Saint-Petersburg State Technological Institute (Technical University)

Was based in 1828 year by imperial command of Emperor Nicholas I

Structural-size effects in the products obtained by the molecular layering method and their application

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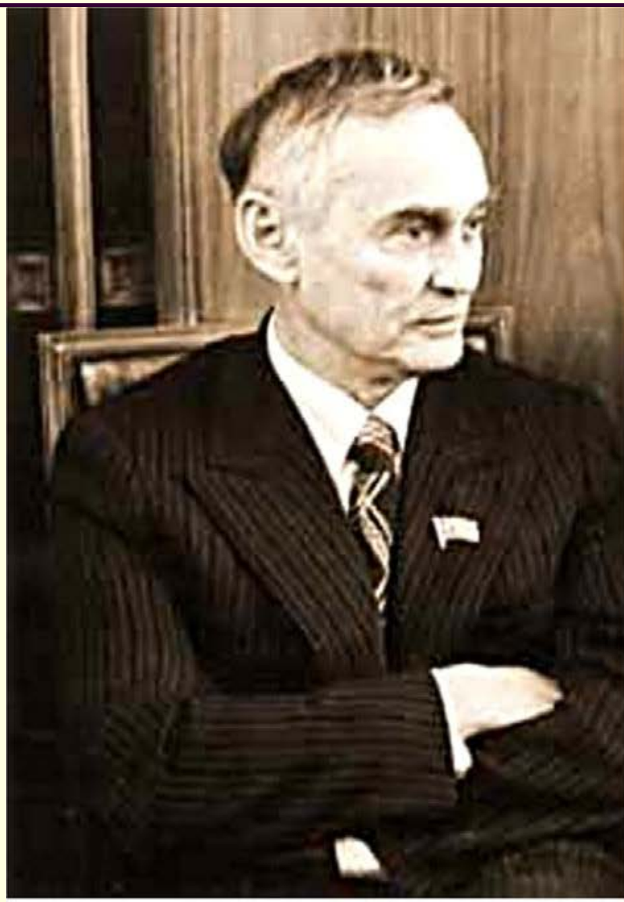
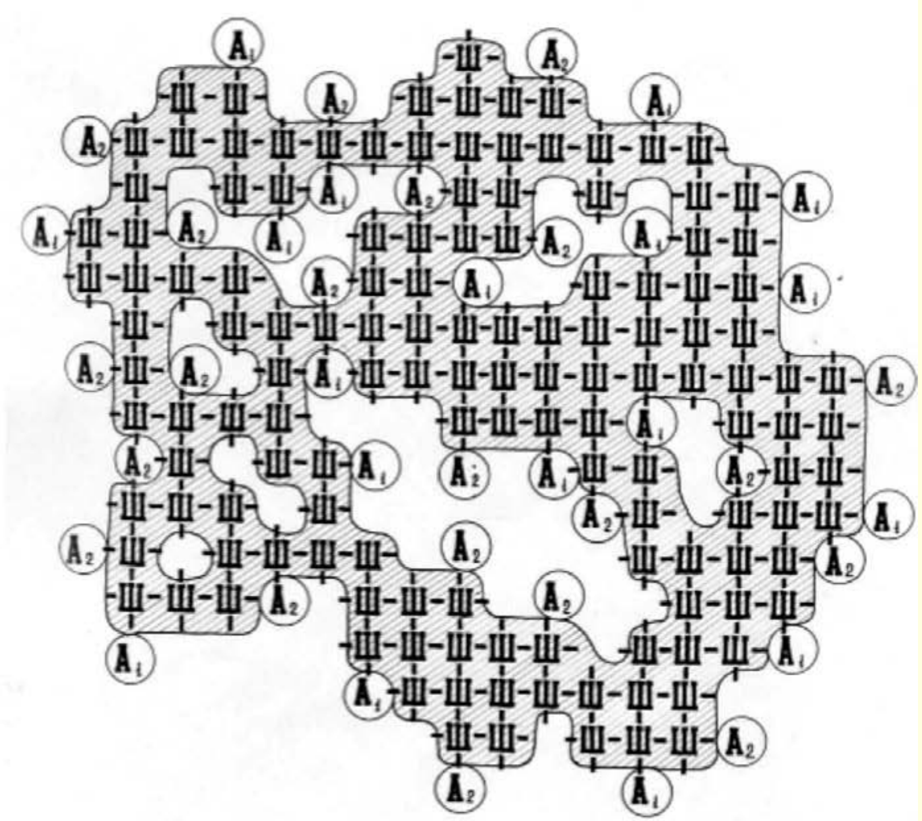
The chemical model of a solid as proposed by V.B. Aleskovskii's "framework" hypothesis (1952, Doctoral dissertation)

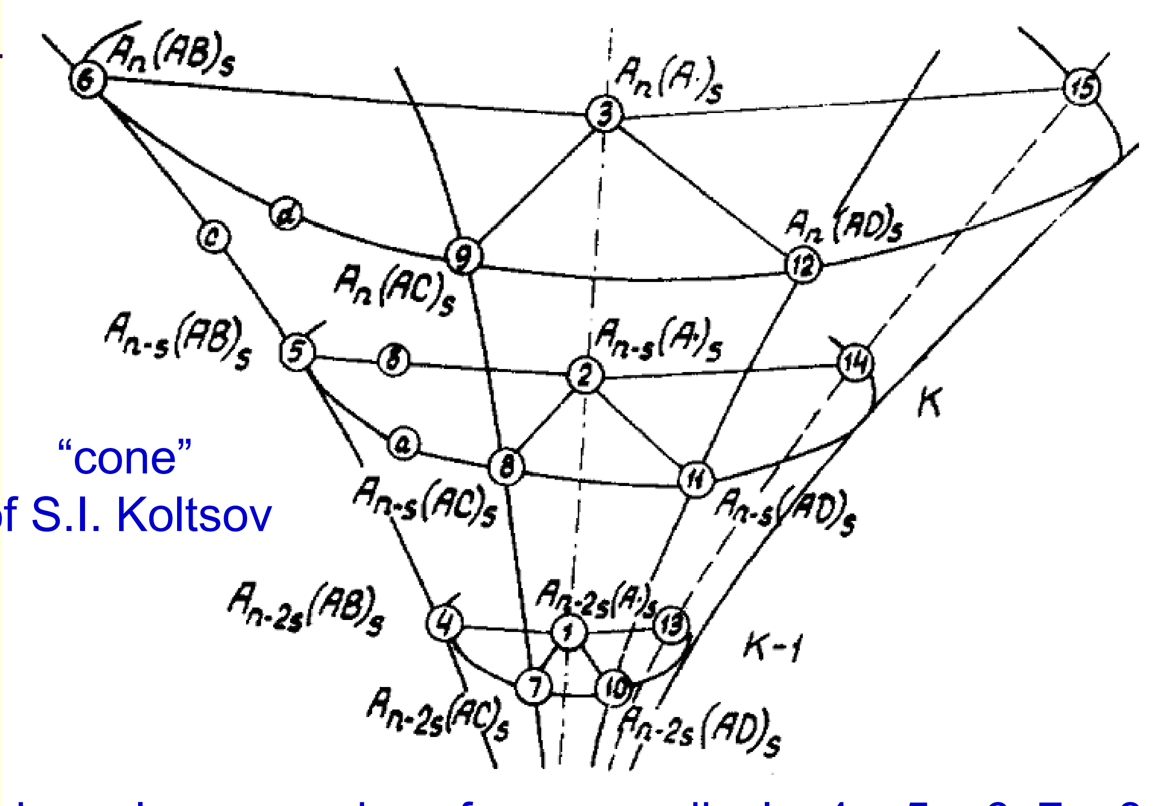




Formula of solid: chemical model of V.B. Aleskovskii can be represented as [Ш]aA In the formula stoichiometric coefficient "a" indicates the amount of chemical equivalents "core" Ш per one chemical equivalent of functional groups.

The relationship of functional transformations in the normal homologous series of solids

(S.I.Koltsov, doctoral dissertation, 1971)

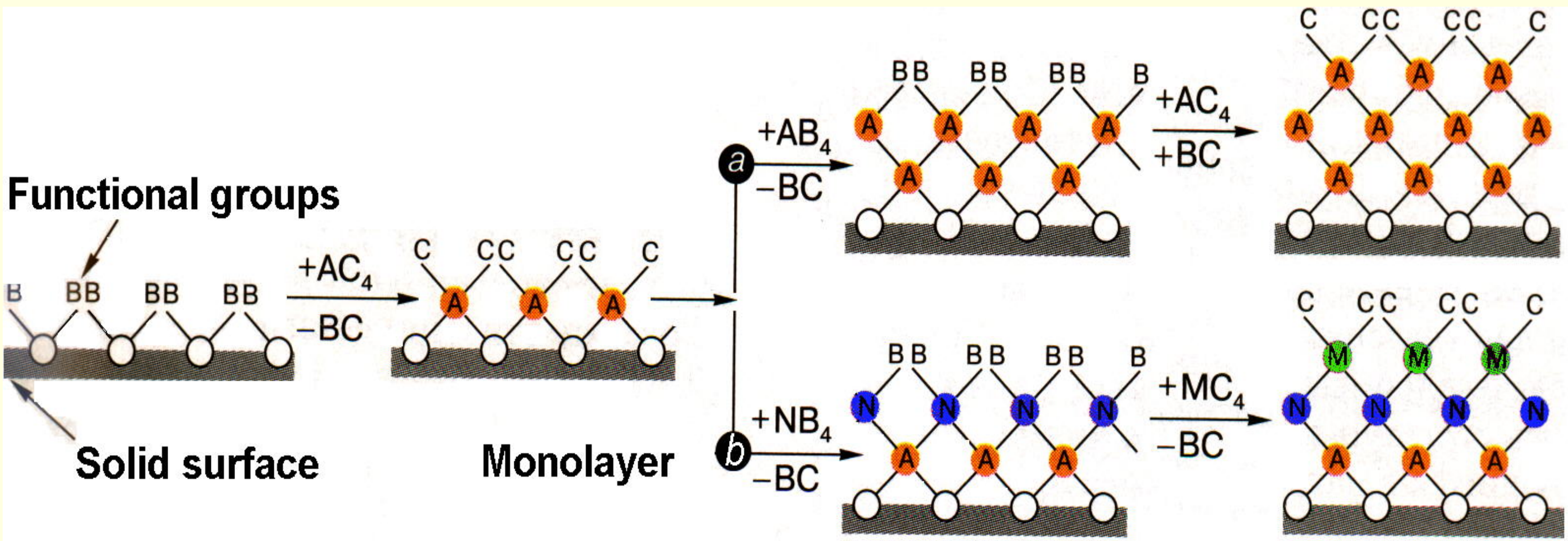


“cone”
of S.I. Koltsov

1-2-3- homologous series of macro radicals; 4 – 5 – 6, 7 – 8 – 9 etc. - homologous series of macromolecules; 4-7-10-13, 5-8-11-14 etc. - series counterparts ; 1-4. 1-7, 2-5, 2-8 etc - isological series; 4-7, 7-10,5-8, 8-11 etc. – genetic series; a, d - Intermediate members of genetic series; b - Intermediate member of isological series; c - an intermediate member of a genetic series molecular layering of structural units; K - number of structural units contained in the radius of the particles ($\Delta K = K_{i+1} - K_i = 1$)

Chemical constructing of nanostructures on the surface of solids by the Molecular layering method (1963 – 1971)

Candidate dissertations: S.I. Koltsov (1963), G .N. Kuznetsova (1965), A.N. Volkova (1969); doctoral dissertation of S.I. Koltsov (1971). Scientific adviser - professor V.B. Aleskovskii



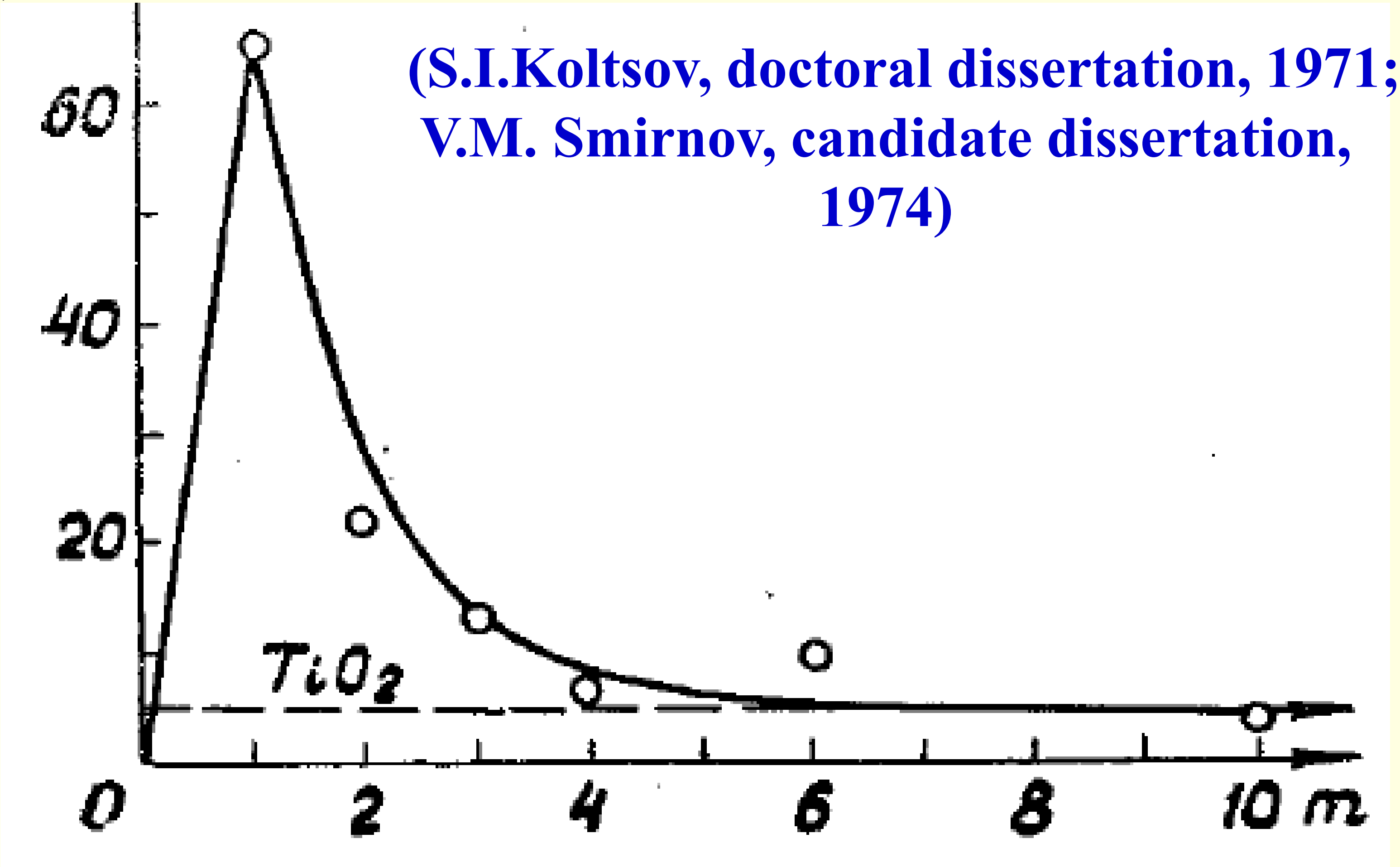
Structurally-dimensional effects in the products of molecular layering

2-D and 3-D structures that synthesized on the surface of solid matrix in ML process and also chemical transformations in system "matrix - surface structure"	Structurally-dimensional effects
A single-component monolayer (from 1 to 4 cycles of ML)	The effect of monolayer - sharp change in the properties of material (after 1-4 ML cycles)
A single-component nanolayers (from 4-6 etc cycles of ML)	The effect of physical overlap surface of the substrate (after at least 4-6 etc. ML cycles)
A many-component layers (mono- and nanolayers)	Effects related to multi-component systems
3-D structure that connected with the surface of matrix by chemical bonds and is in a certain phase state depending on the structure of the substrate surface	Effects related to the mutual coordination between of structural of a substrate surface and thin film formed in ML process

THE EFFECT OF MONOLAYER

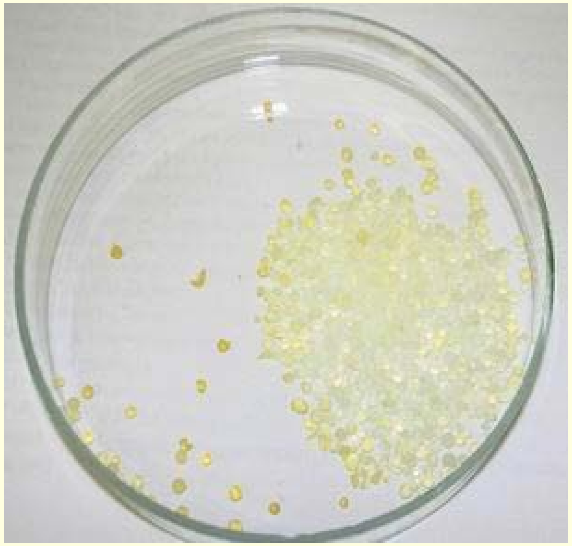
The dependence of the specific rate constants (K_S) hydrolysis of CCl_4 on the number of titanium-containing oxygen monolayers on the surface of silica gel

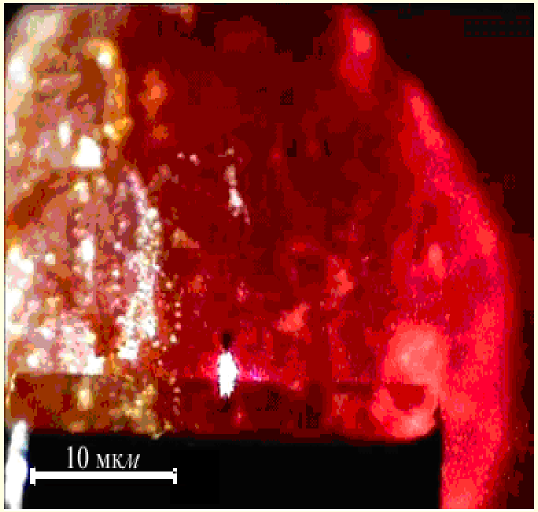
$K_s \cdot 10^4$, mmol·m²·min⁻¹



Change of the color of silica with vanadium oxide monolayer on the surface when contact with water vapor

(A.A. Malygin, candidate dissertation, 1973)





$3(\equiv Si\text{-}OH) + VOCl_3 \rightarrow (\equiv Si\text{-}O\text{-})_3VO + 3HCl$

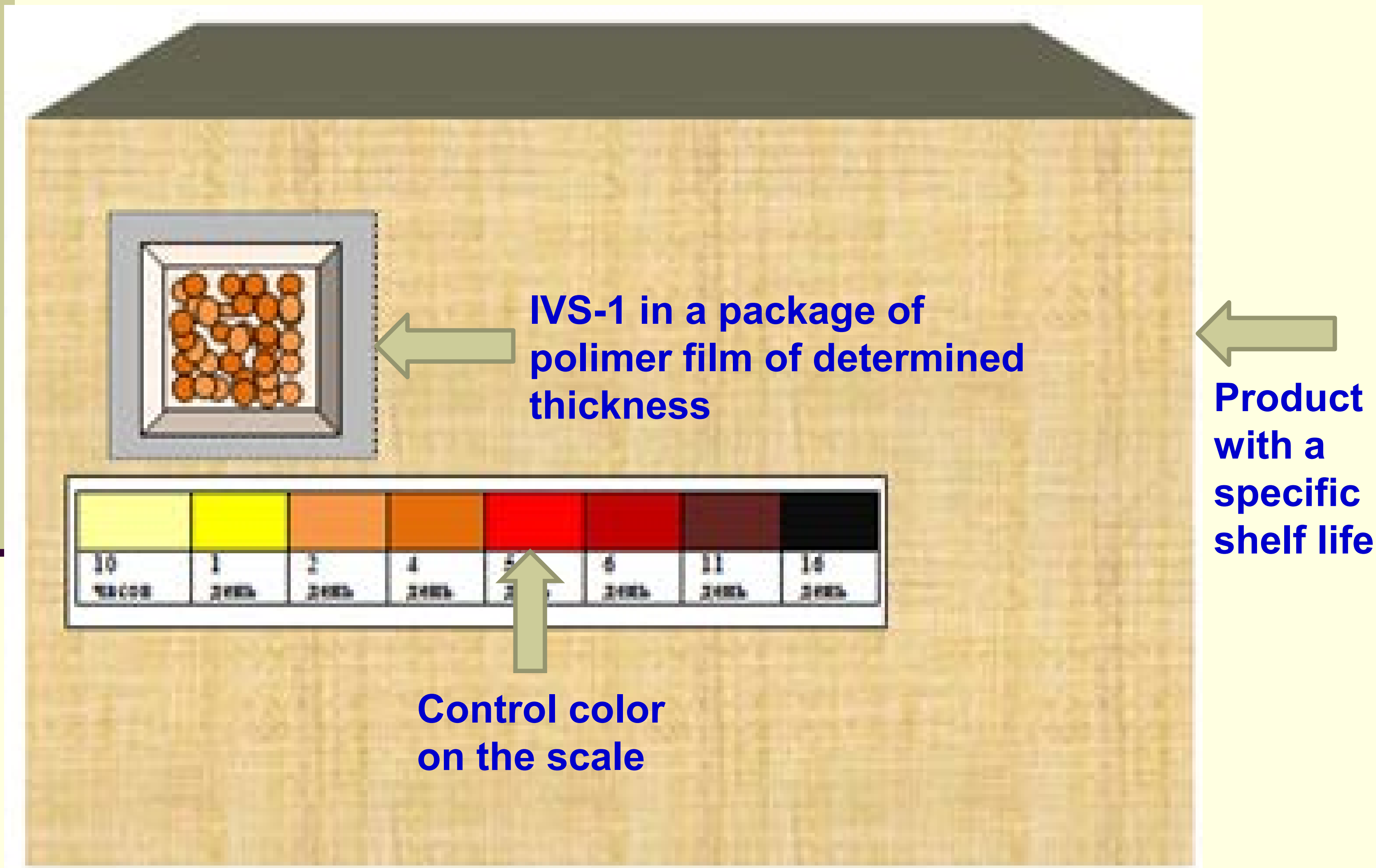
Colouring of vanadium-cotaining silica gel (IVS-1) in closed polymer package

(PVC - 120 microns)

P/P_S	Time to reach the appropriate color, hour							
0,15	0	0,02	1	4	12	24		
0,5	0	0,02	0,5	1	3	4,5	10	
0,85	0	0,02	0,33	0,75	2	3,5	5,5	24
Color								

Depending on the thickness of polymer film the time obtaining of specific color of IVS-1 can regulates from a few minutes to hundreds of hours (initial IVS-1 with out polymer package - from a few minutes to 1 -2 hours)

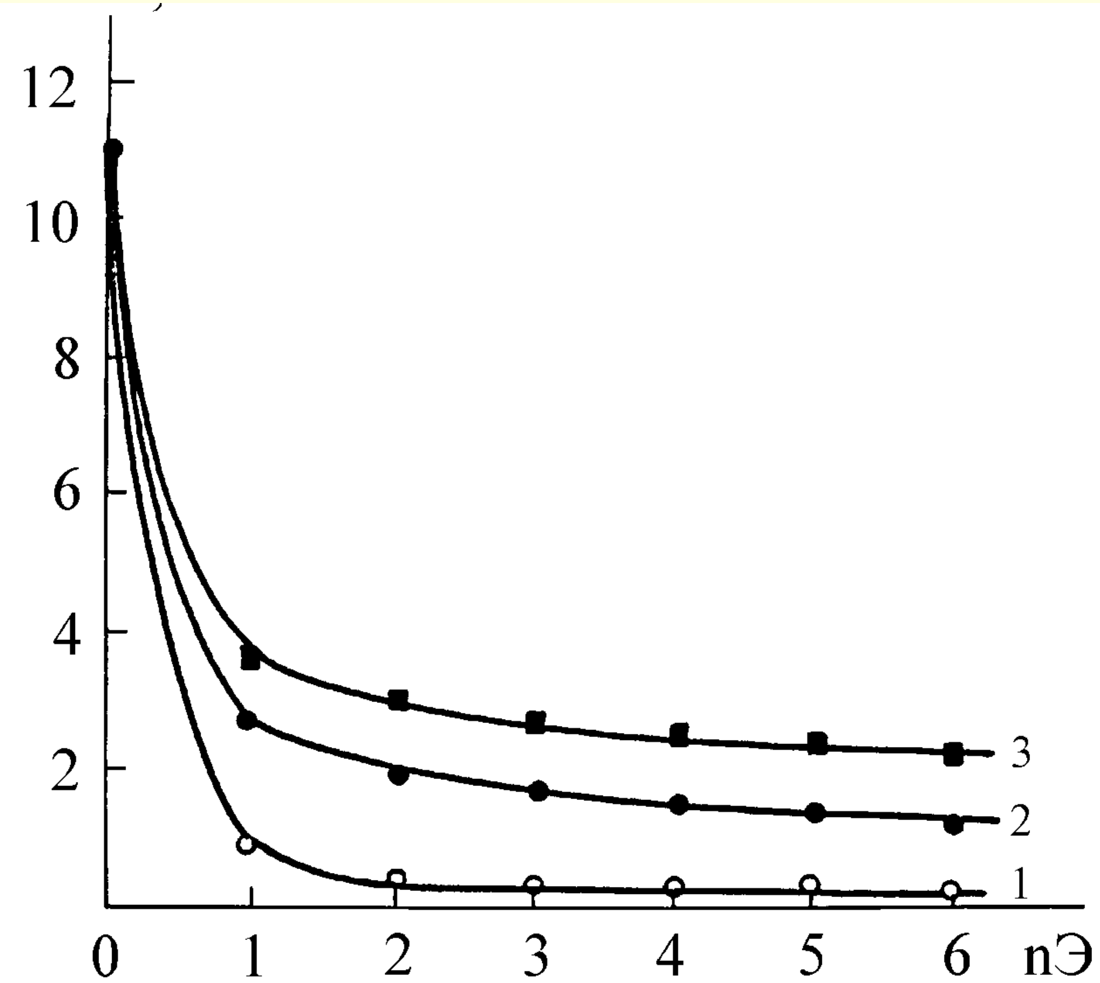
Use of a composition "IVS-1- a polymer film" for the control of shelf life grocery at constant humidity and temperature of the surrounding air atmosphere.



The rate of oxidation of carbon fibers depending on the amount of monolayers of oxide Al^{3+}(1), Si^{4+} (2) and P^{5+} (3)

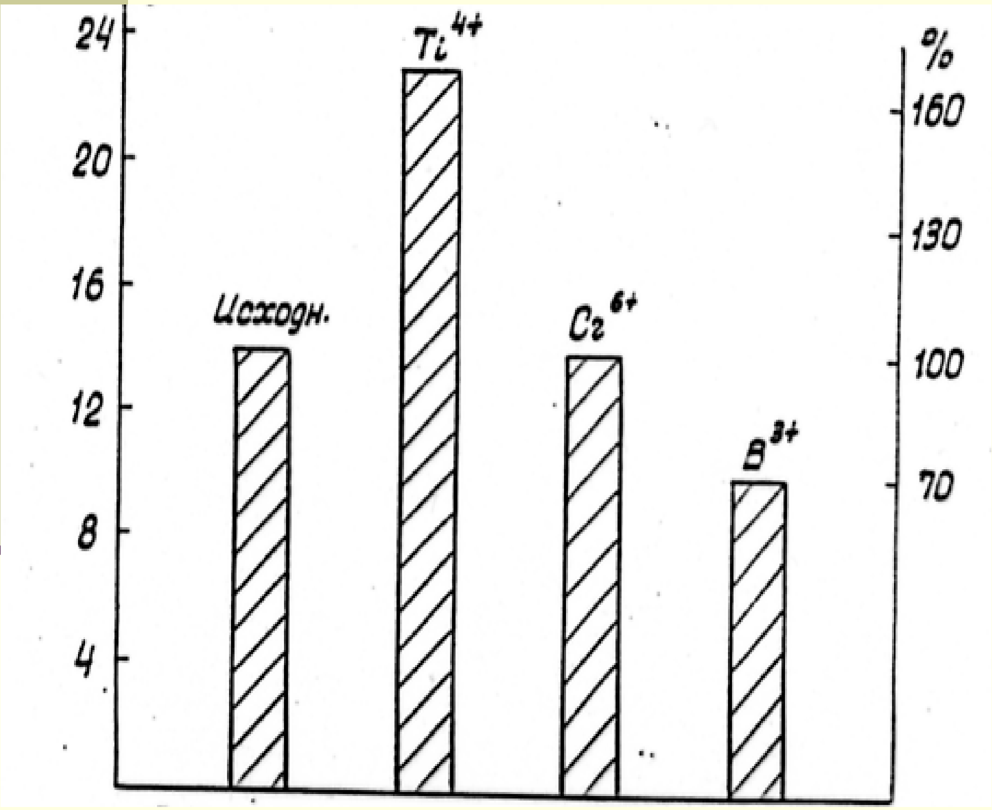
(A.A. Malkov, candidate dissertation, 1977)

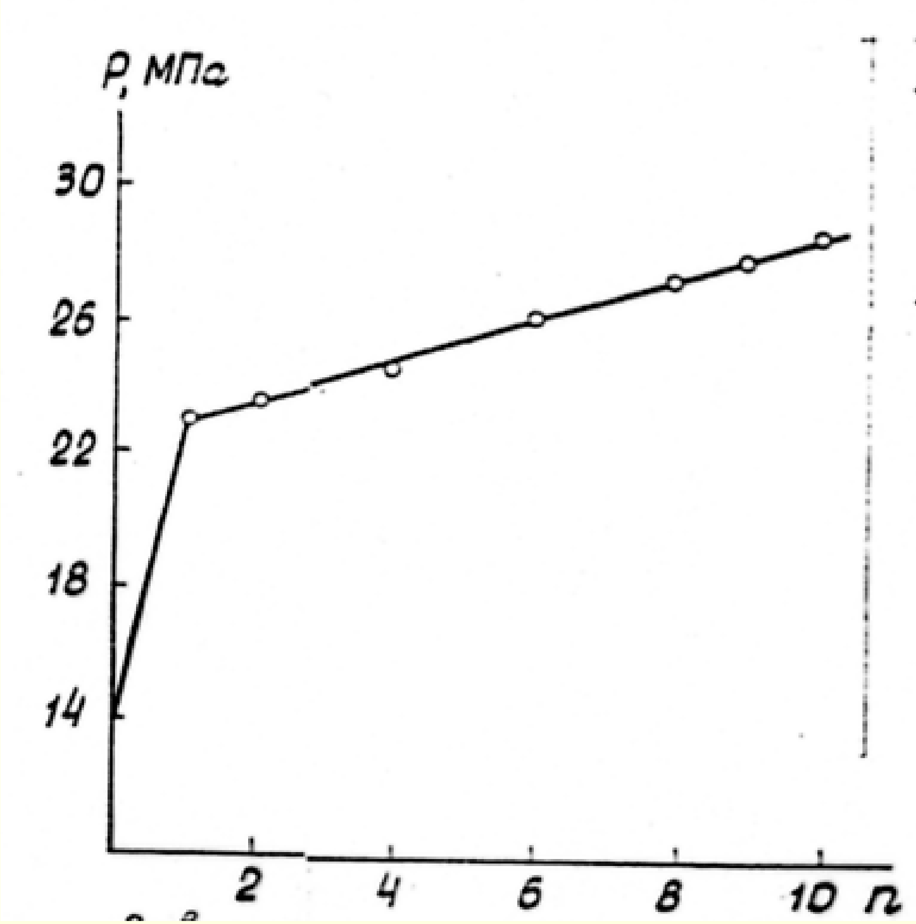
K 10⁵, sec



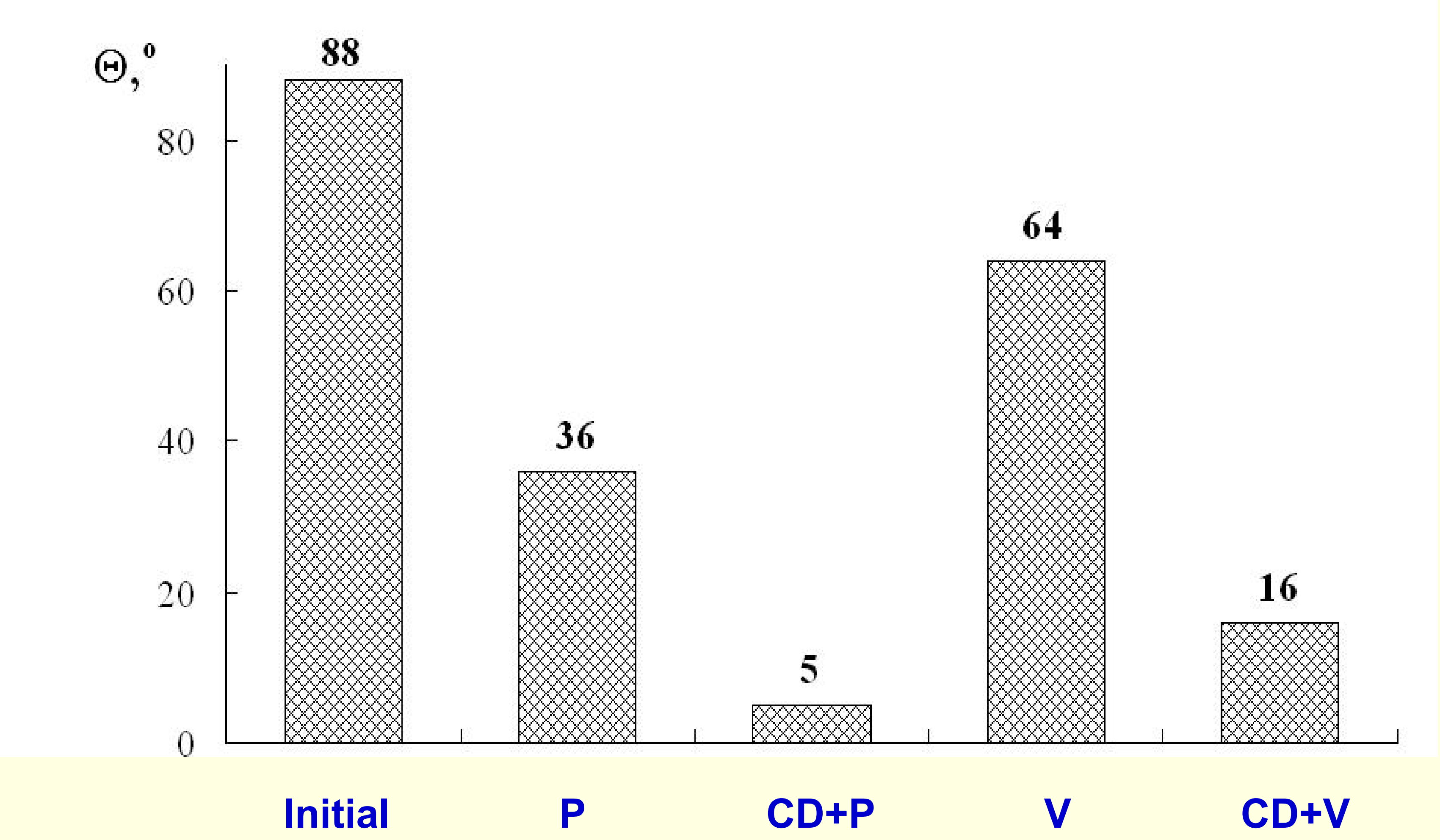
Changing hydrostatic strength (P, MPa) glass spheres depending on the chemical nature of the modifier

P, MPa





Limiting wetting angles of PVC films that treated by corona discharge (CD) and (or) by vapours of PCl_3 (P) and $VOCl_3$ (V)



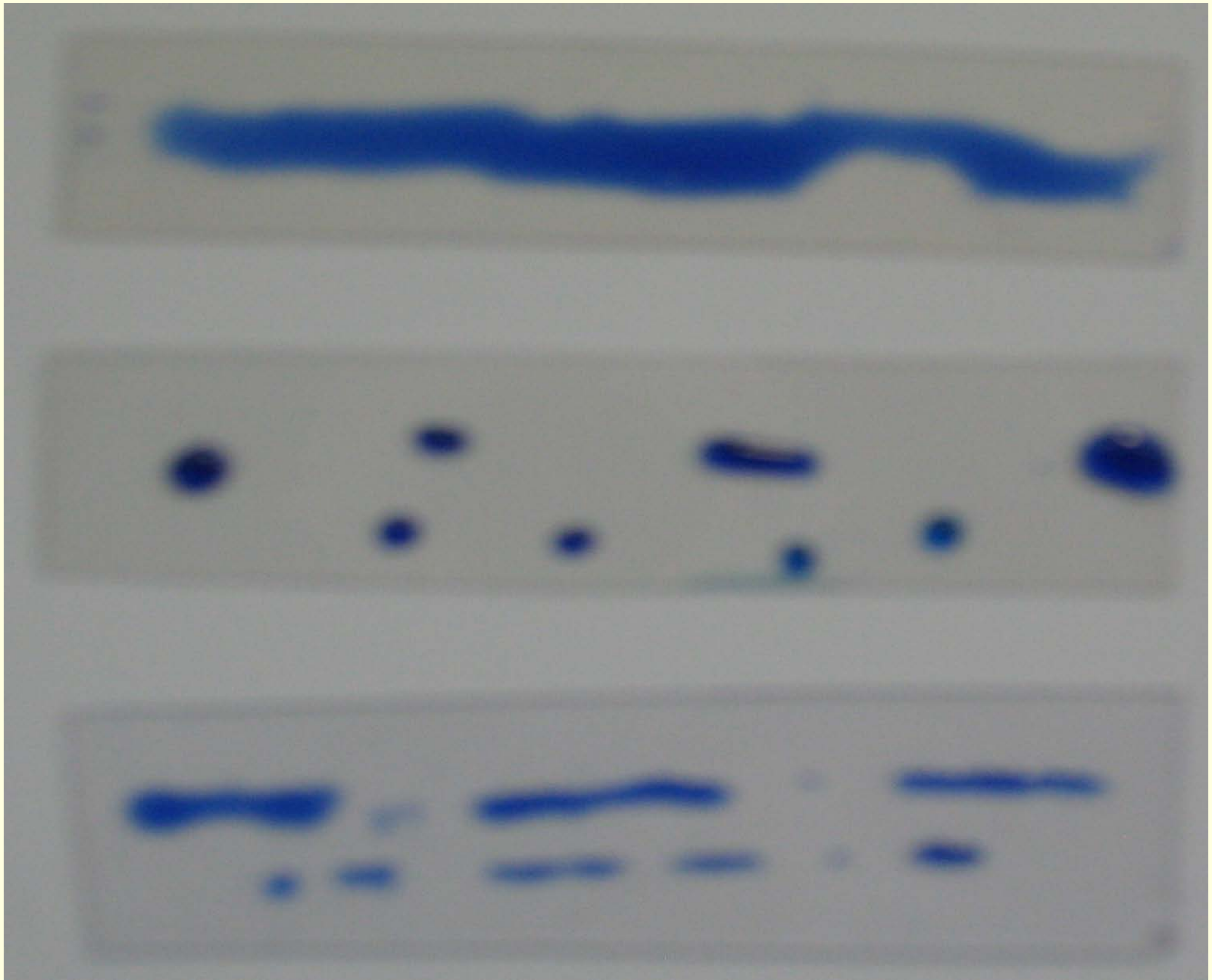
The results of the tests with the use of test liquids

(in the scientific-research center of Klokner Pentaplast)

Mod. by $POCl_3$

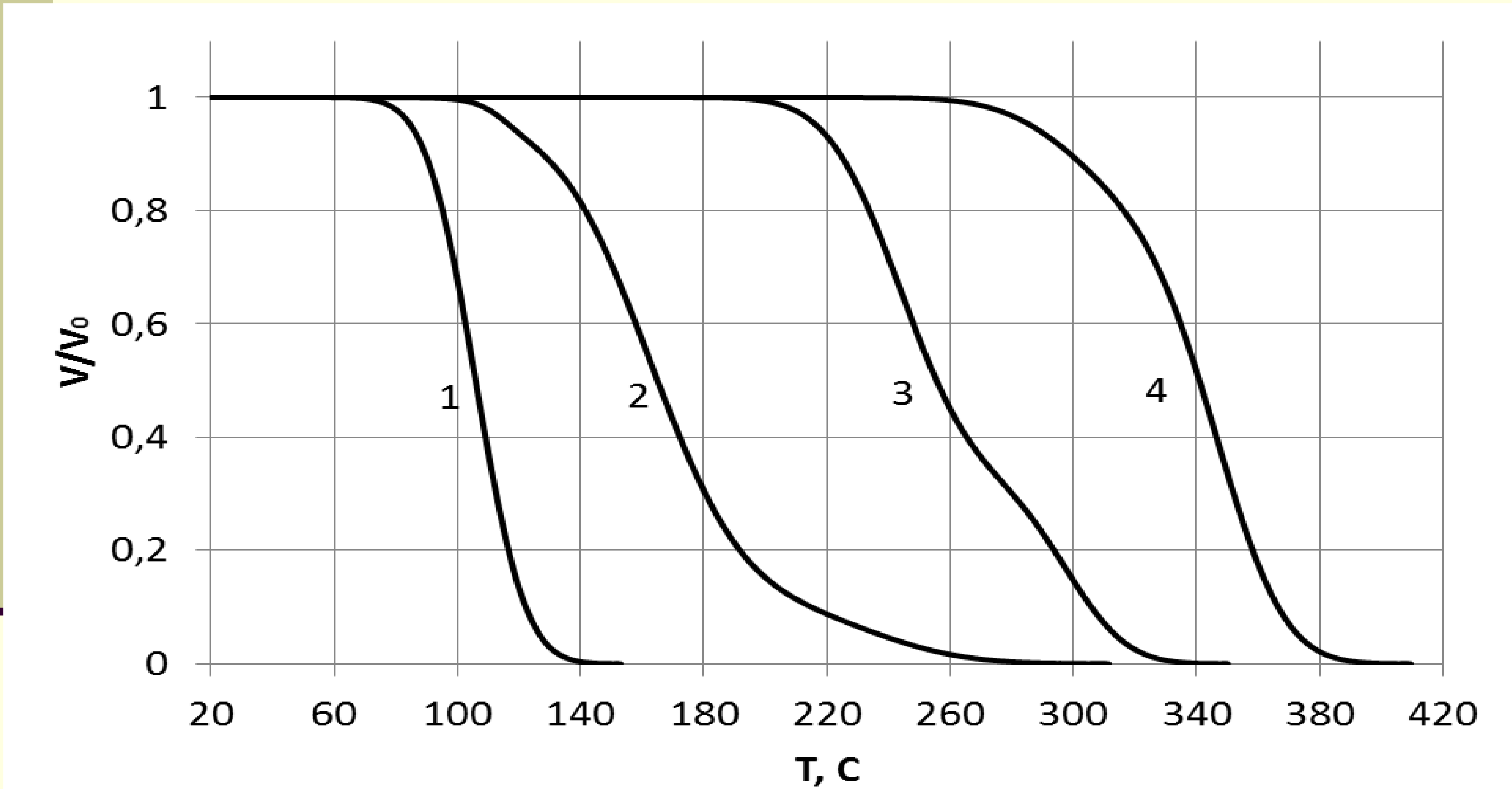
Mod. by $Si(CH_3)_2Cl_2$

Initial



The charge stability of thermally stimulated surface of PTFE nanocomposite

(to create electrets)

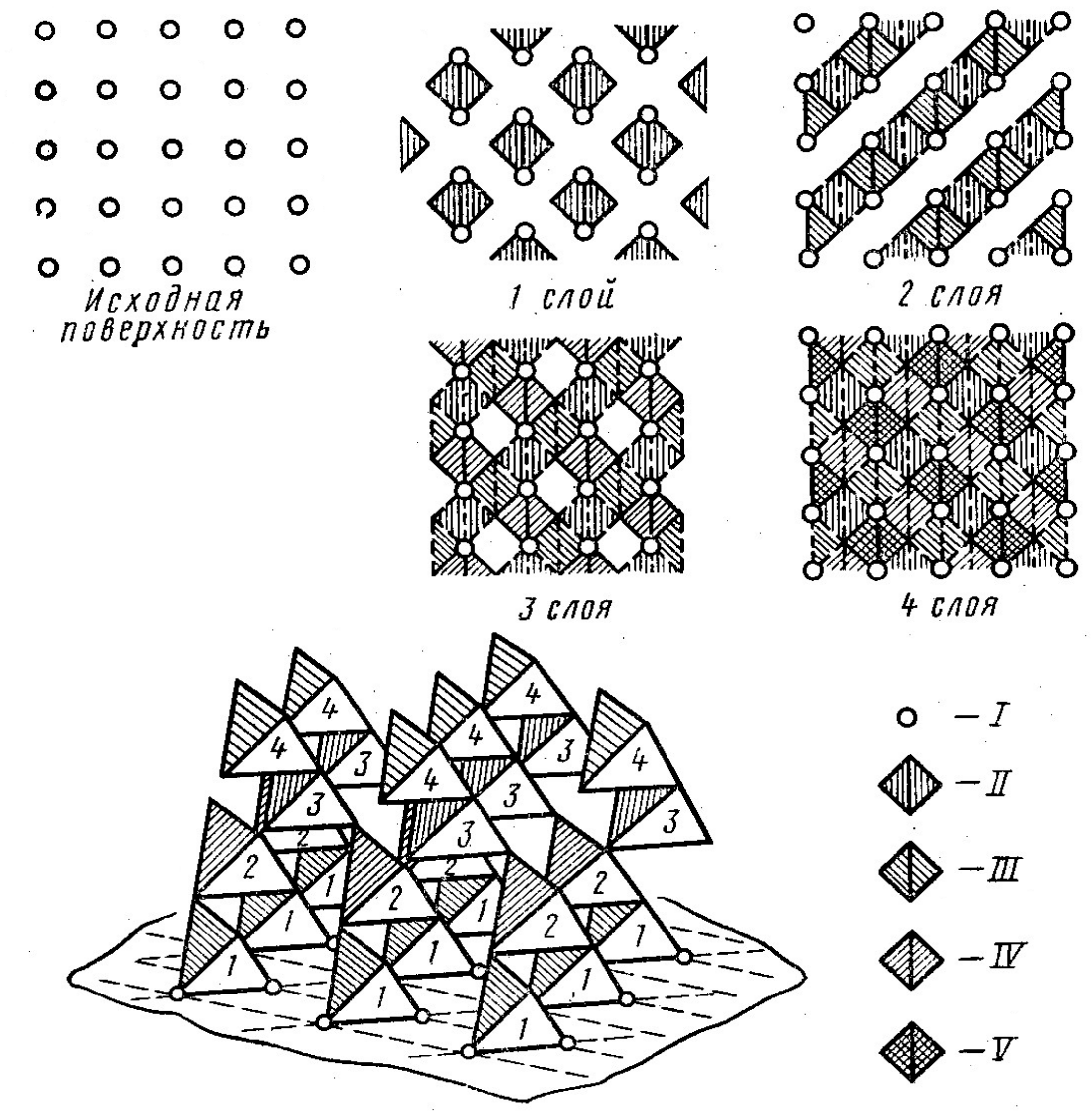


PTFE:1 – original, 2 - plasma treated, 3 – modified by $TiCl_4$ and H_2O, 4 – plasma treated and modified by $TiCl_4$ and H_2O

The effect of overlap the surface of substrate

The effect of overlap of the substrate by four monolayers tetrahedra

(S.I.Koltsov, doctoral dissertation, 1971)



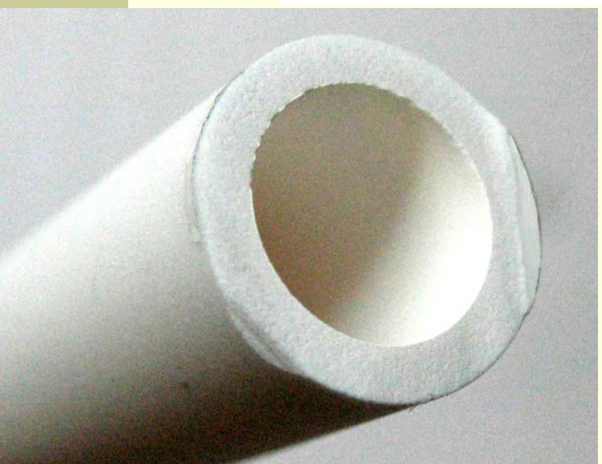
I – functional groups;
II – tetrahedrons of the 1-st monolayer;
III – 2-d monolayer;
IV – 3-d monolayer;
V – 4-th monolayer;

Ceramic tubular membrane

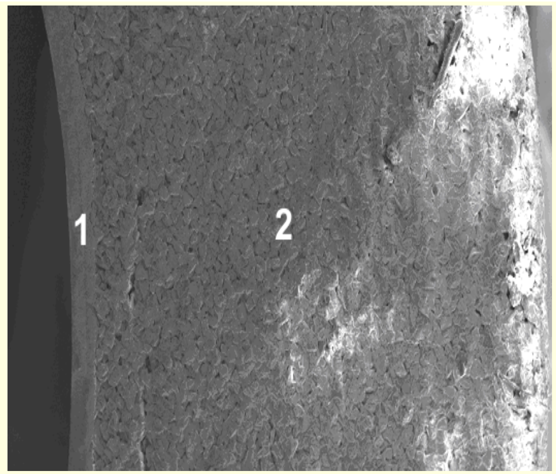
(PaL-Schumacher, Germany)

a - appearance; b, c, d - the cross-section

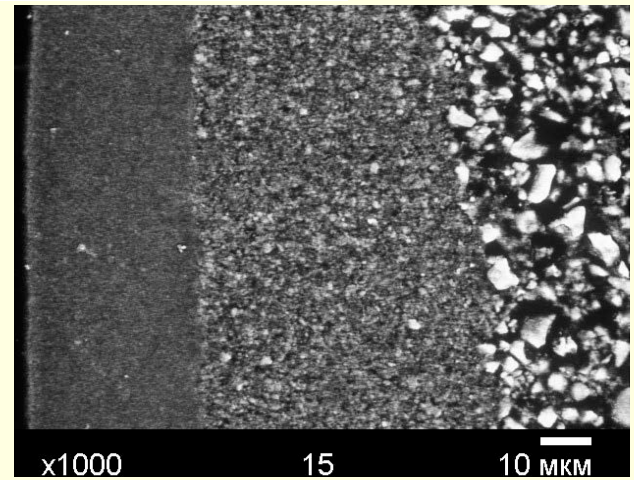
a



b



c

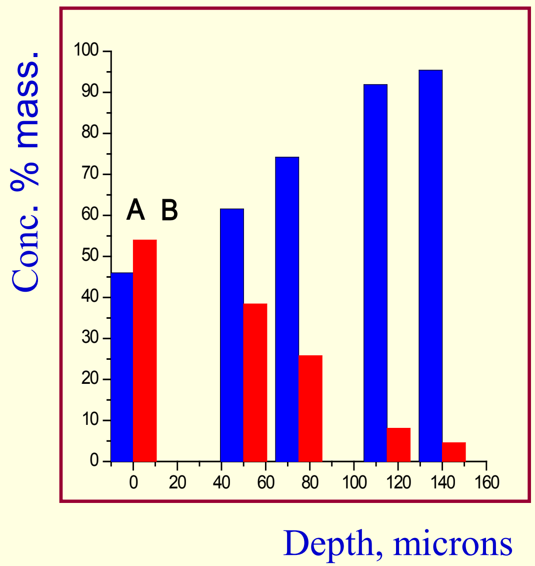


d

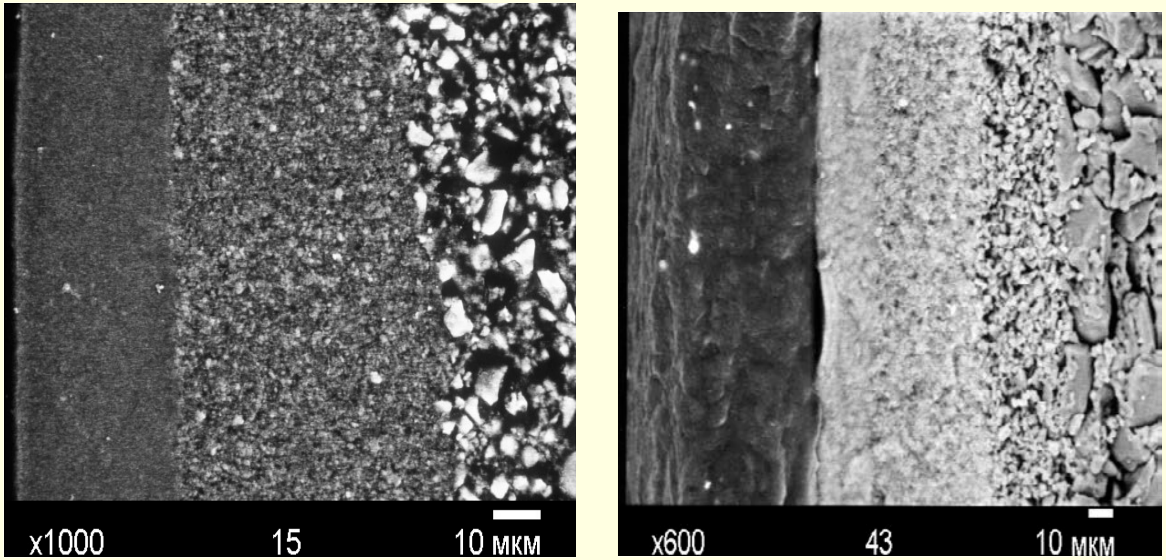
c - (1 - a layer inside the tube consisting of selective and intermediate layers; 2 - base of membrane);

d - the structure of the layer 1 (on the left - the inner side of the wall).

Modification of the composition and morphology of the Al_2O_3 membrane by deposition of titanium oxide nanolayer



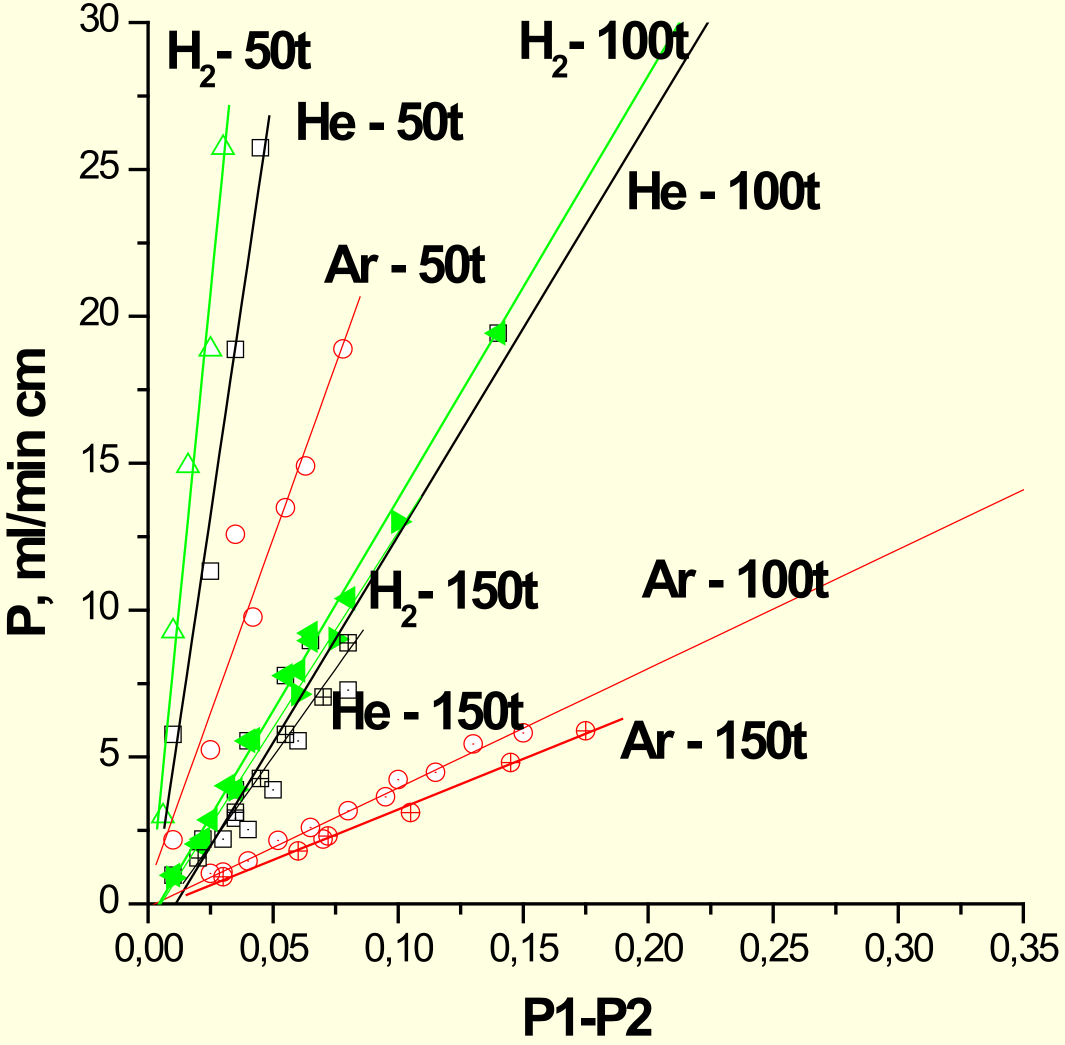
Aluminum content (A) and titanium (B) in the cross section of an membrane with nanolayer of titanium oxide (after 450 cycles of ML)



(a) (б)

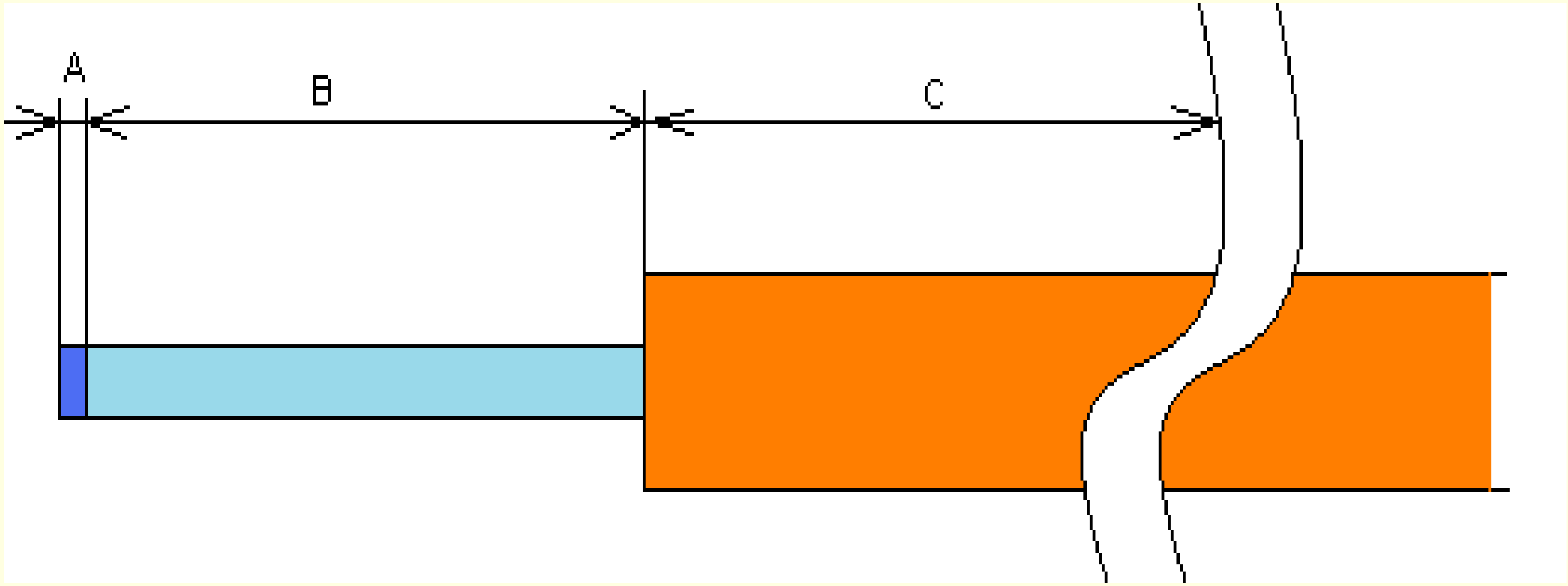
Electron micrographs of the cross-section asymmetrical alumina membranes before (a) and after (b) modifying nanolayer of titanium oxide (after 450 cycles of ML)

The dependence of the rate of permeability of gases from the pressure differential on the membrane after different number of cycles ML of titanium oxide nanolayer



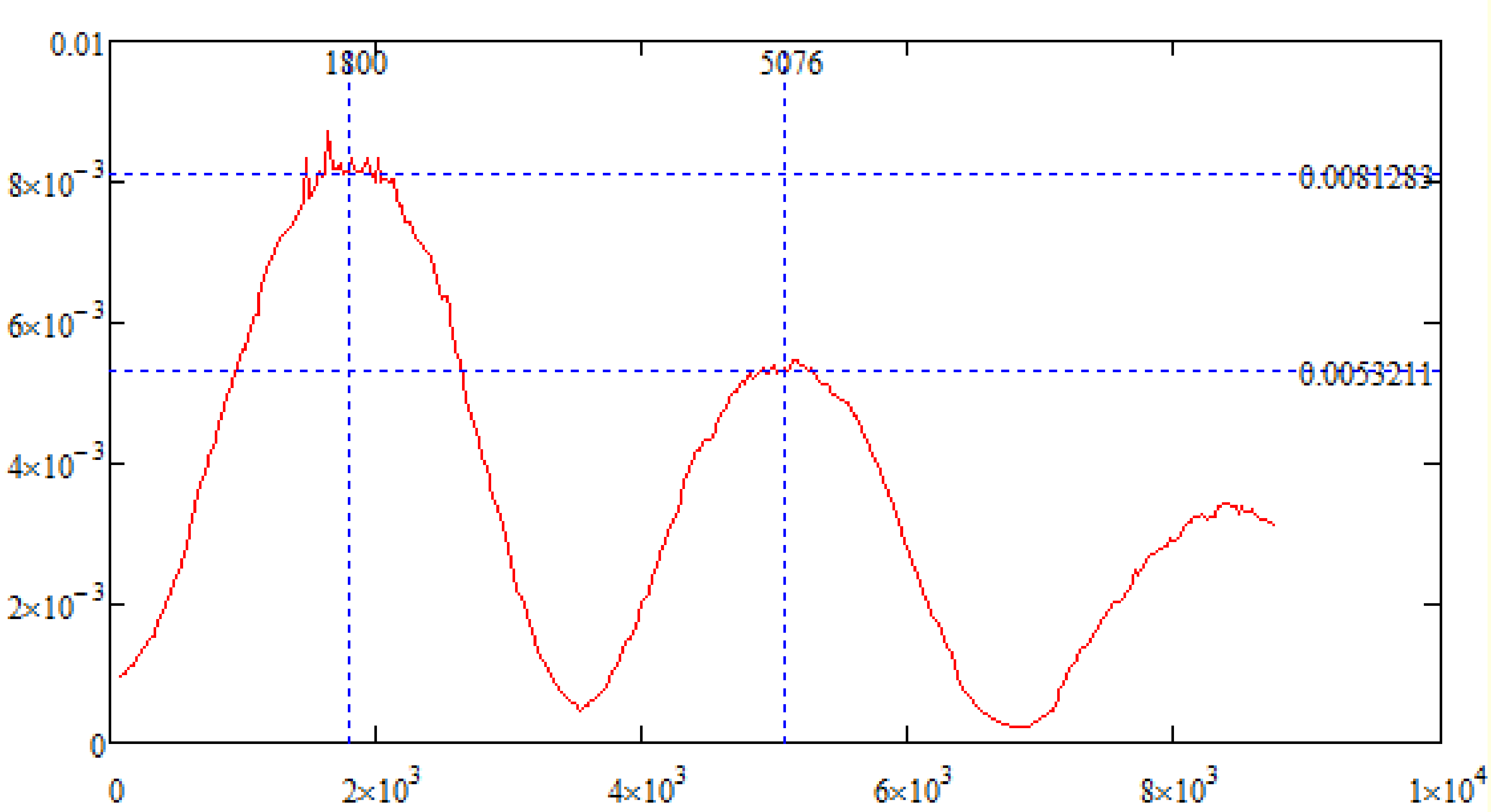
The effect of the substrate overlap in the creation of fiber-optic sensors (FOS) with more better properties

Diagram of the FOS element
A – functional nano-coating; B – quartz optical fiber; C - optical fiber with a polymer coating)



The magnitude of the reflected light power depending on the number of cycles ML

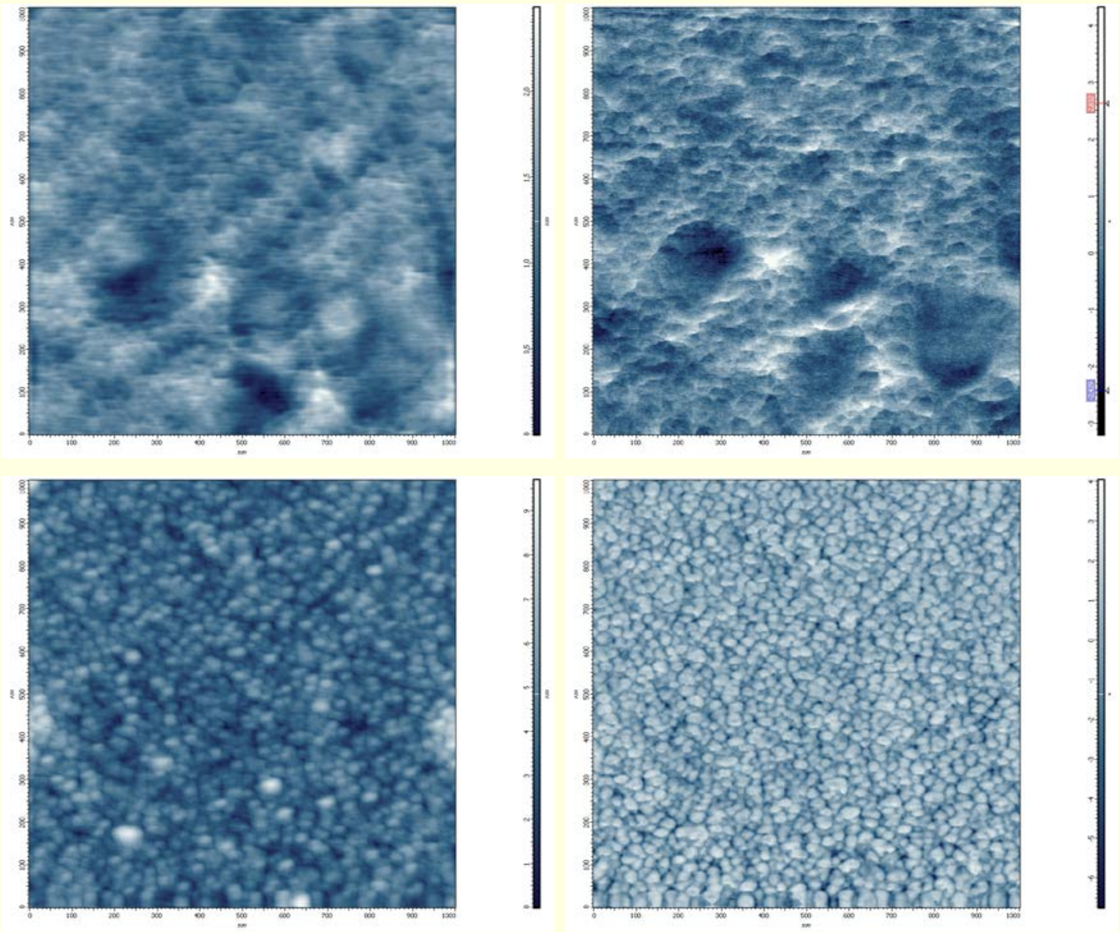
(Laser with a wavelength of 1310 nm)



AFM image of a side surface of the sapphire fiber: the initial (I) and the modified (II) by Zr- oxide layer (400 ML cycles) (scanned area size 1 × 1 microns)

I

II



topography mode

phase contrast mode

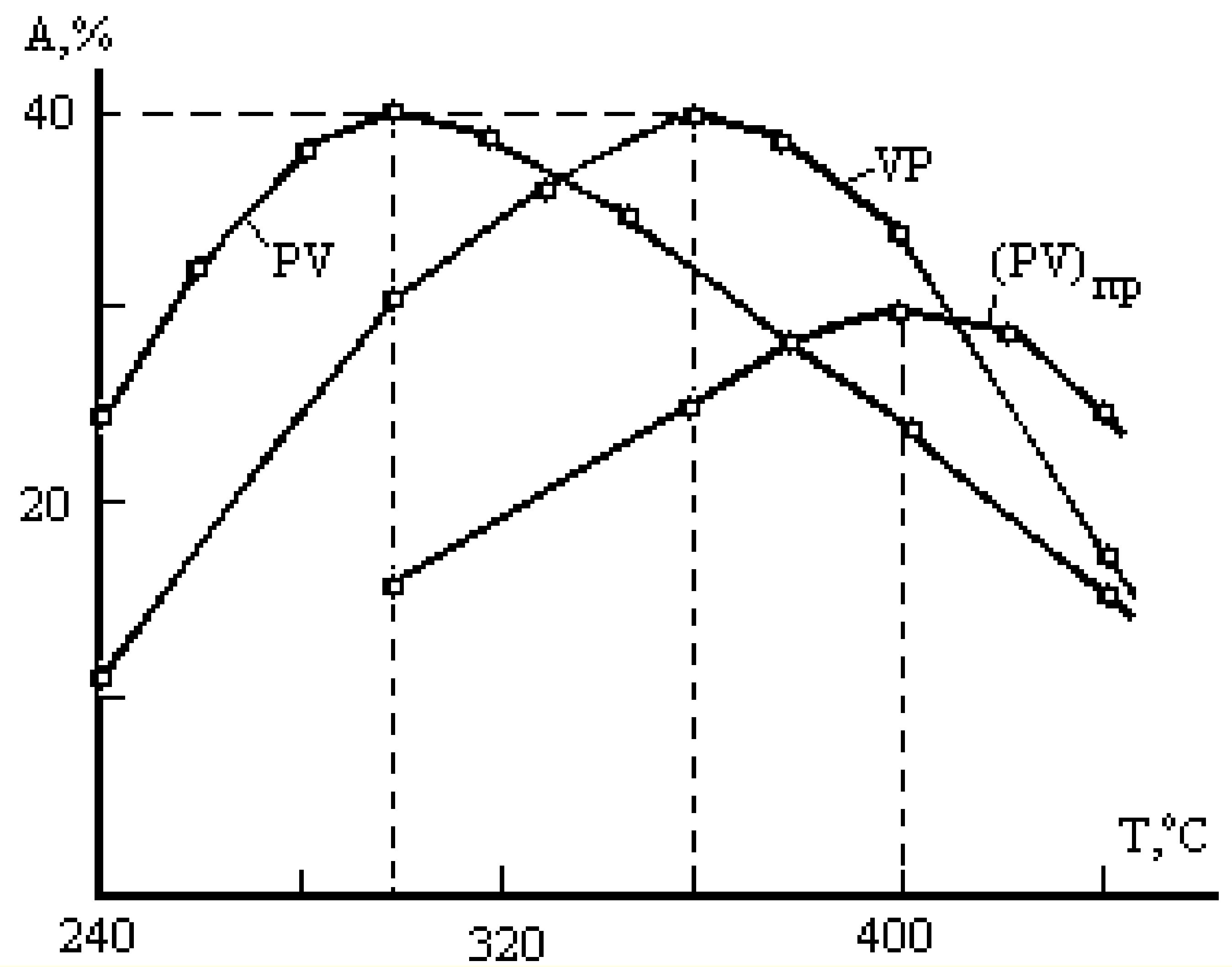
I: sintered particles of diameter ~ 25 nm; recess diameter 150 - 300 nm and a depth of 2 nm.

II: continuous coating of the individual particles with lateral dimensions of 20 - 40 nm, covered with surface defects of the original fiber

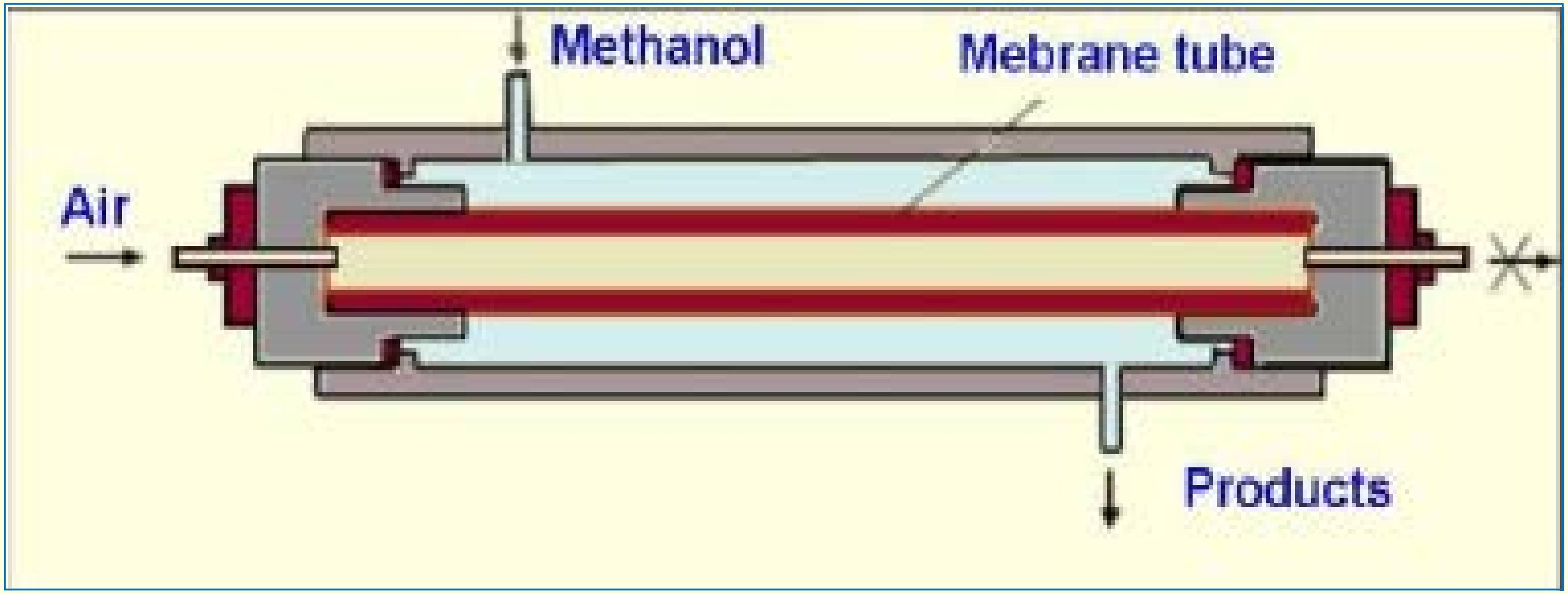
Effects related to multi-component systems

Influence of different relative position of the phosphorus- and vanadium-oxide monolayers on the activity of catalysts for oxidation of a piperilene

Yield of maleic anhydride (A%); (PV), (VP) - obtained by ML; (PV)np - obtained by impregnation



Membrane reactor for deposition of coating in situ by ML and for oxidative dehydrogenation of methanol



Chemical assembly of (V-O-P) catalyst on the surface of membrane catalytic reactor with (-O-Ti-OH) layer

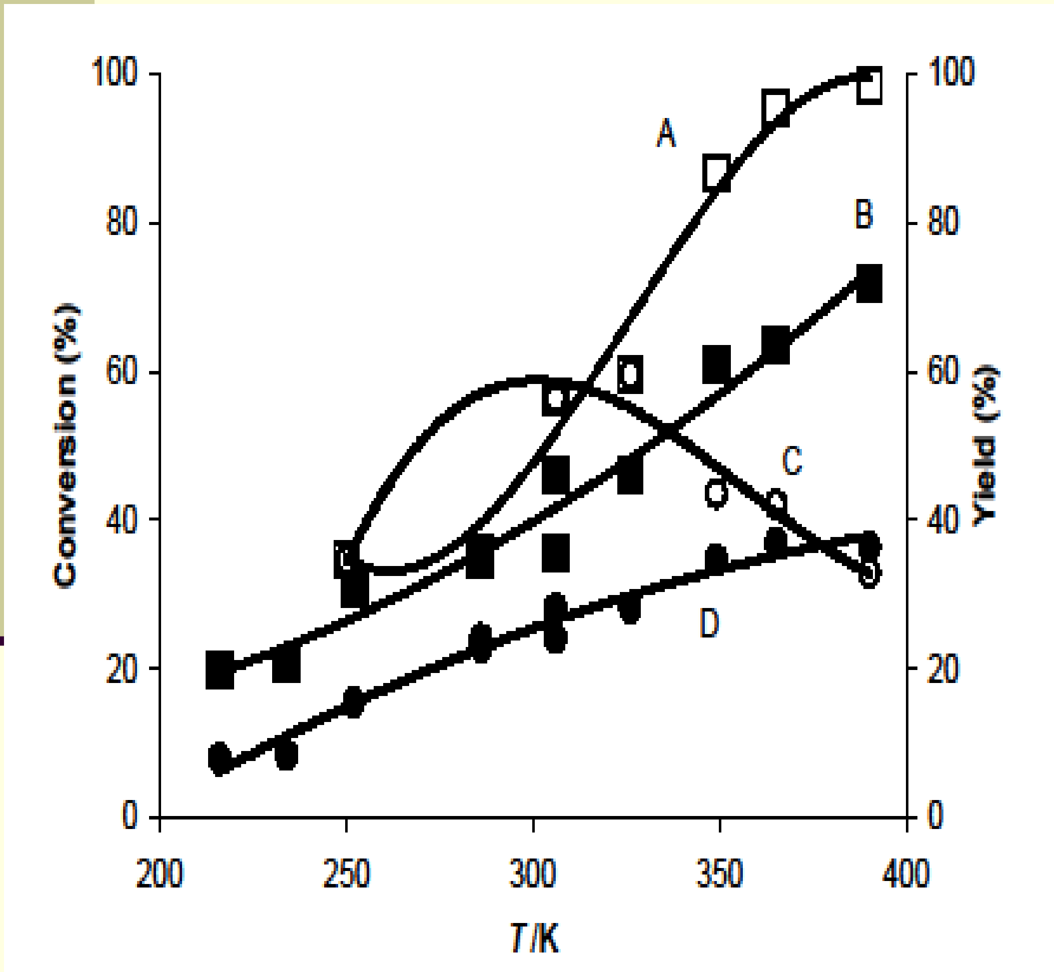
$$3(\equiv Ti\text{-}OH) + VOCl_3 \rightarrow (\equiv Ti\text{-}O\text{-})_3VO + 3HCl$$

$$(\equiv Ti\text{-}O\text{-})_3VO + PCl_3 \rightarrow (\equiv Ti\text{-}O\text{-})_3V \leftarrow OPCl_3$$

$$(\equiv Ti\text{-}O\text{-})_3V \leftarrow OPCl_3 + 3H_2O \rightarrow (\equiv Ti\text{-}O\text{-})_3V \leftarrow P(OH)_3 + 3HCl$$

and then once more treatment by vapors of $VOCl_3$, PCl_3, H_2O and etc.

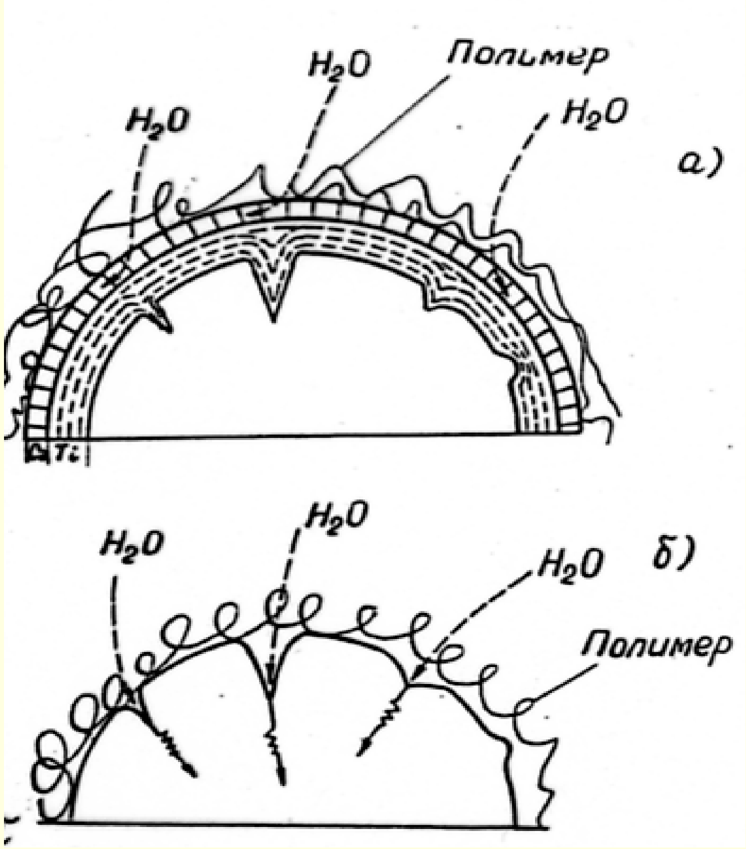
The temperature dependences of the conversion of methanol on the composite membrane catalytic reactor with vanadium-phosphorous catalysts



Conversion of methanol (A,B; solid lines, square marks) and the yield of formaldehyde (C,D; dotted line, circle mark) at the diffusion though the membrane of methanol (A,C; hollow marks) or air (B,D; filled marks).

Optimization using the method ML of composition and structure of the three-components of multi-functional nano-coatings on the surface of the glass spheres

The relative position of the layers of elements - modifiers	Parameter		
	Cr(6+), adhesion	Ti(4+), hydrostatic strength	P(5+), thermal and oxidation resistance
CrTiP	**0**	**0+**	+
TiCrP	**0**	+	+
PCrTi	**0**	**0**	**0+**
PTiCr	+	**0**	**0+**
CrPTi	**0**	**0+**	+
TiPCr	+	+	+

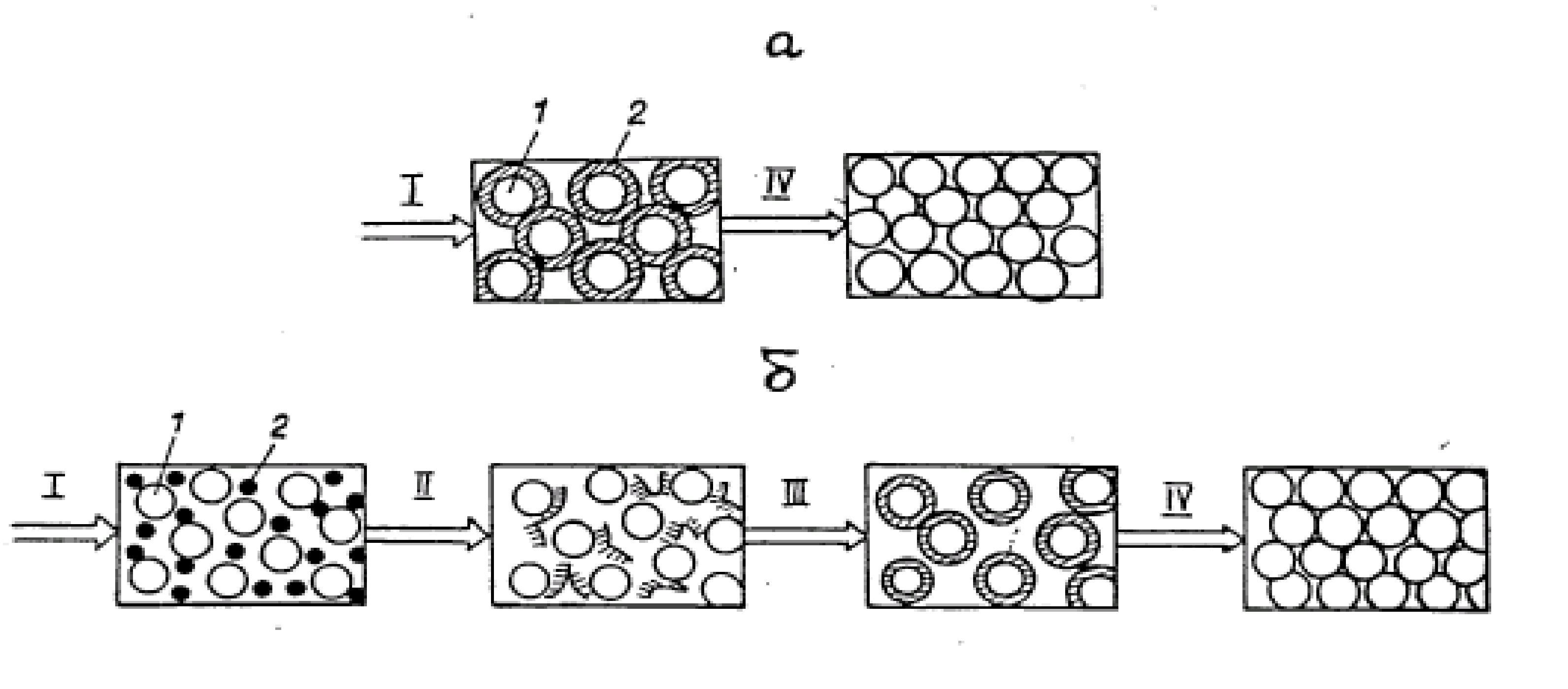


Combustibility of PEN-I (foam based on the phenol-formaldehyde polymers) with P(V)-containing structures on the surface

Sample	Setting fire time, s	Time of indepe-ndent combustion, s	Mass loss, %
V	10	120	63,0
P	10	55	8,6
VP	8	13	4,0
PV	5	30	6,0
VPV	5	24	5,2
PVP	5	8	4,9
VPVP	150	0	3,3
PVPV	8	12	4,1

Effects related to the mutual coordination between of structural of a substrate surface and thin film formed in ML process

Sintering of doped ceramics powder

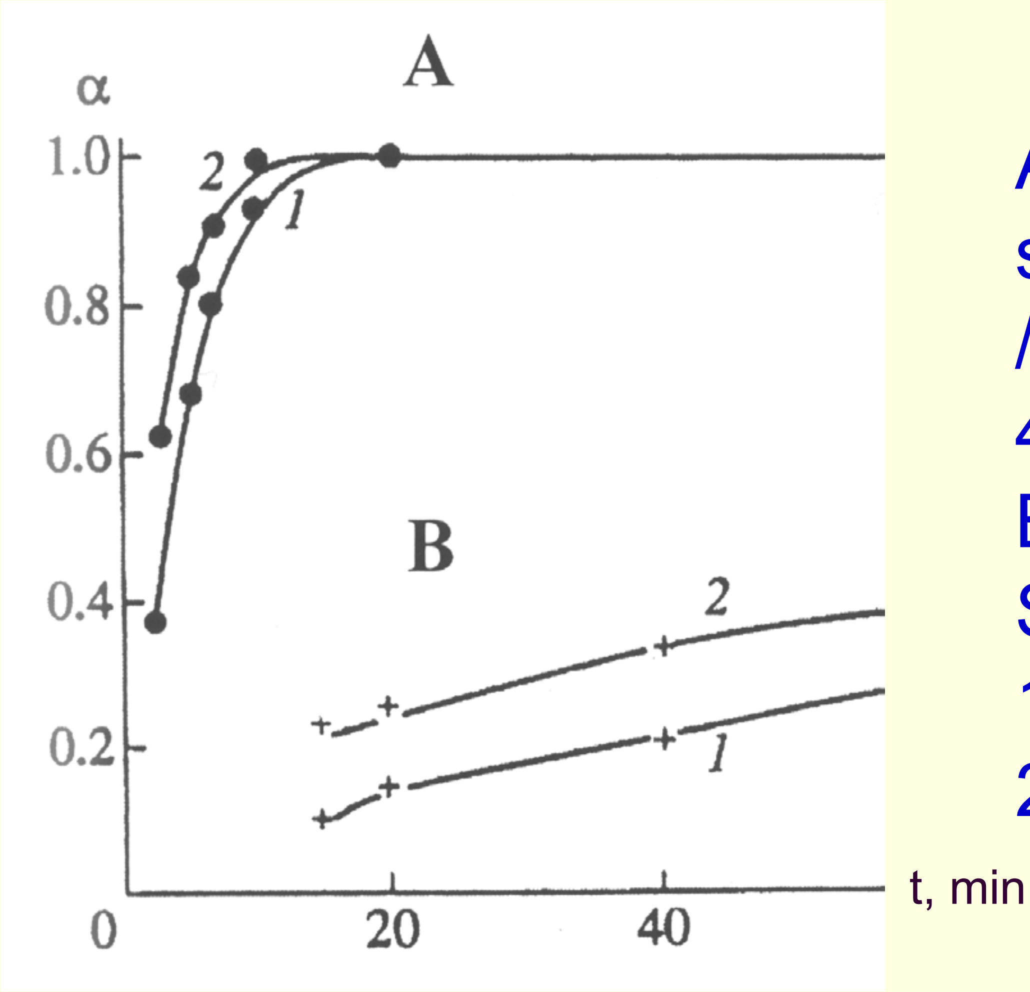


Doping of ceramics powder:

a – synthesis of nanolayers by the Molecular Layering Method:

b – mixing of components; 1 - particle 2 - additive

Transformation (α) of SiO_2 and Al_2O_3 nanolayers into mullite

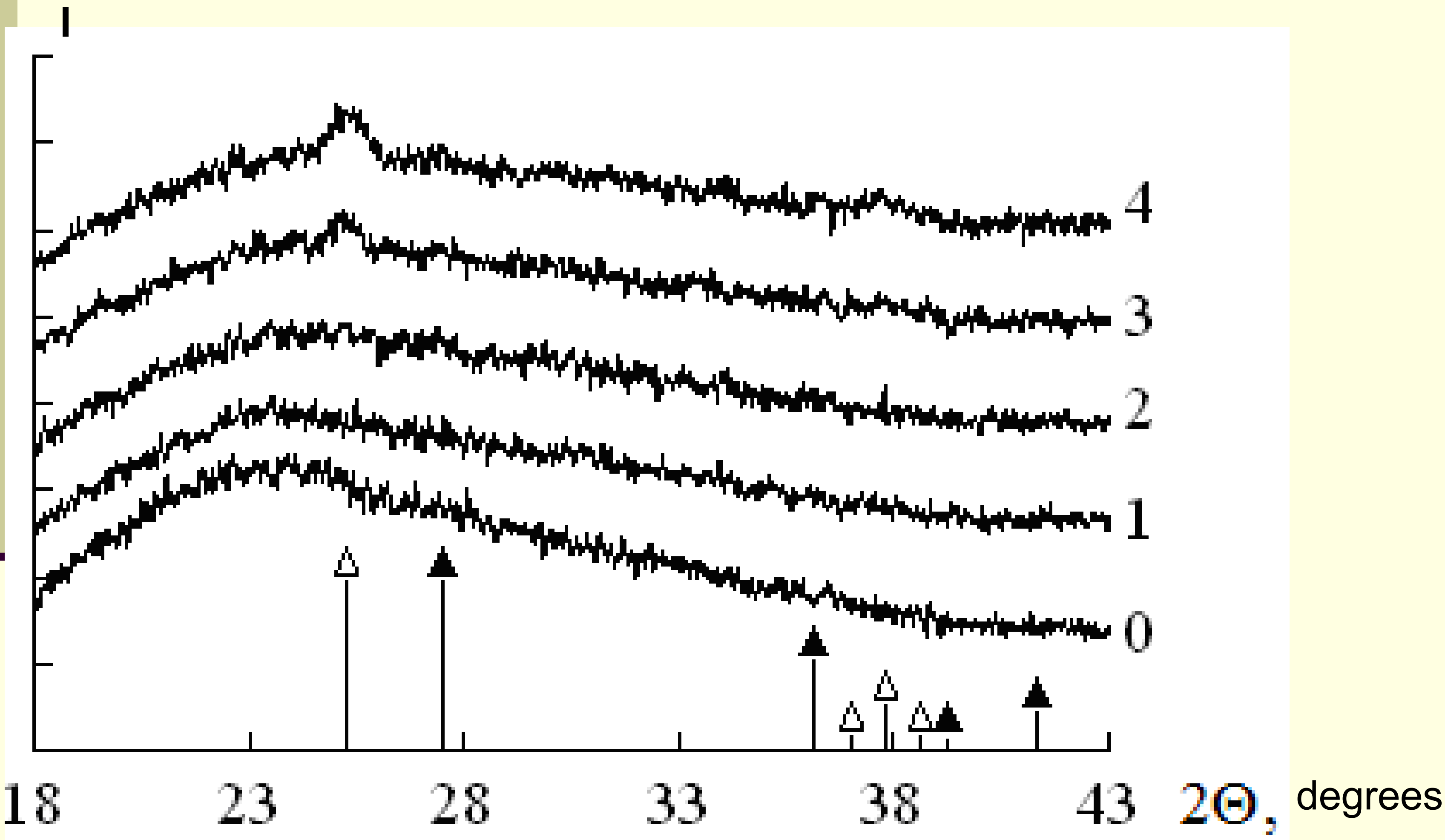


A- in nanosized structure of Al_2O_3 /nanolayer (about of 4 Nm) of SiO_2;
B – in mixture of SiO_2 and Al_2O_3 ;
1 – 1573°K;
2 – 1623°K

Data of X-ray analysis of the titanium oxide layer deposited on the aluminum oxide surface by ML (6 cycles of ML)

Sample	Titanium oxide phase and their content (%)	The parameters of the unit cell (A)
α-$AlO_{1.5}$	rutile like; 100	d/n=3.167 hkl=100
γ- $AlO_{1.5}$	rutile like; 74 ± 4	a=4.597±0.003 b=4.671±0.006 c=2.969±0.002 V=63.6±0.2
	such anatase; 26 ± 4	a=3.797±0.003 b=3.825±0.005 c=9.452±0.008 V=137±0.5

Radiographs modified at 473 K silica SHSKG.
(radiographs number corresponds to the number of synthesis cycles)
The reflexes of anatase (Δ) of rutile (▲)

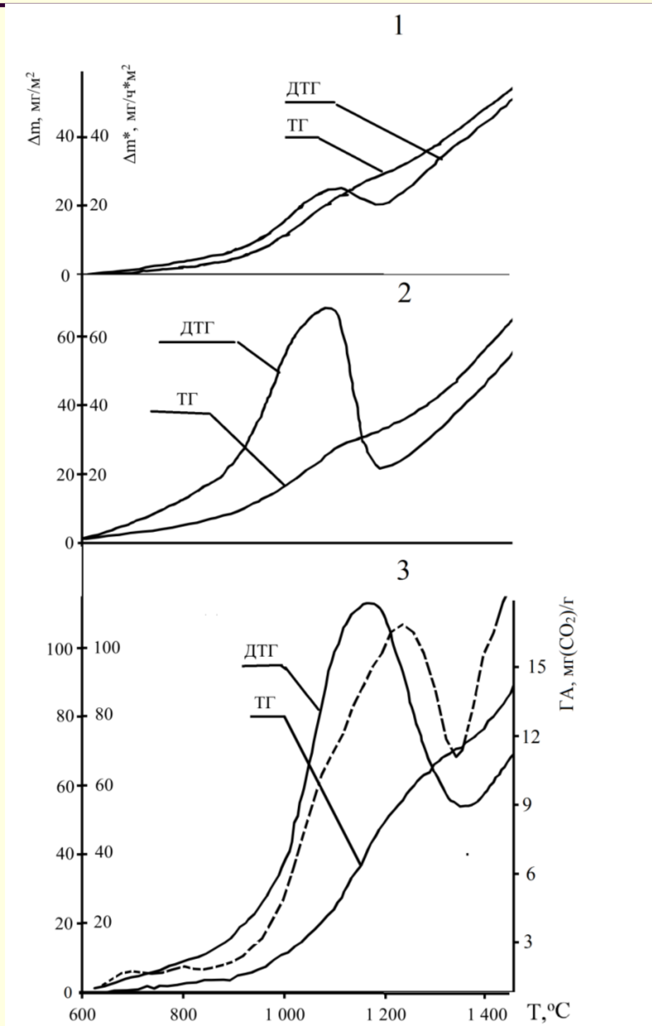


Thermooxidation initial and modified SiC

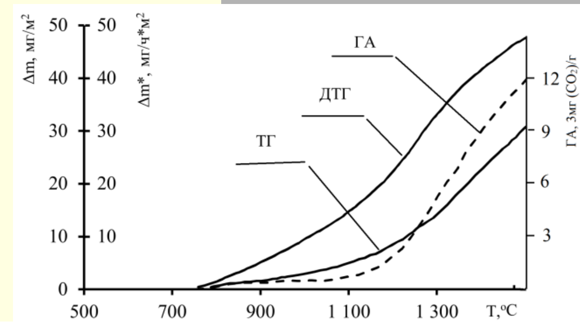
SiC-1V

SiC-4V

SiC-10V



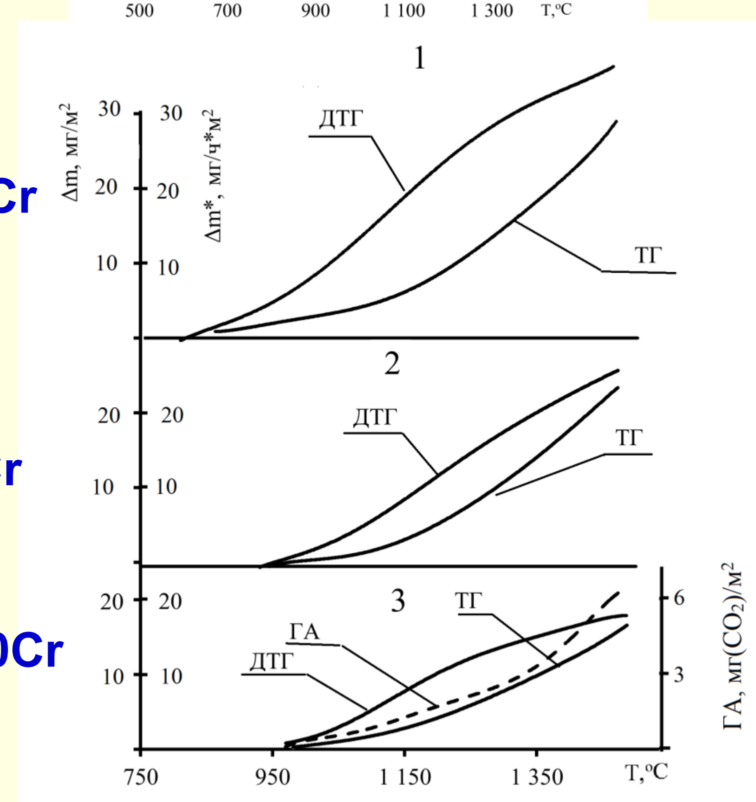
SiC



SiC-1Cr

SiC-4Cr

SiC-10Cr



Conclusion

1. The results presented in the report, of course - this is only a small part of what has been done to date in the application of structural - size effects in the products of atomic layer deposition.
2. The proposed approach may be of interest in the design at the atomic and molecular level, solid-state materials with desired properties. It is often to optimize the properties of the materials necessary to consider not one, but several structural and dimensional effects. For example, when creating sorbents and catalysts, catalytic membrane reactors, fiber optic sensors, polymer composite materials and fillers for their etc.
3. The report focuses on the practical application of structural and dimensional effects. However, in this area ML-ALD have a lot of questions that need basic research. Especially it concerns a deeper study of the effects of a multicomponent system and the mutual coordination structure of the substrate and nanocoating that formed in the ML process . Very perspectively for this purpose to involve quantum chemical, thermodynamic, mathematical models.

Group of participants of the department of chemical nanotechnology and materials for electronics

Research participants.

The main scientists:

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S.D. Dubrovenskii, E.A. Sosnov,
V.F. Dergachev, N.V. Zakharova,
V.V. Antipov

Young scientists:

S.V. Mikhaylovskii,
A.Yu. Shevkina, N.Yu. Efimov,
I.S. Bodalev, A.S. Kochetkova

Students:

Usually 2-3 graduate students, as well as 10-15 students, who will receive the title of Bachelor's or Master's

Thank you very much for attention!