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Investigation of the stability of the modified urea-formaldehyde resin

Summary — Commercial KFMT-15 type urea-formaldehyde resin (UF) was modified with an addition of 4 wt. % of various alcohols (methanol, ethanol, isopropanol, butanol). Changes of pH, relative viscosity, hot gelation time and free formaldehyde content during storage (up to 4 months) were investigated. Chemical interpretation of the results obtained has been proposed. It was found that isopropanol is the most advantageous modifier — from the point of view of UF useful properties (especially emission of formaldehyde).

Key words: urea-formaldehyde resins, modification, aliphatic alcohols, storage stability.

Urea-formaldehyde (UF) resins modified with monohydric and polyhydric alcohols have been well known for a long time, but influence of modifiers added at the stage of polycondensation (1—8 %) on UF resins properties has not been sufficiently investigated [1—3].

It is especially important for the stabilization of UF resins properties during long time storage, for example 1 to 4 months. The problem was interesting for us, and additionally our customers claimed that they wanted to get UF resins with stable properties and technical characteristics. At the same time the modifier content in UF resin should not be high (up to 10 %), because greater amounts of the modifiers make UF resins very expensive.

At the CSC „Lukor" Works the urea-formaldehyde resins are produced by continuous gas phase method according to which urea solution interacts with formaldehyde rich gases derived from the process of methanol oxidation. The technological line of a condensation step consists of the cascade of the reactors.

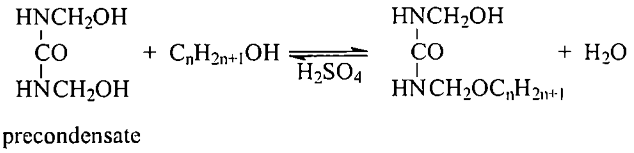
EXPERIMENTAL

A laboratory installation enabled to repeate the work of the cascade of reactors with high accuracy was constructed for the modified resins with stable properties production. Additionally, the installation was equipped with a thermostat with an automatic regulator of temperature and pH-meter.

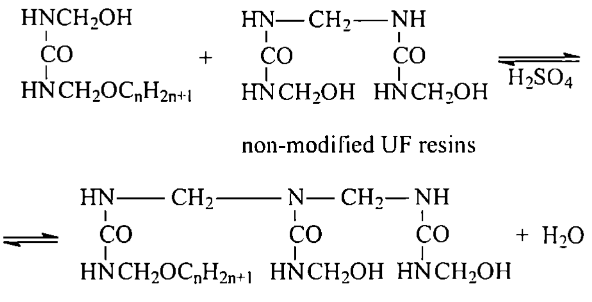
For our tests we used crude UF resins (precondensates) that were formed after the alkaline stage of urea condensation with gas formaldehyde at the molar ratio of 1:1.8 and the modifier was introduced at this stage [4]. This product has been chosen for our investigations.

Crude UF resins modification was made by monohydric alcohols (methanol, ethanol, isopropanol, butanol at amounts 4 wt. %) or dioctyl phthalate (DOP as a plasticizer). To this precondensate, after the stage of acid condensation at pH = 4.3—4.6, the modifier has been added and the resin was heated to 60—90 °C during 1—2 hours.

After the introduction of alcohols to the precondensate, the following reactions (1) and (2) took part between an urea and methylol derivatives of urea at the stage of the acid polycondensation:



$$\begin{array}{c}HNCH_2OH\\|\\CO\\|\\HNCH_2OH\end{array} + C_nH_{2n+1}OH \xrightleftharpoons[H_2SO_4]{} \begin{array}{c}HNCH_2OH\\|\\CO\\|\\HNCH_2OC_nH_{2n+1}\end{array} + H_2O \qquad (1)$$



$$\begin{array}{c}HNCH_2OH\\|\\CO\\|\\HNCH_2OC_nH_{2n+1}\end{array} + \begin{array}{ccc}HN & - CH_2 - & NH\\|&&|\\CO&&CO\\|&&|\\HNCH_2OH&&HNCH_2OH\end{array} \xrightleftharpoons[H_2SO_4]{} \qquad (2)$$

$$\xrightleftharpoons{} \begin{array}{ccccc}HN & - CH_2 - & N & - CH_2 - & NH\\|&&|&&|\\CO&&CO&&CO\\|&&|&&|\\HNCH_2OC_nH_{2n+1}&&HNCH_2OH&&HNCH_2OH\end{array} + H_2O$$

The first reaction (1) took place in the weak acid medium (pH = 5—6), while the reaction (2) — at pH = 3.5—4.5 [5]. As a result of the above processes the modified UF resins were obtained. This product was then stabilized with additional urea (to the molar ratio urea:formaldehyde equal 1:1.2) cooled and analyzed. Modified UF resins were kept during 4 months. Sampling and product analysis were done each month and viscosity, hot gelation time and free formaldehyde content were determined according to [6]. Modified products properties were compared with non-modified KFMT-15 resin, in which the final ratio of urea and formaldehyde was the same: 1:1.2 [7].

RESULTS

As it is shown in Fig. 1, pH of modified UF resins and non-modified KFMT-15 one undergoes the obvious changes in the course of storage time. At the beginning, for the first month of storage, pH of almost all resins decreases. It is the most obvious for the KFMT-15 resin and UF resins modified by ethanol. The decrease is practically the same for the UF resins, modified by the isopropanol or plastified by dioctyl phthalate — DOP. During the longer storage, pH of the resins increase. After 4 months the highest pH value (exceeding the initial one) shows the non-modified resin while the lowest (lower than initial pH) — the resin modified with butanol.

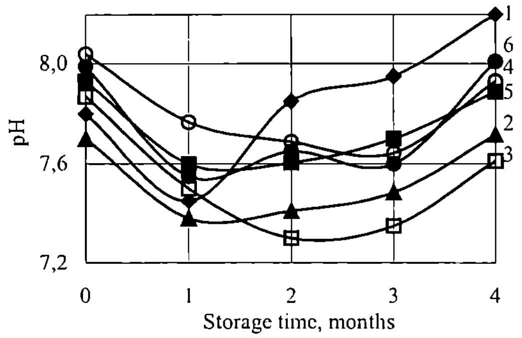


Fig. 1. UF resin pH dependence on storage time: 1 — non-modified UF resin KFMT-15; the resins modified with: 2 — ethanol, 3 — n- butanol, 4 — methanol, 5 — isopropanol, 6 — DOP (plasticizer)

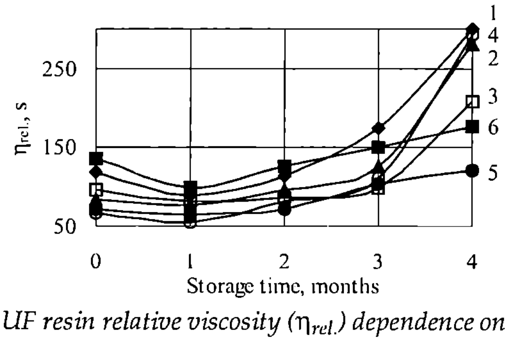


Fig. 2. UF resin relative viscosity ($\eta_{rel.}$) dependence on storage time; for symbols see Fig. 1

As well the viscosity of all UF resins slightly decreased during the first month of storage (Fig. 2), but during the next months of storage the viscosity, as well as pH-value, increased. Significant increase in viscosity after the whole storage was observed in case of non-modified resin or the resins modified with ethanol or methanol.

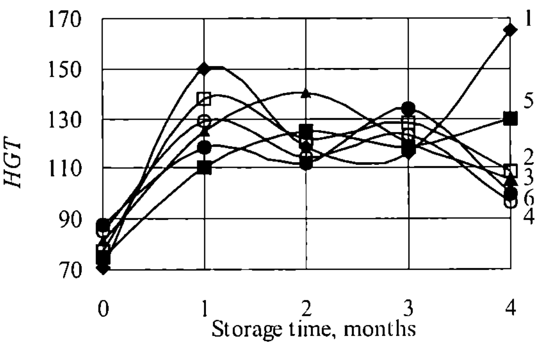


Fig. 3. UF resin hot gelation time (HGT) dependence on storage time; for symbols see Fig. 1

An increase in hot gelation time (*HGT*) of all resins during 1 month of storage (Fig. 3) is connected with the intermolecular reaction taking place in the structure of the resins and a further reaction of UF resins derivatives, that leads to the considerable increase in intermolecular bonds in a resin. *HGT* order of the products of modification is following: ethanol > methanol > butanol > isopropanol so there is no dependence on hydrocarbon chain length. It seems ethanol shows better reactivity towards methylol groups than methanol while in case of isopropanol the steric hindrances decrease the reactivity. Lower reactivity of a modifier prolongs gelation time. After 4 months storage *HGT* values of majority of the modified products are lower. Only the resin modified with isopropanol is an exception.

Our supposition is also confirmed by the changes of free formaldehyde content during storage time shown in Fig. 4.

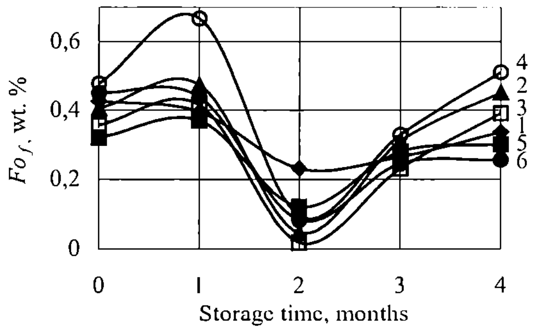


Fig. 4. Dependence of free formaldehyde (Fo_f) content in UF resin on storage time; for symbols see Fig. 1

DISCUSSION

It is clear from the results presented that the certain part of methylol derivative of urea undergoes transformation in the UF resins solutions. Later process in the UF resins seems to undergo a pseudo-stabilization period. This assumption can be confirmed by the stability of viscosity that in fact did not change at this stage during first 45 days of UF resins storage period (Fig. 2). Gelation time stabilizes, too, but only between 1 and 2 month. Apparently, alcohol introduction stabilizes pH value and viscosity. During the second month the changes of free formaldehyde content in the UF resins modified by alcohols are interesting. Formaldehyde content decreases during this storage period from 0.3—0.45 % to 0.05—0.15 %. It can be explained by the fact that pH decreases at the first stage of storage (up to 30 days) what creates the favorable conditions for etherification and aldol condensation reactions. That cannot take place at pH = 7.7—8.1, but can occur at pH = 7.4—7.7.

During storage the free formaldehyde reacts with alcohols and its concentration in UF resins decreases considerably. But the absence of free formaldehyde in the solution causes an increase in pH of UF resins solutions and partial decomposition of the lower molecular derivatives. Free formaldehyde concentration (see Fig. 4) increases for a short time, but the previous values are not achieved. The present contents of free formaldehyde on 90th day of UF resins storage are only 0.2—0.3 %. Only in non-modified resin the free formaldehyde content reaches the initial level.

So, as the result of the research work done it became possible to obtain the new grades of UF resins by the introduction of modifiers. Modification has been made at the stage of synthesis of low-molecular methylol- and methylene derivatives of urea during the process of UF resins manufacturing. This let obtain the UF resins grades modified by the molecules of a modifier build in into their structure, without the changes in the process line.

These resins show some specific properties. The decreased content of residual free formaldehyde gives the possibility to reduce the toxicity of the materials received on their base. Modifications of the resins partly change their molecular weights and structures that influence their solubility in water and organic solvents. It gives a chance to regulate their glue qualities, rheology, solidification and thermal stability.

It was found that the modified resins keep their physico-chemical indices in the permitted limits during 4 months.

On the base of the received results the best modifiers of UF resins on the stage of polycondensation appeared to be isopropanol and butanol as well as dioctyl phthalate — a plasticizer. That is why they could be recommended for the synthesis of modified UF resins, which are used in the production of varnishes and paints, as well as in the paper, woodwork and adhesive industries. The wood-chip and wood-fiber plates received on the base of these modified urea-formaldehyde resins are low-toxic because of the lower free formaldehyde content what is a very important result of the work. The consumers in the branch of adhesives industry are constantly looking for the solution of the problem of free formaldehyde emissions to the environment reduction.

The optimal solution of this problem will improve the ecological situation of the environment.

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