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RESEARCH ON GETTING SAPONIFIED ROSIN GLUES FOR PAPER SIZING IN THE NEAR-INERT MEDIUM

by Jan Mosio-Mosiewski[1] and Ryszard Babicki[2]

Heavy Organic Synthesis Institute, Kędzierzyn Koźle[1)]
Wood Technology Institute, Poznań[2)]

Research was done on the possibility of receiving saponified rosin glue with the purpose of paper-pulp sizing in the near-inert medium. Tall oil rosin was modified with ethylene oxide and maleic acid anhydride, and then saponified with sodium hydroxide solution.

Key words: tall oil rosin, rosin modification, saponified papermakers' glues, sizing in inert medium.

INTRODUCTION

For the production of saponified papermakers' glue most often tall oil rosin is used, modified with maleic acid anhydride, and sometimes, additionally, with paraformaldehyde (Paderin et al. 1989, European patent 1990; US patent 1983; Siwek and Reymann-Piechotta 1980). These glues can be used for paper-pulp sizing in the acid medium at pH = 4.5-5.0 (Charvat et al. 1982), which unlike alkaline medium, has a disadventageous effect on paper strength and endurance (Dąbrowski and Gonera 1995). For paper sizing in weak-acid medium, or even alkaline one, at pH = 5.0-7.5, dispersion glues are used, made of rosin modified with maleic acid anhydride and then partially estrified with polyhydric alcohols (Fallman, Piech and Spyra 1993, European patent 1988, Ronge 1984, Rostek and Wortley 1991). Dispersion glues, however, are more expensive than saponified glues and as water dispersing agents are not resistant to minus temperatures.

Therefore, efforts are made to widen the range of application of saponified glues to use them in neutral or even slightly alkaline medium. Methods which have been developed hitherto are grounded on replacing aluminium sulfate contained in standard glues with other flocculents. They have not found wider

application in the industrial practice (Charvat et al. 1982, Hechler 1985, Krkoška, Kučera and Klokočik 1981, European patent 1990, 1991, Ronge 1984).

The authors are of the opinion that the best solution is to prepare a formula for a saponified resin glue which in the presence of commonly used, cheap aluminium sulfate, would be able to size paper both in the acid medium and the near-neutral one. They made efforts to receive such a type of glues through the selection of proper way of rosin modification. The essence of the solution suggested consists in bringing double system of ester groups into the resin acid structure, and retaining the active carboxyl group. This method however, requires detailed investigation because of complex and variable chemical constitution of rosin.

The purpose of this work was to find out:

- whether the proposed rosin modification will result in getting the resin of properties enabling to obtain saponified papermakers' glue effective in the near-neutral medium,
- to what degree chemical constitution of rosin affects the properties of thus obtained papermakers' glues,
- if retention agents have an effect on paper sizing when using glues prepared according to the formula proposed.

EXPERIMENTS

The tests were carried out using three samples of tall rosin coming from three different tall oil batches manufactured in the Silesian Rafinery at Czechowice-Dziedzice. Content of resin acids, fatty acids and unsaponifiable substances was determined in the primary rosin samples. Physical and chemical properties of the rosin, i.e. softening point, acid value, saponification number and acid number were determined in compliance with binding standards. Chemical constitution of resin acids and fatty acids was examined using Perkin Elmer 900 gas chromatograph equipped with a flame ionization detector. The applied column was made of stainless steel, 1.8 m long and 2 mm in diameter filled with WAW chromosorb (60/80 mesh) and the 10% liquid phase of Silar 9 CP.

Chromatographic resolution took place at the programmable temperature of 140-260°C (8°C/min) and the argon flow rate of 25 cm^3/min. The temperature of the feeder and the detector was 270°C and 320 °C respectively.

Rosin samples were subjected to double-stage modification under identical conditions: first of all ethoxylation and then estrification by means of maleic acid anhydride.

Ethoxylation was carried out at a temp. 170 °C in the presence of sodium hydroxide as a catalyst. Estrification took place at a temp. 230 °C. During tests changes were made to the molar ratio of maleic anhydride (BM) and ethylene oxide (OK) within the following limits:

$$\frac{BM}{OK} = 0.5 \div 0.8$$

Saponification of thus obtained resins was carried out with the use of water solution of sodium hydroxide till well water-soluble glues of 50% dry matter content were received. The degree of paper sizing was determined by Cobb method forming sheets from the bleached kraft in the Rapid-Köthen apparatus. To size the paper pulp the 2% glue portion was added in relation to the fibrous pulp, adjusted to a dry matter basis. In selected samples, sizing was performed with the addition of 0.01% cationic or anionic retention agent (in relation to the dry fibrous pulp).

DISCUSSION OF RESULTS

Physical and chemical properties of rosin samples used for preparation of papermakers' glues were presented in table 1. The tested rosin samples slightly differed in their physical and chemical properties. Apart from the ester number, differences between particular values do not exceed 5% (table 1). However, they greatly varied in the chemical constitution (table 2). So big differences in their constitution referred to the content of fatty acids (2.89-9.63), resin acids (79.01-90.04%) oxy-acids (1.43-3.67%) and unsaponifiable compounds (3.40-9.93%).

Table 1
Tabela 1

Physical and chemical properties of tall oil rosin coming from different production batches
Właściwości fizyko-chemiczne kalafonii talowej z różnych szarż produkcyjnych

Rosin sample symbol Symbol próbki kalafonii	Rosin properties Właściwości kalafonii			
	Softening point Temperatura mięknienia (^{0}C)	Acid value Liczba kwasowa (mg KOH/g)	Saponification number Liczba zmydlenia (mg KOH/g)	Ester number Liczba estrowa (mg KOH/g)
KT-A	63.8	177.1	182.8	5.7
KT-B	64.1	172.7	182.7	10.0
KT-C	65.3	179.5	187.4	7.9

Table 3 presents physical and chemical properties of resins made as a result of modification of three rosin samples with identical amounts of ethylene oxide, followed by estrification with a variable amount of maleic acid anhydride. An increase in amount of the maleic acid anhydride used for rosin modification was accompanied by the slight growth of the softening point and the acid value. It should be mentioned that the applied method of modification resulted in receiving resins with softening point similar to that of the parent rosin (table 1) whereas their acid values were lower by about 40 mg KOH/g than for unmodified rosins. When rosin was modified with the same amounts of maleic

acid anhydride, without initial ethoxylation, obtained resins had their softening point about 10°C higher while their acid values were increased by about 10 mg KOH/g (Reymann-Piechota 1977). No differences were found in resin properties as a result of modification of three different rosin samples having different chemical constitution.

Table 2
Tabela 2

Chemical constitution of tall oil rosin coming from different production batches
Skład chemiczny kalafonii talowej z różnych szarż produkcyjnych

Constituents Składniki	Percentage on constituents in rosin symboled Zawartość składników (%) w kalafonii o symbolu		
	KT-A	KT-B	KT-C
Fatty acids including: Kwasy tłuszczowe, w tym:	2.89	4.42	9.63
palmitic acid palmitynowy	0.05	0.02	0.45
oleic acid olejowy	0.23	0.53	2.16
linoleic acid linolowy	0.50	0.41	1.51
linolenic acid linolenowy	0.03	0.98	1.23
arachidic acid arachidowy	2.08	2.53	4.28
Rosin acids including: Kwasy żywiczne, w tym:	90.04	85.92	79.01
pimaric acid pimarowy	8.62	1.40	1.55
sandarac pimaric acid sandarakopimarowy	3.32	2.29	3.30
isopimaric acid izopimarowy	8.82	9.95	5.81
levopimaric acid lewopimarowy	1.05	1.96	1.17
abietic acid abietynowy	32.66	38.40	25.97
dehydroabietic acid dehydroabietynowy	26.45	20.57	35.81
neoabietic acid neoabietynowy	2.51	4.56	0.04
other resin acids inne żywiczne	6.61	6.79	5.36
Unsaponificable compounds Związki niezmydlające się	3.40	7.31	9.93
Oxyacids Oksykwasy	3.67	2.35	1.43

The low softening point and low acid value of resins are advantageous from the point of view of papermakers' glue production. Saponified glues made from rosins characterized by the high softening point in the presence of aluminium ions, form resinates of high sintering point, which may hinder melting of the glue sediment in the drying part of the paper-making machine (Khetan 1985).

The low acid value of the parent resin makes it possible to use smaller amounts of soda lye in the process of saponification, which indirectly lowers the consumption of the aluminium sulfate during the operation of paper-pulp sizing.

Table 3
Tabela 3

Properties of rosin modified with ethylene oxide (OK) and maleic anhydride (BM)
Właściwości kalafonii zmodyfikowanej tlenkiem etylenu (OK) i bezwodnikiem maleinowym (BM)

Resin symbol Symbol żywicy	Rosin symbol Symbol kalafonii	Molar ratio Stosunek molowy n = OB/OK	Rosin properties Właściwości kalafonii	
			softening point temperatura mięknienia (°C)	acid value liczba kwasowa (mg KOH/g)
KTA-1	KT-A	0.50	62.1	133.4
KTA-2	KT-A	0.65	63.0	137.2
KTA-3	KT-A	0.80	63.7	138.9
KTB-1	KT-B	0.50	62.4	132.0
KTB-2	KT-B	0.65	63.3	136.8
KTB-3	KT-B	0.80	63.9	138.1
KTC-1	KT-C	0.50	64.3	133.4
KTC-2	KT-C	0.65	65.4	137.2
KTC-3	KT-C	0.80	67.1	138.7

Table 4
Tabela 4

Properties of glue obtained by saponification of modified rosin coming from different production batches
Właściwości klejów otrzymanych przez zmydlenie zmodyfikowanej kalafonii z różnych szarż produkcyjnych

Glue symbol Symbol kleju	Amount of NaOH used for saponification of 100 g rosin Ilość NaOH użyta do zmydlenia 100 g kalafonii	Properties Właściwości				
		Viscosity of 50% solution lepkość 50%-owego roztworu (mPa·s)	Degree of paper sizing for parameters: Stopień zaklejenia papieru dla parametrów:			
			$\%Al^{+3}$=3.5 pH = 6.2%	Al^{+3}=3.5 pH = 7.2%	Al^{+3}=2.0 pH = 6.2%	Al^{+3}=2.0 pH = 7.2
Z/KTA-1	8.8	4980	18.3	19.1	20.1	24.3
Z/KTA-2	8.9	3470	17.7	16.4	16.6	22.3
Z/KTA-3	9.1	2240	20.0	23.3	22.4	35.7
Z/KTB-1	8.9	3790	24.2	26.3	27.5	30.9
Z/KTB-2	9.1	3730	22.0	29.8	32.4	41.3
Z/KTB-3	9.2	3050	23.1	38.6	28.2	54.6
Z/KTC-1	9.1	2750	22.7	40.1	23.3	66.1
Z/KTC-2	9.3	2640	21.3	39.1	21.5	69.8
Z/KTC-3	9.5	2020	23.9	42.7	23.4	82.3

Table 4 presents the properties of glues made by saponification of resins mentioned in the table 3. The attention should be paid to small amounts of NaOH used for rosin saponification, varying between 8.8-9.5 g/100 g of resin. In case of standard resins saponification, NaOH consumption is about 50%

higher (Mosio-Mosiewski 1991). Differences found in the consumption of saponifying lye are caused by the fact, that the product of reaction of ethoxylated rosin with maleic anhydride contains only one carboxyl group able to neutralize, while the rosin adduct has three groups potentially reacting with NaOH. The decrease in the amount of the saponifying lye in the process of glue production makes it possible to reduce the consumption of aluminium sulfate during paper-pulp sizing.

The bigger amount of maleic acid anhydride used for rosin modification, the smaller viscosity of glues. All glue samples are characterized by high effectiveness of paper sizing in the weak-acid environment (pH = 6.2), and the reduction of aluminium sulfate portion from 3.5% to 2.0% causes only insignificant worsening of the degree of paper sizing.

The distinct effect of rosin constitution on the degree of paper sizing can be seen in the weekly alkaline medium (pH = 7.2). If glues made from the KT-A symbolled rosin, containing 90% resin acids and only 3.4% unsaponifiable compounds are still highly effective, then glues coming from the KT-C rosin, containing only 79% resin acid, more than 9.5% fatty acids and about 10% unsaponifiable compounds are characterized by the lower effectiveness of paper sizing, especially with the reduced portion of aluminium sulfate. The sizing effectiveness of glues made from the KT-B rosin containing about 86% resin acids, 4.4% fatty acids and 7.3% unsaponifiable compounds is medial in comparison to glues made from the KT-A and KT-C rosins.

The tests showed that in order to receive saponified glues for high sizing of paper in the near-inert medium it is necessary for modification to use the rosin of the highest possible content of resin acids and the lowest content of fatty acids and unsaponifiable compounds. The character of changes in the degree of paper sizing let us believe that the effectiveness of the glue is determined not only by the content of resin acid in the rosin material, but also by the content of remaining rosin consistents, which take part in chemical changes occurring during the process of modification. It is particularly visible in case of paper sizing in the weakly alkaline medium. For example, at pH = 7.2 and 2% addition of aluminium sulfate, the degree of paper sizing with the Z/KTC glues is 2-3 times lower than with the Z/KTA glues, while the resin acid content in the KT-C rosin is only 11% lower than that in the KT-A rosin. For each kind of rosin, there is a different optimum dose of maleic acid anhydride which depends on the chemical analysis of resin material used for modification.

Table 5 presents results of research on paper sizing with the use of three selected glues, made from the modified rosin marked with KT-A, KT-B and KT-C symbols, with or without 0.01% cationic or anionic retention agent. It was found that the addition of the retention agent just as in case of dispersing glues, caused a great improvement in paper sizing, whereas the presence of retention agents during the process of paper sizing with traditional saponified glues had not a distinct effect on the degree of paper sizing. From the table 5 it is evident that for the accepted range of sizing parameters, the addition of the anionic retention agent is most effective with the 2.0% portion of aluminium sulfate and pH = 6.2. In remaining cases, bigger improvement in paper sizing was obtained while using the cationic retention agent. The addition of

retention agents causes the evident improvement in paper sizing, especially in the weakly-alkaline medium and with the lowered portion of aluminium sulfate. The best sizing was obtained while using the glue made from the KT-A rosin with the biggest resin acid content, and the worst sizing was made by the glue coming from the KT-C rosin characterized by the highest content of fatty acids and unsaponifiable compounds.

Table 5
Tabela 5

The effect of retention agents on the degree of paper sizing by saponified rosin glues
Wpływ środków retencyjnych na stopień zaklejenia papieru kalafoniowymi klejami zmydlonymi

Glue symbol Symbol kleju	Type of retention agent Typ środka retencyjnego	Properties Właściwości			
		Degree of paper sizing for parameters: Stopień zaklejenia papieru dla parametrów:			
		$\%Al^{+3}$=3.5 pH = 6.2	$\%Al^{+3}$=3.5 pH = 7.2	$\%Al^{+3}$=2.0 pH = 6.2	$\%Al^{+3}$=2.0 pH = 7.2
Z/KTA-1	-	18.3	19.1	20.1	24.3
Z/KTA-1	anionic anionowy	18.5	13.3	10.6	12.1
Z/KTA-1	cationic kationowy	12.0	13.1	12.2	10.4
Z/KTB-1	-	24.2	34.8	25.5	49.9
Z/KTB-1	anionic anionowy	25.7	25.4	16.6	20.4
Z/KTB-1	cationic kationowy	16.1	19.7	17.3	17.6
Z/KTC-1	-	22.7	40.1	23.3	66.1
Z/KTC-1	anionic anionowy	27.1	33.4	18.7	28.6
Z/KTC-1	cationic kationowy	18.8	20.0	19.5	22.4

CONCLUSIONS

1. Saponification of rosin modified with ethylene oxide and maleic acid anhydride resulted in obtained the papermakers' glue effective in the near-neutral medium.

2. Chemical constitution of rosin used for the modification largely affects sizing properties of the product, particularly in the slightly alkaline medium.

3. The addition of retention agents to the paper pulp greatly improves paper sizing with no regard to the content of chemical compounds, not being resin acids, in the rosin.

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BADANIA NAD OTRZYMYWANIEM ZMYDLONYCH KLEJÓW KALAFONIOWYCH DO ZAKLEJANIA PAPIERU W ŚRODOWISKU ZBLIŻONYM DO OBOJĘTNEGO

Streszczenie

Wykonano badania nad możliwością otrzymywania zmydlonego kleju kalafoniowego z przeznaczeniem do zaklejania masy papierniczej w środowisku zbliżonym do obojętnego. Kalafonię poddawano modyfikacji tlenkiem etylenu i bezwodnikiem maleinowym, a następnie zmydlano roztworem NaOH. Stwierdzono, że z tak zmodyfikowanej kalafonii można uzyskać kleje papiernicze o poszerzonym zakresie stosowania, a właściwości kleju w znacznym stopniu zależą od składu chemicznego kalafonii wyjściowej.

Authors' addresses:
Prof. dr hab. Jan Mosio-Mosiewski
Instytut Ciężkiej Syntezy Organicznej
47-225 Kędzierzyn-Koźle ul. Energetyków 9 POLAND
Prof. dr hab. Ryszard Babicki
Instytut Technologii Drewna
60-654 Poznań ul. Winiarska 1 POLAND