Analysis of interaction processes between the silver nanoparticles and the surface of fur semi-finished products within conditions of HF plasma at decreased pressure

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Abstract. In order to impart the bactericidal properties and the additional strength to the fur semi-product, it is proposed to perform its treatment with the silver nanoparticles within conditions of high frequency (HF) plasma at decreased pressure. Silver comes to the fur surface in atomic and ionized form, which significantly facilitates its interaction with keratin, provides their efficient adsorbing on the surface of fur semi-product and forming the stable compositions.

1. The Introduction. One of the methods to impart bactericidal property to material is coating it with silver nanoparticles. In case of treatment of the fur material, the treatment evenness was provided by using HF plasma at decreased pressure. When applying the coating, the functional purpose of plasma is activation of nanoparticles their transporting to the surface of specimen, removing from the surface the weakly adsorbed particles and strengthening the well adsorbed ones, that will form further on the final coating [1]. In this connection, in theoretical researching a process of the silver nanocoating application onto fur semi-product, it is necessary to consider the effects that occur while nanoparticles transporting with plasma and directly during the coating deposition on the fur surface.

2. Materials, methods and equipment
In the course of research, the possibility of imparting bactericidal properties to fur materials as the object of study were used sheepskin and a colloidal aqueous solution of silver nanoparticles “Agbion-2” The feature of the product "Agbion-2" is that the silver nanoparticles have a spherical shape and their size lies in the range of 5-9 nm. In order to ensure uniform distribution of nanoparticles and their strong fixation on the surface of the fur material, the deposition was carried out from a colloidal solution under the conditions of RFI plasma. To obtain an induction discharge, an experimental RFI plasma device was used, the sprayed nanoparticles were introduced into the plasma by passing a plasma-forming gas through a bubbler containing a colloidal silver solution.
3. Results
As known, any object is being negatively charged in plasma. Besides, in high frequency plasma of decreased pressure, due to significant amplitude of the electronic gas oscillation (~10⁻³ m) in HF electric field, a positive charge layer (PCL) with thickness up to 2mm is being formed at the object surface, and the object becomes an additional electrode. Positive ions of plasma-supporting gas are accelerated in PCL and acquire energy of 10 to 100 eV. Coming onto a surface of polymeric material, ions of plasma-supporting gas transfer their kinetic energy to the surficial atoms of material. Moreover, when ion clashing with surface, its recombination is possible with emission of correspondent energy. The mutual influence of kinetic and potential energy of the plasma-supporting gas ion results in modification of a surface: contaminants desorption, micro-unevenness diffusion etc. The density of ion current on a surface of polymeric specimen in the course of HF plasma treatment amounts to 0,3-0,9 А/m², which corresponds to the ion flow density of 2-6 10⁻³ ion/(nm²⋅s). The typical terms for relaxation of atomic states amount around 10⁻¹³ s. It means that there is no effect of influence cumulation onto surface by various ions [2]. When bombarding a surface of fur semi-product by the low-energy argon ions, the following effects may occur:

1) a combination of Ar⁺ ion with electron staying on a surface; here, energy of 15,76 eV is emitted and being consumed for ionization of argon atom in plasma, and a fast atom of Ar is formed;

2) a combination of Ar⁺ ion with electron emitted from the material surface under influence of ion’s electric field; it leads to forming a fast atom of Ar, and a molecule of collagen and keratin is ionized;

3) transmission of ion’s kinetic energy to atoms of molecular chain.

In plasma, ion’s electric field is compensated with PCL field which thickness, depending on treatment mode, amounts to 0,5-2 mm. Taking into consideration that the time of emission is around 10⁻⁸ s and the above evaluations of ions speed, we find out, the process of ion Ar⁺ recombination with the electron emitted from the specimen surface is quite probable. Therefore, it is most likely that Ar⁺ ions will recombine when flying to the specimen surface, and it will be the «fast» atoms of Ar having the kinetic energy of 70-100 eV [3] that will interact with surface.

The sizes of used nanoparticles (5-9 nm) are much less than Debye layer, λD~70 nm, that is why the provisions of the above-mentioned theory of the low temperature plasma interaction with the solid object and, in particular, their obtained potential, in this specific case shall be clarified. The fusion bonded to be introduced into plasma while plasma-supporting gas passing through bubbler tank containing the silver colloidal solution. The concentration of Ag⁺ nanoparticles in the solution does not exceed 10⁸ 1/m³, which is by 17-18 orders of magnitude less than the atoms concentration in the plasma-supporting gas and by 13-14 orders of magnitude less than the ions concentration in plasma. Therefore, it’s enough to consider the issue on interaction of a single nanoparticle with plasma, without considering the other nanoparticles influence. One nanoparticle includes 10⁵ – 10⁶ atoms and ions of silver. The flying time of a silver nanoparticle from an inlet opening of plasmatron to the fur surface is ~10⁻³ s or ~10⁶ oscillation periods of electromagnetic field. The electrons and ions concentration in plasma of HF discharge at decreased pressure amounts to 10¹⁵-10¹⁸ 1/m³, which corresponds to the presence of one charged particle (electron or ion) in the volume with radius of ~10⁻⁶-10⁻⁴m. The length of free run amounts to ~10⁻⁵ m for electrons, ~10⁻⁴ m for ions. This means than during one oscillation period of electromagnetic field, ~10⁻⁵-10³ electrons and ~10⁻¹⁻10⁵ ions fly through this volume. Without consideration of Coulomb interaction, a probability of an electron clash with a nanoparticle during one oscillation period of the field amounts to ~10⁻⁴, for ion ~10⁻⁵-10⁻⁴, or during the flying time of a nanoparticle to the specimen surface, it is ~10⁻¹⁻1 for electron and ~10⁻²⁻10⁻¹ for ion. A nanoparticle entering plasma is positively charged since it is formed in result of «combination» of ions contained in solution. The total charge of particle is ~1,6 10⁻¹⁶ - 5·10⁻¹⁷ C. While recombining electron with Ag⁺ ion, energy of 7,5 eV is emitted, which is almost 3 times higher than energy required for evaporation of Ag atoms from surface. In this connection, a question arises on the status of nanoparticle in the moment of its interaction with the fur surfacea [4]. The presented pattern
describes interaction of HF plasma at decreased pressure with silver nanoparticles, approximately, at qualitative level. For understanding, how exactly the flow of low-energy ions interacts with the polymeric surface, the more precise quantitative evaluations with the use of mathematical model shall be performed.

The model is created on the assumption that nanoparticles are move with the speed of plasma-supporting gas, so that in coordinates system connected with nanoparticle, ions are motionless, and electrons oscillate in-phase with changing the tension of electric field. A uniform flow of electrons was modelled flying through elementary cell in which a positively charged silver nanoparticle is present. Let us consider this nanoparticle on its fly to area of HF inductor, is area of gas temperatures of 500-1500 K and concentrations of electrons of $10^{15}$-$10^{18}$ m$^{-3}$ at plasma flow speed of 150-500 m/s. The flying time of silver nanoparticle from the inlet opening of plasmatron to the fur surface amounts to $\sim 10^{-3}$ s, or $\sim 10^3$ oscillation periods of electromagnetic field. With a silver nanoparticle diameter of 5-9 nm, it occupies a volume of around $113-381$ nm$^3$ and contains $Z_d=(2-3)\times 10^3$ ions and $5\times 10^3-22\times 10^3$ atoms of silver. The speed of electron in HF plasma at decreased pressure with energy of $\sim 1$ eV is $\sim 10^4$ m/s. It means that its time for passing an elementary cell amounts to $\sim 10^{-10}$ s. A nanoparticle entering plasma is charged positively since it was formed in result of aggregation of ions and atoms contained in solution. The total charge of particle is $Q=(3.2-4.8)\times 10^{-16}$ C=($2-3)\times 10^1$ e. Since an ion’s radius is smaller than a radius of neutral atom, then when an electron heats a nanoparticle containing the silver ions, it volume will increase by $0.56 \times 10^{-29}$ m$^3$, and its radius will increase by $\sim 1.1 \times 10^{-10}$ m and one Ag$^+$ ion will recover to a neutral Ag atom. After each heat with electron, the nanoparticle charge drops and its energy increases due to emission of energy of recombination Ag$^+$ ions (7.5 eV) and adsorption of electron’s kinetic energy ($\sim 1$ eV in HF argon plasma). Due to increase of internal energy of nanoparticle, its temperature first increases till the melting temperature, then the energy is spent to a phase transition into liquid phase (melting), and a particle continues becoming hotter till the temperature of atoms (ions) evaporation from its surface. To heat a silver nanoparticle from the room temperature up to boiling temperature, it shall receive the energy equal to 4000 eV. This energy will be received by a nanoparticle when clashing with $\sim 330$ electrons, which will occur within $66 \times 10^{-7}$ s. To define a number of electron’s clashes with a charged silver nanoparticle, let’s calculate a target distance $R$ – which is a distance where the kinetic energy of electron equals to the energy of its potential interaction with a charged nanoparticle, as per formula:

$$\frac{m v_t^2}{2} = \frac{Ze e}{4\pi \varepsilon_0 R^4}.$$  

Using the target distance at the edge of elementary cell, it’s possible to define an area passing through which, an electron will hit a nanoparticle. The probability for an electron, flying into elementary cell, to hit a nanoparticle is determined by ratio of the hit area to the cell edge area. Dependence of the target distance on the probability of an electron hitting the nanoparticle surface is given in Table 1.

| $Z_d$ | I | II | III |
|-------|-------|-------|-------|
|       | $2 \cdot 10^4$ | $1 \cdot 10^4$ | $5 \cdot 10^2$ | $10^5$ | $10^9$ |
| $R$, m | $0.071 \times 10^{-6}$ | $0.038 \times 10^{-6}$ | $0.022 \times 10^{-6}$ | $0.009 \times 10^{-6}$ | $0.00332 \times 10^{-6}$ |
| $p$ | $5 \times 10^{-3}$ | $15 \times 10^{-4}$ | $5 \times 10^{-4}$ | $81 \times 10^{-6}$ | $11 \times 10^{-3}$ |

To evaporate an ion or a silver atom from the nanoparticle surface at the temperature of silver boiling, the energy equal to 2.65 eV is required. At the temperature of silver boiling, each electron hitting nanoparticle will provoke the fusion or evaporation of three silver ions or atoms, and sech fourth electron that hits – of four ones. The most probable composition of the fused particles is given in Table 2.
Table 2. Dependence of composition of diffused particles on charge

| Charge number of nanoparticle | Composition of diffused particles |
|------------------------------|-----------------------------------|
| 0.5 \(Z_d - Z_d\)           | \(\text{Ag}^0, \text{Ag}^+, \text{Ag}^+\) |
| 0.25 \(Z_d - 0.5 Z_d\)       | \(\text{Ag}^0, \text{Ag}^0, \text{Ag}^+\) |
| 0-0.25 \(Z_d\)               | \(\text{Ag}^0, \text{Ag}^0, \text{Ag}^0\) |

4. Conclusions

Upon the modelling results, it was found that within 1-3 oscillation periods of electromagnetic field, the complete fusion of a nanoparticle to Ag atoms and Ag+ ions occurs. Ionization energy of silver atoms equals to 7.5 eV, which is over 2 times less that ionization energy of argon atom (15.76 eV). The rate of gas ionization from Ag atoms is not less than ~10^{-1}. Therefore, silver comes to the fur surface in atomic and ionized form which significantly facilitates interaction with its keratin and formation of the stable compositions.

Based of the above said, the following conclusion can be made: the silver particles are spurted as an atomic&ionic flow, which provided their efficient adsorbing of the surface of fur semi-product.

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