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## Synthetic polyfunctional ionites

It is presented the results of reaction of a nucleophilic replacement of the chlorine humic acids with various nucleophiles. It is shown that reactions proceed on aliphatically bound atom of chlorine and lead to formation of functional derivative coals of molar structure 1:1–2 (HU:Nu). It is established that 60–70 % bound coal chlorine participate in reaction with nucleophiles. Depending on conditions of reaction and the applied reagents on nucleophilic groups 30–50 % of chlorine are replaced.

*Key words:* humic acids, polyampholytes, complexing agents, extractants, amino products.

In literature the processes of chlorination of coals and humic acids, an interaction of these compounds with amines and other nucleophiles, research of a structure and their properties are little studied and there are necessary more in-depth studies in this area. The modified coals received on the basis of chlorination are perspective as cationic and polyampholytic complexing agents and extractants for waste water treatment, as a polymeric basis for lacquer coats [1, 2].

The synthesized chlorine humic acids (ChHA) belong to the class of haloaryl and the reactions of nucleophilic replacement  $S_N2$  are characterized to them. We investigated the interaction of the chlorinated humic acids with aliphatic (di) amines for the purpose of strengthening their ion-exchange and the complexing properties [3, 4]. Reactions of this type are widely used in synthesis of multifunctional anionite and polyampholytes.

It is investigated the interaction of ChHA with monoethanol amine (EA), diethyl amine (DEA) and ethylene diamine (EDA) in the environment of organic solvents. As solvents there were used dimethylformamide (DMFA) and methylethylketone (MEK). For experiences it is taken chlorine humic acids received by electrochemical chlorination of Maykuben brown coals (ChHA<sub>1</sub>) and humic acids from the Shubarkol oxidized coals (ChHA<sub>2</sub>). Some characteristics are provided in Table 1.

Table 1

Characteristics of the initial chlorine humic acids

Coal	Chlorine humic acid	$W_a$ , %	$A_a$ , %	$\Sigma\text{COOH}+\text{OH}$ , mg-eq/g	The amount of chlorine, %
Maykuben brown coal	ChHA <sub>1</sub>	4,30	2,05	3,46	23,8
Shubarkol oxidized coal	ChHA <sub>2</sub>	5,94	10,09	5,71	18,4

### Experimental part

The chlorinated humic acids (ChHA) were received by the technique described in [4]. Synthesis of the aminochlorine-derived humic acids was carried out at a ratio of the initial reagents ChHA:amine = 1:1 (mol), ChHA:solvent=1:1–10 (mass), temperature 70–80 °C with in 2–4 hours at an intensive hashing. Reaction proceeds with an exothermic effect. On the course of reaction it is dropped out the sediment of the amino product which was washed out water and dried at low temperatures. When carrying out reaction in DMFA there are formed the soluble products. From reactionary solutions in vacuum DMFA was driven away and residual products of amino derivatives were washed out water and dried.

The formed for condensates of aminoproducts for the purpose of deepening of reaction of chlorine atoms replacement with amino groups and polycondensation on these groups, and also for decrease in solubility, were subjected to curing in vacuum at a temperature 80–120 °C within 4–7 hours (the 2<sup>nd</sup> stage). It is judged about the course of reaction according to the content of chlorine, nitrogen and the sum of acidic groups in the amino chlorine-derived of HA. Data of the made experiments are presented in Tables 2–4.

Table 2

The interaction of chlorine humic acids with amines (1 stage)

№ of experience	Amine	Solvent, composition of solution, volume parts	The content of chlorine in AHA (1 stage), %	The amount of the chlorine which reacted, %	The content of chlorine in AHA after a curing, %
1	MEA	MEK, 1:7	8,35	64,9	5,29
2	DEA	MEK, 1:7	7,96	66,6	Undefined
4	EDA	MEK, 1:1	10,48	56,0	3,03
5	EDA	MEK, 1:2+NaOH	13,12	44,9	7,93
6	EDA	MEK, 1:10	7,97	66,5	5,93
3	EDA	DMFA	10,74	54,9	5,12
7	EDA-F, 1:8	MEK+NaOH +water	8,03	66,3	6,05
8	EDA	MEK, 1:10	7,12	70,1	5,31

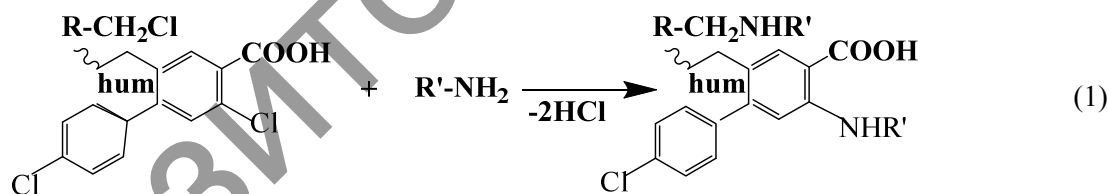
Note. 1–7 experiences for ChHA<sub>1</sub> with chlorine 23,8 %, the 8<sup>th</sup> experience — for ChHA<sub>2</sub> with chlorine 18,4 %.

### The results and discussion

Presence at the structure of ChHA of chlorine bound with aromatic and aliphatic carbon, defines feature of the reaction course of ChHA with various nucleophiles.

Apparently from Table 2, the content of chlorine in products decreases from 23,8 % (or 18,4 %) to 7–13 % depending on the nature and concentration of amine and solvent. It is established that at the first stage 45–70 % of the bound with HA chlorine participate in interaction with nucleophiles, at the vacuumized heat treatment extent of participation of chlorine increases to 66–78 %. From this the amount of chlorine, judging by the content of residual chlorine and nitrogen, 35–70 % of atoms of chlorine are replaced on nucleophilic groups, other quantity is chipped off in the form of chloride hydrogen or it is removed in the form of salt with residual amine during cleaning of a product.

It is assumed that amines interact with the chlorine bound both with an aliphatic and aromatic link of humic acid if there are carboxyl group in ortho- and/or para- provisions to atom of chlorine. Process of amination proceeds according to the following scheme (1):



Amination process of the chlorine humic acids depends on the amine nature (Table 2) a little. There is the dependence of the content of residual chlorine on concentration of initial amine in reactionary mix. In case of use as the DMFA solvent at a ratio amine:solvent = 1:1, solvent remains as a part of a condensate and it is removed from the product in the course of the curing.

Process of amination of ChHA depends on nature of the solvent. The maximum attached quantity of nitrogen in compounds is received in DMFA. In the preparative plan it is preferable MEK as the final product is allocated easily from the reactionary mix with filtering. The content of sour groups in the aminated samples is lower than in the initial ChHA that is caused by formation of the ammonium salts on carboxyl groups of ChHA.

The content of nitrogen in the amine chlorine humic acids (AChHA) is 2,3–5,6 % (Table 3) that corresponds to entry into HA 4,5–12 % of amine depending on the amine nature and conditions of carrying out of the replacement reaction.

The received aminederivants after a thermocuring represent black-brown powders partially soluble in alkalis and insoluble in organic solvents.

Table 3

**The characteristic of aminochlorinederivants of HA after a curing (2 stage)**

№ of experience	Yield, %	$\Sigma\text{COOH}+\text{OH}$ , mg-eqv/g	N, %	The content of amine, %	Solubility			
					MEK	DMFA	NaOH	H <sub>2</sub> O
1	82,1	3,71	3,3	7,4	Insol.	Slightly sol.	Slightly sol.	Slightly sol.
2	84,5	3,93	2,3	11,9	Insol.	Insol.	Slightly sol.	Insol.
3	80,0	2,10	5,6	12,0	Insol.	Sol.	Slightly sol.	Insol.
4	86,7	4,20	2,3	4,9	Insol.	Insol.	Slightly sol.	Slightly sol.
5	81,2	3,50	4,2	9,1	Insol.	Insol.	Slightly sol.	Insol.
6	80,3	2,02	4,5	4,5	Insol.	Insol.	Sol.	Insol.
7	79,1	1,76	4,8	-	Sol.	Insol.	Slightly sol.	Insol.
8	87,8	2,94	3,8	8,2	Insol.	Slightly sol.	Sol.	Insol.

Note. 1–7 experiences — for ChHA<sub>1</sub>, the 8<sup>th</sup> experience — for ChHA<sub>2</sub>.  $\Sigma\text{COOH}+\text{OH}$  =5,71 mg-eqv/g.

On the basis of data of the element and functional analysis it is counted a content of aminoderivants of the chlorine humic acids (Table 4).

Table 4

**The content of aminoderivants of the chlorine humic acids**

№	Amine	Solvent, the solvent content	The content of the initial mixture, %			The content of amin-HA, %		
			Amine	Chlorine	HA	Amine	Chlorine	HA
1	MEA	MEK, 1:7	13,2	20,7	66,1	7,4	5,3	87,3
2	DEA	MEK, 1:7	15,5	20,1	64,4	11,9	Undefined	
4	EDA	MEK, 1:1	13,0	20,7	66,3	4,9	3,0	92,1
5	EDA	MEK, 1:2+NaOH	13,0	20,7	66,3	9,1	7,9	83,0
6	EDA	MEK, 1:10	13,0	20,7	66,3	4,5	5,9	89,6
3	EDA	DMFA	13,0	20,7	66,3	11,9	5,1	83,0
7	EDA-F, 1:8	MEK+NaOH +water	13,0	18,1	76,2	Undefined	6,1	
8	EDA	MEK, 1:10	13,0	20,7	66,3	8,2	5,3	86,5

Note. 1–7 experiences — for ChHA<sub>1</sub> with chlorine 23,8 %, the 8<sup>th</sup> experience — for ChHA<sub>2</sub> with chlorine 18,4 %.

In IR-ranges of the cured samples it is not fixed absorption strips of chlorine hydrocarbon (780–550 cm<sup>-1</sup>). There are absorption strips, characteristic for stretching vibrations of aromatic amines (1250–1360 and 1650 cm<sup>-1</sup>) and aliphatic compounds (1020–1220 cm<sup>-1</sup>). Associates of the amino groups bound hydrogen bounds are shown in the field of 3500 cm<sup>-1</sup> and above.

Thus, new aminochlorinehumic acids represent gel multifunctional compounds with a set of groups, different in the nature: chlorine, amino group, carboxyl, phenolic and other acid groups. At heat treatment of the aminochlorinehumic acids it is occurred polycondensation on chlorine- and amino groups, which leads to increase of molecular weight (mass). When applying plenty of high temperatures and excerpts (150 °C, 2 hours) it is occurred cross-linking and formation of gel insoluble structures. It is defined optimum parameters of the amination reaction of the chlorine humic acids (ChHA) by ethylene diamine (EDA) in the environment of DMFA.

The reaction of amination was carried out at a variation of three factors: temperatures ( $x_1$ ), concentration of EDA in solvent ( $x_2$ ) and synthesis duration ( $x_3$ ). Conditions of the reaction of amination are given in Table 5.

The reaction proceeds with exothermic effect, on the course of reaction it is dropped out a sediment of an aminoproduct. Reactionary mix after the end of the synthesis was diluted with water, the sediment was filtered, washed out water and dried in a vacuum drying cabinet at 60 °C. Control of reaction was carried out on the attached amine and on residual chlorine.

Amines interact with bound both with an aliphatic and aromatic link of humic acid if there is electroacceptor group in orto- and/or para- provisions to atom of chlorine, and also it is possible formation of quarternary ammonium salts on carboxyl group which are easily hydrolyzed in water.

Table 5

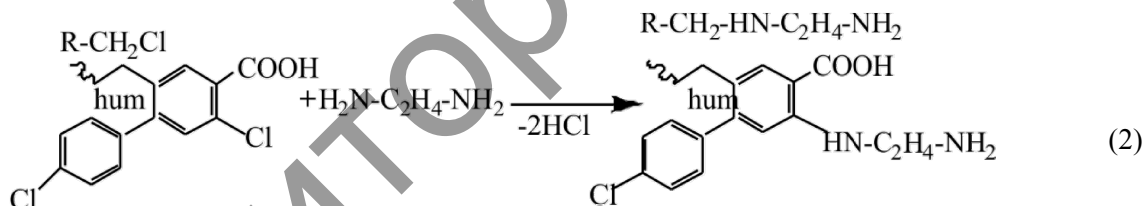
## Amination of the chlorine humic acids

№ o/e	$x_1$ , °C	$x_2$	$x_3$ , hour	Yield, g	Cl, % (res.)	Cl, mg-eq/g (react.)	N, mg-eq/g	$\Sigma$ COOH+OH, mg-eq/g	
1	40	1:2	4	2,5	10,8	3,3	3,0	4,4	
2	50			3,0	13,2	2,5	3,4	3,0	
3	60			3,1	10,6	3,4	3,3	4,2	
4	80			2,9	10,5	3,4	3,2	4,4	
5	60	1:1	4	2,4	14,9	2,14	4,0	5,0	
6		1:1		2,7	15,3	2,00	2,6	4,1	
7		1:2		3,1	10,6	3,40	3,3	3,8	
8		1:5		1,7	10,7	3,40	2,9	3,9	
9		1:5		2,1	10,5	3,38	2,8	3,9	
10		1:8		3,2	13,5	2,50	2,8	3,3	
11		1:2	2	2	1,9	8,4	3,97	3,2	4,4
12				2	3,2	12,6	2,80	2,8	3,8
13				4	2,6	10,5	3,38	3,5	4,6
14				5	2,6	8,5	3,9	3,3	4,3

Experimental data show that it isn't observed considerable differences according to the content of the attached nitrogen in the range of the varied values, therefore further amination reaction of the chlorine humic substances is carried out at a temperature 60 °C, ratios of the initial amine to DMFA 1:2, synthesis duration is 4 hour. The sum of sour groups in amination reaction decreases slightly.

It was investigated reactions of a hydroxyl methylation of aminochlorinehumic acids. Polycondensation was carried out in two stages. At the first stage it was received aminochlorinehumic acid, through interaction of ChHA with ethylene diamine in DMFA or MEK solution.

It is supposed that the reaction proceeds according to the following scheme (2):



Then the received AChHA was processed with formaldehyde, as a result it is received aminomethylol-derivat (AChHA-F) which is condensed at pH, equal 3–4 in the presence of 2 % oxalic acid within 40 minutes before receiving viscous condensation solution. Some indicators of the received polymer are given in Table 6.

Table 6

## Polycondensates of ChHA with ethylene diamine and formaldehyde

Solvent	Yield, %	Chlorine, %	Nitrogen, %	COOH+OH, mg-eqv/g	$\eta$ , dl/g	COE Na <sup>+</sup> , mg-eqv/g	COE Cu <sup>2+</sup> , mg-eqv/g
DMFA	60	13,2	3,40	2,5	0,11	4,18	2,9
MEK	72	12,3	8,27	3,6	0,09		

Then mix was subjected to vacuum condensation for removal of excessive water. Mix was cured within 2 hours at 150 °C. Curing occurs onmethylol and amino groups.

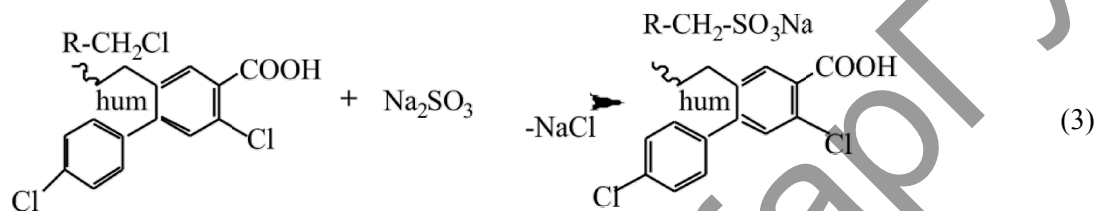
For introduction of sulfonate group to methylol chlorine humic acids and ChHA it is carried out their interaction with sodium sulfite on Shtrekker's reaction (Table 7).

Synthesis of the sulphoderivants from ChHA and AChHA-F

Solvent	Yield, %	Chlorine, %	Sulfur, %	COOH+OH, mg-equiv/g	COE Cu <sup>2+</sup>	COE Na <sup>+</sup>
DMFA	50–60	3–4	2,15–3,0	2,8–3,3	1,2–2,9	2,7–5,5

The received sulphomethylol chlorine humates and humates are insoluble in DMFA and in aqueous-alcoholic solution. The functional content of the received derivants is defined.

An introduction reaction of sulfonate group to chlorine derivants of HA occurs according to the scheme (3):



Thus, in the article it is shown an ability of the chlorine humic acids to reactions of nucleophilic replacement of chlorine atoms to amino groups. Optimum conditions of the reaction and the products characteristic are defined.

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#### Синтетикалық полифункционалды иониттер

Мақалада хлоргуминді қышқылдардың әр түрлі нуклеофилдермен әрекеттесу реакцияларының нәтижелері келтірілген. Реакциялар хлордың алифатты байланысқан атомдары бойынша жүріп, құрамы 1:1–2 (ХУ:Nu) мольдік құрамды көмір туындыларының түзілуіне алып келетіні анықталды. Нуклеофилді реакциялар кезінде көмірмен 60–70 % байланысқан хлор қатысатыны анықталған. Реакцияның жүру жағдайына және қолданылатын реагенттерге байланысты 30–50 % хлор нуклеофилді топтарға ауысады.

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#### Синтетические полифункциональные иониты

В статье представлены результаты реакции нуклеофильного замещения хлоргуминовых кислот с различными нуклеофилами. Показано, что реакции протекают по алифатически связанным атомам хлора и приводят к образованию функциональных производных углей мольного состава 1:1–2 (ХУ:Nu). Установлено, что в реакции с нуклеофилами участвует 60–70 % связанного с углем хлора. В зависимости от условий реакции и применяемых реагентов на нуклеофильные группы замещаются 30–50 % хлора.

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Репозиторий Қарғу