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Structure of Naphthol Modified Urea-Formaldehyde Resins by Using The Method of Nuclear Magnetic Resonance.

Nikolay Pavlovich Plotnikov*, and Galina Pavlovna Plotnikova.

FGBOU VPO "Bratsk state university" Russia, 665709, Irkutsk region, Bratsk, Makarenko St. 40.

ABSTRACT

The scale of phenol consumption is significant but to meet the industry needs not only phenol is necessary but naphthols and different phenol homologs are important either. Both naphthols (α - and β -type) have a great technical significance; β -naphthol is the most important one among the simple intermediate products of a naphthalene number. Naphthols are used in the manufacture of azo-dyes as azo-components and they are the initial products for producing of naphtholsulfoacids which are also widely used in the manufacture of azo-dyes. In this article the main regularities of naphthol influence on toxicity of modified adhesive composition are identified. The quantitative interrelation of resin toxicity reduction from the amount of a led modifier is established. The composition and structure of naphthol modified urea-formaldehyde resins by the method of NMR spectroscopy are considered.

Keywords: toxicity, urea-formaldehyde resin, naphthols, condensed benzene nuclei compound, NMR-spectroscopy.

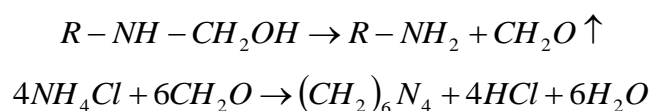
*Corresponding author

INTRODUCTION

A great range of synthetic glues are used in industry, which differ from each other by reliability, technological parameters, toxicity and cost [1-2]. Many of these qualities are determined by the properties of the original polymer.

One of the dominant types of glue in timber industry is a type of glue based on urea-formaldehyde resin (UFR). It is distinguished by high speed of curing (2-2,5 times higher than phenol-formaldehyde resins), adhesion strength, colorless glue joint, low cost [3-5]. Besides this fact, there are some rich sources of raw materials for its manufacturing. But now in the world there is a tendency to reduce the use of binders based on UFR because they are toxic both in liquid and in cured state which is caused by emission of formaldehyde (CH_2O) into the environment [6-8].

In liquid form UFRs are a mixture of oligomer and low-molecular products of condensation – mono-, di-, tri-, tetra- methylolureum. A general formula of methylol compounds of UFR can be represented in the following form $R-NH-CH_2OH$. [9-11] The toxicity of this type of resins is explained by the availability of these products, where formaldehyde is given off in a free form:



The investigation of reduction of the toxicity index, use of different methods of synthesis, introduction of modifiers in the process of resin synthesis and in finished products were carried out. The low toxicity resins with the content of free formaldehyde $< 0,18\%$ were synthesized. [12-14] But the question about the decreasing of toxicity is urgent.

The research aim is to study of α - and β - naphthols modified urea-formaldehyde resin structure by NMR-spectroscopy.

METHODS

The method of nuclear magnetic resonance (NMR) is one of the leading methods among the other physical and chemical methods of analysis when the structure of organic and non-organic substances should be determined. The empirical correlations between the parameters of NMR-spectra – chemical shift (δ) and constant of spin-spin interaction (T), on the one hand, and the composition and structure of the mode on the other hand - are the base of NMR-spectroscopy application to determine the structure of unknown substances. The electronic environment of nuclei is defined by the value of chemical shift, and, therefore, the changing of the nuclei charge. Spectroscopy of nuclear magnetic resonance allows to reveal the influence of dissolved substances on a dissolvent state. The relaxation time T_1 is called the time corresponding to longitudinal or spin-lattice relaxation which characterizes the speed constant of perturbed system transition in the equilibrium state, and the time T_2 is called the time of cross or spin-spin relaxation which characterizes the energy exchange between the individual spins.

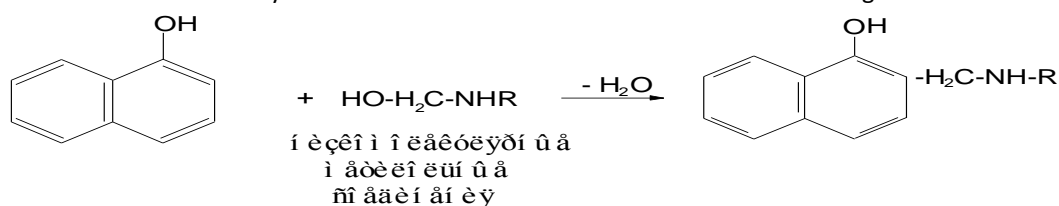
Registration conditions of NMR spectra

- Resonance frequency of oxygen nuclei – 67,76 MHz (for VXR-500 S);
- Evolvent width – 8000 Hz;
- Duration of 90°- impulse – 51,8 μ s;
- Relaxation time of delay – 0,1 s;
- Ratio signal/noise – not less than 150;
- Number of scans NS – 100-600;
- Temperature into the sensor - 26°C.

Parameters of NMR spectra were obtained with the help of the spectrometer «Varian VXR 500 S» having the operating frequency for oxygen nucleus of 67,76 MHz. Chemical shifts were measured in regard to the signal of distilled water (measurement accuracy $\pm 0,1$ ppm). The values of spin-spin relaxation time (T_2) of oxygen nucleus relaxing on quadrupole mechanism, in the studied systems, were determined from the width of a line on the semi-height by using the ratio $\Delta\nu^{17}\text{O} = 1/\pi T_2$ and by a standard procedure on the basis of Carr-Purcell-Meyboun-Gill impulse sequence. The accuracy of the spin-spin relaxation time T_2 was defined in the condition of impulse sequence $\pm 10\%$. Semi-width of a line was determined in approximate accordance with Lorenz form, the accuracy measurement $\Delta\nu^{17}\text{O}$ of nucleus ^{17}O was $\pm 0,1$ Hz.

THE MAIN PART

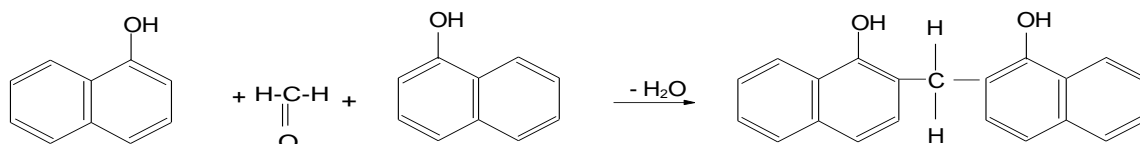
Modifiers α - and β - naphthols are the polyaromatic compounds with condensed benzene nucleus which have high chemical activity. [15]. It can be assumed that the interaction of modifiers and low-molecular compounds of urea-formaldehyde resin is carried out in accordance with the following scheme:



(low-molecular methylol compounds)

As naphthols in structure and properties are similar to phenols, the reaction of their interaction with free formaldehyde is possible:

for α - naphthol

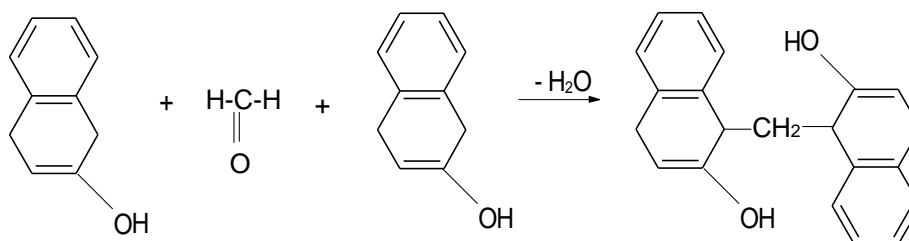


α - naphthol formaldehyde

bis- (1-hydroxi 2-naphthyl) methane)

And further condensation bis – (1-hydroxi 2-naphthyl) of methane with the formation of resinous products

for β - naphthol



In alkaline environment regardless of molar ratios of reacting substances, much larger number of formaldehyde moles than naphthols starts the reaction and as the temperature raises, the formed naphthol-alcohol are subject to polycondensation with the water isolation by methyl hydroxyl groups and unsubstituted hydrogen atoms of an aromatic ring, which is located in ortho- and parapositon to naphthol hydroxyl.

The polycondensation reaction proceeds with the formation of more complex products, which are the resin components of rezol type. Thus, the number of low-molecular products of condensation in the resins is reduced, and it was confirmed by the conducted research.

Naphthol modified urea-formaldehyde resin probably contains the fragments which are similar to phenol-formaldehyde resin of rezol type or to resorcinoformaldehyde resin having the three-dimensional structure and characterized by a great number of connections between the molecular chains that is proved by naphthol structure, in comparison with the pure urea-formaldehyde resins. The increased water resistance and mechanical strength of adhesive compounds, obtained on the basis of modified adhesive composition can be explained by it.

A full analysis of NMR spectra ^{13}C of KF-MT-15 urea-formaldehyde resin with the using of simulation software allows to make a conclusion that the quantitative NMR spectrum ^{13}C is presented by the groups of signals by singlets (area of carbonyl carbon in the range of XC 154-164 ppm) and the presence of CH_2 -groups (triplets in the area of 40-80 ppm). MNR spectra are registered in off-resonance with the meaning of constants of spin-spin interaction of carbon nuclei ^{13}C with the nuclei of ^1H . The detailed analysis of XC ^{13}C carbonyl area shows the presence of 5 signals of carbonyl groups $>\text{N}-\text{C}(\text{O})-$: the intensive signals have the value of XC 161.9, 160.2 and 158.7 ppm and broadened signals of medium intensity have the value of 159.8 and 158.4 ppm. Maximum intensity corresponds to the first group of signals. If we take the total intensity of carbonyl groups as 100%, each carbonyl group has the following content: 161 ppm (15.9%), 160 ppm (31.7%), 158.7 ppm (35.7%); 159.8 ppm (5.%), 158.4 ppm (11.46%). If we take the total integral intensity of signals of carbonyl groups and methylene groups as 100%, we will get the following ratio of carbon atoms in the carbonyl and methylene fragments: $\text{CO}/\text{CH}_2 = 37.2/62.8$. I.e. the content of methylene groups is more 1.7 times. The analyzed range of XC methylene groups of urea-formaldehyde resin is shown in table 1. If we take the sum of the integral intensity in the area of methylene groups as 100%, we will get the ratio of methylene groups (CH_2) in each of the specified ranges which are presented in table 1. It should be noted that monomethyl, dimethyl and tetramethyl of carbomides at the level of 0.1% are not exposed. Two signals of $\text{C}(\text{O})$ with XC 155.1 and 156.5 ppm are exposed at the level of 0.5% in the area of carbonyl groups.

Table 1: Main structural fragments of UFR

XC ppm	Multipletness	Intensity %	Structural fragment
46.1	Triplet	19.6	OH
54.3	two triplets	31.6	$>\text{N}-\text{CH}_2-\text{N}<$
63.4	Triplet	22.2	$\text{HO}-\text{CH}_2-\text{N}<$
68.2-75.3	Three-four triplets	26.6	$>\text{N}-\text{CH}_2-\text{O}-\text{CH}_2-\text{N}-\text{N}-\{\text{CH}_2-(\text{OH})\}_2$ where the groups of CH_2 belong to different spatial conformers

When α -naphthol, which has in an inert dissolvent the following signals with the value of XC 151.3, 134.7, 120-127 and 108.7 ppm), is introduced into a sample of urea-formaldehyde resin, it has been found that both XC of the main substance (UFR) and naphthol have not practically changed (within 0.1 ppm). It is evidence that the donor-acceptor coupling, which should be observed at least through the fragments which can take part in it, just containing the carbonyl groups and nitrogen atoms of UFR and OH-group of naphthol is not observed. Without speaking about the chemical processes. It should be noted the following fact: if the width of signals in NMR spectra ^{13}C UFR has not practically changed by adding of naphthol, the signals of the naphthol in the UFR solution are significantly broadened relatively to the signals of naphthol in the solution of acetone. It proves that in the samples of modified urea-formaldehyde oligomers, the relaxation processes associated with the exchanged processes between naphthol and UFR affecting molecules in general, play a significant role. Probably it is connected with the diffusion processes of naphthol penetration in the globule voids of UFR. We believe that naphthol diffuses into size various voids, the structure cells of macromolecules of UFR, filling them and thus changing of the structural matrix of UFR, and it essentially condenses the structure. It can fundamentally change the width of signals in the naphthol spectrum by changing of their relaxation characteristics of nuclei ^{13}C .

I.e. both α - and β - naphthols change the permolecular structure of UFR by eliminating of voids in the

macromolecule of urea-formaldehyde resin. To confirm this version, we have studied these systems by the method of NMP spectroscopy on oxygen nuclei ^{17}O . The relaxation time of nuclei ^{17}O characterizing a water matrix « H_2O – naphthol - UFR» and « H_2O -UFR» was counted. It was found that the value $T_{1/2}^{17}\text{O}$ (relaxation time of oxygen nuclei expressed in Hz. $T_{1/2}^{17}\text{O} = 1/\kappa T_2$) is a matrix « H_2O -UFR»-269 Hz; matrix « H_2O -UFR- α -naphthol» -228 Hz.; « H_2O -UFR- β -naphthol» -199 Hz.; standard water has a value– 86,7 Hz.

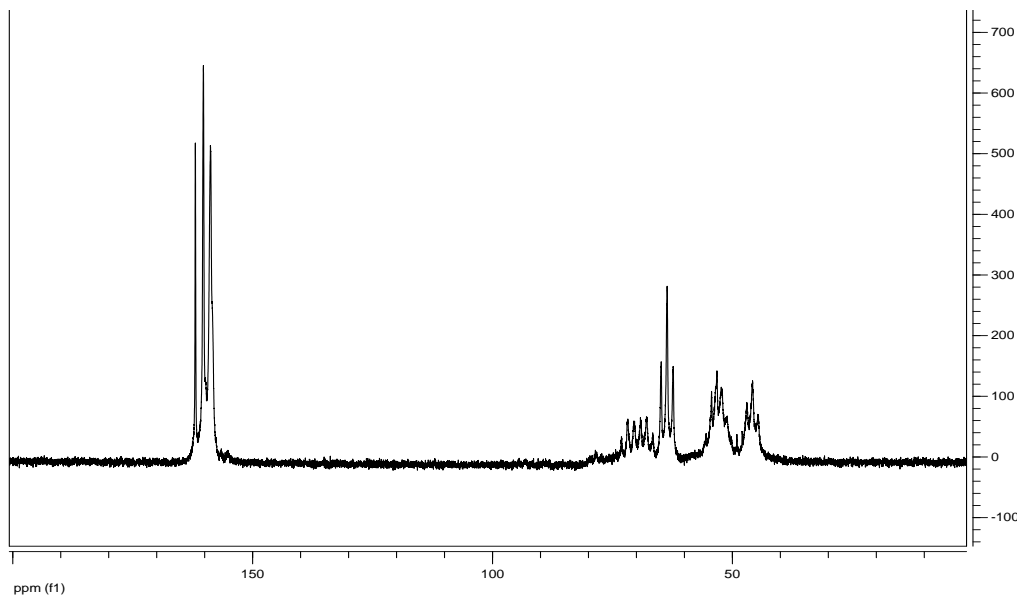


Figure 1: NMR-spectroscopy of UFR on nuclei of carbon atom ^{13}C

The significant width of the line of nuclei ^{17}O in the matrix « H_2O -UFR» 269 Hz was found. It corresponds to $T_{1/2}^{17}\text{O} = 1/T_2 = 0.0037$ s. It is a very fast relaxation time. I.e. the water in the system « H_2O - UFR» is highly structured by binding and filling of voids (cells, local cavities) with water molecules in macromolecules UFR.

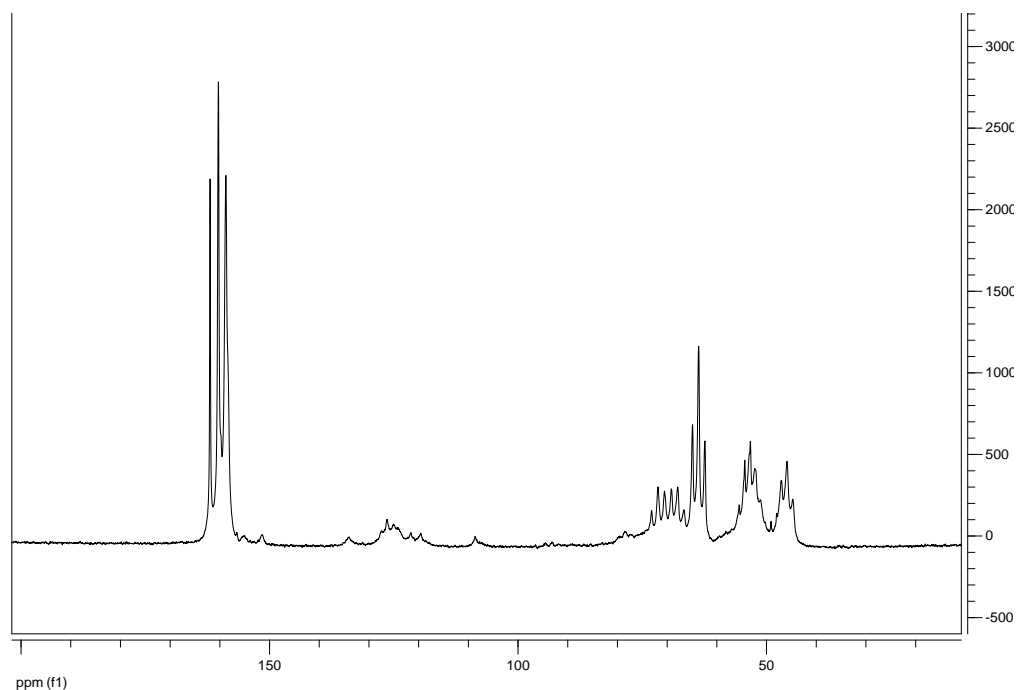


Figure 2: NMR-spectroscopy of modified by α -naphthol of UFR-oligomers on nuclei of carbon atom ^{13}C

Introduction of naphthol partially destroys the order in the system “ H_2O -UFR- 228” and 199 Hz respectively. It is naturally because aromatic hydrocarbons really destroy water structure. But naphthol

changes the permolecular structure of UFR significantly. I.e. the remaining in the cavities of UFR water changes the mechanism of exchange processes in the matrix « water-UFR-naphthol» fundamentally, namely, it slows down the exchange processes. It is reflected in the XC ¹³C of naphthol. As a result naphthol modified UFR will show new properties for various chemical and physical influences on it.

CONCLUSION

The general regularities of naphthol influence on toxicity of modified adhesive composition are defined. The quantitative interrelation of resin toxicity reduction from the amount of introducing modifier is established. The composition and structure of naphthol modified urea-formaldehyde resins are considered by using the method of NMR-spectroscopy.

CONCLUSIONS

In accordance with the research results of the naphthol modified structure of urea-formaldehyde resins by the method of NMR-spectroscopy it is possible to make the following conclusions:

- The complex analysis of NMR spectra ¹³C of naphthol modified UFR with the involvement of simulation software allows to make a conclusion that the quantitative NMR spectrum ¹³C is presented by the groups of signals by singlets (area of carbonyl carbon in the range of XC 154-164 ppm) and the presence of CH₂-groups (triplets in the area of 40-80 ppm).
- In the samples of modified urea-formaldehyde oligomers, the relaxation processes associated with the exchange processes between naphthol and UFR, affecting the naphthol molecules in general, play a significant role. Naphthol diffuses into voids of different sizes, cells of the structure of UFR macromolecules, and fills them and thus it changes the structural matrix of UFR, condenses it essentially.
- With the introduction of α- and β-naphthols in UF-oligomer a decreasing of a number of low-molecular products of condensation in resin is observed, it is confirmed by the results of the research. This fact also confirms the possibility of obtaining of low-toxicity of oligomers by naphthol binding of free formaldehyde in urea-formaldehyde resins.

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