

PRODUCTS OF ETHOXYLATION OF ROSIN

*Jan Mosio-Mosiewski**, *Ryszard Babicki***

Instytut Ciężkiej Syntezy Organicznej w Kędzierzynie-Koźlu*
Instytut Technologii Drewna w Poznaniu**

Attempts were made to introduce to the structures of resin acids of new function group by the way of ethoxylation of rosin. Presence of the hydroxyl group in ethoxylate will change physico-chemical properties of resin and will enable its modification by the new groups of chemical compounds. Ethoxylation was carried out at low molar ratio of ethylene oxide to rosin, namely in the range 0.0 - 3.0. Together with the increase of molar ratio of ethylene oxide to rosin in substrates are decreasing: softening point, viscosity, and acid number of product, and most fast drop has been observed in the range of molar ratio of substrates 0.0 - 1.0.

INTRODUCTION

The basic raw material used for the production of paper resin glues as well saponified as of dispersion kind is the rosin. At present for the production of glues with raised effectiveness of paper gluing is applied improved rosin. In this purpose is carried out modification of rosin most often with the use of maleine anhydride of fumaric acid, paraformaldehyde or additionally alcohols [6-9]. Particularly for production of dispersion glue is used partially esterified rosin [1], where the stabilizer function plays caseine. Caseine is sensitive for the microbial decay and gives glues of relative low stability with considerable susceptibility to foaming. In connection with that alternative solutions are needed. As the emulsifiers found application the products modified previously with maleine anhydride ethoxylation, which are then transformed into salts of derivatives of sulphosuccinic acid [2, 4]. Instead of ethoxylation could be carried out esterification of rosin with the ethylene polyglycol [3, 5]. Dispersing agents contain in the ethylene polyglycol chain complex of oxyethylene groups.

Till to this time methods of modification of rosin are based on the presence of reactive unsaturated bonds contained in the cyclic ring e.g. esterification of rosin with alcohols. In presented work attempts were taken to introduce to

structure of resin acid of the new function group on the way of rosin ethoxylation. It is expected that the presence of hydroxyl group in the ethoxylate will change physico-chemical of this resin and will enable their modification by the new groups of chemical compound e.g. by the estrification with the use of organic acids or their anhydrides. In contrary to rosin for the production of the rosin emulsifiers, ethoxylation is carried out at low molar ratio of ethylene oxide to rosin, namely in the range 0.0-3.0.

METHODS OF STUDIES

For the research tall oil rosin has been used. Ethoxylation was conducted in metal reactor of capacity 2 dm³ in the periodical way in presence of NaOH as catalyst. Into reactor containing melted rosin in temperature 170°C was dosed in portions liquid ethylene oxide in amounts resulting from adopted programme of studies. In the subsequent tests was increased quantity of the introduced ethylene oxide each next 0.5 mol on the rosin mol. Content ethoxylated rosin was determined by the use of gas chromatography method with the use of chromatograph Perkin - Elmer - model 8500 with flame - ionisation detector. As the fluid phase Dexil 400 GC spread on Chromsort GAW-DMCS was used. Samples of rosin were transferred into sililil derivatives with the use of BSA (Bistrimethylsilil acetamid). Kinetic viscosity of ethoxylated rosin were measured in temperature 100°C with the use of Ubbelohd viscosimeter.

DISCUSSION OF RESULTS

In the Table 1 presented are results of determinations of contents of ethoxylated rosin in dependence upon the average degree of ethoxylation. Products of ethoxylation reaction are always mixtures of adducts of ethylene oxide of various degree of polyaddition. Average degree of ethoxylation denotes mean quantity of moles of ethylene oxide in one mol of hydrophobic substrate. For calculation mean mass molar of rosin as for abietic acid, which is main its constituent. Accordingly to the adopted method of studies in tall oil rosin is 1.0% of light fraction and 3.5% of heavy fraction. Carried out by authors experiments revealed, that light components are fatty acids, while heavy are products of esterification of resin acids by higher alcohols. With the increase of average degree of ethoxylation of rosin increases content in the product of light in form of polyglycols formed as the adventive product. Increase of mean degree of ethoxylation from 0.0 up to 1.0 cause raising of ethoxylates in rosin, but quantity of heavy fraction did not undergoes greater change. After surmounting of limit, there is observed stepwise increase of a heavy fraction content on the expense of ethoxylates, while content of free

Table 1

Contents of rosin ethoxylation products
Skład produktów oksyetylowania kalafonii

Average ethoxylation Średni stopień oksyetylowania	Contents of constituents in product (weight %) Zawartość składników w produkcie (% wag)				
	light fraction frakcja lekka		rosin kalafonia	ethoxylates of rosin oksyetylaty kalafonii	heavy fraction frakcja ciężka
	unidentified components składniki niezidentyf.	polyglycols poliglikole			
0,0	1,9	—	94,6	—	3,5
0,5	0,2	—	43,9	51,7	4,2
1,0	0,4	—	3,9	91,8	3,9
1,5	0,2	0,3	1,2	55,4	42,9
2,0	0,1	1,1	1,3	58,3	39,2
2,5	0,5	2,3	1,4	58,2	37,6
3,0	0,1	7,7	2,3	64,4	25,5

rosin establishes on the level 1.2 - 2.3%. Over the mean degree of ethoxylation 1.0. takes part great growth of heavy fraction content accompanied by rapid decrease of ethoxylates quantity. From that, it can be concluded, that heavy fractions is the product of secondary reaction, which occur in conditions of ethoxylation process content of creating as the result of ethoxylation of rosin polyglycols and ethoxylates is presented in Table 2.

Polyglycols are created just after overreaching of mean degree of ethoxylation 1.0. At first forms only tri - and tetraethylene glycol - and at average degree of ethoxylation equal 3.0. are formed also higher polyethylene glycols. In this last case content of polyglycols in the product is considerable, because equals 7,7%.

Due to that, it is to be taken into account their presence in processes covering further modification of rosin or production of paper glue. Accordingly to expectations main products of ethylene oxide addition to rosin are mixture of resin acids derivatives of various content of oxyethylene groups in molecule. In the Table 2 quantity of linked oxyethylene molecules was described in the symbol of ethoxylate type with arabic number eg KS OE - rosin containing 5 oxyethylene groups in the chain. With the increase of molar ratios of ethylene oxide to rosin in substrates increases distribution of chain polyoxyethylene length. In the products of reaction besides ethoxylate containing quantity of ethylene oxide with the molar ratio of ethylene oxide to rosin in the substrates, are ethoxylates of smaller and greater length of polyoxyethylene chain. In the Table 3 are tabulated properties of adducts of rosin with various quantities of ethylene oxide. With the growth of average of ethoxylation of rosin decreases softening temperature, and acid number of product. At the molar ratio of substrates 1-1 esterification undergoes 96% of carboxyl groups contained in resin acids.

Kinetic viscosity of melted product measured at the temperature 100°C, rapidly decreases with the increase of average degree of rosin ethoxylation

Table 2

Content of polyglycols and adducts of rosin in products of its ethoxylation
 Skład poliglikoli i adduktów kalafonii w produktach je oksyetylowania

Constituent name Nazwa składnika	Content of polyglycols and ethoxylation (weight %) in fractions for the average degree of ethoxylation of rosin Zawartość poliglikoli i oksyetylatów (% wag.) we frakcjach dla średniego stopnia oksyetylowania kalafonii:						
	0,5	1,0	1,5	2,0	2,5	3,0	
Diethylene glycol	-	-	-	-	-	-	
Glykol dietylenowy	-	-	-	-	-	-	
Triethylene glycol	-	-	45,5	71,0	63,9	39,4	
Glykol trietylenowy	-	-	45,5	71,0	63,9	39,4	
Tetraethylene glycol	-	-	54,5	29,0	36,1	26,4	
Glikol tetraetylenowy	-	-	54,5	29,0	36,1	26,4	
Pentaethylene glycol	-	-	-	-	-	18,1	
Glikol pentaetylenowy	-	-	-	-	-	18,1	
Hexaethylene glycol	-	-	-	-	-	9,5	
Glikol heksaetylenowy	-	-	-	-	-	9,5	
Heptaethylene glycol	-	-	-	-	-	6,6	
Glikol heptaetylenowy	-	-	-	-	-	6,6	
Oxyethylate typu K10E	83,3	80,2	54,0	40,2	26,0	17,6	
Ethoxylate typu K10E	83,3	80,2	54,0	40,2	26,0	17,6	
Ethoxysylate typu K20E	16,7	19,7	35,9	39,7	35,6	29,2	
Oksyetylat typu K20E	16,7	19,7	35,9	39,7	35,6	29,2	
Ethoxysylate typu K30E	-	0,1	8,7	15,1	22,2	24,9	
Oksyetylat typu K30E	-	0,1	8,7	15,1	22,2	24,9	
Ethoxysylate type K40E	-	-	1,3	4,2	10,2	15,7	
Oksyetylat typu K40E	-	-	1,3	4,2	10,2	15,7	
Ethoxysylate typu K50E	-	-	0,1	0,7	3,0	7,2	
Oksyetylat typu K50E	-	-	0,1	0,7	3,0	7,2	
Ethoxysylate typu K50E	-	-	-	0,1	2,4	4,0	
Oksyetylat typu 560E	-	-	-	0,1	2,4	4,0	
Ethoxysylate typu K70E	-	-	-	-	0,6	1,4	
Oksyetylat typu K70E	-	-	-	-	0,6	1,4	

Properties of ethoxylated rosin
Właściwości oksyetylenowej kalafonii

Table 3

Average degree of ethoxyetylation Średni stopień oksyetylenowania	Properties of ethoxylated rosin Właściwości oksyetylenowanej kalafonii		
	softening temperature temperatura mięknięcia (°C)	Acid number liczba kwasowa (mg KOH/g)	Viscosity in lepkość w $t=100^{\circ}\text{C}$ (10^{-6} m ² /s)
0,0	67,0	177,4	557,8
0,5	27,6	88,1	288,4
1,0	16,5	6,5	75,1
1,5	15,0	4,8	59,9
2,0	15,0	3,5	55,4
2,5	15,0	3,4	41,6
3,0	15,0	3,3	30,9

from 0.0 to 1.0. After surmounting of this interval decrease of viscosity is much slower. As it is known, as well softening temperature, viscosity as acid number of rosin has great influence on the properties of paper glues. Those properties can be controlled by the change of average ethoxylation degree or by application of the proper modification chemicals reactive with oxyethylene groups.

REASSUMPTION

Modified was rosin on the way of the ethylene oxide addition maintaining in particular experiments ratio of thylene oxide to rosin in the range 0.0-3.0. Studied was content of products. It was found, that if the process is carried out at molar ratio – of ethylene oxide to rosin up. to 1.0, are not are formed residual products in form polyglycols, and the product contains mainly rosin ethoxylates. After surmounting this ratio are formed glycols, and considerable part of ethoxylates is transformed in to compounds of lower volatility, described as the heavy fraction ratio of increase of molar ratio of ethylene oxide to rosin in the substrates decreases softening temperature, viscosity and acid number of product, and the fastest drop is observed in the range of molar ratio of substrates 0.0-1.0.

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PRODUKTY OKSYETYLOWANIA KALAFONII

Streszczenie

Prowadzono modyfikację kalafonii tlenkiem etylenu utrzymując w poszczególnych próbach stosunek molowy tlenu do kalafonii w zakresie 0,0-3,0.

Określono skład jakościowy i ilościowy produktów oksyetylenowania kalafonii. Oznaczono takie właściwości otrzymanych żywic jak temperatura mięknięcia, liczba kwasowa oraz lepkość w temperaturze 100°C.

Authors addresses:

Prof. dr hab. inż. Jan Mosio-Mosiewski
Instytut Ciężkiej Syntezy Organicznej
ul. Energetyków 9
47-225 Kędzierzyn-Koźle

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