



Formation principles of layers from active carbon microparticles with grafted amine derivatives of PVC on substrate

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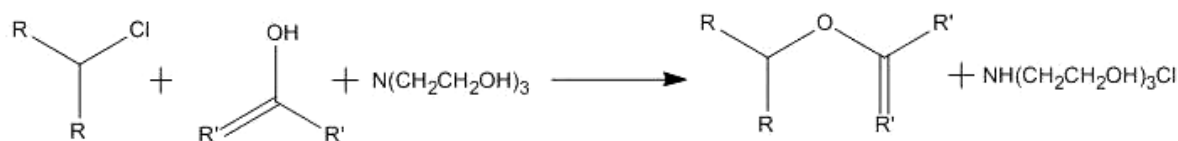
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Abstract: Porous layers from activated carbon with macro-molecular cyclic amines based on PVC and modified by primary amines were synthesized and its properties were described. Layers were grafted to the surface of a PVC film, cotton medical gauze and asbestos fabric. The nature of benzyl alcohol solvation and the mechanism of suspension formation within layers of macro-molecular cyclic amines were investigated by methods of IR-spectroscopy and luminescence spectroscopy and described. The structural features of grafted PVC was identified and the influence of the substrate nature on the structure was traced. Upon contact of particles with benzyl alcohol molecules from solvatocomplexes PVC-related aromatic groups replace benzyl alcohol in solvatocomplexes. This leads to non-covalent binding of groups on the surface of the particles. It was shown that sorption of organic molecules does not affect the number of structural types of oxoamines.

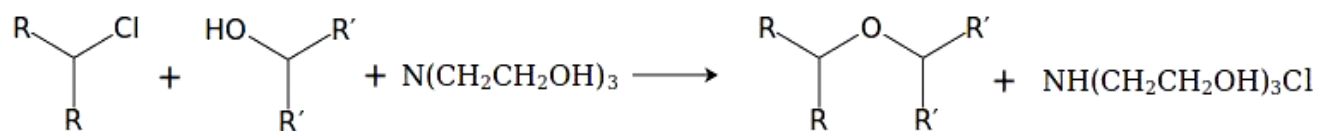
Key words: PVC, layer, active carbon, grafting, amine derivatives of PVC, luminescence, sorption.

Introduction: The layers of chemically modified active carbon with grafted PVC or its derivatives, synthesized at the substrate, are the basis of block sorbents and sorption-active electrochemical materials [1-3]. Of particular interest are the layers of active carbon microparticles with grafted ethanolamine and sodium or potassium glycinate derivatives of PVC. They are grafted to the surface of PVC materials, cellulose and asbestos fibers [4-8]. Layers are electron-conductive and luminescent active. They absorb acids, salts and hydroxides of alkali metals and complexes of nickel, copper and other metals, as well as organic molecules. The properties of the layers due to the method of their synthesis. Active carbon, in which there are hydroxy groups, is dispersed in a PVC solution of a mixture of tetrahydrofuran (THF), benzyl alcohol (BA) and triethanolamine (TEA) by grinding. A suspension consists of spherical particles ranging in size from 0.5 to 7 microns. It is applied to the substrate, THF is evaporated and in the gel-like layer using the reaction

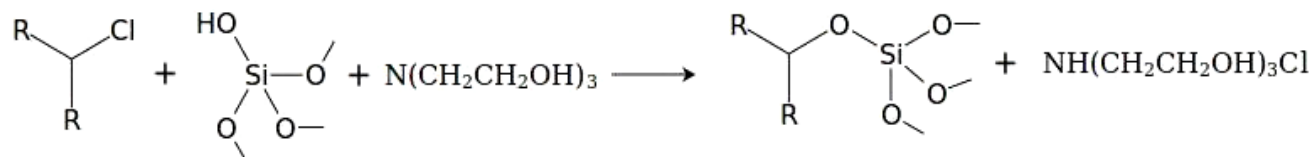


where R – elements of PVC, R' - elements of activated carbon, at 105 - 110 °C graft PVC to the surface of the particles. At the same time, the layer is grafted to the substrate. In the case of PVC, it is based on

the participation of surface macromolecules in the grafting to the particles adjacent to them. For grafting to the fibers, the following reactions are used:

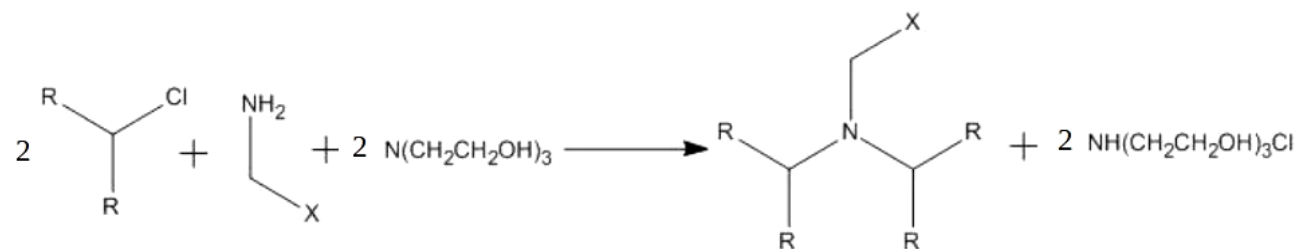


and



where R – elements of PVC, R' – elements of cellulose, OH – groups of cellulose or magnesium hydrosilicate.

Then, using the reaction -



where R – elements of PVC, X – substituent in amine, using ethanolamine, or concentrated solutions of sodium or potassium glycinate, at 105 - 110 ° C turn PVC into derivatives - macromolecular nets of jointed NR cyclic amines where X are -CH₂OH, -COONa, -COOK. They are grafted to particles via cyclic oxoamine bridges with carbon radicals. When PVC is transformed into derivatives, the structure, shape and size of particles are retained. They approach each other sufficiently for electronic exchange. The groupings are similar to organic phosphors with aromatic radicals.

It should be noted that in suspension the particles of active carbon are equally distributed, despite the fact that the density of the PVC solution is almost 2 times greater than that of active carbon. According to [9], PVC forms solvated complexes with BA. BA molecules, when in contact with a developed surface, promote the adsorption of macromolecules. It can be assumed that during grinding of the source of active carbon around the particles, shells are formed from sections of macromolecules. The particles will be bound by such macromolecules and, accordingly, equally distributed in suspension. Obviously, the shell structure will remain in the gel after evaporation of THF. After grafting areas of macromolecules from the surface of the particles form a shell around them, similar to the shells in the gel. After the transformation of the PVC layer on the film with oxoamines nets of cyclic amines joints, the ends of them are not chemically linked to the substrate. In the case of cellulose fabric, the ends of the individual nets will be connected through the >CH-O-CH< group, and in the case of asbestos - through -O₃Si-O-CH< group. It is possible that grafting the layer to the substrate may affect the structure of oxoamines, through which the sorption into particles of carbon occurs.

The purpose of this work: To investigate the nature of BA solvation and to justify the mechanism of suspension formation, to identify the structural features of grafted PVC and to trace the influence of the substrate nature on the structure of oxoamines

Experimental: Materials and reagents: crushed activated carbon (birch activated carbon, production of Russia, active surface area 750 sq m per g, iodine adsorption activity 60 %, porosity by water 1,6 cm³/g), PVC film (grade PR-M180/09-09/9406, production of China, FUSHIYUAN PLASTIC CO., LIMITED), PVC resin (SG -7, production of China), cotton medical gauze GOST 9412-93 (Russia), asbestos cloth grades AT-16 (Russia), THF, BA, TEA and ethanolamine, sodium glycinate, potassium glycinate, toluene, 1,4-dioxane, dimethyl sulfoxide, qualification "pur".

Devices: holder collapsible cuvette of two metal plates 3 mm thick and rectangular windows 16x30 mm.

For the investigation were prepared: a solution of PVC in BA, suspension according to the technique [4], samples of layers of grafted PVC on a PVC film according to the technique [4], samples of layers of particles grafted with ethanolamine and sodium or potassium glycinate derivatives of PVC on PVC films according to the technique [4, 5] and, samples of layers of particles with grafted ethanolamine PVC derivatives on cellulose fibers (gauze) and asbestos material according to the technique [3], as well as samples of the same layers with sorbed organic solvents

Research methods: IR - Fourier spectroscopy, luminescent spectroscopy.

IR Fourier spectra were recorded on Perkin-Elmer 2000 IR Fourier spectrometer (Detector type MCT, operating range 5 – 40 °C wave length range 7,800 – 600 cm⁻¹).

The luminescence spectra were recorded on a spectrofluorimeter «Fluorolog» (Optics: All reflective optics for high sensitivity at all wavelengths, and for microsamples; Source: 450 W CW Ozone-free Xenon arc lamp (250 to 2500 nm); Monochromators: Czerny-Turner design with plane gratings for optimized focus at all wavelengths and minimum stray light; Excitation grating: 1200 groove/mm blazed at 330 nm; Emission grating: 1200 groove/mm blazed at 500 nm; Bandpass: 0 to 30 nm (single mono, 1200 gr/mm grating), continuously adjustable; 0 to 15 nm (double mono, 1200 gr/mm grating), continuously adjustable; Wavelength Accuracy: ± 0.5 nm; Integration Time: 1 ms to 160 s; Base detector: Photomultiplier R928P, spectral coverage 200 to 870 nm; Reference Detector: UV enhanced silicon photodiode; Water Raman S/N: >30000:1 RMS (> 15,000:1 FSD)).

The IR spectra of the PVC solution in BA and pure BA (Figure 1) and the spectra of the layer of particles grafted with PVC on PVC film and of the original PVC (Figure 2) were recorded, as well as the luminescence spectra of layers of particles grafted with ethanolamine derivatives of PVC on PVC film, on the fibers of cellulose fabric and asbestos material and the same layers sorbed with toluene, 1,4-dioxane, dimethyl sulfoxide (Figure 3a, b, c)

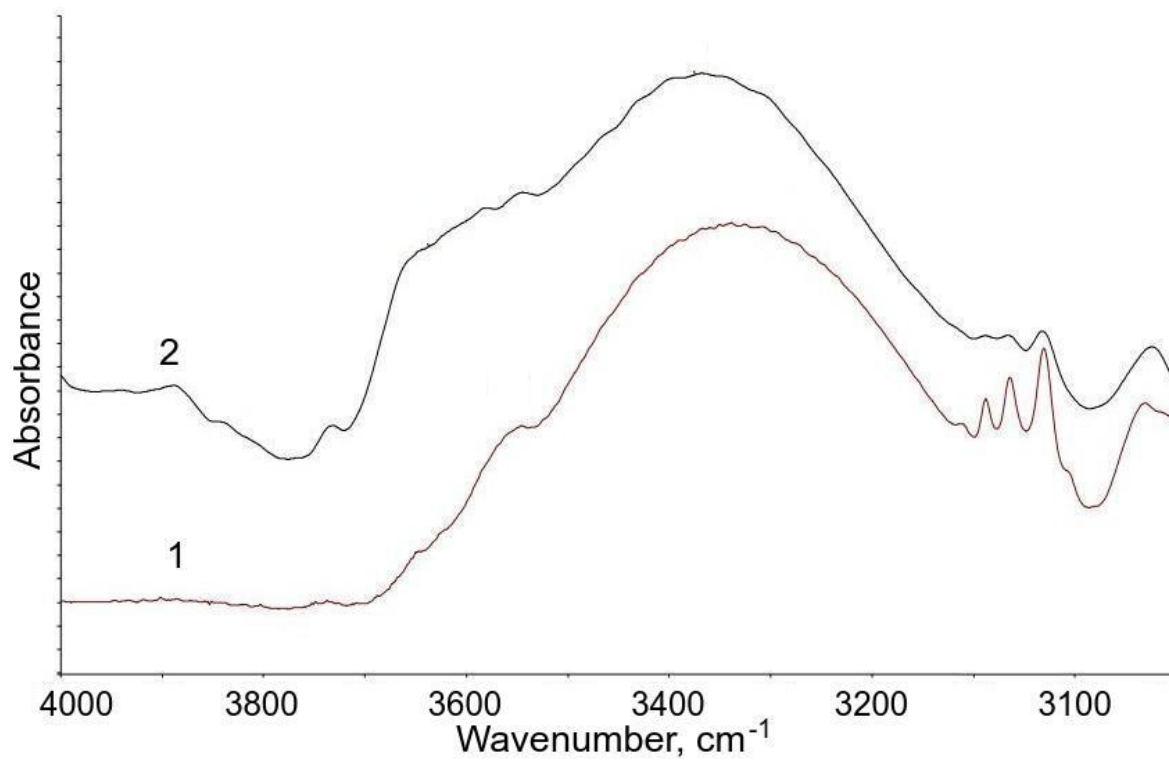


Figure (1): IR spectra of BA (1) and PVC solution in BA (2).

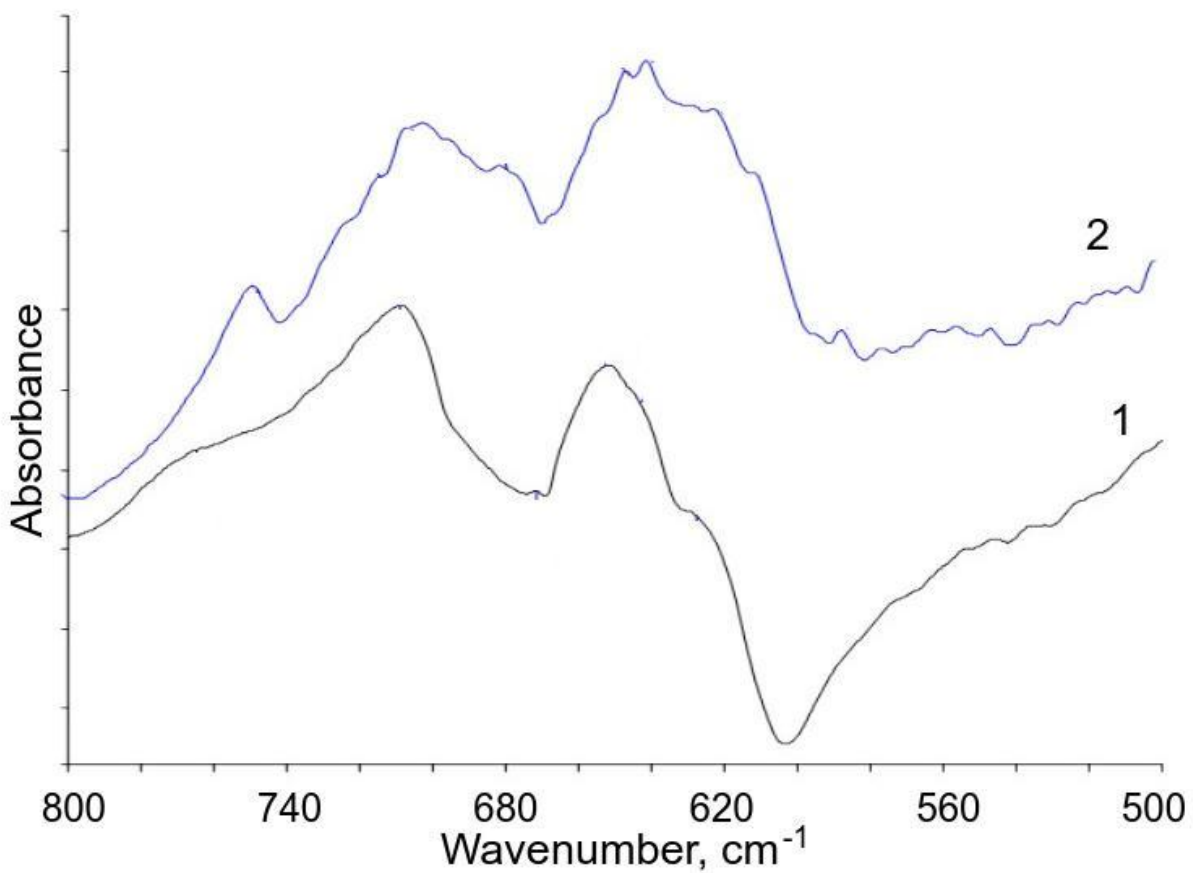


Figure (2): IR spectra of original PVC (1) and PVC grafted to particles (2).

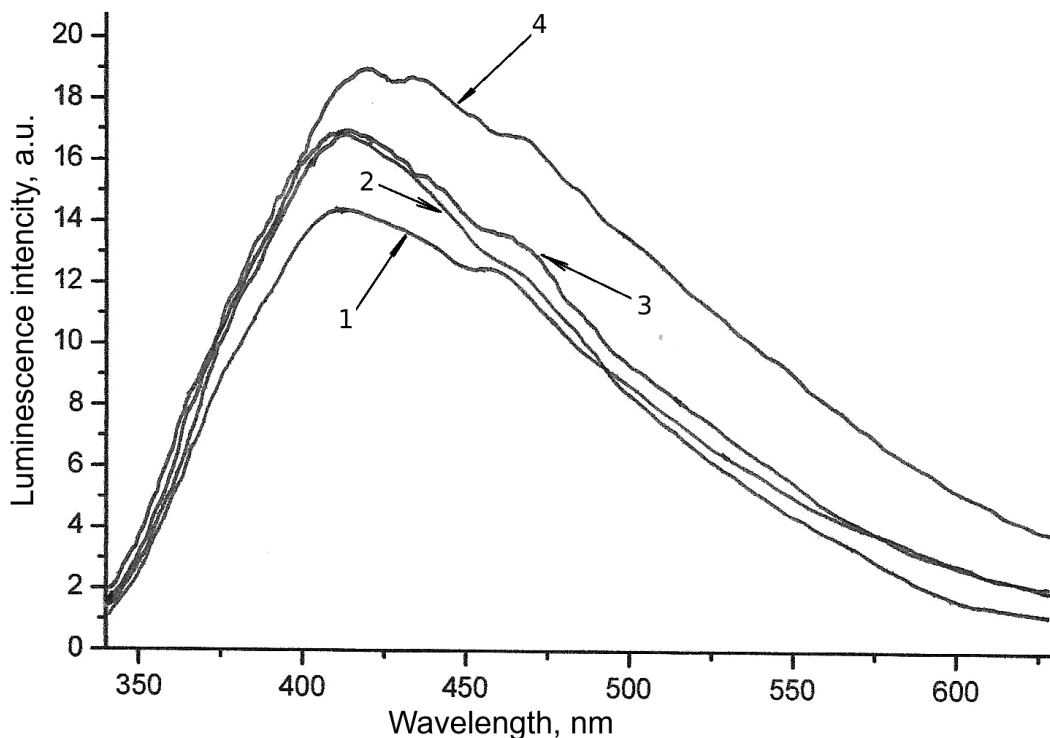


Figure (3a): Luminescence spectra of layers of particles grafted with ethanolamine derivatives of PVC on PVC film and the same layers sorbed with toluene, 1,4-dioxane, dimethyl sulfoxide.

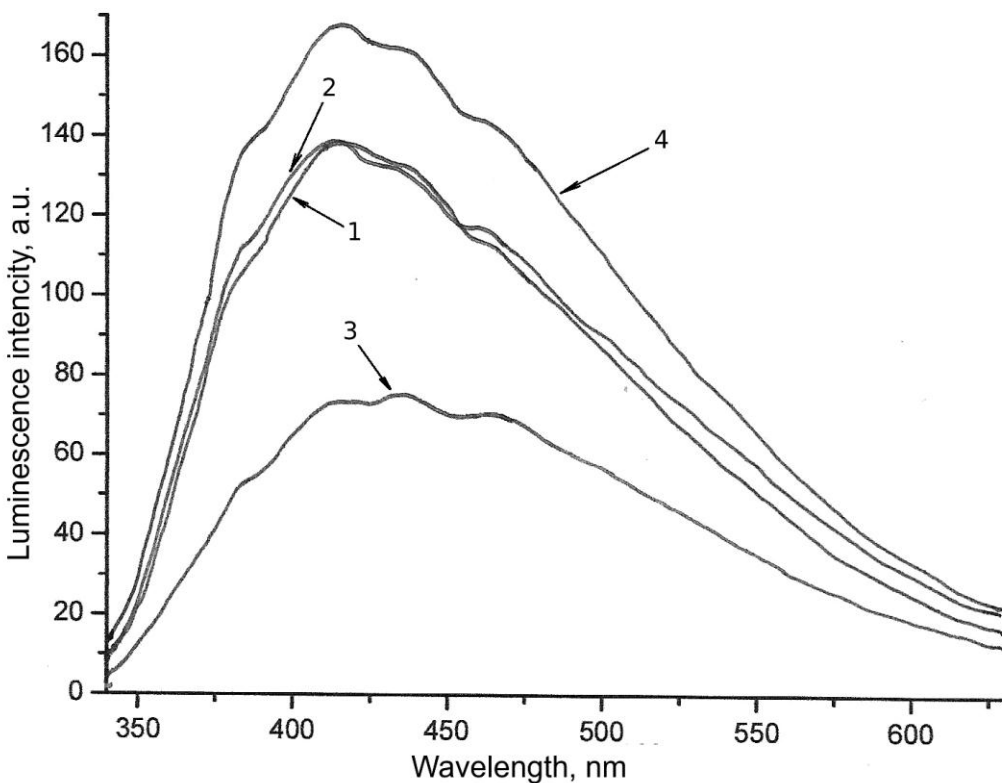


Figure (3b): Luminescence spectra of layers of particles grafted with ethanolamine derivatives of PVC on the fibers of cellulose fabric and the same layers sorbed with toluene, 1,4-dioxane, dimethyl sulfoxide

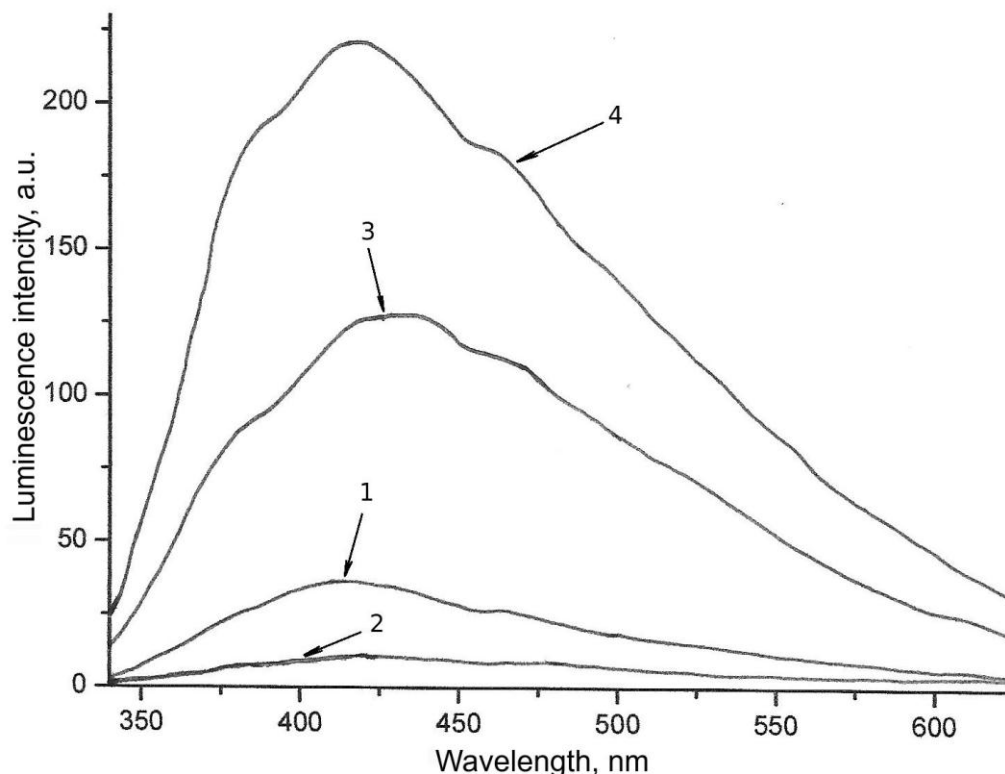


Figure (3c): Luminescence spectra of layers of particles grafted with ethanolamine derivatives of PVC on asbestos material and the same layers sorbed with toluene, 1,4-dioxane, dimethyl sulfoxide

Results and Discussion: From Figure (1) it can be seen that in the IR spectrum of the PVC solution in BA have bands of 3830 cm^{-1} and 3373 cm^{-1} , and in the BA spectrum there are only bands at 3373 cm^{-1} . According to [10], the O–H vibrational bands in alcohol vapor are about 3830 cm^{-1} . In liquids, they shift to the long wavelength region due to the formation of intermolecular hydrogen bonds. The band at 3830 cm^{-1} is in the region of oscillations of a “weak hydrogen bond”, that is, in the $\text{C}_6\text{H}_5\text{CH}_2\text{-OH}\cdots\text{Cl-CH}$ groups. In the structures that form the developed surface of the initial particles there are OH groups. In them, the mobility of hydrogen is approximately the same as that of phenols [11]. In systems with solvation, the hydrogen bond strength of alcohols correlates with the mobility of hydrogen [15]. Upon contact of particles with BA molecules from solvatocomplexes PVC-related aromatic groups replace BA in solvatocomplexes. This leads to non-covalent binding of Cl-CH groups on the surface of the particles. Apparently, as the particle size decreases to $0.5\text{-}7\text{ }\mu\text{m}$, a shell is formed around them. In the spectrum of grafted PVC, as can be seen from Figure 2, there are bands at 708 cm^{-1} and 671 cm^{-1} , related to vibrations in amorphous areas and intense 652 cm^{-1} complex band, characteristic of dissolved PVC with disordered chains. At the same time, the spectrum of the original PVC contains a band of 640 cm^{-1} and bands of 709 cm^{-1} and 679 cm^{-1} , that is characteristic of crystalline and amorphous regions of the polymer, a band of 645 cm^{-1} , and a band of 620 cm^{-1} , that are related to vibrations in chains with conformational defects and with a non-planar configuration, the same weak band at 586 cm^{-1} is characteristic of disordered PVC chains [11 - 16]. Consequently, in the layer of particles grafted with PVC, the structure of PVC sections connected with the particles is close to the structure of PVC bound to particles through hydrogen bonds. When heated under the action of TEA, the intermolecular groups -> C-OH * Cl-CH < are converted to ester groups. At the same time, the structure of PVC areas emanating from the surface is similar to the structure of dissolved PVC.

In the luminescence spectrum of a layer of particles with grafted ethanolamine derivatives on a PVC film with and without solvents accordingly with Figure (3a), there are two strips on the cellulose fabric

— four strips and layers on the asbestos material — three strips. The frequency values of the band maxima and their peak intensity are given in Table (1).

Table (1): The frequency and wavelengths values of samples luminescence spectra maxima.

Substrate	Original		DMSO		Dioxane		Toluene	
	λ_{\max} , nm	Intensity, a.u.	λ_{\max} , nm	Intensity, a.u.	λ_{\max} , nm	Intensity, a.u.	λ_{\max} , nm	Intensity, a.u.
PVC	412	14.5	418	16.5	414	16.8	425	19
	468	11.9	469	12.2	469	12	471	16
Cellulose tissue	388	105	387	104	390	55	386	127
	416	132	418	142	420	74	414	164
	437	127	437	132	440	75	437	160
	470	110	468	117	471	69	468	140
Asbestos material	387	20	380	21	381	67	385	177
	411	23	412	32	424	129	420	220
	470	18	457	24	472	116	469	177

The bands refer to the $\pi^* \rightarrow \pi$ transitions in the conjugated carbon structures in oxoamines, excited as a result of non-emitting $\sigma^* \rightarrow \sigma$ transitions in the amino and oxo groups [15]. Each band corresponds to a cycle with a certain state of π electrons in carbon structures in cycles. It depends on steric tension cycles. In a layer on PVC, there are two structural types of oxoamines. The band in the 410 – 420 nm region refers to the $\pi^* \rightarrow \pi$ transition in the more stressed — and in the 467 – 470 nm region — to the less stressed carbon structures in cycles. In layers on the cellulose fabric and on the asbestos canvas there are oxoamines with the same intensity as in the PVC layer. In this case, a more intense cycle appears, characterized by a band of 387 - 390 nm. In addition, in the layer on the pulp tissue, another band appears at about 437 - 440 nm. Thus, as a result of chemical grafting of the layer, the number of structural types of oxoamines increases. The energy flux $\pi^* \rightarrow \pi$ is distributed between the emitting and the flow rate for conformational oscillations of the cycles. As can be seen from the table for the solvent-free layer, depending on the substrate, the quantum yield increases in the series PVC < Sodium hydrosilicate (asbestos) < Cellulose. Fiber asbestos fabric consists of rolls of magnesium hydrosilicate. $(-O)_2OSi-O-H$ groups on the surface of the rolls are involved in the grafting of the layer. Cellulose fiber consists of fibrils, between which there are macropore-type vacancies. Particles before the transformation of PVC can fill these pores. The number of asbestos groups that bind nets is less than that of cellulose. Probably, in the asbestos layer, the conformational vibrations of oxoamines are more limited than in the layer on PVC, and in the layers on cellulose fabric they are restrained, on PVC they are not restrained.

Conclusions: Sorption of organic molecules does not affect the number of structural types of oxoamines, in almost all cases leads to an increase in the intensity of luminescence. For layers on PVC and asbestos material, it increases in the following line: a layer without solvent < a layer with dimethyl sulfoxide < layer with dioxane < a layer with toluene, and for a layer on cellulose fabric: a layer with dioxane < layer without solvent \approx layer with dimethyl sulfoxide < toluene layer. Apparently, the filling of cavities leads to the difficulty of conformational vibrations. Dioxane associates with cellulose, as a result of which, through its molecules, a part of the energy flow can be dispersed into the substrate.

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