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**UTILISATION OF NANOSCALE ORGANOSILOXAN COATINGS
TO IMPART SPECIFIC PROPERTIES TO NONWOVEN MATERIALS***V.M. GORCHAKOVA, B.A. IZMAYLOV**(The Moscow State Textile University named after A.N. Kosygin)*

Over the last ten years we have been carrying research work with the aim of developing nonwoven textile materials with a package of tailor-made properties; the areas of research are as follows:

– processes of fixation of functional-active organic, inorganic and elementorganic compounds on the surface of fibrous materials are studied;

– methods of immobilisation of nanoscale organosiloxan polymer coatings (covalently bound to the surface of fibrous material) of tailor-made composition and structure to the surface of fibrous materials, consisting of functional oligomers which are soluble or self-dispersing in water, are developed;

– methods of designing of nanoscale laminated templated siloxan-organo-inorganic polymer coatings of tailor-made structure, composition and texture on the surface of flexible fibrous materials are developed;

– methods of adjusting and controlling properties of such laminated coatings and their performance specifications are developed.

Through the use of such laminated coatings nonwoven materials are endowed with hydrophobic, bactericidal, aromatic, strengthening and other special properties. Very small quantity of silicone is used to obtain such coatings. This fraction accounts for millimols (10^{-3} g/mol) and micromols (10^{-6} g/mol) of silicone per 1 square meter of specific surface of fibrous material. Nanoscale organosiloxane polymer coatings demonstrate dimensional effects. In particular, high chemical activity of functional groups man-

ifest itself, both directly bound with silicon atoms, as well with the ones which are in carbofunctional radicals, which are covalently bound to silicon atoms.

Nanocoatings are fixed very strong on the surface of fibrous materials, so that they can be removed only with hydrofluoric acid or by boiling for extended time in a concentrated alkaline solution.

Organosiloxane polymer coatings are steam and gas-permeable. Therefore, fibrous material "breathes" even under a thick layer of siloxane film, retaining its comfort properties during usage.

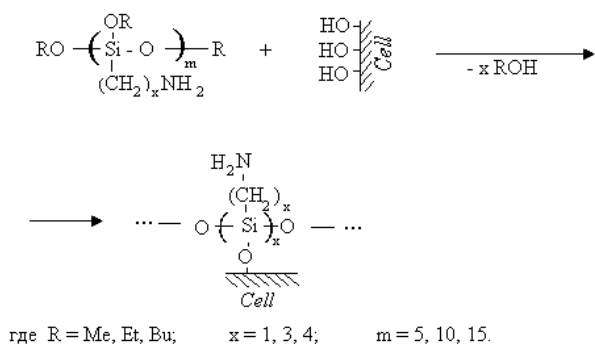
Silicon atoms of such coatings possess carbofunctional radicals, covalently bound to them, which are capable of further chemical transformations. Therefore, by using methods of nanochemistry and nanotechnology, we have developed a method of molecular design on the surface of organosiloxane polymer coatings of the second, third and fourth generation. Coatings can be organic, inorganic or elemento-organic.

Such methods enable to obtain conceptually new generation of flexible laminated composite materials on the surface of which nanoscale laminated templated siloxane-organo-inorganic polymer coatings are located (positioned coaxially in relation one to another) of tailor-made structure, composition and texture.

Let us consider as an example a formation of complexing laminated nanoscale siloxane-organo-inorganic polymer coatings on the surface of fibres having on the surface highly active and high-selective complexing ligands.

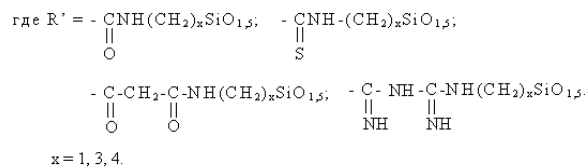
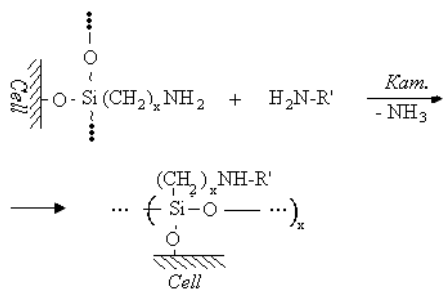
1. Immobilization of complexing ligands onto the surface of fibres. Fixation of complexing ligands is carried out by method of molecular design on the surface in two stages. During the first stage aminoalkyl silyl ($\equiv\text{Si}(\text{CH}_2)_x\text{NH}_2$) groups are fixed covalently on the surface of fiber by means of treatment of fibers with oligoalkoxy(aminoalkyl)-siloxane (Diagram 1).

Diagram 1



During the second stage condensation of aminoalkyl groups with carbamide, dicyandiamide is carried out (Diagram 2).

Diagram 2



As a result complexing carbamide, thiocarbamide, malonodiamide, biguanidine ligands are fixed.

Content of complexing ligands is varied from 5 to 30 mol %.

Thermal and chemical stability of sorbents on the basis of acetate, acetate-cellulose and viscose fibers is determined by nature of the fibrous carrier.

All sorbents are distinguished by a wide range of sorption activity. They withdraw efficiently toxic, precious metals and a large group of heavy metals from liquids, thus forming nanoscale metal-containing coating of the third generation. Such coatings are of interest in terms of application:

2. Adsorption of toxic elements. Toxic elements Hg(II), As (V), Bi (III), Cd (II), Sb (III), Pb (II) are active complexing agents, and consequently can form stable ion-coordinating ligands with the above mentioned complexing groups in more acidic environments. The highest degree of adsorption for Hg(II), As (V) and Bi (III) is found in 1-3M solutions of mineral acids and is characterized by quite high values of sorption capacities (Table 1). The investigated materials with thiocarbamide ligands manifest the highest activity with regard to Hg(II) ions, for which the value of capacity reaches 400 mg/g.

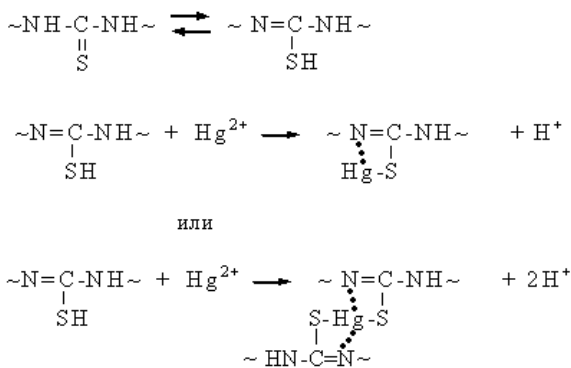
Table 1. Values of static sorption capacities (CCE) of fibers for toxic elements

CCE, mg/g					
Hg(II)	Bi (III)	Cd (II)	As (V)	Sb (III)	Pb (II)
179 (1m HNO ₃)	40 (1m HNO ₃)	40 (pH=1)	145 (3m HNO ₃)	110 (pH=1)	131 (pH=1)
128 (1m HCl)	134 (pH=6)	127 (pH=6)	-	-	-
210 (3m HNO ₃)	-	-	-	-	-
400 (1m H ₂ SO ₄)	-	-	-	-	-

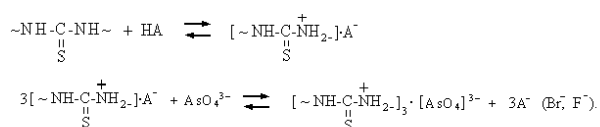
Such values of capacities for Hg(II) for known sorption materials are found extremely rare.

High efficiency of these materials in relation to Hg(II) ions and other toxic metals is a result of forming strong complexes in the sorbent phase.

With due consideration of thion-thiol tautomerism which is inherent to thioamides, and especially to thiocarbamides, one can assume that sorption of cations of toxic metals proceeds according to mechanism of ion coordination:



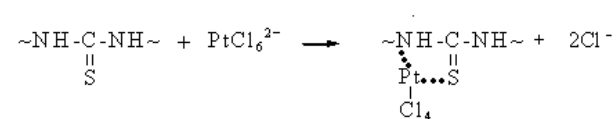
Anion metabolic activity of the thiocarbamide with regard to oxo complexes AsO_3^- and SbO_2^- is related to the known capability of thiocarbamides to form iso-thyronine salts in acidic solutions. The discovered ability of sorbents containing thiocarbamide groups to extract anions of bromine and fluorine from solutions can also be attributed to the above said.



Solutions of 6M HCl serve as all-purpose desorbents for regeneration of sorbents saturated with toxic metals; effect of excessive acid on metal-saturated sorbents causes complete outwashing of them from the surface of the sorption material.

3. Sorption of precious metals. Highly selective recovery of precious metals Ag (I), Au (III), Pt (IV), Pd (II), Rh (III), Ir (III), Ru (III), Os (IV) by new sorbents can proceed in concentrated solutions of hydrochloric and sulphuric acids in the presence of dominant amount of diverse non-ferrous and heavy metals. Sorbents with thiocarbamide groups manifest maximum efficiency and selectivity.

Process of complex formation with ions of precious metals proceeds according to the following scheme:



and is accompanied by displacement of two to four chlorine atoms from the coordination

sphere of metal-acido complex.

Statistical sorptive capacity (SSC) of sorbents on the basis of fibrous glass in sulphate solutions at 100°C is the following:

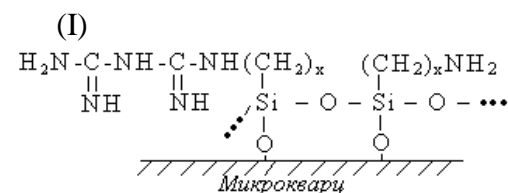
- Ir (IV) – 48 mg/g (4.5m H_2SO_4),
- Ru (III) – 31 mg/g (6.0m H_2SO_4),
- Os (IV) – 46 mg/g (7.5m H_2SO_4).

It should be noted that, in case of extraction of Au (III) by a sorbent on the basis of glass "microquartz" fiber, insignificant portion (up to 20%) of gold (III) passes to the zero-valent state, i.e. is regenerated to Au (0).

4. Sorption materials with biguanidine ligands. Most of organic biguanidine derivatives are biologically active substances. For instance, biguanidine grouping is part of palauamine and styloguadine alkaloids (which have cytotoxic, antibiotic, antifungal and immunomodulatory action) of the antibiotic glyformin preparation.

Besides, organic compounds containing polydentate biguanidine grouping are known as selective complexing agents. Until now there was no information in technical literature regarding biguanidine derivatives.

We have developed zol-gel method for designing organosiloxane polymer coatings on the surface of fibers of different nature which possess high sorption activity, especially with regard to silver (statistical sorption capacity of coating (I) amounts as to Ag (I) 544 mg/g). It is determined by high tendency of Ag (I) ions to complex formation with nitrogen-containing ligands.



Change of sorption activity of coatings (I) in the range of the examined metals Au (III), Pt (IV), Pd (II) is related to the higher stability of coordination compounds Ag (I) with amines in comparison with Au (III), Pt (IV), Pd (II).

Coating (I) has been examined as adsorbent of precious metals Ag (I), Au (III), Pd (II) и Pt (IV). Sorption has been carried out in

acidic medium 0.5-0.6M HNO₃ for Ag (I), 3M HCl for Au (III), Pd (II) and Pt (IV) in static mode. Results of determining statistical sorptive capacity (SSC) of the coating with regard to the examined metals (elements) are given in Table 2.

Table 2. Results of determining SSC of coating with regard to examined metals (elements)

Sorbate	SSC, mg/g
Ag (I)	544
Au (III)	6,6-22
Pt (IV)	30
Pd (II)	30,8

CONCLUSION

In summary, the examined sorption-active complexing laminated nanoscale templated siloxane-organo-inorganic polymer coatings on the surface of fibers of different nature, which contain carbamide, thiocarbamide, malonodiamide biguanidine ligands, represent promising sorption materials for extraction of toxic metals – As (V), Cd (II), Sb (III), Hg(II), Pb (II), Bi (III), precious metals - Ag (I), Au (III), Pt (IV), Pd (II), Rh (III), Ir (IV), Ru (III), Os (IV); and some rare elements – V (V), Mo (VI), W (VI), Th (IV), U (VII) from natural objects and technological facilities (liquids, gas media, fume, suspensions, emulsions, etc.).

In terms of application aspects, it is of some interest to utilize coatings of the 1st, 2nd, 3rd generation both separately and in different combinations to solve different technical tasks, such as:

– to impart predefined electrophysical (nonlinear optical and luminescent, electrochromic, magnetic, conducting and other) prop-

erties (rare earth elements) to fibers,

– to impart resistance to radioactive exposure and other high-energy rays (¹⁰B, ¹¹³Cd, ¹⁴⁹Sm, ¹⁵¹Eu, ¹⁵⁵Gd, ¹⁵⁷Gd),

– to impart fire-resistance (P, N, Si),

– to impart antimicrobial properties, biocide (Ag (I), Cu (II), Zn (II), Fe (III)),

– acaricide properties, i.e ability to repel encephalitic ticks,

– to impart hydrophobic, hydrophilic, antistatic and other properties,

– metal-organic paintable coatings made of conjugate of rare metals for nonwoven new-generation materials under the accepted "Intelligent Textile" program,

– development of optical sensors to determine metal cations (Cu (II), Zn (II), Cd (II), Fe (III) and others) in aqueous solutions.

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