РЕСУРСОСБЕРЕГАЮЩИЕ ТЕХНОЛОГИИ

DOI 10.15593/2409-5125/2017.02.08
UDC 676.011:544.77

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THE CREATION AND IMPLEMENTATION OF THE RESOURCE-CONSERVING TECHNOLOGY OF PAPER AND PAPERBOARD SIZING WITH HYDRO-DISPERSIONS OF MODIFIED ROSIN IN THE MODE OF HETERO-ADAGULATION OF PEPTIZED PARTICLES

The specific features of the application of hydro-dispersions of modified rosin (HDMR) in dispersed systems have been studied, and the technological mode of hydrophobicity rise, paper and cardboard strength increase has been developed. It has been shown the necessity of controlling the processes of MRH electrolyte coagulation and peptization of coagulants by changing the content of a particular type of aluminum hydroxide compounds ($Al(H_2O)_6^{3+}$, $Al(H_2O)_5(OH)^{2+}$, $Al(H_2O)_4(OH)_2^{+}$, $Al(H_2O)_3(OH)_3^{0}$ и $Al(H_2O)_2(OH)_4^{-}$). The proposed new technological method allows obtaining new sizing complexes in the form of fine-dispersed (size 180–220 nm) positively charged particles (charge from +22 to +30 mV) of peptized particles. Such particles are able to be uniformly distributed by a monolayer and firmly fixed on the surface of negatively charged cellulose fibers, which facilitates the process of hydrophobization in a more efficient mode of heteroadagulation. This effect is achieved due to the peptization (disaggregation) of electrically neutral coagulates (size not exceeding 1800 nm) formed in the first coagulation zone of the HDMR, while according to the existing technology, the role of sizing complexes is performed by electrically neutral coagulates (size 2000–3800 nm and more) formed in the second area of HDMR coagulation.

The developed technology to ensure the peptization coagulates formed in the first area of rapid coagulation of neutral and high-resin HDMR, enables to obtain new sizing systems in the form of finely-dispersed positively charged peptized particles. Hexa aqua aluminium ions $Al(H_2O)_6^{3+}$ have a peptizing effect on the coagulates. The structure of peptized particles differs from that of coagulums in the content of ions $Al(H_2O)_6^{3+}$, $Al(H_2O)_5(OH)^{2+}$, $Al(H_2O)_4(OH)_2^{+}$ и SO_4^{2-} in the adsorption and

Chernaya N.V., Fleisher V.L., Zholnerovich N.V. The creation and implementation of the resource-conserving technology of paper and paperboard sizing with hydro-dispersions of modified rosin in the mode of hetero-adagulation of peptized particles. PNRPU. Applied ecology. Urban development. 2017. No. 2. Pp. 87-101. DOI: 10.15593/2409-5125/2017.02.08

Черная Н.В., Флейшер В.Л., Жолнерович Н.В. Создание и внедрение ресурсосберегающей технологии проклейки бумаги и картона гидродисперсиями модифицированной канифоли в режиме гетероадагуляции пептизированных частиц // Вестник Пермского национального исследовательского политехнического университета. Прикладная экология. Урбанистика. – 2017. – № 2. – С. 87–101. DOI: 10.15593/2409-5125/2017.02.08

diffusion layers. The implementation of the developed resource-saving technology at five paper and paperboard enterprises confirmed the results of the research and demonstrates the feasibility of economy in the production of each ton of paper and cardboard up to 30–40% of hydro-dispersion of modified rosin and reduce the electrolyte consumption by 1.5–2.0 times.

Keywords: technology of paper, hydro-dispersions of modified rosin, peptized particles, hetero-adagulation

Introduction. Various sizing agents in the form of hydro-dispersions of modified rosin (HDMR) [1–8] are widely used in the technology of glued paper and paperboard. They contain negatively charged particles of the dispersed phase sized d_o and differ in the content of sodium resonates (RCOONa, $R(COONa)_2$ and $R(COONa)_3$) and the free rosin acids (RCOON, $R(COOH)_2$ and $R(COOH)_3$) and, consequently, in the colloid-chemical properties. At present, at paper and paperboard factories neutral HDMR (for example, TORM (tall oil rosin modified), ORM (oleo-resin modified), TORMHA-2 (tall oil rosin modified with higher alcohols, etc.) are widely used for sizing in an acidic environment and in a neutral environment (pH 6.5–7.2) – high-resin HDMR (TORMHA-2N (tall oil rosin modified with higher alcohols), TORMAA-3N (tall oil rosin modified with amino alcohols) and Sacocell-309, etc.)

It should be noted that the aluminum compounds in the form of solutions of aluminum sulphate $Al_2(SO_4)_3$, sodium aluminate, $NaAlO_2$, oxy-chlorides of aluminum ($Al(OH)Cl_2$ and $Al_2(OH)_5Cl$) and alums (aluminum-potassium, aluminum-sodium or aluminum-ammonium) are traditionally used as electrolytes. The pH of the electrolyte solution affects the content of the forms of aluminium hydroxo-compounds $(AHC)^2$: $Al(H_2O)_6^{3+}$, $Al(H_2O)_5(OH)^{2+}$, $Al(H_2O)_4(OH)_2^{+}$, $Al(H_2O)_3(OH)_3^{0}$, $Al(H_2O)_2(OH)_4$, etc. Positively charged forms of AHC are involved in colloid chemical interactions with the particles of the dispersed phase to form the HDMR sizing complexes differing, as determined by us [9–11], in the structure, dispersion, electro-kinetic potential and hence, the nature of distribution and fixation strength on the surface of fibers.

Since the sizing complexes as coagulates are formed in the first (developed technology) and the second (existing technology) areas of rapid coagulation, they may be coarsely-dispersed and electrically neutral (existing technology) or, conversely, after peptization (disaggregation) finely-dispersed (d_p) and positively charged (developed technology). A subsequent heat treatment (115–135°C) of paper and paperboard in the dryer section of a paper and board machine promotes melting and sintering of sizing complexes to form a hydrophobic ”film” on the surface of fibers. Therefore, reducing the thickness and ensuring its homogeneity contributes to, on the one hand, reducing the consumption of the HDMR and the electrolyte and, on the other hand, the maximum preservation of the original strength of

the paper sheet. This can be achieved, in our opinion, not only by reducing the size of gluing complexes d_{medium} to the size of peptized particles d_p, where $d_p \approx d_o$, and providing a uniform distribution of a monolayer on the surface of the fibers, but also by increasing the strength of their fixation with the fibers by significant displacement of their electro-kinetic potential to the range of positive values. This scientific hypothesis is the basis of the creation of the resource-conserving technology of paper and paperboard sizing, providing savings of HDMR (by peptization of coagulates and synthesis of new sizing complexes in the form of peptized particles) and reducing the electrolyte consumption (due to the transfer process of electrolytic coagulation from the second area of rapid coagulation to the first one).

The research, previously carried out by us, demonstrated [10, 11], that the coagulates formed in the first area of rapid coagulation of HDMR after the adding of the first (small) portion of the electrolyte can be peptized after the subsequent addition of a second (small) portion of the electrolyte, and coagulates formed in the second area of rapid coagulation due to the presence of "excessive" amount of electrolyte based on the famous stoichiometric ratio of HDMR: electrolyte = 1 : 3 (1 : 5) – are coarsely-dispersed and are not able to be peptized. In the first case, the electrolyte is added; the sizing complexes are finely-dispersed positively charged peptized particles capable of being uniformly distributed in the form of a monolayer and firmly fixed on the surface of negatively charged fibers that promotes the sizing process in the mode of hetero-adagulation of peptized particles. In the second case, the sizing complexes are coarsely-dispersed electro-neutral coagulates not capable of being uniformly distributed and firmly fixed on the surface of the fibers which leads to the flow of the sizing process in the mode of homo-coagulation.

The purpose of the research is to substantiate scientifically and develop a resource-saving technology of paper and paperboard sizing with hydrodispersions of modified rosin by replacing of the sizing process in the mode of homo-coagulation by a more effective mode of hetero-adagulation providing the peptization of coarsely-dispersed electro-neutral coagulates and obtaining finely-dispersed positively charged peptized particles.

Experimental. To achieve this goal the work was carried out in three stages: *at the first stage* the influence of the forms of aluminium hydroxo-compounds (AHC) (Table 1) and electrolyte consumption (aluminum sulphate) on the kinetics of electrolytic coagulation of neutral and high-resin HDMR, the degree of aggregation of coagulum (N_m), the dispersion of coagulates (d_{medium}) formed in the first and second areas of rapid coagulation, and their ability to peptization were studied; *at the second stage* the peptization conditions of coagulates were determined, formed during the electrolytic coagulation of the

studied neutral and high-resin HDMR; the dispersion, electro-kinetic potential, aggregate stability and specific interaction energy of peptized particles were studied as well; *at the third stage* we performed an industrial testing and implementation of the developed resource-conserving technology of paper and paperboard sizing in the mode of hetero-coagulation of the peptized particles.

Table 1

The influence of pH of electrolyte solution on the content of aluminium hydroxo-compounds (AHC) forms

Таблица 1

Влияние pH раствора электролита на содержание форм гидроксосоединений алюминия (ГСА)

pH of electrolyte solution (S_{el})	Content of aluminium hydroxo-compounds (AHC) forms, %				
	$Al(H_2O)_6^{3+}$	$Al(H_2O)_5(OH)^{2+}$	$Al(H_2O)_4(OH)_2^{+}$	$Al(H_2O)_3(OH)_3^{0}$	$Al(H_2O)_2(OH)_4^{-}$
1.95	100	–	–	–	–
2.70	95	5	–	–	–
3.50	90	10	–	–	–
3.75	88	12	–	–	–
4.30	85	10	5	–	–
5.30	10	40	40	10	–
6.80	–	–	20	80	–
9.10	–	–	–	60	40

The following results of the research on the managing the process of electrolyte coagulation of neutral and high-resin HDMR by means of a purposeful change not only the content of the electrolyte in the dispersed system (S_{el}, wt.h. / wt. h. of the dispersed phase of HDMR), but also the qualitative and quantitative distribution of aluminium hydroxo-compounds (AHC) forms [9].

The results of our turbidimetric studies have shown that the turbidity (τ, cm^{-1}) of the dispersed system and, hence, the dispersion of coagulates depends on the amount of the added electrolyte (S_{el}) and the pH of its solution. It was determined that after the coagulation of HDMR in the first area of rapid coagulation, when a dispersed system contains an electrolyte in an amount of $R_{1,\,s} \le S_{el} \le R_{1,\,e}$, coagulates capable of being peptized are formed. This is evidenced by a decrease in turbidity from the maximum (τ_{max}) to the initial (τ_o) values and a decrease in the coagulation rate (W) to zero at $R_{1,\,e} \le S_{el} \le R_{2,\,s.}$.

The laws of kinetics of the electrolyte coagulation of HDMR allowed to develop the technology of reducing the aggregation of coagulum (N_m) and sizes

of coagulates (d_{medium}) and increase the ability of coagulates to peptization. The data presented in Table 2 for the dispersed system "High-resin hydro-dispersion TORMHA-2N – electrolyte", reveal the influence of pH of the electrolyte solution and the content of aluminium hydroxo-compounds forms (AHC) in it (Table 1) on N_m and d_{medium}. A similar trend is observed for hydro-dispersions TORM, ORM, TORMHA-2, TORMAA-3N and Sacocell-309. The difference lies in the properties of coagulates (N_m and d_{medium}) depending on the conditions of coagulation and their ability to peptize. It is found that the peptization of coagulates can occur fully ($\tau = \tau_o$ and $W = 0$) or partially ($\tau_{max} > \tau > \tau_o$ and $W_{max} > W > 0$). We were the first to have discovered the existence of the area of finely-dispersed peptized particles. In this area, $\tau = \tau_o$ and $W = 0$. However, the subsequent addition of the electrolyte in an amount of $R_{2,s} \le S_e l \le R_{2,e}$ changes the structure of peptized particles that violates their aggregate stability and leads to the flow of the coagulation process in the second area of rapid coagulation.

The coagulates formed in the first area of rapid coagulation of HDMR and having $2 \le N_m \le 12$ and $400 \le d_{medium} \le 1080$ nanometers, are peptized, while in the second area of rapid coagulation coagulates of different sizes and coarsely-dispersed ($900 \le d_{medium} \le 3200$ nanometers) coagulates are formed, not capable of being peptized. The dispersed system comprising, for example high-resin hydro-dispersion TORMHA-2N, has a certain pH* value (Table 2). It was obtained that in the first area of rapid coagulation for the investigated HDMR the ph* of the dispersed system is in the range from 6.5 to 7.5, while in the second area of rapid coagulation – from 4.8–6.4.

Table 2

The properties of coagulates depending on the conditions of the coagulation of high-resin hydro-dispersion TORMHA-2N

Таблица 2

Свойства коагулятов в зависимости от условий коагуляции высокосмоляной гидродисперсии ТМВС-2Н

pH of electrolyte solution (S_{el})	S_{el}				pH* of a dispersed system	Properties of coagulates		
	$R_{1,s}$	$R_{1,e}$	$R_{2,s}$	$R_{2,e}$		N_m	d_{medium}, nanometers	Ability to be peptized
1	2	3	4	5	6	7	8	9
The first range of rapid coagulation								
1.95	0.06	0.13	–	–	7.3–7.5	7–10	1350–1800	yes
2.70	0.10	0.17	–	–	7.3–7.5	6–9	1100–1620	yes
3.50	0.20	0.37	–	–	7.3–7.5	5–9	900–1620	yes
3.75	0.22	0.39	–	–	7.3–7.5	5–9	900–1620	yes

1	2	3	4	5	6	7	8	9
4.30	0.55	0.90	–	–	7.3–7.5	5–8	900–1400	yes
5.30	0.61	1.00	–	–	7.3–7.5	5–7	900–1300	yes
6.80	2.22	3.67	–	–	7.3–7.5	5–7	900–1300	yes
9.10	90.0	148.4	–	–	8.5–8.8	4–8	740–1400	no
The second range of rapid coagulation								
1.95	0.06	0.13	2.01	8.17	5.0–6.4	10–18	1800–3200	no
2.70	0.10	0,17	2.72	9.03	5.0–6.4	8–16	1450–2880	no
3.50	0.20	0.37	3.00	12.2	5.0–6.4	8–12	1450–2425	no
3.75	0.22	0.39	3.32	13.5	5.0–6.4	8–11	1450–2000	no
4.30	0.55	0.90	3.67	21.6	5.0–6.4	5–10	900–1800	no
5.30	0.61	1.00	4.48	31.2	5.5–6.4	5–10	900–1800	no
6.80	2.22	3.67	24.5	48.4	6.8	5–10	900–1800	no
9.10	90.0	148.4	The second range of coagulation is not reached					

The microphotographs (Fig. 1) for the dispersed system “High-resin hydro-dispersion TORMHA-2N – electrolyte (pH 3.75)” suggest that under full peptization of coagulates the condition $d_p \approx d_o$ is met (best option), and at partial peptization – $d_p > d_o$. Therefore, to carry out the process of sizing paper and cardboard in the mode of hetero-adagulation it is necessary to provide a complete peptization of coagulates to form peptized particles.

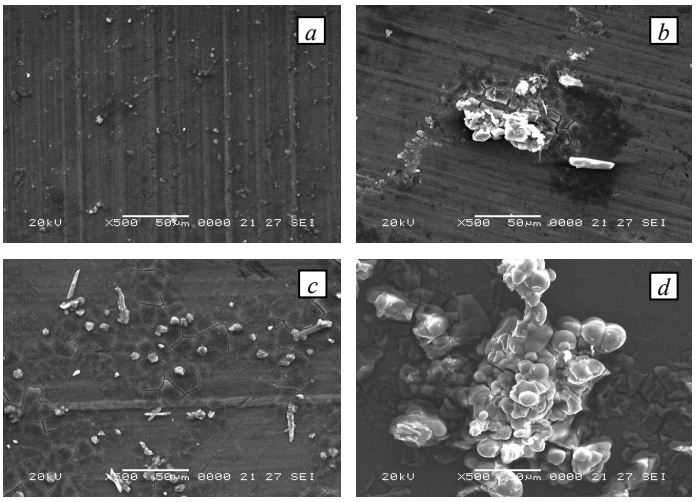

Figure 1. Micrographs of dispersed systems (*a* – initial HDMR;
b – coagulates (the first area of rapid coagulation); *c* – peptized particles;
d – coagulates (the second area of rapid coagulation))
Рис. 1. Микрофотографии дисперсных систем (*а* – исходная ГМК;
б – коагуляты (первая область коагуляции); *в* – пептизированные частицы;
г – коагуляты (вторая область коагуляции))

It was established that to manage the processes of coagulation and peptization a necessary amount of forms of aluminium hydroxo-compounds (AHC)(C_{AHC}) must be present in each specific dispersed system (Table 3). Thus hexa aqua aluminum ions $Al(H_2O)_6^{3+}$ have a peptizing effect[9].

Table 3

The peculiarities of ensuring the peptization of coagulates depending on the HDMR type and the conditions for coagulation

Таблица 3

Особенности обеспечения пептизации коагулятов в зависимости от вида ГМК и условий коагуляции

Type of HDMR	pH* of a dispersed system	The content of AHC forms (%) in a dispersed system			
		$Al(H_2O)_6^{3+}$	$Al(H_2O)_5(OH)^{2+}$	$Al(H_2O)_4(OH)_2^{+}$	$Al(H_2O)_3(OH)_3^{0}$
Coagulation (first area)					
TORM	6.0–6.5	–	5	30	65
TORMHA-2	7.1–7.4	–	–	5	95
ORM	5.7–7.5	5	10	20	65
TORMHA-2N	7.3–7.5	3	–	4	96
TORMAA-3N	7.3–7.5	–	–	4	96
Sacocell-309	6.1–6.5	–	5	30	65
Peptization of coagulates					
TORM	5.6–5.9	15	25	45	15
TORMHA-2	6.3–7.0	10	15	25	50
ORM	5.3–5.6	35	30	35	–
TORMHA-2N	7.0–7.2	5	10	10	75
TORMAA-3N	7.0–7.2	5	10	10	75
Sacocell-309	5.7–6.0	15	25	45	15
Coagulation (second area)					
TORM	4.0–5.0	60	35	5	–
TORMHA-2	4.6–5.6	50	40	10	–
ORM	4.3–4.8	60	35	5	–
TORMHA-2N	5.0–6.4	5	25	45	25
TORMAA-3N	5.0–6.4	5	25	45	25
Sacocell-309	5.0–5.3	10	40	40	10

It is found that depending on the conditions of providing the peptization of coagulates the peptized particles have high ($d_p \approx d_0$), medium ($d_p > d_0$) or low ($d_p >> d_0$) aggregate stability (Table 4). The duration (t) of the observation of the dispersed system ranged from 0.5 to 60.0 min. Certain conditions for obtaining peptized particles should be set up for each specific dispersed system.

Table 4

Aggregate stability of peptized particles depending on the conditions of providing the peptization of coagulates

Таблица 4

Агрегативная устойчивость пептизированных частиц в зависимости от условий обеспечения пептизации коагулятов

pH of electrolyte solution (S_{el})	S_{el}			pH* of a dispersed system	Properties of peptized particles		
					d_p, nanometers		Aggregate stability
	R_s	$R_{p,1}$	$R_{p,2}$		at t = 0.5 min	at t = 60.0 min	
1	2	3	4	5	6	7	8
Dispersed system “Neutral hydro-dispersion TORM – electrolyte”							
3.50	0.38	0.45	0.67	5.6–5.9	190	250	Medium
3.75	0.40	0.50	0.82	5.6–5.9	190	190	High
4.30	0.46	0.56	0.91	5.6–5.9	190	245	Medium
Dispersed system “Neutral hydro-dispersion TORMHA-2 – electrolyte”							
5.30	1.40	1.65	2.46	6.3–7.0	580	850	Low
6.80	2.24	2.72	4.95	6.9–7.0	175	610	Low
Dispersed system “Neutral hydro-dispersion ORM – electrolyte”							
1.95	0.38	0.61	1.65	5.3–5.6	196	355	Medium
2.70	0.46	0.67	1.80	5.3–5.6	196	320	Medium
3.50	0.83	0.69	2.46	5.3–5.6	250	320	Low
Dispersed system “High-resin hydro-dispersion TORMHA-2N – electrolyte”							
1.95	0.14	0.16	0.45	6.5–7.2	260	440	Low
2.70	0.18	0.27	0.49	6.5–7.2	240	375	Low
3.50	0.38	0.45	1.00	6.5–7.2	180	400	Low
3.75	0.40	0.61	1.49	6.5–7.2	180	250	Medium
4.30	0.91	1.35	2.23	6.5–7.2	180	180	High
5.30	1.01	1.49	5.47	6.5–7.2	180	180	High
6.80	3.68	9.03	13.46	6.9–7.2	180	220	Medium
Dispersed system “High-resin hydro-dispersion TORMAA-3N– electrolyte”							
1.95	0.09	0.22	0.61	6.5–7.2	185	700	Low
2.70	0.18	0.27	0.90	6.5–7.2	500	800	Low
3.50	0.46	0.61	1.00	6.5–7.2	300	580	Medium
3.75	0.68	1.00	1.82	6.5–7.2	185	185	High
4.30	0.83	1.22	1.88	6.5–7.2	185	185	High
Dispersed system “High-resin hydro-dispersion Sacocell-309 – electrolyte”							
1.95	0.14	0.22	1.22	5.7–6.0	216	216	High
2.70	0.23	0.37	1.28	5.7–6.0	216	216	High
3.50	0.38	0.45	1.65	5.7–6.0	216	300	Medium
3.75	0.50	0.82	2.01	5.7–6.0	216	310	Medium
4.30	0.61	0.95	3.22	5.7–6.0	216	500	Low

For the conducting the process of sizing paper and paperboard in acidic and neutral media in the mode of hetero-adagulation of peptized particles it is necessary to ensure that the basic condition: $d_p \approx d_0$ is met. Table 4 shows that the peptization of coagulates starts at a certain content of the electrolyte $R_{p,1}$ in each specific dispersed system and ends at $R_{p,1}$. The peptized particles continue to maintain their aggregate stability with a subsequent increase in the electrolyte content from $R_{p,}$ to $R_{п,2}$. It was found that the structures of coagulum, coagulates and peptized particles differ.

Coagulum formed in the presence of an electrolyte-coagulator in an amount insufficient to ensure the coagulation when the absolute value of ξ-potential is higher than the critical value ($-\xi_{cr}$), have the structure:

• application of *neutral* HDMR:

$$\{[R(COOH)_2]_m\, n(R(COO^-)_2)(2n/3 - z)\, Al(H_2O)_6^{3+}\}^{-3z}\, z\, Al(H_2O)_6^{3+}, \quad (1)$$

$$\{[R(COOH)_2]_m\, n(R(COO^-)_2)(n - m)Al(H_2O)_5(OH)^{2+}\}^{-2m}\, m\, Al(H_2O)_5(OH)^{2+}, \quad (2)$$

$$\{[R(COOH)_2]_m\, p(R(COO^-)_2)\, (2p - q)Al(H_2O)_4(OH)_2^{+}\}^{-q}\, q\, Al(H_2O)_4(OH)_2^{+}, \quad (3)$$

• application of *high-resin* HDMR:

$$\{[R(COOH)_2]_s\, t(R(COO^-)_2)f(NH_2–R^{IV}–COO^-)\, ((2t + f)/3 - y)Al(H_2O)_6^{3+}\}^{-3y}\, y\, Al(H_2O)_6^{3+}, \quad (4)$$

$$\{[R(COOH)_2]_s\, t\, (R(COO^-)_2)\, f\, (NH_2–R^{IV}–COO^-)((t + f/2 - a)\times \times Al(H_2O)_5(OH)^{2+}\}^{-2a} \cdot a\, Al(H_2O)_5(OH)^{2+}, \quad (5)$$

$$\{[R(COOH)_2]_s\, t(R(COO^-)_2\, f(NH_2–R^{IV}–COO^-)\times \times (2t + f - b)Al(H_2O)_4(OH)_2^{+}\}^{-b} \cdot b\, Al(H_2O)_4(OH)_2^{+}. \quad (6)$$

Coagulum which formed coagulates in the first area of rapid coagulation (area of critical values of ξ-potential) have the structure:

• application of *neutral* HDMR:

$$\{[R(COOH)_2]_m\, n(R(COO^-)_2)\, (2n/3)\, Al(H_2O)_6^{3+}\}^0, \quad (7)$$

$$\{[R(COOH)_2]_m\, n(R(COO^-)_2)\, nAl(H_2O)_5(OH)^{2+}\}^0, \quad (8)$$

$$\{[R(COOH)_2]_m\, n(R(COO^-)_2)\, 2nAl(H_2O)_4(OH)_2^{+}\}^0, \quad (9)$$

• application of *high-resin* HDMR:

$$\{[R(COOH)_2]_s\, t(R(COO^-)_2)\, f(NH_2–R^{IV}–COO^-)\, ((2t + f)/3)\, Al(H_2O)_6^{3+}\}^0, \quad (10)$$

$$\{[R(COOH_2]_s\, t(R(COO^-)_2)\, f(NH_2–R^{IV}–COO^-)((2t + f)/2)\, Al(H_2O)_5(OH)^{2+}\}^0, \quad (11)$$

$$\{[R(COOH)_2]_s\, t\, ((RCOO^-)_2)\, f(NH_2–R^{IV}–COO^-)(2t + f)\, Al(H_2O)_4(OH)_2^{+}\}^0. \quad (12)$$

Peptized particles have a structure:

• application of *neutral* HDMR:

$$\{[R(COOH)_2]_m\ n(R(COO^-)_2)\ (2n + z)/3)Al(H_2O)_6^{3+}\ ((z - x)/2)\times \times SO_4^{2-}\}^{+x}\ (x/2)\ SO_4^{2-}, \quad (13)$$

• application of *high-resin* HDMR:

$$\{[R(COOH)_2]_q\ s(R(COO^-)_2)\ t(NH_2–R^{IV}–COO^-)((2/3)s + + (1/3)t + y)Al(H_2O)_6^{3+}\cdot(3y/2 – a)\ SO_4^{2-}\}^{+2a}\ a\ SO_4^{2-}. \quad (14)$$

Coagulum which formed coagulates *in the second area of rapid coagulation*, have the structure:

• application of *neutral* HDMR:

$$\{[R(COOH)_2]_m\ n(R(COO^-)_2)(2n/3 + x)\ Al(H_2O)_6^{3+}\ 3x/2\ SO_4^{2-}\}^0, \quad (15)$$

$$\{[R(COOH)_2]_m\ n(R(COO^-)_2)(n + y)\ Al(H_2O)_5(OH)^{2+}\ y\ SO_4^{2-}\}^0, \quad (16)$$

$$\{[R(COOH)_2]_m\ n\ (R(COO^-)_2)\ (2n + z)\ Al(H_2O)_4(OH)_2^+\ z/2\ SO_4^{2-}\}^0, \quad (17)$$

• application of *high-resin* HDMR:

$$\{[R(COOH)_2]_s\ t(R(COO^-)_2)\ f(NH_2–R^{IV}–COO^-)\ ((2/3)t + (1/3)f + a)\times \times\ Al(H_2O)_6^{3+}\ (3/2)\ a\ SO_4^{2-}\}^0, \quad (18)$$

$$\{[R(COOH)_2]_s\ t\ (R(COO^-)_2)\ f\ (NH_2–R^{IV}–COO^-)\ (t + (1/2)f + b)\times \times\ Al(H_2O)_5(OH)^{2+}\ b\ SO_4^{2-}\}^0, \quad (19)$$

$$\{[R(COOH)_2]_s\ t\ (R(COO^-)_2)\ f\ (NH_2–R^{IV}–COO^-)\ (2t + f + c)\times \times\ Al(H_2O)_4(OH)_2^+\ c/2\ SO_4^{2-}\}^0. \quad (20)$$

The research revealed that the structure of the peptized particles differs from that of coagulum in the content in the adsorption and diffusion layers of ions $Al(H_2O)_6^{3+}$, $Al(H_2O)_5(OH)^{2+}$, $Al(H_2O)_4(OH)_2^+$ and SO_4^{2-}. The peptized particles have the structure (13) and (14) when sizing the paper and paperboard with neutral and high-resin HDMR respectively.

The peptized particles as shown in Table 5, are finely-dispersed ($d_p \approx d_o$) and positively charged (ξ-potential is in the range of +22 to +37 millivolts (mV).

The values of the ξ-potential of peptized particles depend on the type and amount of potential-determining ions in the adsorption layer. It has been established that the optimal content of peptizing cations $Al(H_2O)_6^{3+}$ is $3.19\cdot10^{-3}$ and $7.88\cdot10^{-4}$ mol/l in sizing paper and paperboard with neutral and high-resin HDMR respectively.

The specific interaction energy of peptized particles ($–U(h_0)$) does not exceed 10 mJ/m^2 (Table 6), does not contradict the modern theory of DLFO [12–14] and the data obtained by a research team led by E.D. Shchukin [15]

[p. 292–293] for the other types of peptized particles (formed from sodium alkyl sulphonate, and the methylated aerosil and propyl alcohol). The following symbols are used in Table 6: h_o·– distance between the particles, m; n_a·– concentration of the particles of the dispersed phase in an aggregated state,%; n_p·– concentration of the particles if the dispersed phase in a peptized state, %.

Table 5

The properties of the peptized particles depending on the kind of HDMR

Таблица 5

Свойства пептизированных частиц в зависимости от вида ГМК

Type of HDMR (hydro-dispersion of modified rosin)	Properties of peptized particles	
	d_p, nm	ξ-potential, mV
Neutral hydro-dispersion TORM (d_o = 190 nm)	190	from +27 to +30
Neutral hydro-dispersion TORMHA-2 (d_o = 175 nm)	175	from +22 to +25
Neutral hydro-dispersion ORM (d_o = 196 nm)	196	from +22 to +25
High-resin hydro-dispersion TORMHA-2N (d_o = 180 nm)	180	from +30 to +35
High-resin hydro-dispersion TORMAA-3N (d_o = 185 nm)	185	from +32 to +37
High-resin hydro-dispersion Sacocell-309 (d_o = 216 nm)	216	from +28 to +32

Table 6

The influence of pH of the electrolyte solution on a specific interaction energy of peptized particles ($–U(h_0)$)

Таблица 6

Влияние pH раствора электролита на удельную энергию взаимодействия пептизированных частиц ($–U(h_0)$)

pH of electrolyte solution (S_{el})	$h_o \cdot 10^{-10}$, m	$n_a \cdot 10^{-2}$, %	$n_p \cdot 10^{-2}$, %	$–U(h_0)$, mJ/m^2
1,95	2,00	0,22	1,78	10,33
2,70	2,80	0,17	1,83	12,90
3,50	2,95	0,15	1,85	13,98
3,75	3,21	0,12	1,88	14,56
4,30	3,32	0,10	1,90	16,37
5,30	3,44	0,06	1,94	17,92
6,80	4,05	0,88	1,12	20,98

The following facts indicate the course of the process of peptization of coagulates: first, the rate of coagulation of HDMR decreases from the maximum values of W_{max} to zero (W = 0); secondly, the average/median diameter (d_p) of the peptized particles is minimal and with a certain content of the electrolyte (S_{el}) and aluminium hydroxo-compounds (AHC) forms in the dispersed system the condition $d_p \approx d_o$ is met.

The microphotographs of pulp (Figure 2) indicate that, when it is sized with high-resin hydro-dispersion TORMHA-2N (flow rate 1.5% abs. dry. fibers) in the mode of homo-coagulation (a) coarsely-dispersed coagulates and those of different sizes are formed. However, the peptization of coagulates provides sizing complexes in the form of finely-dispersed particles (*b*).

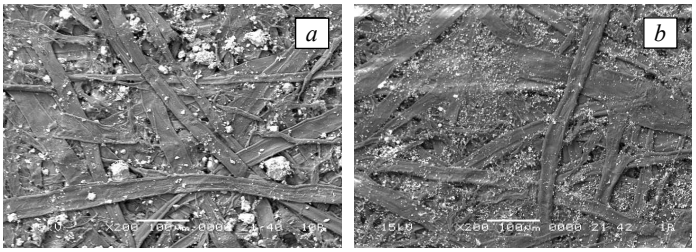

Figure 2. Micrographs of the paper pulp sized in the mode of homo-coagulation (*a*) and hetero-adagulation (*b*)
Рис. 2. Микрофотографии бумажной массы, проклеенной в режимах гомокоагуляции (*а*) и гетероадагуляции (*б*)

Paper and paperboard made of pulp with a sizing in acidic (pH 4.8–5.2) and neutral (pH 6.5–7.2) environments in the mode of hetero-adagulation of peptized particles, possess a high water repellency and durability.

Table 7

The quality of paper made from pulp with sizing in the modes of homo-coagulation (existing technology) and hetero-adagulation of peptized particles (developed technology)

Таблица 7

Качество бумаги, полученной из бумажной массы с проклейкой в режимах гомокоагуляции (существующая технология) и гетероадагуляции пептизированных частиц (разработанная технология)

Indicator	Indicator value	
	Existing/current technology	Developed technology
Size of gluing complexes, nm	3500–4500	180–250
Type of sizing complexes	Coagulates	Peptized particles
ξ-potential, mV	from –10 to +10	from +35 to +50
Mode of sizing paper pulp	Homo-coagulation	Hetero-adagulation
Degree of sizing according to the barcode method, mm	1.6	2.4
Absorbency at unilateral wetting, g/m^2	18–22	10–12
Stress at break, H	64–67	86–90
Tensile strength, kN/m	4.2–4.4	5.3–5.5
Breaking length, m	5700–6000	7600–7800

The data on the use of high-resin hydro-dispersion TORMHA-2N for paper sizing according to the existing/current (homo-coagulation) and developed (hetero-adagulation) technologies are given as examples in Table 7.

As it follows from Table 7, the sizing complexes differ in dispersion and electro-kinetic potential. Finely-dispersed peptized particles having ξ-potential ranging from +35 to +50 mV and the size of which does not exceed 250 can be uniformly distributed and firmly fixed on the surface of the fibers. This results in high values of hydrophobic quality indicators: the degree of sizing paper according to the barcode method is 2.4 mm and its absorbency at unilateral wetting is not more than 12 g/m^2. In this case the original maximum strength of a paper sheet is retained.

The comparative analysis of the data provided in Table 7 indicates, on the one hand, the advantages in the gluing process in the developed mode of hetero-adagulation of peptized particles over the traditional sizing process in the mode of homo-coagulation and, on the other hand, the advisability to reduce costs of the HDMR by 30–40% and the electrolyte by 1.5–2.0 times, which indicates the creation of a resource-saving technology for glued types of paper and cardboard.

The developed technology of sizing paper and cardboard in the mode of hetero-adagulation of peptized particles after testing in an industrial environment has been implemented on five paper and cardboard factories. 35 kinds of paper and cardboard, differing in requirements for their quality and field of application have been produced. Various types of fibrous materials were used for their production. Neutral and high-resin HDMR were used for sizing pulp and wastepaper suspensions having a degree of grinding 30–55 ShR, or the compositions obtained from them. The small introduction into the pulp containing the particles of the dispersed phase of HDMR, the required amount of electrolyte solution (aluminum sulphate) enabled first (after the first portion) in the first area of rapid coagulation of HDMR to obtain peptizing coagulates, and then (after the second portions) to ensure their peptization with the obtaining of new sizing complexes in the form of finely-dispersed positively charged particles. The industrial tests of the developed technology have shown that the total flow of the electrolyte inputted from the first (in the machine pool) and the second (in the mixing pump) by portions 1.5–2.0 times less then the flow rate of the electrolyte that is added to the pulp according to the existing technology. The increasing of the retention degree of sizing complexes in the structure of paper and cardboard from 58–65 to 89–94% due to the uniform distribution of the monolayer and firm fixation of peptized particles on the fiber surface can reduce the consumption of the HDMR by 30–40%, which has an important techno-economic and environmental value.

Conclusion. Thus, the developed technology to ensure the peptization coagulates formed in the first area of rapid coagulation of neutral and high-resin HDMR, enables to obtain new sizing systems in the form of finely-dispersed positively charged peptized particles. Hexa aqua aluminium ions $Al(H_2O)_6^{3+}$

have a peptizing effect on the coagulates. The structure of peptized particles differs from that of coagulums in the content of ions $Al(H_2O)_6^{3+}$, $Al(H_2O)_5(OH)^{2+}$, $Al(H_2O)_4(OH)_2^{+}$ и SO_4^{2-} in the adsorption and diffusion layers. The implementation of the developed resource-saving technology at five paper and paperboard enterprises confirmed the results of the research and demonstrates the feasibility of economy in the production of each ton of paper and cardboard up to 30–40% of hydro-dispersion of modified rosin and reduce the electrolyte consumption by 1.5–2.0 times.

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Получено 27.02.2017

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СОЗДАНИЕ И ВНЕДРЕНИЕ РЕСУРСОСБЕРЕГАЮЩЕЙ ТЕХНОЛОГИИ ПРОКЛЕЙКИ БУМАГИ И КАРТОНА ГИДРОДИСПЕРСИЯМИ МОДИФИЦИРОВАННОЙ КАНИФОЛИ В РЕЖИМЕ ГЕТЕРОАДАГУЛЯЦИИ ПЕПТИЗИРОВАННЫХ ЧАСТИЦ

Изучены особенности применения гидродисперсий модифицированной канифоли (ГМК) в дисперсных системах и разработан технологический режим повышения гидрофобности и прочности бумаги и картона. Показана необходимость управления процессами электролитной коагуляции ГМК и пептизации коагулятов путем изменения содержания в дисперсной системе кон-

кретного вида гидроксосоединений алюминия (Al(H2O)63+, Al(H2O)5(OH)2+, Al(H2O)4(OH)2+, Al(H2O)3(OH)30 и Al(H2O)2(OH)4-). Предложенный принципиально новый технологический прием позволяет получить новые проклеивающие комплексы в виде мелкодисперсных (размер 180–220 нм) положительно заряженных (заряд от +22 до +30 мВ) пептизированных частиц. Такие частицы способны равномерно распределяться монослоем и прочно фиксироваться на поверхности отрицательно заряженных целлюлозных волокон, что способствует протеканию процесса гидрофобизации в более эффективном режиме гетероадагуляции. Этот эффект достигается за счет пептизации (дезагрегирования) электронейтральных коагулятов (размер не более 1800 нм), образовавшихся в первой области коагуляции ГМК, в то время как по существующей технологии роль проклеивающих комплексов выполняют электронейтральные коагуляты (размер 2000–3800 нм и более), образующиеся во второй области коагуляции ГМК.

Разработанная технология для обеспечения пептизации коагулятов, образовавшихся в первой области быстрой коагуляции нейтрального и высокомолекулярного ГМК, позволяет получать новые системы в виде мелкодисперсных положительно заряженных пептизированных частиц. Алюминиевые ионы Hexa aqua Al(H2O)63+ оказывают пептизирующее действие на коагуляты. Структура пептизированных частиц отличается от структуры коагулятов содержанием ионов Al(H2O)63+, Al(H2O)5(OH)2+, Al(H2O)4(OH)2+ и SO42- в адсорбционном и диффузионном слоях. Внедрение разработанной ресурсосберегающей технологии на пяти предприятиях по производству бумаги и картона подтвердило результаты исследования и продемонстрировало возможность экономии при производстве каждой тонны бумаги и картона до 30-40% ГМК и уменьшить потребление электролита в 1,5–2,0 раза.

Ключевые слова: технология бумаги, гидродисперсии модифицированной канифоли, пептизированные частицы, гетероадагуляция.

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