FOLIA FORESTALIA POLONICA Seria B, zeszyt 26, 1995

POSSIBILITY OF PAPER SIZING WITH ROSIN GLUES IN NEUTRAL MEDIUM

by Jan Mosio-Mosiewski ¹, Ryszard Babicki ²

The Heavy Organic Synthesis Institute at Kędzierzyn-Koźle¹ The Wood Technology Institute in Poznań²

Three kinds of papermakers' glues were made basing on modified rosin and the research was conducted to use them for paper-pulp sizing particularly in the medium close to neutral.

INTRODUCTION

In the world there is a growing interest in papermakers' glues enabling to size the paper-pulp in a slightly acid or even slightly alkaline medium. Sizing in the medium close to neutral results in lower corrosivity of the paper-making machine, improves paper age-resistance, allows to reduce the consumption of aluminium sulphate commonly used as a coagulant, and finally makes it possible to use chalk as a filler. This paper presents types of the most commonly used papermakers' glues and their general characteristics. It contains results of research made on sizing the paper-pulp with the use of rosin glues obtained by the authors and characterized by higher sizing efficiency in the medium close to natural.

CHARACTERISTICS OF PAPERMAKERS' GLUES

Different kinds of papermakers' glues are used for sizing of paper. Considering the kind of basic material; those glues can be numbered among the class of rosin or synthetic glues. Rosin glues can be divided into sizes made from common rosin and the so called supported glues made from modified rosin [7].

Such modification aims at the reduction of its crystallisability as well as the improvement of physical and chemical properties. Most often used modifiers are α, β - unsaturated diacarbonyl compounds, e.g. maleic anhydride, fumaric acid [4, 5, 11] and formaldehyde [3, 6]. Thus modified rosin can be used for the production of saponified glues as well as dispersive glues. Production of saponified glues is a simple operation since it consists in converting resin acids into salts by means of alkaline water solutions. Unfortunately, the growth of rosin modification degree is accompanied by the growing consumption of coagulant, mainly aluminium sulfate, used in the sizing process.

It was found, that saponified glues are most effective if the sizing process is carried out at pH = 4.5 [9, 10]. The necessary amount of aluminium sulfate added to the paper-pulp mainly depends on the glue portion and the degree of rosin modification, and varies between 0.5 and 1.5%. with reference to the dry fibrous pulp. When the pH value grows then paper sizing is less effective, and if the pH value is close to 7, then even multiplied portion of glue does not give the required degree of sizing. In the respect dispersive glues are much better. They are obtained by way of dispergation of melted resin in water in the presence of protective colloids and stabilizers. During their production process, you can face the problem connected with selection of the effective protection enabling to obtain and stabilize fine-dispersive colloidal system, and with defining the optimum dispergation temperature range. The use of dispersive resin glues makes it possible to size paper effectively at pH - 5.0-5.5 [10] with much smaller quantities of aluminium sulfate. Due to the introduction of cation dispersing agents and the use of rosin partially esterified with polyhydric alcohols, it was possible to widen the pH range of paper-pulp during the sizing process. Thus obtained glues are characterized by high sizing effectiveness in the neutral medium, i.e. at pH - 7.0-7.5 [1, 10]. Considerable influence on the degree of paper sizing and retention of fillers have retention agents [2]. It should be noted, however, that the use of costly auxiliaries and higher capital costs connected with building of process installation, make dispersive glues more expensive than the saponified ones.

Efforts undertaken to size paper with saponified glues in the alkaline medium in the presence of sodium aluminate have not resulted in spreading that method on the industrial scale. More importance is given to synthetic glues in the form of alkyloketene dimmers and alkyl derivatives of succinic anhydride as they can be used for paper sizing in the alkaline or neutral medium to get a product of higher moisture resistance and fastness to different liquids. Those glues, however, show definite imperfections, namely, the glue made from succinic anhydride hydrolyzes in the presence of water and precipitates deposits, and the complete sizing of paper with alkyloketene glue is obtained only after a given time of storage [8]. Within this research three kinds of papermakers' glues were prepared basing on the modified rosin and investigations were made to check their application for paper-pulp sizing, particularly in the medium close to neutral.

RESEARCH METHODS

Three kinds of rosin glues were made, namely, dispersive glue, modified saponified glue and standard supported saponified glue as a comparative glue. The dispersive glue was made from thallic rosin modified with maleic anhydride (6%) and paraformaldehyde (2%). The colloid mill was filled with 70.0 g of rosin, 2.5 g of refined montan wax and 20.0 g of paraffin and heated to the temp. 100 °C. Next, to the mill, intensively mixed, 40.0 g of water solution containing 1.7 g of casein and 5.0 g of triethanolamine was added. After diluting with cold water, 30% glue was obtained. The modified saponified glue was obtained from thallic rosin, subjected to chemical changes consisting in its partial decarboxylation, and bringing definite amount of ester groups into the structure of resin acids. Rosin modification method will be a subject of patent application. The resin obtained was saponified at a temp. 100°C with NaOH water solution to give a glue of 50% concentration and 15 mg KOH/g acid value.

The comparative saponified glue was obtained from thallic rosin which was modified with 6% at maleic anhydride and 2% of paraformaldehyde. The rosin was saponified at a temp. 100°C with NaOH water solution to give the glue of 50% concentration and 15 mg KOH/g acid value.

Glue effectiveness was tested on paper which recipe corresponded to that of offset paper, using fibrous pulp containing 75% of bleached birch cellulose and 25% of bleached pine cellulose. The paper pulp was beaten to reach 27°SR.

In case of loaded paper, the cellulose pulp was mixed with kaolin in weight ratio of 3:1. The retention agent was added to the paper pulp as the last constituent. Those tests aimed at:

- a) determination of pH effect on the degree of paper sizing made by three kinds of glues.
- b) learning the effect of adding the selected retention agent and the filler on the degree of paper sizing with dispersive glue.
- c) determination of the effect of the filler and portions of dispersive glue and retention agent on paper resistance properties.

The sizing process was conducted at pH - 5.5. Polymin SK was used as the retention agent, and aluminium sulfate - as the coagulant.

DISCUSSION

Fig. 1 presents the effect of paper-pulp on the degree of paper sizing in case of standard saponified glue, dispersive glue and modified saponified glue. The curve 1 shows that the standard saponified glue effectively sizes the paper to pH - 4.2. With the growth of pH value, sizing effectiveness dramatically declines. The use of dispersive glue widens optimum range of glue application up to 5.5 pH, and after exceeding that value, the degree of sizing slightly deteriorates (curve 2). The curve 3 has an interesting characteristics corresponding to the rosin saponified glue obtained from the rosin modified as per

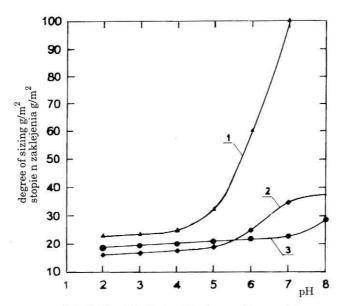


Fig. 1. The pH effect on the degree of paper sizing
1. saponified glue, 2. dispersive glue, 3. modified saponified glue
Rys. 1. Wpływ pH na stopień zaklejenia papieru
1. klej zmydlony, 2. klej dyspersyjny, 3. klej zmydlony, zmodyfikowany

the authors' original recipe. This glue is effective in the whole range of acid medium, and even in the slightly alkaline medium, as a result of partial decarboxylation and bringing ester and ether groups into the structure of resin acids.

Fig. 2 shows changes in softening point and acid number proceeding as a consequence of catalytic decarboxylation conducted at a temp. 230°C. Thus obtained alicyclic hydrocarbons increase the water-repellent properties of rosin, whereas oxygen bonds present in the modified rosin make it possible to create coordinate bonds with products of aluminium sulfate hydrolysis formed in the medium close to neutral, which is the condition of the proper course of the sizing process.

The effect of the retention agent portion on the degree of paper sizing and ash contents has been shown in Fig. 3. Increasing the portion of Polymin SK to 0.06% causes big rise in the degree of paper sizing and ash content, whereas further addition of the retention agent does not result in any distinct changes. Therefore, in case of use of the dispersive glue it is advisable to add the retention agent to the paper pulp.

Through the selection of proper ratio: dispersive glue retention agent it is possible to obtain well-sized paper of high filler content in the slightly-acid medium.

Table 1 compares properties of paper made while using different portions of dispersive glue and retention agent. In case of unloaded paper, its sizing improves with the increase of amount of glue and retention agent. The effect

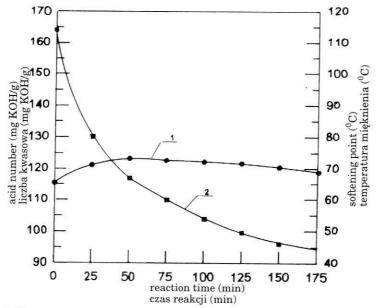


Fig. 2. Changes in properties of decarboxylated rosin depending on the reaction time
1. softening point, 2. acid number
Rys. 2. Zmiany właściwości dekarboksylowanej kalafonii od czasu reakcji

1. temperatura mięknienia, 2. liczba kwasowa

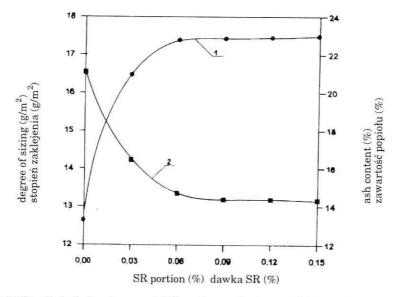


Fig. 3. The effect of retension agent (SR) portion on the degree of sizing and ash content in the paper

1. ash content, 2. degree of sizing

Rys. 3. Wpływ dawki środka retencyjnego (SR) na stopień zaklejenie i zawartości popiołu w pa-

Table 1 Tabela 1

Właściwości papierów zaklejonych klejem dyspersyjnym (nie wypełnionych N i wypełnionych W) w obecności zmiennej ilości środka retencyjnego (SR) Properties of paper sized with dispersive glue (unloaded N and loaded W) in the presence of the retention agent (SR)

Paper properties	Paper type				ÖĞ	Glue portion (%) Dawka kleju (%)	%) %)			
Właściwości papieru	Typ papieru		1.0			2.0			3.0	
		W.C	SR portion (%) dawka SR (%)	6) 0)	<i>8</i> . 0	SR portion (%) dawka SR (%)	69	or o	SR portion (%) dawka SR (%)	~ ~
		0.00	0.05	0.10	0.00	0.02	0.10	0.00	0.05	0.10
Degree of sizing (g/m²) Stopień zaklejenia (g/m²)	≯z	17.6	16.8 15.3	- 16,8 14.7	17.0	16.5 13.8	15.8	15.1 14.9	14.7	14.2
Breaking length (km) Samozerwalność podłużna (km)	3 z	12.3 7.9	11.6	11.3 5.6	11.9	11.0	10.7 5.3	11.4	10.3 5.3	10.3
Burst (kPa) Przepuklenie (kPa)	≥z	276.1 158.2	276.2	266.2 108.3	276.3 158.5	266.6 108.8	256.1 99.1	266.7 157.9	247.7 99.2	227.8 99.3
Relative tear (mN) Przedarcie względne (mN)	≥ z	810.0 897.8	889.9 818.9	881.1 818.9	854.4 883.1	892.9 813.0	898.8 804.1	885.0 815.0	907.7 754.8	908.7 703.5
Ash content (%) Zawartość popiołu	W	12.9	23.6	23.9	13.1	22.7	22.8	13.3	22.5	22.6

of the retention agent on sizing is much bigger in case of the loaded paper. It was found that while using the dispersive glue under research, the loaded paper had better sizing than unloaded one made in a similar way. Breaking length and burst mainly depend on paper loading, and much less on the amount of glue. The presence of the retention agent is of bigger importance. In case of unfilled papers, tear strength improves with the increase of the glue portion and in the presence of the retention agent, whereas in case of loaded paper those agents cause a certain change of this properly for the worse.

Bringing 0.06% of the retention agent into the paper pulp causes almost double increase of the filler amount in the paper. It disadvantageously effects the paper strength, particularly lowers its burst and self-breaking properties.

Received in June 1995

6. REFERENCES

- 1. G a z i ń s k i J.: Sacocell 309, dyspersja zmodyfikowanej kalafonii jako środek do zaklejania papieru w masie, zarówno w środowisku kwaśnym jak i neutralnym. Materiały z Sympozjum "Środki chemiczne w papiernictwie". Łódź Arturówek (1994).
- 2. Hechler E.: Neutralleimungen mit einem neuentwickelten Leimungsmittel. Papier 1985, 2, 57-65.
- 3. Opherden A., Schurig G.: Harzleimtypen und Hinweise zum kolophoniumsparenden Leimeinsatz in den Papierfabriken. Zellst. und Pap. 1985, 2, 69-71.
- Paderin W. Ja. i in.: Novyj kompozicionnyj klej pasta na osnove kanifoli tallovoj i EMO. Gidroliz. i lesochem. prom. 1989, 5, 21-22.
- 5. Patent RFN No 0018007(1980). German patent.
- 6. Patent USA No 4404034(1983). USA patent.
- 7. Przybysz K.: Technologia celulozy i papieru. Technologia papieru 2. Wydawnictwa Szkolne i Pedagogiczne. Warszawa 1983.
- 8. Riebeling H. U., Auhorn W. J.: Syntetische Massleimungsmittel Einflussgrössen und Grenzen. Woch. f. Papierfabr. 1987, 22, 1006-1013.
- 9. Ronge H.: Harzleimung in Gegenwert von Kreide. Woch. f. Papierfabr. 1984, 5, 147-149.
- Rostek P. C., Wortley B. H.: Coping with Carbonate: Neutral pH rosin sizing. Pulp and Paper Canada. 1991, 6, 60-61.
- 11. S i w e k K., R e y m a n n P i e c h o t a E.: Wpływ sposobu modyfikacji żywicy lub kalafonii oraz warunków ich zmydlania na właściwości otrzymanych, wzmocnionych klejów papierniczych. Prace Inst. Technol. Drewna Poznań. 1980, 3/4, 66-97.
- 12. Sturmer L., Poppel G.: Papierleimung mit Harzdispersionen im neutralen pH Bereich. Woch. f. Papierfabr. 1983, 19, 713-715.

MOŻLIWOŚCI ZAKLEJANIA PAPIERU KLEJAMI KALAFONIOWYMI W ŚRODOWISKU OBOJĘTNYM

Streszczenie

Scharakteryzowano różne rodzaje klejów papierniczych z uwzględnieniem możliwości ich stosowania w środowisku obojętnym. Stwierdzono, że standardowy kalafoniowy klej zmydlony

wymaga środowiska silnie kwaśnego, a klej dyspersyjny sporządzony w oparciu o ten sam surowiec żywiczny środowiska słabo kwaśnego, przy czym korzystne jest oddziaływanie środka retencyjnego.

W wyniku modyfikacji kalafonii polegającej na jej częściowej dekarboksylacji i wprowadzeniu grup estrowych i eterowych można otrzymać kleje zmydlone efektywne w środowsku obojętnym.

Authors addresses: Prof. dr hab. Jan Mosio-Mosiewski Instytut Ciężkiej Syntezy Organicznej 47-225 Kędzierzyn-Koźle, ul. Energetyków 9

> Prof. dr hab. Ryszard Babicki Instytut Technologii Drewna 60-654 Poznań, ul. Winiarska 1