

Application of Methods of Preparation of Plasm-Chemical Nanocoatings Designated to Hydrophobic and Oleo Phobic Correction of Surface Working of Textile Materials for Filtration Protective Suit

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Abstract

The possibility of creation of nanocoatings with hydrophobic or oleo phobic properties on textiles materials designated for protective suits with plasma-chemical procedures with the employment of atmospheric plasma without vacuum has been verified. On four samples of selected textile materials without any additional modification (Ba, PES+Ba, PES+Ba+Nomex, Ba+Nomex) has been at the Masaryk's University (MU) in Brno applied with a plasma nozzle with ten different ways nanocoatings based on siloxane (HMDSO, OMCTS) and nanoglass. Prepared samples have been assessed at the MU in Brno even from the behaviour against freely lying drops of the sulphur mustard point of view. At the Military Technical Institute of Protection (VTUO) some selected samples have been subsequently evaluated even from the behaviour of freely lying drops of sulphur mustard. Supposed behaviour of the Chemical Warfare Agent (CWA) of the VX type, sulphur mustard and Soman have been simulated within selected samples with observation of freely lying drops of the olive oil, nitrobenzene, and propanol with similar values of the surface tension as above-mentioned CWA. Founded values of contact angles have been compared with contacts values of contacts angles founded in the scope of two developed materials of the coating textiles for modernized filtration protective garment with classical hydrophobic or oleo phobic modification which have been provided with the company of B.O.I.S. – Filtry, Ltd. Within all samples the change of contact angles in time and also the homogeneity of the modification have been considered. The stability and mechanical sustainability of applied sets against washing has not been evaluated. It has been proved that with the help of plasma-chemical modification is possible to prepare nanocoatings even with ultra-hydrophobic (the contact angle for water is bigger than 150 °) and super oleo phobic (the contact angle for water is bigger than 136 °) properties on suitable textile materials. The best results, so called the effect of a lotus flower, have been reached mainly within two samples of textile materials contented a part of nomex fibres.

KEY WORDS: *Hydrophobic modification, oleo phobic modification, chemical warfare agents, chemical resistance, harmful substance, nanocoatings, effect of lotos flower*

1. Introduction

Protection suits used in the body surface chemical protection against the effects of toxic compounds with percutaneous effects are made not only from non-porous polymeric materials (isolative protection) but also from textile of permeable porous character (filtration protection). The task of these suits is to prevent the permeation of gas, solid and liquid harmful substances with percutaneous effects to the body surface. While hermetic isolative suits made from non-porous materials can protect the user against rain and harmful substances in any form, filtration suits of an adsorption type which is produced from untreated textile materials, and they are less resistant against rain and permeation and penetration of harmful substances in a form of drops or roughly dispersive aerosols. Drops of water and drops of harmful substances tend to feather on porous materials in consequence of capillary forces.

This problem is usually solved with hydrophobic and oleo phobic modification of an upper (coating) textile. This classical hydrophobic or oleo phobic impregnation is not cheap, increases the weight of carried textile and even negatively affects their air permeability, flammability, camouflage, or physiological properties. This textile can cause an allergic reaction within more sensitive persons. With the development of nanotechnology is very important to find a way how to replace the impregnation. As one from possible solution is usage of a plasma chemical way of coating

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of nanocoatings with hydrophobic and oleo phobic properties which are better than classical impregnation from the reason of achievement of the super hydrophobic and super oleo phobic effect.

2. Theoretical part

Preparation of surfaces with super hydrophobic and super oleo phobic properties is not practically possible without the employment of nanotechnologies. Very quality and durable hydrophobic and oleo phobic adjustment, however only to the values of a contact angle of 130° can be reach with common used impregnation procedures. For reaching of the effect of a lotos flower when drops are not kept on the surface and has the tendency to roll down is necessary to reach the contact angle of more than 150 . Bhushan in his large study introduces a lot of interesting information which explains not only a principle of the lotos flower effect but also of its evaluation.

Generally it possible to claim that if we drip the drop of water or another liquid on the surface of porous material we reach the state when the drop is soaked immediately or the drop with measurable contact angle from 0 to 180° is formed. From the value of 0° to 50° the material is considered as hydrophilic, from the value of 0° to 90° it is considered as hydrophobic and finally from the value of 90° to 180° it is oleo phobic whereas for drops of the water the values from 150° to 180° the material is considered as super hydrophobic and for drops of oils and solvents it is super oleo phobic. Values of the contact angle from 0° to 20° they are considered as super hydrophilic. These values are clear from the figure 1.

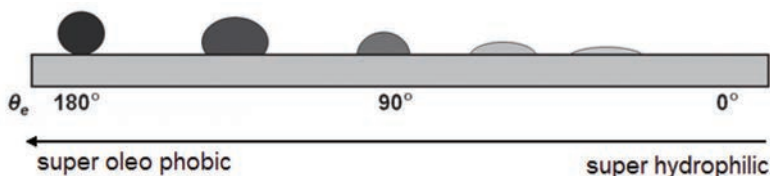


Fig. 1 Characterization of the quality of the solid surface in accordance to the drop behavior

Evaluation of an achieved level of hydrophobity and oleo phobity is performed with the measurements of the contact angle (angle of wetting) or with tested ink. The exactness of the measurement is $\pm 1 \text{ mN}\cdot\text{m}^{-1}$. For easier manipulation and simpler marking a row of tested liquids is in descriptors which are suitable for determination of the surface tension on different materials. Values of the surface tension of some liquids introduced in literature are summarized in the table 1. In the table 2 there are introduced the values of chemical warfare agents and model chemical compounds which have been chosen on the base of comparable surface tension.

Table 1.

Surface tension of selected liquid harmful substances ($\text{mN}\cdot\text{m}^{-1}$)

acetone	23,30	n-pentane	16,00
aniline	40,50	olive oil	33,00
benzene	28,90	ricinus oil	36,40
diethylhere	16,40	terebinthine oil	27,00
ethanole	22,55	petroleum	27,00
glycerol	62,50	propanole	23,70
chloroform	26,50	mercury	476,00
formic acid	37,80	carbon disulphide	33,80
acetic acid	28,00	tetrachloromethane	25,90
methanole	22,70	toluene	28,40
n-hexane	18,40	water	72,75

Table 2.

Selected model compounds for chosen Chemical warfare agents

somane	25,50	propanole	23,70
sulfur mustard	42,90	nitrobenzene	41,80
VX compound	32,00	olive oil	33,00

Within textile or other soaked materials it is possible to create the hydrophobic or oleo phobic surface (or both at the same time) in a different way. The first way is that material is coated or impregnate with the compound with high surface tension (usually on the base on silicone or fluoru polymers) which ensures that the drop of water or oil is not soaked into material and it stays on its surface. The second possibility how to reach hydrophobic or oleo phobic effect is to create the surface of the material with suitable micro or nano structure with self-cleaning properties thus the same effect which occurs on the lotos flower or a common leaf. These effects are visible on the figure 2.

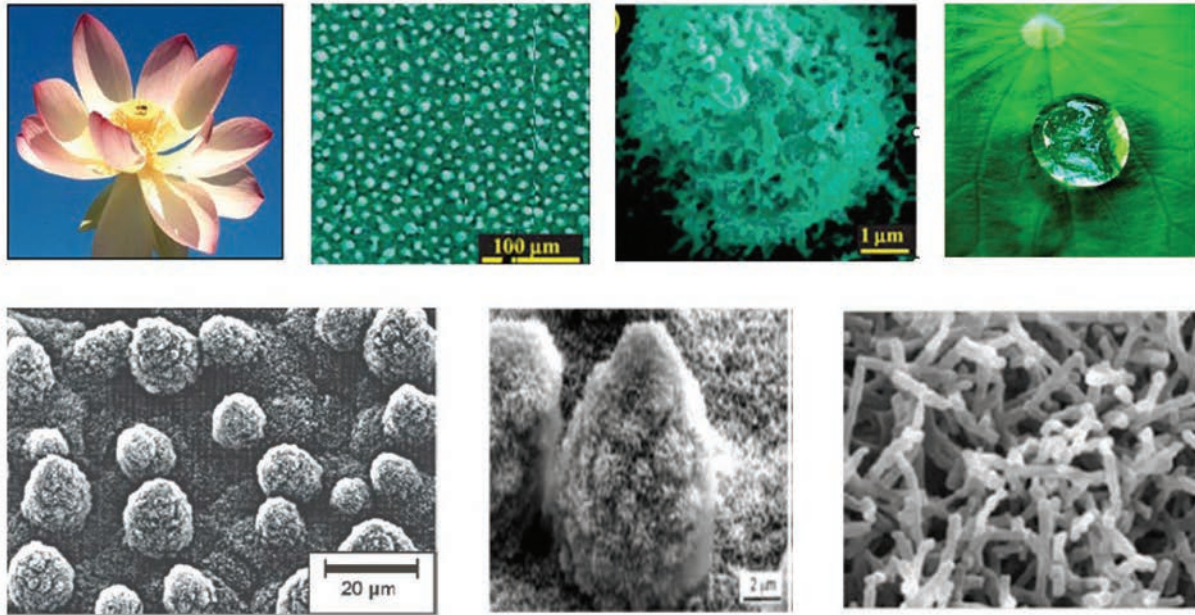


Fig. 2 Microstructure and nanostructure of the surface of lotos flower or the leaf

Very important role plays mainly hierarchic structure both natural and artificially prepared surfaces which is the base of super hydrophobic or super oleo phobic effect. These effects are visible on the figures 3 and 4.

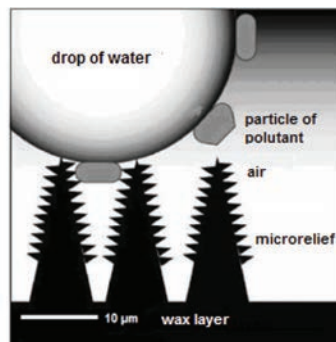


Fig. 3 Schematic illustration of a self-cleaning function of the lotos flower

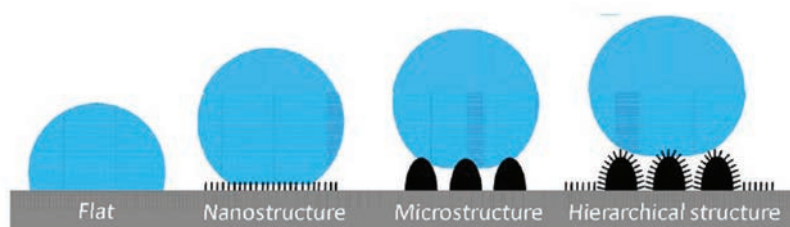


Fig. 4 Hierarchic structure of super hydrophobic or super oleo phobic surfaces

Artificially it is possible to prepare similar microstructures and nanostructures in the different way and in the different form - as ribbing or as nanotubes or other suitable shapes. One from possibilities of preparation of hydrophobic surfaces is for example nanostructures with the employment of special nanowaxes, nanopigments, or nanofiber structures prepared with electro spinning from fluoropolymers as it is visible on the figure 5.

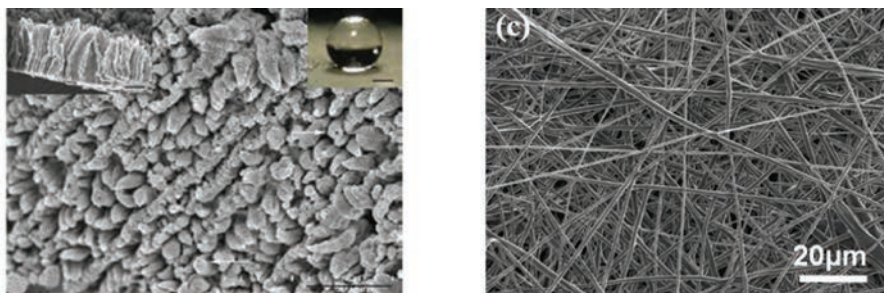


Fig. 5 Examples of the employment of nanofilaments from nanowaxes and nanotubes from PTFE for preparation of hydrophobic and oleo phobic surfaces

In current time a lot of companies also offer applications of some super hydrophobic and super oleo phobic preparatives, usually based on nanoglass, soaking or spraying. However, the effectiveness is discussable. For reaching of quality result, it is necessary to apply suitable reagents with the help of special procedures. A way of coating with the low temperature plasma with usage of a plasma nozzle suits well to this purposes in atmospheric pressure. A principle of this method is visible from the figure 6.

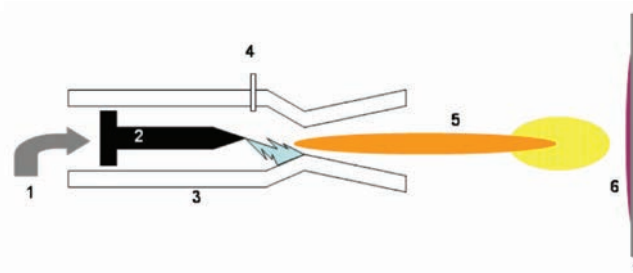


Fig. 6 Principle of the plasma nozzle suitable for coating of hydrophobic and oleo phobic substances on textile materials: 1-income of plasma gas, 2-catode, 3-anode, 4- doser of precursors for deposition, 5-plasma, 6-layer after deposition, 7-substrate

If we prepare textile or another material with hydrophobic and oleo phobic surface with some from above mentioned ways it is necessary to verify its resistivity against real drops of water, oils or other harmful substances. Verification is performed with the help of measurement of the contact angle of the freely lying drop as it is visible from the figure 7 and below introduced diagram on the figure 8. This one describes the drop behavior (Wetzel's, or Cassi's model) in accordance to the fact if the surface under nanostructures is wetted or non-wetted.



Fig. 7 Calculation of the contact angle of the freely lying drop of the tested liquid

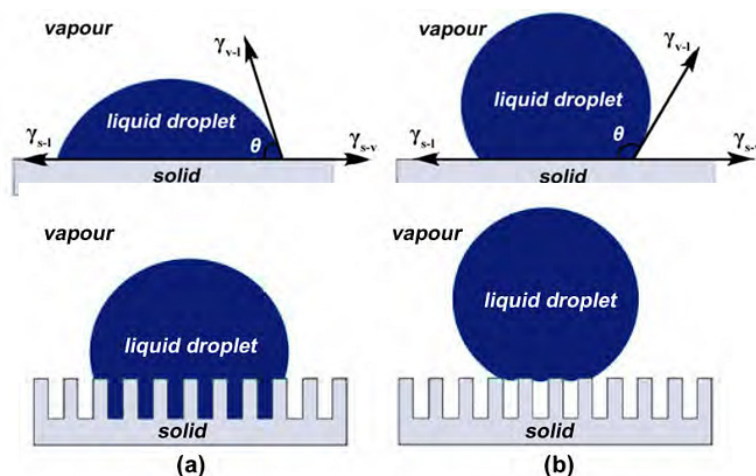


Fig. 8 Behavior of drops on the solid surface (a) Wenzel's model, (b) Cassi's model

3. Experimental part

3.1 Samples preparation

For verification of possibilities of plasma chemical coating of hydrophobic and oleo phobic nanosurface on textile materials 4 types of textile samples have been chosen with no modification.

- cotton shirting form military shirt (homespun weave, ba), weight 220 g/m²;
- material of field uniform (pattern 90) made from the mixture of polyester and cotton fibers (twill weave, ba-PES in the ration of 50/50), weight 360 g/m²;
- development sample of a mixture fabric from SPOLSIN made from the mixture of cotton, polyester and nomex fibres (knitted fabric, ba-PES-NOMEX in the ration of 40/30/30), weight 280 g/m²;
- development sample of a mixture fabric from SPOLSIN made from the mixture of cotton, polyester and nomex fibres (homespun weave, ba-NOMEX in the ration of 50/50), weight 105 g/m²;
- Two development samples designated for modernized filtration protective suit with classical hydrophobic and oleo phobic impregnation in a framework of cooperation from the company of B.O.I.S., Filtry, Limited Company have been used for comparison and evaluation.
- development sample of cower textile TENCATE DWFENDER M with hydrophobic, oleo phobic and fire-resistant modification made from polyamide fibres (weave ripstioip plain, FR-ARAMID – PAD in the ration of 65/25/10) with camouflage Woodland or Desert, weght 210 g/m²;
- development sample of cower textile TATRALAN 140, pattern 95 made with the twill weave from clear cotton with the hydrophobic and oleo phobic modification with camouflage of “jungle” or “dessert”, weight 186 g/m²;

At least three cut-out samples, dimension of 10 x 10 cm, tempered on demanded temperature have been used for measurement of the contact angle of the freely lying drop of test chemical.

3.2 Used procedure of plasma chemical modification

Equipment developed at the Masaryk's university in Brno working with the system of plasma nozzles which generate high frequency non- isothermal plasma within atmospheric pressure in accordance to solvers' patent (CZ 286310, US 6,525,481, EP 1077021 - in current time within the legal protection) has been used for plasma chemical modification of textile samples. Forming thin ultra hydrophobic nanostructure layers on textiles with the help of plasma has been realized based on patents registrations EP 07466017 a CZ – PV 2008-290 (in current time within the legal protection). Real appearance of the equipment enabling continual modification of fabrics in the wide of 30 cm is presented on the figure 9.

All four tested samples of textile materials (1 - clean cotton, green, 2 - PES + cotton, green, 3 - PES + cotton + Nomex, brown, 4 - Nomex, blue) have been modified with overall 10 ways described below:

- 01 modification with plasma with OMCTS dosed through argon and nitrogen;
- 02 modification with plasma with OMCTS dosed through nitrogen;

- 03 modification with plasma with OMCTS dosed argon + HMDSO dosed through nitrogen;
- 04 modification with plasma with OMCTS dosed argon + HMDSA dosed through nitrogen;
- 05 without plasma, coating of Nanopool preclean, after drying coating nanoglass;
- 06 pre-modification with plasma, coating nonoglass;
- 07 pre-modification with plasma, coating nanoglass, subsequent modification with plasma OMCTS dosed through argon or nitrogen;
- 08 pre-modification with plasma, coating nanoglass, subsequent modification with plasma HMDSO dosed through nitrogen;
- 09 pre-modification with plasma, coating nanoglass, subsequent modification with plasma OMCTS dosed through argon + HMDSO dosed through nitrogen;
- 10 pre-modification with plasma, coating nanoglass, subsequent modification with plasma OMCTS dosed through argon + HMDSA dosed through nitrogen.

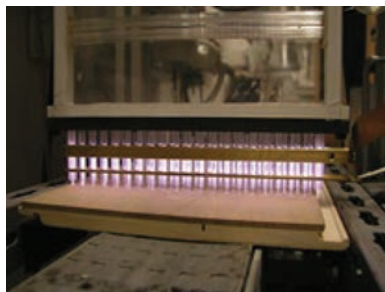


Fig. 9 System of plasma nozzles for plasma chemical coating of nano coatings

All modified samples have been evaluated from the size of the contact angle for drops of water and olive oil point of view - measured values are always the average of three measurements. The calculation of surface energy of nano coating forming on the sample surface has been performed within 4 selected samples with the highest values of the contact angle for drops of water and olive oil. The surface energy has been calculated with the method of OWRK (Owens, Wendt, Raberl, Kaelble) for tested liquids, thus water and glycerol with the employment of Young's equation.

$$\sigma_s = \gamma_{sl} + \sigma_l \times \cos\theta$$

where σ_s is the surface tension or surface energy of the solid surface
 σ_l is the surface tension of the tested liquid
 θ is the measured contact angle
 γ_{sl} is divergence of the surface tension of liquid and the solid surface

Results of these evaluations are introduced in the table 3, 4 and 5 in the subsequent chapter.

3.3 Measurements of the contact angle of freely lying drops of tested compounds

The equipment SeeSystem, SW SeeSystem 6.3 has been used for measurement of the contact angle of freely lying drops. Dosage of drops within the volume of 2,5 μ l has been performed with the micropipettes. Testing equipment consists of digital micro camera DigiMicro 2 (with the software for measurement of the contact angle and the size of the drop) and rustles, altitude set tripod enabling horizontal observation of freely lying drop of tested chemical (its timely reduced evaporation) on horizontally lying sample has been used at the Military technical Institute of Protection. This equipment enables to take figure made within observation and save them into the computer and further to use them. Within working with Chemical Warfare Agents this equipment has been placed into a digester and within measurement have been used protective equipment. A simple drawing of the equipment and an illustrative figure of the observed drop are introduced on the figure 10.

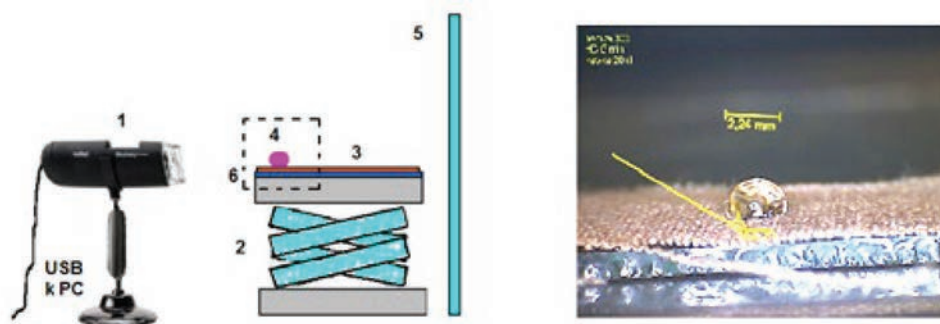


Fig 10 Equipment for measurement of the contact angles of freely lying drops of liquids 1 - digital micro camera DigiMicro2.0 Scale with the software for measurement of contact angles, 2 - altitude set tripod, 3 - tested sample. 4 - tested liquid, 5 - foil, 6 – slide picture - the example of the picture of freely lying drop of tested compound (left)

4. Results and discussion

In the chart 3 there are introduced results of measurements of the contact angles of freely lying drops of water and olive oil (size $2,5 \mu\text{m}$) gained at the Masaryk's university in Brno on the sample 1 and 2. From the results it is clear that for drops of water have been received relatively good result concerning high values of the contact angle (around 140°) within all used ways of coating. Initiative good hydrophobity, however, decreased in time, probably as the result of small thickness of the created nanocoating. From the demanded oleo phobic effect point of view, however, these samples has not satisfied at all because the drop of olive oil has feathered immediately (til 10 s).

Table 3.

Contact angels measured at the Masaryk's University Brno on modified samples 1 and 2

Number of sample	Number of modification	Contact angel		Number of sample	Number of modification water	Contact angel	
		water	Olive oil				Olive oil
1	01	145,9	-	2	01	145,0	-
	02	142,6	-		02	143,9	-
	03	146,9	-		03	138,9	-
	04	147,6	-		04	140,3	-
	05	141,9	-		05	133,4	-
	06	141,5	-		06	137,5	-
	07	148,4	-		07	141,1	-
	08	141,7	-		08	147,1	-
	09	146,3	-		09	141,6	-
	10	146,1	-		10	140,8	-

In the chart 4 there are introduced results of measurements of the contact angles of freely lying drops of water and olive oil (size $2,5 \mu\text{m}$) gained at the Masaryk's university in Brno on the sample 3 and 4. From the results it is clear that within these samples have been received high values of the contact angle (around 150°) for water in the scope of all used ways of coating. However, for drops od olive oil values were worse (mostly about 130°) and they heva been reached after application of modification from the fifth way and further. Moreover, the quality of modification has not been stabile and homogenous enough within some procedureds. It can again be determined due to small thickness of nano cover.

Table 4.

Contact angels measured at the Masaryk's university Brno on modified samples 3 and 4

Number of sample	Number of modification	Contact angel		Number of sample	Number of modification water	Contact angel	
		water	Olive oil				
3	01	153,4	-	4	01	151,0	-
	02	154,2	-		02	147,9	-
	03	153,9	-		03	157,8	-
	04	152,4	-		04	147,6	-
	05	150,7	137,2		05	158,9	-
	06	153,6	139,7		06	160,7	139,7
	07	155,2	123,6		07	154,0	137,0
	08	153,2	130,0		08	154,2	93,3
	09	151,7	136,7		09	153,5	112,1
	10	153,0	134,8		10	155,0	134,8

By four samples with the highest values of the contact angle and the most durable hydrophobic and even oleophobic surface energies have been calculated at the Masaryk's University introduced in the chart 5.

Two groups of chemical compounds – antecedents – which have given huge differences in results have been used within application of plasma chemical modification of the samples' surfaces. The first group of surface modification has been based only on application of different combination of siloxanes or silazanes. By samples from this group have been, in accordance with expectation, reached almost super hydrophobic surface properties which are connected with forming of nanostructure on the surface of the material and their chemical composition. These very thin nanostructure layers are fully continuous for water gas. If we compare reached results with referential samples without any modifications it could be said that came to important increasing of hydrophobic properties on the modified surface because samples without modification have been totally wettable or liquid-absorbing.

Based on reached results it can be said that plasma surface modification with siloxanes enables to achieve essentially higher hydrophobicity in all cases for particular underlay material (the best value in different conditions 145,0° and 154,2°) than within procedure without employment of plasma. The highest values of hydrophobicity within surface modification with plasma with siloxanes have been reached in selected conditions by the sample 4-03 (cotton + Nomex, blue), where the contact angle was 157,8°.

As the reached results for the group with application of nanoglass show very positive result has been achieved. It concerns mainly water by the sample 3-05 with the part of nomex fibres (PES + cotton + Nomex, brown, contact angle for water 150,7°, for oil 137,2°). By application with pre-modification of samples with plasma have again been reached positive results only by samples with the part of nomex fibres, 3-06 (PES + cotton, Nomex, brown, thew contact angle for water 153,6°, for oil 132,3°) and 4-06 (cotton + Nomex, blue, contact angle for water 160,7°, for oil 139,7°) what is the best result from all. Technologies of application of pre-modification with plasma, coating of nanoglass and subsequent modification with plasma with antecedents has reached the most stabile positive results by samples 3-09 (PES + cotton + Nomex, brown, the contact angle for water 151,7°, for oil 136,7°) and 4-07 (cotton + Nomex, blue, the contact angle for water 154,0, for oil 137,0), 4-09 (cotton + Nomex, blue, contact for angle 153,5o, for oil 112,1o). By samples 3-07, 3-08, 3-10 and 2-07 have been reached very good results of contact angels not only for water but also for oil. However, probably small thickness of layers has caused gradual percolatin of oil. This lack is, however, possible to remove by forming of thicker and more homogenous nanostructure layer by longer affection of plasma with bigger amount of antecedents and more intensive cooling by carried gas, eventually with bigger amount of used nanoglass.

Samples prepared at the Masaryk's University have been further evaluated at the Military Technical Institute of Protection. Regarding the fact that due to a personnel computer accident all date from the measurement angles has been lost. From that reason it was necessary to verify, at least by in the best way modified samples, the behavior of freely lying drops of water and olive oil from the point of view of stability of hydrophobic and oleophobic effect in time. The problem was in homogeneity of performed modifications because of plasma nozzles. Although these ones are tightly side-by-side they do not cover uniformly the whole surface of modified material and the stripes with smaller amount of coated components are formed. It can be removed either with some rows of nozzles side-by-side which are covered each other or cik-cak moving of nozzles, eventually thereby that material will be modified two times after

slewing about 90°. Thanks to in homogeneity, however, on all modified samples were places with bigger or smaller value of the contact angle. It has sometimes caused that on one place the drop or other tested materials has kept without soak for relatively long time while on another place it was relatively quickly soaked into even the fact that initial value of the contact angle has been considerably high.

Moreover it was necessary to consider how these modifications will behave against the affection of freely lying drops of Chemical Warfare Agents. It has been found during orientation probe that drops of somane and even its model chemical compound (n-propanole) after coating on any prepared sample immediately soaked. Next attempts with them have not been performed. Due to high toxicity of VX compound it has been used olive oil instead of it. From real Chemical Warfare Agents the contact angel has been measured only with the employment of drops of sulfur mustard. Because of measurements with nitrobenzene as its model compound has not given any comparable results the measurement has been finished without any continuation.

The figure 11 represents the typical texture of the surface of the sample of 3 and 4 with a share of nomex fibres. These ones are suitable than other textile materials after their modification with plasma chemical modification. They have typical contact angles for freely lying drops of water and olive oil for different modification of the sample

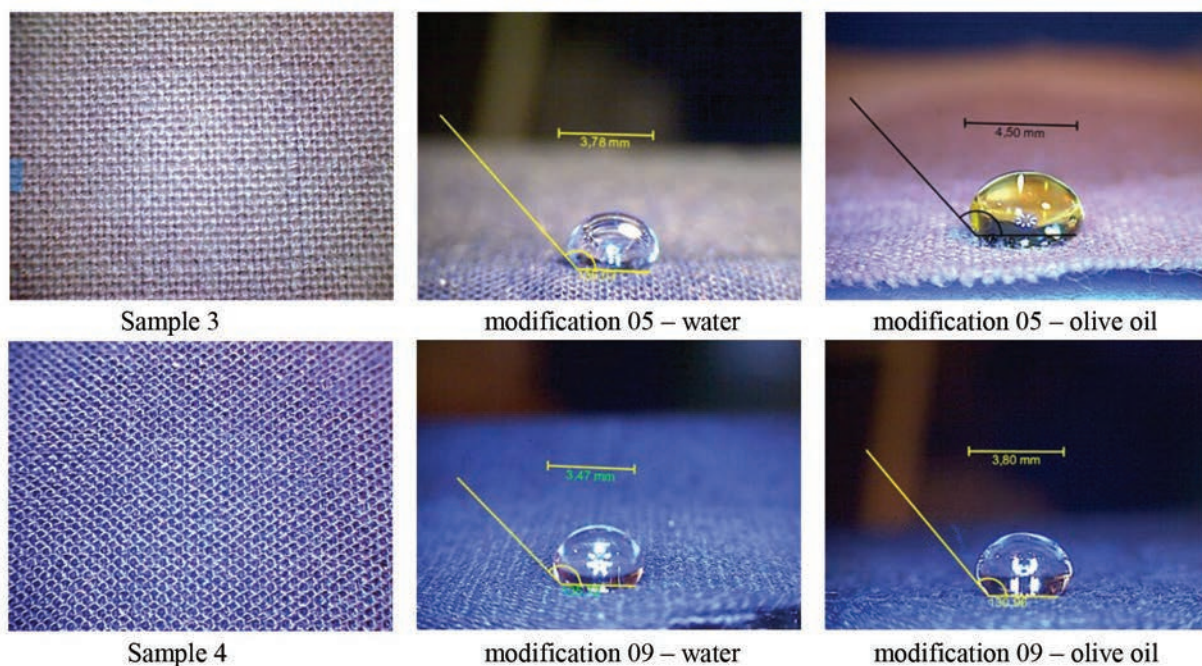
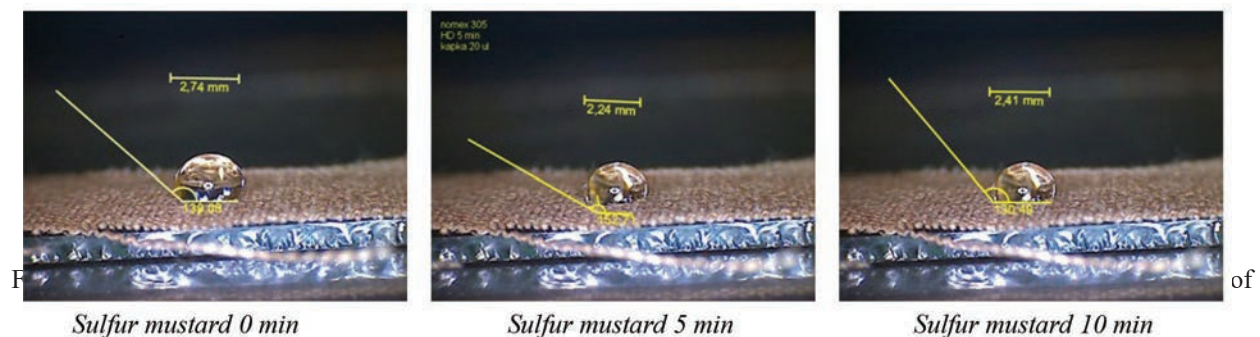
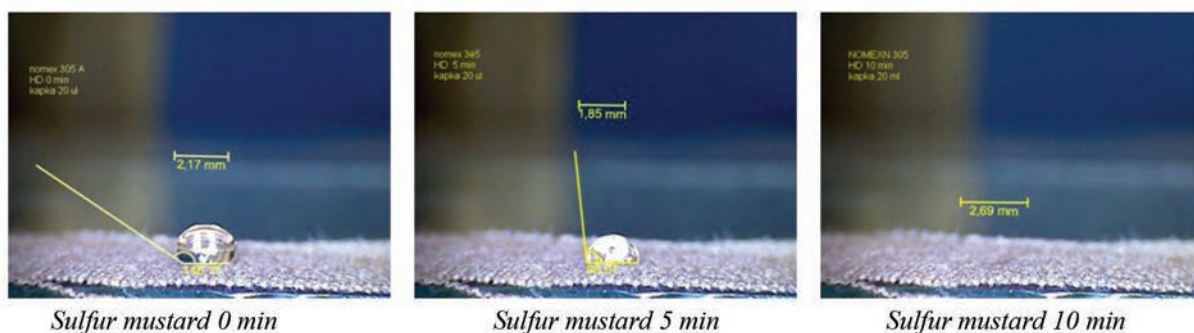


Fig. 11 Behavior of freely lying drop of water and olive oil (volume 20 μ l, temperature 25 °C) on nomex fibres

The objective example which verifies presence of inhomogeneity of nanocoatings forming on the surface of material 3 with the help of procedure 5 are measured values of contact angels for drops of sulfur mustard (Volume 20 μ l). These ones in the long term embody high value of the contact angle (till 24 hours) on one place on the material while on another place the value of the contact angel decreases till the time when the drop is totally soaked (Figure 12).





Whether sulfur mustard has been replaced by drops of nitrobenzene as an effort to use it as a model compound it has come to relatively quick soaking on all tested materials regardless of placing as it is seen on figure 13. Similarly as drops of sulfur mustard behave freely lying drops of the olive oil as it is seen on figures 14 and 15 while drops of water has not changed within the same conditions.

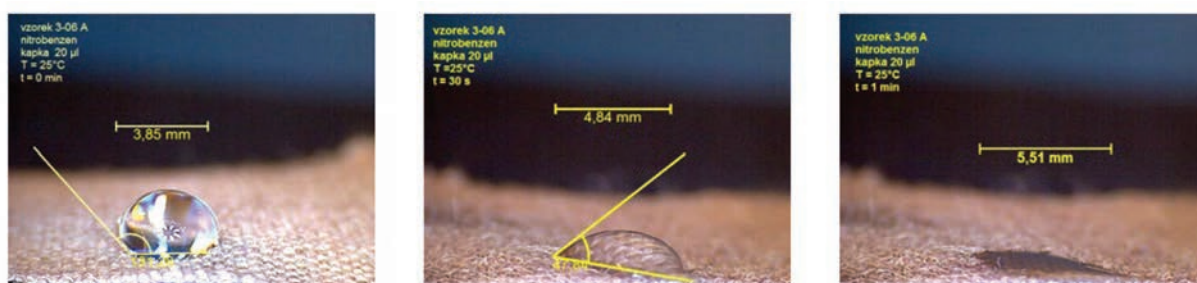


Fig. 13 Behavior of freely lying drop of nitrobenzene (volume 20 μ l, temperature 25 $^{\circ}$ C on material 3 modified with the procedure 06 and 19

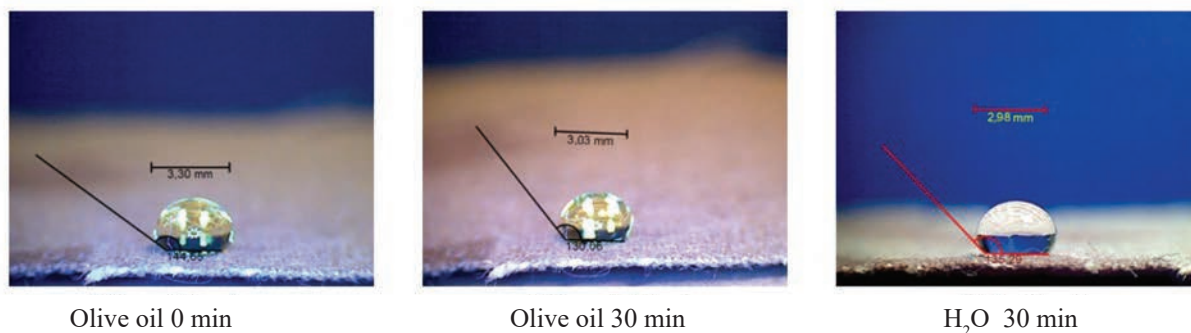


Fig. 14 Behavior of freely lying drop of olive oil (volume 20 μ l, temperature 25 $^{\circ}$ C on material 3 modified with the procedure 06

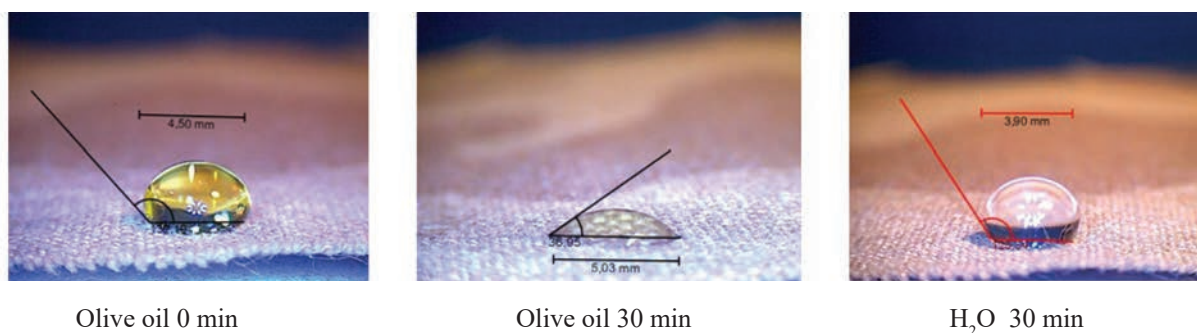


Fig. 15 Behavior of freely lying drop of olive oil and water (volume 20 μ l, temperature 25 $^{\circ}$ C on the surface of material 3 modified with the procedure 05

Photos on pictures 16 and 17 illustrate texture of surface of developed textile KT TECATE for a modernized filtration protective disguise with permanent hydrophobic and oleo phobic modification and its behavior against freely lying drops of water and olive oil. In both cases very good and stabile hydrophobic and oleo phobic effect have been reached and contact angles have achieved the value around 135 ° for water and oil. In comparison with the best values of contact angels measured within plasma chemical modified textile samples these values are little bit lower, however for this purpose quite suitable. The same consideration is valid even for another developed material TATRALAN. Surface modification of this material and behavior against freely lying drops of water and olive oil are illustrated on the figure 18.

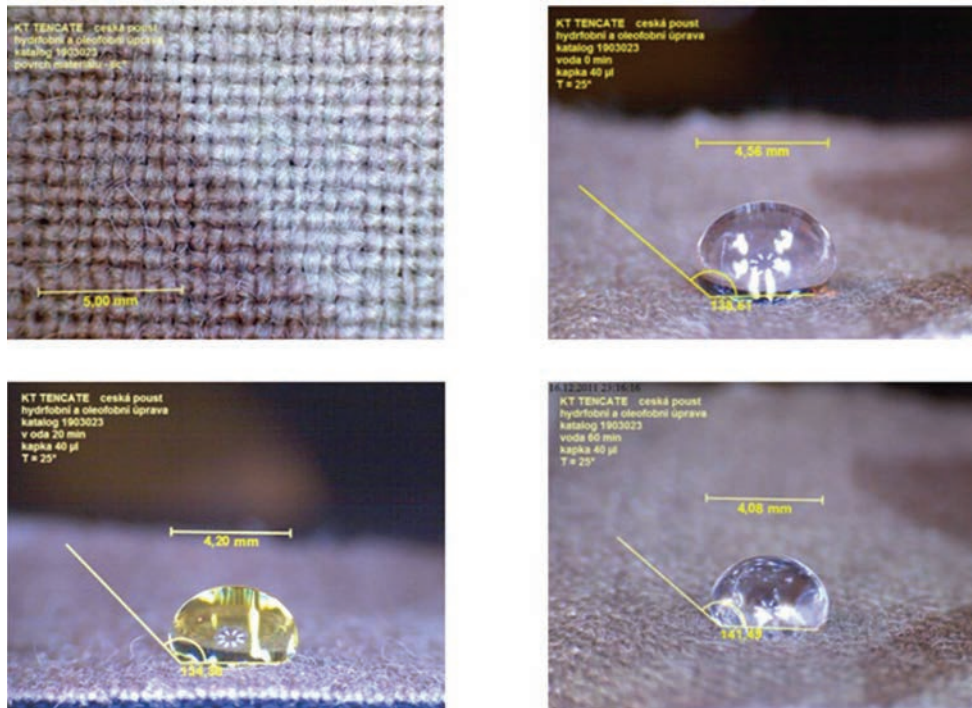


Fig. 16 Structure of the surface of new KT TECATE and behavior of freely lying drop of water

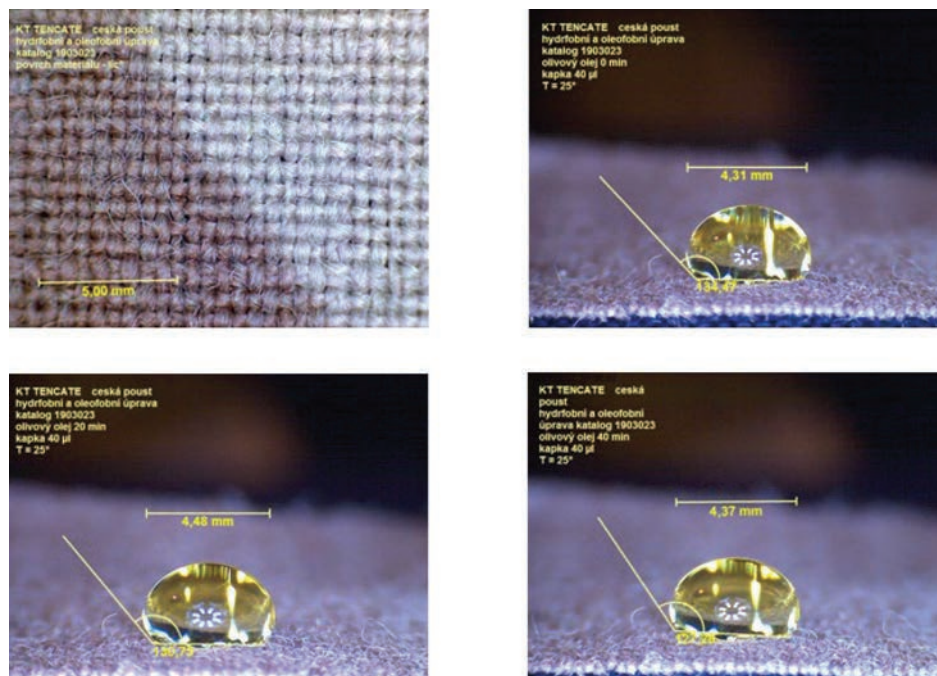


Fig. 17 Structure of the surface of new KT TECATE and behavior of freely lying drop of olive oil

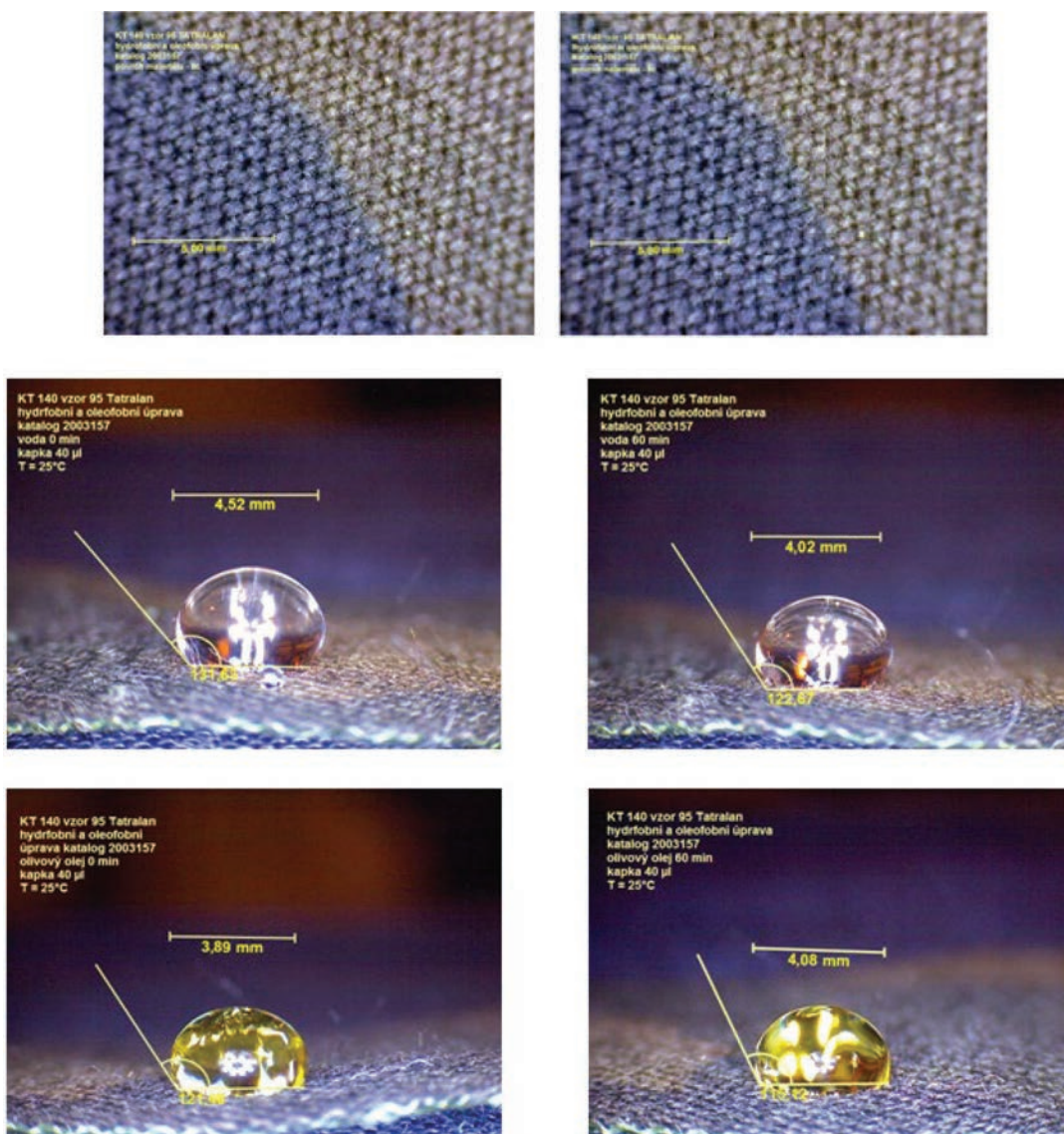


Fig. 18 Structure of the surface of new KT 140 pattern of 95 Tatalan. Behavior of freely lying water drop and olive oil

5. Conclusion

It has been experimentally verified that with the help of plasma chemical procedures with combination with siloxane or silazane antecedents and nanoglass is possible to apply nanocoatings with super hydrophobic and super oleophobic properties on suitable textile materials. These properties can significantly increase not only the resistance of the field uniform against the rain but also to significantly increase resistance of textile constructive materials of resistance against drops of chemical warfare agents or other liquid harmful substances. Because the best results have been reached by samples with the part of nomex fibres it is possible to assume that the main reason is above all better terminal stability of these samples. Further research should be focused on this direction. Regarding the fact that the presented information concerned the first orientation experiments the used technologies have not been optimized yet and neither mechanical nor another resistance has been evaluated of prepared nanocoatings. It can be supposed that with further research in this area would be proposed procedures enhanced and confirmed even commercial demands.

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