEK, w= 9.5%), 10.80 g ofHCI (w=37%) and 7.20 g of triethanolamine (w=100%); after sonication for 15 min., the dispersion was manually shaken for 1-2 min. Influence of dispersion composition on CeO_2 NP characteristics the Auriga model workstation produced by Carl Zeiss SMT Germany FESEM-FIB with GEmin column field emission source for the electron beam, was used. The SEM micrographs (fig.11) show that, in the case of UPW and solvent CeO_2 dispersion, these have a structure with a relatively uniform morphology made up of CeO_2 NPs polyhedron shaped with sizes ranging between 10 nm and 50 nm (the octagon shapes are visible). The statistical indicators: average, coefficient of variation and standard deviation were calculated in order to compare data sets.

$$X_{med} = \frac{\sum_1^n X_n}{n};\ C_v = \frac{A_s}{X_{med}} \times 100;\ A_s = \sqrt{\frac{(X_1 - X_{med})^2 + (X_2 - X_{med})^2 + \ldots + (X_n - X_{med})^2}{n-1}} \quad (1)$$

Dispersion indices of CeO_2 dimensions in the case of dispersion in UPW and solvent reveal the following aspects:

- the average of the values obtained for the NP size is larger in UPW dispersion case (23.11 nm as compared 18.2 nm) as compared to the solvent dispersion;
- the standard deviation is higher in solvent CeO_2 dispersion (5.8 as compared to 3.6);
- the variation coefficient of the NP size in solvent dispersion is higher as compared to UPW dispersion (31.8 % as compared to 15.5%).

The shown values indicate a certain NP agglomeration tendency in UPW dispersion but it is made up ofmore uniform NP size wise (Fig.12). The EDS spectrogram of the UPW CeO_2 dispersion shown in figure 13, *a* highlights stressed peaks for: Al (>25cps/eV), Oxygen O_2 (around 18 cps/eV) and Ce (around 14 cps/eV). It also highlights other elements: Fe, Cu, Ca, Cl. The element with the highest weight is Ce (Ce–62.0%), followed by oxygen (O_2–25.4%) and carbon (C–10.6%). The spectrogram of the solvent Ce O_2 dispersion (fig.13,*b*) highlights that the highest peak is obtained for Al, Al>82 cps/eV, followed by oxygen, copper, cerium, carbon and iron.

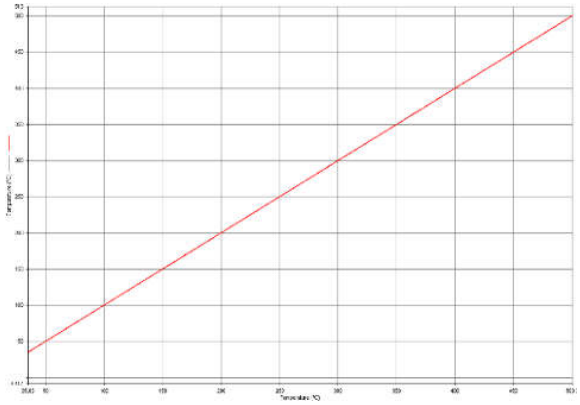

Fig. 10. DSC thermogram

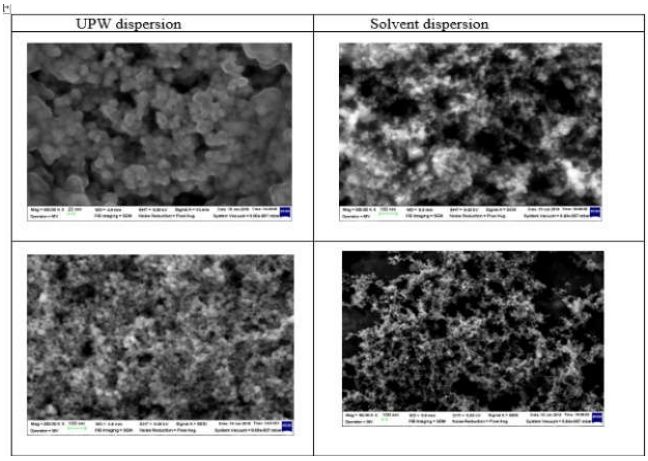

Fig.11. SEM images

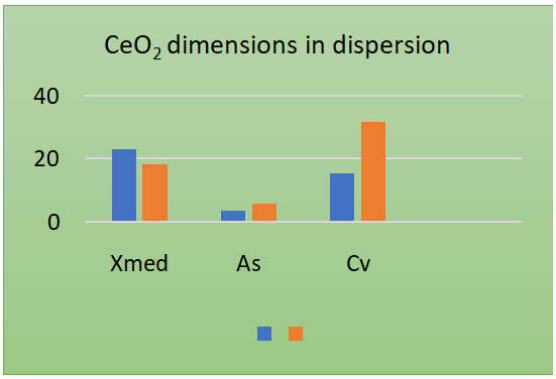

Fig. 12. CeO_2-dimensions in dispersion

From the point of view of the weight of the various elements, in this case, cerium appears to be Ce=24.5% as compared to carbon, C=35.4% and oxygen, O_2=35.2%. The comparative analysis of the data shows that the UPW CeO_2 dispersion has a higher amount of NPs (62%) as compared to the solvent dispersion (24.5%). The white and dyed knits (made up of the following fiber mixtures – 100% cotton, 45% cotton/55% pes and 100% pes) were functionalized using the padding technology which comprised oleophobization treatments with Nuva N2114 and Rukostar EEE 6 and CeO_2 NP during the same stage of the technological process, followed by twisting and drying/condensation. The following recipes were used for treatment: 70 g/l Nuva N2114/Rukostar EEE6, 20 ml/l CeO_2 NP 5% dispersion in ethylene glycol/water, 0.5 ml/l acetic acid 60% (1 ml/l for the 100% pes mixture), taking over level: 80%, dried at 110ºC, condensation at 140 ºC, for 2 minutes

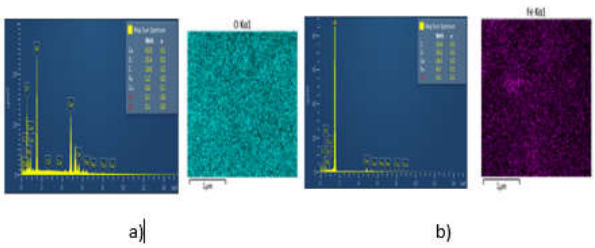

Fig.13. EDS spectra:a)dispersion with UPW, b) dispersion with solvent

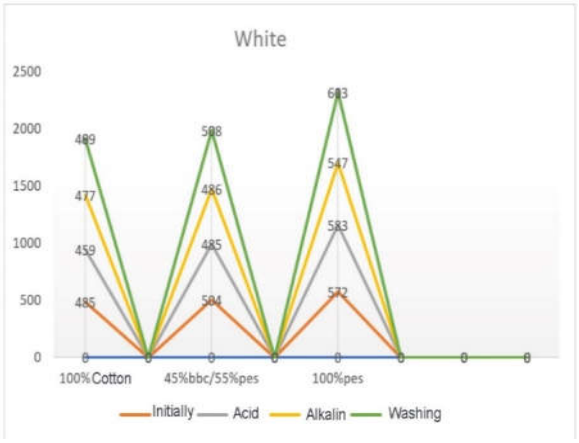

Fig. 14. White knited materials

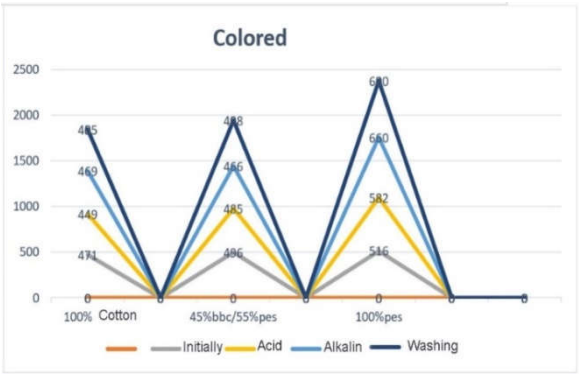

Fig. 15. Colored Knited materials

RESULTS

Evolution of the amount of CeO_2 on the surface of knits depending on the treatment of resistance to acid/alkaline perspiration and washing: The amount of CeO_2 on the surface of the knits was determined for the following knit versions: white and dyed 100% cotton, 45% cotton/55% pes and white and dyed 100%, oleophobized with Nuva N2114 and functionalized with UPW and CeO_2 dispersion. The knits were subjected to the acid/alkaline perspiration resistance tests, carried out according to SR EN ISO-104-E 04 and washed according to the SR EN ISI 105-CO8/ standard. The CeO_2 amount was determined using the ICP-OES method. The optical emission spectrometer with the inductive coupled plasma, Optima 8300 Perkin Elmer, was used. The CeO2 NP amount evolution on the surface of the textile materials is shown in figure 14 for the white knit and figure 15 for the dyed knit. The analysis of the data shown in figures 14 and 15 highlights the following ideas:

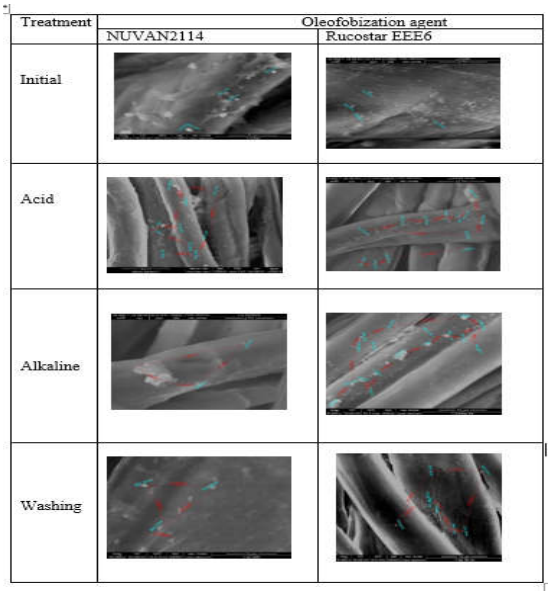

Fig.16. SEM images

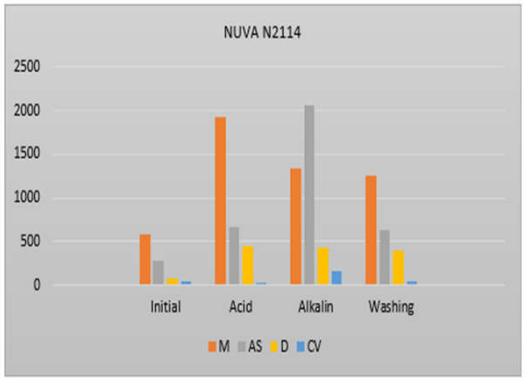

Fig. 17. Diminsions evolution(NUVA N2114)

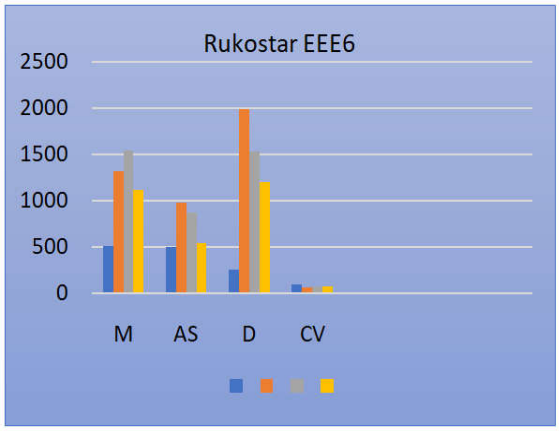

Fig.18. Diminsions evolution (Rukostar EEE6)

In the case of the knits initially treated with Nuva N2114 oleophobization agent and functionalized with UPW CeO_2 dispersion, the highest amount of NPs is found with the white and dyed 100% pes knits (572 mg/kg, for the white and 516 mg/kg, for the dyed);

- The 100% (white and dyed) cotton knits lose the highest amount of NPs after the acid perspiration test (5%);
- For all the fiber, white or dyed mixtures, there is a drop of max. 5% of the NP amount on the surface of the knits following the acid, alkaline perspiration and washing tests.

Statistical indicators of dimensions and distances distribution of CeO_2 on the surface of knits depending on the nature of the oleophobic agent: The evolution of the statistical indicators regarding the CeO_2 size and distance distribution on the surface of the knits oleophobized with Nuva N2114 or Rukostar EEE6 and functionalized with UPW and solvent CeO_2 dispersion was analyzed using the SEM scanning microscope following the acid and alkaline perspiration and washing tests. The analysis was made for the 100% cotton knits. The SEM images are shown in figure16. The evolution of the statistical indicators related to CeO_2**size** distribution on the surface of the knits oleophobized with Nuva N2114 or Rukostar EEE6 and functionalized with UPW CeO_2 dispersion is shown in figures17 and 18, respectively. The analysis of the data shown in figures 17 and 18 displays the following aspects:

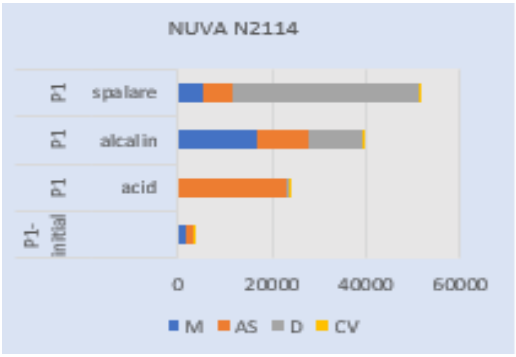

Fig.19. Evolution of distances (NUVA N2114)

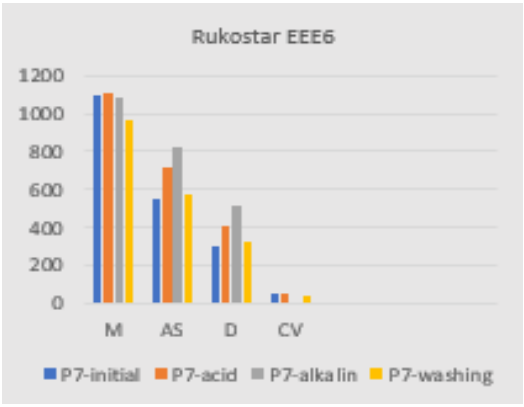

Fig.20. Evolution of distances (RUKOSTAR EEE6)

- the average value of the initial size of the conglomerates on the surface of the 100 % cotton knits oleophobized with Nuva N2114 and functionalized with UPW CeO_2 dispersion are not significantly different as compared to the version oleophobized with Rukostar EEE6 (580.6 as compared to 510.6 nm); the variation coefficient is higher with the solvent dispersion variant (98.36 as compared to 46.8%)
- the growth of the average values of the conglomerate size is not significantly different from the Nuva N2114 oleophobized version as compared to the Rukostar EEE6 oleophobized version in the case of all the three treatment categories: acid, alkaline perspiration and washing; in the case of theNuva N2114 version, there is a higher conglomerate growth in the case of the acid perspiration treatment (1922.1 nm as compared to 580.6 nm initially); in the case of the Rukostar EEE6 version, this growth is seen in the case of the alkaline perspiration treatment (1540 nm as compared to 510.68 nm).

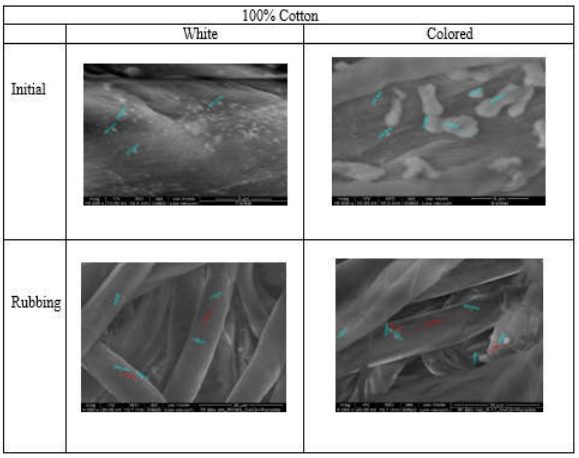

Fig. 21. SEM images– rubbing test

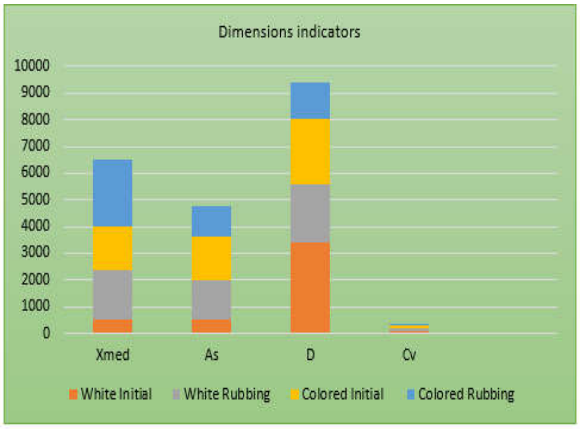

Fig.22. Dimension evolution – rubbing test

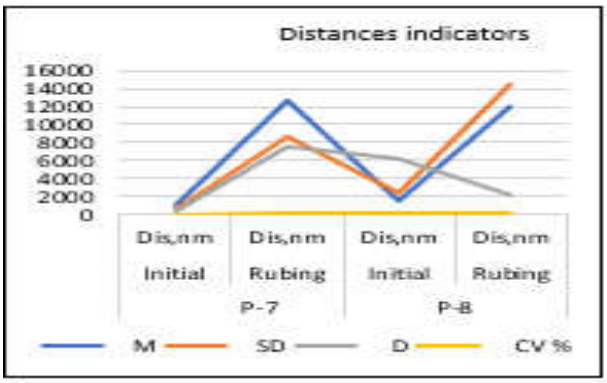

Fig.23. Distances evolution-rubbing test

The evolution of the statistical indicators regarding the CeO_2 distance distribution on the surface of the knits oleophobized with Nuva N2114 or Rukostar EEE6 and functionalized with CeO_2 in UPW dispersion is shown in figures19 and 20.

Evolution of statistical indicators of distribution of dimensions and distances between CeO_2 on the surface of knits after the wear test (friction): The analysis of the data shown in figures 19 and 20 displays the following aspects:

- The average value and the variation coefficient regarding the CeO_2 distances on the surface of the knits oleophobized with Nuva N2114 are higher as compared to that oleophobized with Rukostar EEE6 and operationalized with CeO_2 in UPW dispersion (1705.7nm as compared to 1092.18nm and 91.63% as compared to 50.58%);
- The evolution of the average distances between the CeO_2 conglomerations is significantly more balanced in the case of the version oleophobized with Rukostar EEE6 and subjected to the acid/alkaline perspiration and washing treatments (max. 1110 nm of the acid perspiration treatment as compared to the 1092 nm of the initial variant), as compared to the variant oleophobized with Nuva N2114 (the lowest value – acid perspiration – 376.1 nm and the highest, 5336.6 nm with the washing as compared to 1705.7 nm of the initial variant)
- The evolution of the variation coefficients of the distances between the CeO_2 conglomerations is balanced both in the case of the version oleophobized with Rucostar EEE6, and in the case of the Nuva N2114 and subject to acid/alkaline perspiration and washing treatments (the highest alkaline perspiration value – 66.2% as compared to the initial 50.58% and 117.8 % respectively, to a, as compared to the initial 91.63%)

The analysis was performed by reviewing the SEM images produced by the Quanta 200 scan microscope and shown in figure21, using a comparison between the initial variants and those subject to the rubbing test on the Martindale device. The evolutions of the NP size on the surface of the white and dyed 100% cotton knits, oleophobized with Rukostar EEE6 and functionalized with UPW Ce O_2 dispersion, initially and after the rubbing test are shown in figure 22.

The analysis of the data shown in figure 22 displays the following aspects:

- The average value and the variation coefficient of the size of the conglomerations on the surface of the 100% cotton knits oleophobized with Rukostar EEE6 and functionalized with UPW CeO_2 dispersion are higher with the dyed knits (1592.79 nm as compared to 510.6nm and 104.7 as compared to 98.36%);
- Following the rubbing test, the average size value increases with the two variants, but with a difference: 3.6 times with the white variant and 1.58 times with the dyed version where the variation coefficient decreases as compared to the initial (45.7% as compared to 98.36%).
- Figure 23 shows the evolution of the distances between the NPs on the surface of the white and dyed 100% knits, oleophobized with Rukostar EEE6 and functionalized with UPW Ce O_2 dispersion, initially and following the rubbing test.
- The analysis of the data shown in figure 22 and 23 displays the following aspects:
- The average value of the distances between the NPs is higher with the dyed 100% cotton knit variant, oleophobized with Rukostar and functionalized with UPW CeO_2 dispersion as compared to the white variant (1429nm as compared with 1092nm); the variation coefficient has the same evolution (172.8% as compared to 50.58%)
- The average value of the distances following the rubbing test increases significantly, both with the white knit variant (12580 nm as compared to 1092 nm) and the dyed one (12111.4 nm as compared to 1429.4 nm); the variation coefficient has a different evolution: it increases with the white knit following the rubbing test (68.8% as compared to 50.58 %) and decreases with the dyed knit (119.27% as compared to 172.8%)

Conclusion

SEM and TEM analysis of CeO_2 and dispersions of CO_2 in UPW (ultrapure water) and solvent have evidenced the medium dimension (10–50nm) and thepolyhedral shape; EDS analysishas evidenced that dispersion with CeO_2 with UPW contains a greater quantity of NP (62%) when compared with solventdispersion (24,5%).

Knitted materials from 100% cotton, 45% cotton/55% PES and 100% PES, raw and dyed were treated after oleophobic treatment in same process with CeO_2 NP by padding technology.

The quantity of NP deposited on knitted materials surface by impregnation technology has evidenced a value>400mg/kg which do not decrease significantly after acid/alkaline perspiration tests, washing, rubbing tests.

Statistic indicators ofdispersion have evidenced the evolution of dimensions and distances between CeO_2 on surface knittingin initial phase and treated of acide/alkaline perspiration, washing and rubbing tests, which are depending on:nature of oleophobic agent, andpresence ofdyestuffon the textile material.

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