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NEW POLYMERS SYNTHESIS BASED ON RESIN ACIDS AMIDES FOR WASTE PAPER HARDENING

Strengthening effect on the kinds of junk paper provides nitrogen poly-measures based on amides of resin acids. Conditions developed modification of resin acids and polycondensation of adipic acid with a polyamine allow to obtain a polymer with an acid number of 20–30 mg KOH/g and infinitely miscible with water. The resulting polymer of the physico-chemical properties and hardening effect is not inferior to the best imported counterpart Melapret PAE/A.

Introduction. At the present stage pulp and paper industry is characterized by increased consumption of secondary semi-finished goods for the manufacture of paper and cardboard. This allows to significantly reduce material and energy costs, as well as to recover some production and consumption wastes.

It is known that recycled fibers possess reduced papermaking properties, this reduction progressing due to a cycling use of waste paper. The main reasons for the decrease of hardness indexes are hornification of fibre surface layers during contact drying; polysaccharide thermal destruction; fibre destruction during defibering and pulp beating; and the presence of non-fibrous inclusions caused by intensive use of different kinds of auxiliary chemicals [1]. Consequently, the hardening of waste paper and cardboard is an urgent problem facing the pulp and paper industry of the Republic of Belarus. The most effective way to solve this problem is the use of hardening polymer additives in the composition of paper and cardboard. A variety of different high molecular weight compounds (natural and synthetic) act as such substances in paper technology. In our country, for the manufacture of paper and cardboard very costly imported hardening additives are used, that is why the necessity of developing our own additives is urgent.

Recently a wide range of hardening agents based on acrylamide copolymers, and epichlorohydrin modified polyamines and polyamides etc. is widely used. However, in spite of minor expenses for the production of such functional additives, the material costs of their using in paper composition to achieve the desired complex of physico-mechanical properties are very high.

Main part. The purpose of research is to develop techniques and conditions for the synthesis of new nitrogen-containing polymer on the basis of resin acids amides and a polyamine polycondensation product with hexane diacid, the application of which will compensate the loss of paper and cardboard strength in their manufacture based on recycled fibrous raw materials.

High molecular weight compounds used for paper and cardboard hardening should have a relatively high molecular weight, contain amido- and amino groups capable of forming a hydrogen bond with the hydroxyl groups of cellulose macromolecules, and possess good solubility in water.

For this reason, we have developed a technique for the synthesis of new nitrogen-containing polymers based on resin acids amides.

As a raw material for a new nitrogen-containing polymer we used resin acids (abietic and dehydroabietic acids or their mixture – oleoresin and tall oil rosin), polyamine (diethylenetriamine (DETA), triethylene tetramine (TETA)), and hexane diacid. Monitoring of the nitrogen-containing polymer manufacture at each stage of the synthesis was carried out by the acid number.

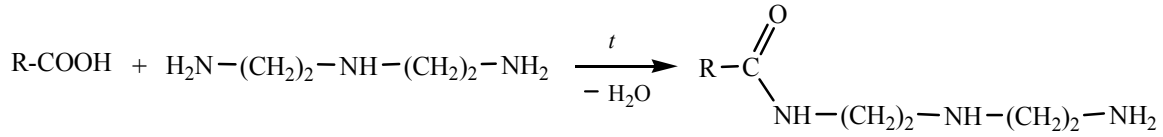
Chemistry stages of nitrogen-containing polymer formation on the amide-based resin acids is represented in the figure below.

Synthesis of a new nitrogen-containing polymer was carried out in two stages.

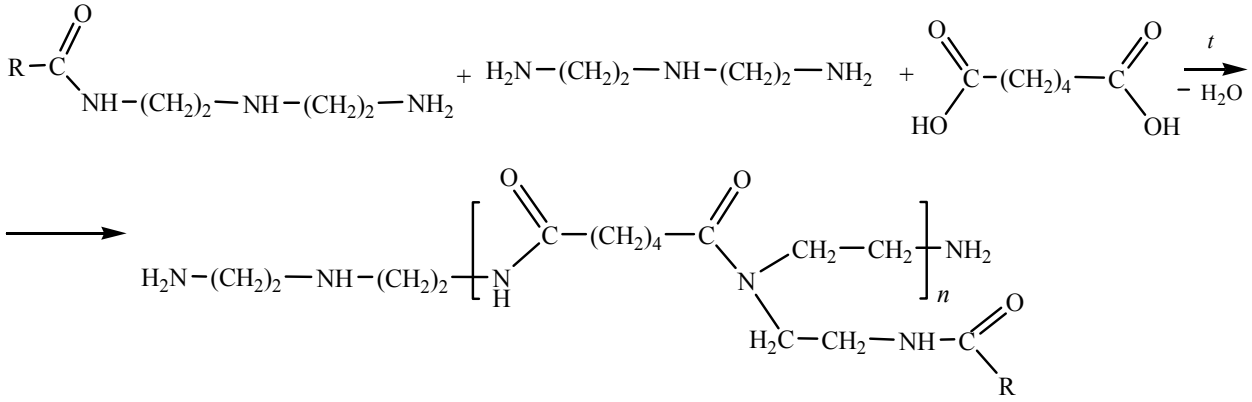
Stage 1. A 250 cm^3 three-necked flask, equipped with a stirrer, a thermometer and a Dean-Stark trap was charged with a sample of resin acids and added by 1/3 of the required amount of polyamine, the ratio being 1.0 mole of polyamine to 0.05–0.15 moles of resin acid. Then, under constant stirring, the reaction mixture was heated to a temperature 170–190ºC. The mixture was kept under constant stirring up to the acid number 20–30 mg KOH/g. The fullest interaction between polyamine and resin acid followed by the formation of monoaminoamides proceeded under these conditions.

Stage 2. Resin acid amide (formed during the 1-st stage) was added with the remaining amount of polyamine and equimolar dose of hexane diacid, which ensures the formation of high molecular weight, water soluble polyamide resin having improved hardening and hydrophobic properties. The duration of the second condensation stage was about 2.0 h at a temperature 160–200ºC.

Stage 1. Resin acids amides formation



Stage 2. Resin acids polyaminoamides formation



where R – resin acid residue

Chemistry stages of nitrogen-containing polymer formation on the amide-based resin acids

Synthesis was carried out with constant stirring at a temperature 210°C, defining the acid number of the reaction mass every 0.5 h. On reaching the acid number (20 ± 5) mg KOH/g, the reaction mass temperature was lowered to 85–95ºC, whereupon the estimated amount of water was added, the temperature of water being 90°C.

The above technique was used to manufacture a number of nitrogen-containing polymers, the synthesis conditions are given in Table 1. The synthesized nitrogen-containing polymers are light brown substances miscible with water with no limit.

It can be assumed that a large number of reactive amido and amino groups in the nitrogen-containing polymer composition will contribute to a fiber-to-fiber type bonding due to the formation of additional hydrogen bonds between the polymer amide groups and the hydroxyl groups of cellulose fibres macromolecules. The presence of resin acids residues will promote hydrophobization of the paper web.

Paper samples and elemental cardboard layers were produced using a sheet making apparatus Rapid-Ketten (firm Ernst Haage, Germany).

Table 1

Conditions for obtaining nitrogen-containing polymers based on resin acids amides

Polymer sample number	Reagents ratio, mole			Polyamine type	Resin acid type	Reaction time, h		Reaction temperature, °C	
	polyamine	adipic acid	resin acid			1-st stage	2-nd stage	1-st stage	2-nd stage
1	1.0	1.0	0.10	DETA	AA	2.0	2.0	180	190
2	1.0	1.0	0.10	DETA	DAA	2.0	2.0	180	190
3	1.0	1.0	0.10	DETA	OR	2.0	2.0	180	160
4	1.0	0.95	0.12	TETA	AA	2.0	2.0	190	170
5	1.0	0.90	0.05	DETA	OR	2.0	2.0	190	200
6	1.0	1.1	0.15	TETA	OR	2.0	2.0	170	200
7	1.0	1.0	0.10	TETA	TOR	1.5	2.0	170	190
8	1.0	1.0	0.10	DETA	TOR	2.5	2.0	190	180

Notes: DETA – diethylenetriamine, TETA – triethylenetetramine, AA – abietic acid, DAA – dehydroabietic acid, OR – oleoresin rosin, TOR – tall oil rosin.

Table 2

Properties of nitrogen-containing polymers and paper samples

Polymer sample number	Polymer properties		Paper sample properties		
	relative viscosity, s	polyamide resin consumption, %	breaking length, m	stroke method sizing degree, mm	wet strength, %
1	70	0.2	5050	2.2	8.4
2	60	0.2	4850	2.4	7.2
3	100	0.2	4900	2.2	6.1
4	43	0.2	4800	2.2	5.5
5	65	0.2	4700	2.2	5.0
6	110	0.2	4750	2.2	5.8
7	70	0.2	4900	2.4	6.5
8	75	0.2	4850	2.2	6.5
Melapret	120	0.2	4650	2.0	4.8

Fibrous slurry preparation was performed as follows. 1% fibrous slurry was prepared by defibering and pulp beating. Cellulose defibering was carried out in a BM-3 disintegrator where 1500 sm^3 of water and 22 g of bone dry substance (a. d. s.) were charged in series. The duration of defibering was 7–8 min. Thereafter, the defibered mass was transferred to a laboratory roll bath, the beating rate being 30–40° SR. After completion of beating, a sample of fibrous slurry was taken for the manufacture of paper samples and elemental cardboard layers weighing 80 g/m^2.

Hardening effect of a synthesized nitrogen-containing polymer was compared to that of imported functional additive Melapret PAE/A, which is a polyamide-amine of epichlorohydrin resin and is widely used at paper and cardboard enterprises in the Republic of Belarus and abroad. Therefore, breaking length, stroke method sizing degree and wet strength were determined for test and reference samples. Properties of a nitrogen-containing polymer and paper samples are shown in Table 2.

As is seen from Table 2, paper samples on the basis of resin acids amides developed at our Department possess higher wet strength in comparison with the imported analogue Melapret PAE/A. Other quality indicators, such as breaking length and stroke method sizing degree have comparable consumption parameters of a nitrogen-containing polymer, 2.0% by weight of a. d. s.

Conclusion. Nitrogen-containing polymer on the resin acids amides basis has a hardening effect on waste paper types. It is shown that the developed resin acids modification conditions and hexane diacid polycondensation with polyamine make it possible to manufacture a polymer with the acid number 20–30 mg KOH/g, which is miscible with water with no limit. The polymer obtained is equal in its physical and chemical properties and hardening effect to the best imported analog Melapret PAE/A.

References

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