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**FILLERS AND CATALYSTS EFFECT
ON THE PHYSICOCHEMICAL PROPERTIES
OF UREA-FORMALDEHYDE RESINS**

In the present research the effect of different fillers on the composition of urea-formaldehyde resins (UFR) was studied. The usage of fillers in the composition of urea-formaldehyde resins makes it possible to reduce the resin consumption by 10–20%. Aluminum silicate type of fillers cannot be used conveniently in plywood technology because resin particles initially agglomerate; then their swelling and hydration lead to the significant viscosity growth of the adhesive especially at a filler consumption rate more than 8% by weight of the resin.

Sulfate and carbonate types of fillers can be used more preferable because in this case there are no agglomeration of resin particles and no quick solidification of adhesive composition. Viscosity of the adhesive composition decreases vice-versa with the adding of silicate type filler into the urea-formaldehyde resin. Combining of different fillers types allows controlling the rheological properties of the adhesive composition.

Compounds containing ions of three-valence metals are effective catalysts of urea-formaldehyde resins. The usage of such catalysts in plywood technology leads to condensation time reduction of urea-formaldehyde resins at 1.8–2.3 times which opens up additional possibilities for application of low-emission resins with a low formaldehyde content. Gelatination time of adhesive compositions prepared using the new effective catalysts for the condensation process of urea-formaldehyde resins remains for 2–4 hours.

Key words: urea-formaldehyde resins, kaolin, marble calcite, silica, calcium sulfate, ammonium salt, aluminum salt, complex salt.

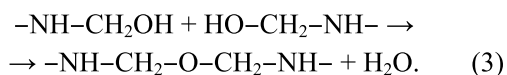
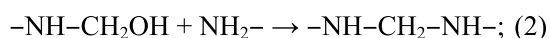
Introduction. Nowadays the woodworking enterprises of the Republic of Belarus are being modernized. When modernization of the enterprises will be completed (2016–2017) the production capacity of the process lines will increase 1.5–2.5 times. Thus, the production of plywood will be increased up to 290,000 m³ and chipboard up to 1,300,000 m³. The needs of the internal market of the Republic of Belarus are 50,000 m³ of plywood and 800,000 m³ of chipboard. Thus, the major part of abovementioned wood products has to be sold abroad in a highly competitive market place. For this reason, the products should meet two major requirements: high quality and relatively low cost. This may be achieved by a number of technological, organizational and logistical procedures.

The present paper deals with two techniques improving the technology of plywood and chipboard production, namely, inclusion of fillers in the binder composition and selection of efficient catalysts for resins curing. Nowadays urea-formaldehyde resins (UFR) of different brand marks are mainly used in the plywood and chipboard manufacture. They are either produced by the plant itself if it manufactures plywood or chipboard or purchased abroad, mainly in Russia. The share of the resin cost in the finished goods cost value is rather high and amounts to about 25–30%.

The usage of cheap fillers in the binder (or adhesive) composition reduces the consumption of

resin and, thus, lowers the production costs and improves its quality by reducing the content of free formaldehyde in the finished product. The literature describes the cases of including fillers into the adhesive composition while manufacturing plywood and solid glued woodproducts. The fillers mentioned above were products of organic and inorganic origin: wood flour, lignin, flour of cereals and legumes, starch and its derivatives, flour of a variety of nuts, kaolin, chalk, charcoal, silica gel [1, 2]. However, the fillers involved were used only in phenol-formaldehyde resins. A number of patents on the use of fillers in urea-formaldehyde resins, for example, wastes of crystalline silicon production [3], cured urea-formaldehyde polymer [4], natural aluminum silicates [5], schungites [6] are known.

However, in the literature there are practically no data on the effect of fillers on physical-chemical properties of binders based on urea-formaldehyde resins. It is equally important to find effective catalysts for curing UFR. The action of the classic catalysts used for curing urea-formaldehyde resins, for example ammonium chloride is shown by the following reactions [7]:



The reactions foregoing show that the more free formaldehyde is contained in the initial resin, the more formic acid is formed and, accordingly, the faster is the polycondensation reaction with the formation of methylene and methylene-ester bonds.

The given scheme of the reactions does not work for modern UFR containing 0.01–0.05% of free formaldehyde [8–11], so classical catalysts are poor curing agents for them.

The present work has been aimed at the study of the effect of fillers on the physical-chemical properties of the urea-formaldehyde resins and selection of effective catalysts for UFR curing.

Main part. In the experiments involved urea-formaldehyde resin of KF-MT-15 brand mark was used. Characteristics of this resin and the requirements claimed are given in Table 1. Mineral compounds of various types were used as fillers: aluminum silicate (kaolin), carbonate (marble calcite), silicate (SG – technical silica gel), sulfate (PG – technical calcium sulfate or gypsum).

Ammonium salts (chloride and sulfate), aluminum salts (sulfate), complex salts (aluminum-ammonium alum) and complex compounds containing salts of several metals (PMC) were studied as UFR curing catalysts. The experiment technique was as follows: to the resin sample weighing 150 g, 1.5–45.0 g of filler were added at 1.5 g intervals, the mixture was stirred for 10 min, and then the following parameters were determined: viscosity (dynamic viscosity) by using VZ-4 viscometer, the pH value by EV-74 ionomer, gelling time at 100°C according to GOST 14231–88. Additionally it was determined the viability (gelling time at 20°C), as well as aggregate and sedimentation sustainability.

The influence of different types of fillers on the change in dynamic viscosity of the adhesive composition is shown in Fig. 1.

When crushed kaolin is added (curve 1) to the resin balling occurs, followed by swelling and dissolution. Due to the hydration of the filler the viscosity of the adhesive composition increases. The increase being particularly substantial at the dosage of more than 8%. The curve of viscosity versus dosage is of parabolic type due to the decrease of free water fraction in the composition, caused by hydration of the kaolin. As for fillers of carbonate (marble calcite) and sulfate (technical calcium sulfate of PG mark) types (2 and 3), the dynamic viscosity of the adhesive composition also increases with their addition, but the dependence curve is close to linear one, indicating the absence of hydration of these fillers.

A totally different type is the curve of the dependence of viscosity on the amount of filler when using silicate type one (4). While adding technical silica gel of SG mark to the resin viscosity of the adhesive composition decreases. In the studied dosage range (1–30% by weight of resin) viscosity reduction is of linear character. This phenomenon is probably due to the interaction of the methylol groups of urea-formaldehyde oligomers with hydroxyl groups of the disperse filler. For this reason, water bound to hydrophilic methylol groups of oligomers, is released going over to a free state, and the viscosity of the composition decreases.

It should be noted that the viscosity of the adhesive composition has restrictions on both the top and bottom limit. In the manufacture of plywood viscosity should be from 80 to 200 s, and in the production of chipboard it is 20–40 s. Water content of the adhesive composition should be as small as possible, since in the process of hot pressing all the water turns into steam, which leads to its increased pressure inside the product, and to the destruction of insufficiently hardened binder and product when the platens of hydraulic press are opened.

Table 1

Properties of urea-formaldehyde resin of KF-MT-15 mark

Parameter	Norm according to RB TS 600012243.036-2007	Results of the analysis
Appearance	Homogeneous suspension from white to light yellow color without mechanical inclusions	Homogeneous white suspension without mechanical inclusions
Solid content, %	66 ± 2	64.0
Mass ratio of free formaldehyde, %, no more than	0.15	0.13
Viscosity (20.0 ± 0.5)°C by VZ-4 viscometer, s	30–120	85
The concentration of hydrogen ions, pH	7.4–8.5	7.5
Gelling time at 100°C, s	40–70	60
Marginal miscibility of resin with water when coagulation is observed, in ratio by volume	1 : 2–1 : 10	1 : 3

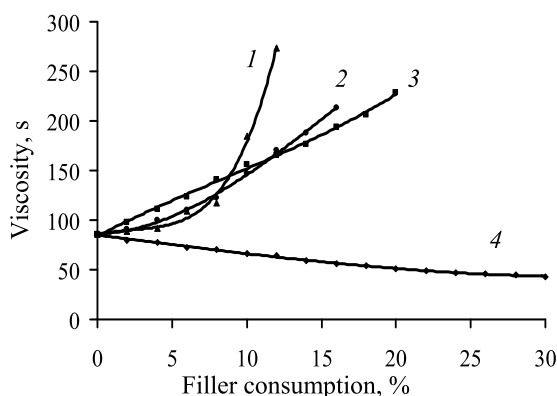


Fig. 1. Change in composition viscosity when fillers are added:
 1 – kaolin; 2 – marble calcite;
 3 – PG technical calcium sulfate;
 4 – SG technical silicon oxide

Thus, in the manufacture of plywood kaolin in the amount of up to 10%, marble calcite and PG technical calcium sulfate in the amount of up to 15% can be used. Technical silica gel of SG mark can be applied in the manufacture of chipboard instead of or together with water to reduce the viscosity of the adhesive composition. Promising is the use of a mixture of fillers of multi-directional action, such as filler of SG with PG marks and SG mark with kaolin, as these mixtures allow to control the dynamic viscosity of the adhesive compositions in any given range. Together with the viscosity of freshly prepared adhesives the stability of the composition over time is of great importance. Table 2 shows the VZ-4 change of dynamic viscosity of the filled composition based on urea-formaldehyde resin of KF-MT-15 mark during five days (120 hours).

As it is seen from Table 2, when all of the studied fillers are used sufficient stability of the adhesive composition is ensured within three days. With the maximum allowable filler content the

composition viscosity increases by no more than 10–20% during the first three days, which is quite sufficient for plywood or chipboard technologies. It should be noted that when using SG mark filler for more than four days there is gelling of the resin, indicating that the filler involved has certain catalytic character. This phenomenon is positive since it will contribute to the additional curing of the adhesive in the inner layers of the material during the product storage.

Classic UFR catalyst is ammonium chloride. However, in the EU countries the use of ammonium chloride is prohibited due to the possible formation of highly toxic dioxins during the combustion of chipboard and plywood [12]. For this reason, the selection of the curing catalysts for UFR, that would provide effective curing and would not form toxic compounds during exploitation and utilization of plywood and chipboard, is of great practical importance. According to the data given in special literature, effective catalysts for curing urea-formaldehyde resins are salts of iron and aluminum (Fe^{3+} , Al^{3+}) [13]. However, their influence on the physical and chemical properties of the adhesive compositions is not well investigated.

To study the effect of catalysts on the properties of UFR the following experiment was carried out. 0.1–2.1 g of the investigated catalysts were introduced into the sample of the resin with the mass of 150 g with a range of 0.3 g. The mixture was stirred for 5 min until the catalyst was completely dissolved, the following parameters of the adhesive being subsequently measured: the gelling time of the adhesive at the temperature of 100 and 20°C (viability), pH and funnel viscosity. Change of the time of adhesive gelling with different catalysts added at the temperature of 100°C is shown in Fig. 2. For comparison Fig. 2 shows data that have been obtained using ammonium chloride.

Table 2

Change in viscosity of filled adhesive composition during storage

Time, h	Filler type / Filler consumption by weight of the resin			
	Technical calcium sulfate of PG mark / 10%	Technical silica gel of SG mark / 30%	Kaolin / 12%	Marble calcite / 16%
	Viscosity determined by VZ-4, s			
0	140	43	270	240
24	142	48	268	290
48	148	65	264	310
72	154	110	265	320
96	161	Gel	265	340
120	172	Gel	264	360

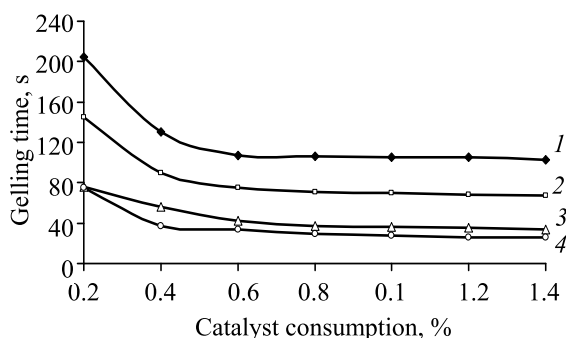


Fig. 2. Influence of catalyst consumption on the resin gelling time:
1 – ammonium sulfate; 2 – ammonium chloride;
3 – PMC; 4 – aluminum sulfate

The data in Fig. 2 show that for all studied curing catalysts the gelling time decreases by increasing their dosages from 0.2 to 0.6% by weight of the resin, and then it stabilizes at a certain level. The minimum curing time with the use of ammonium chloride is 70 s, with ammonium sulfate – 105 s, with PMC – 38 s, with aluminum sulfate 30 s. Thus, concentration of catalysts being equal, the activity of PMC and aluminum sulfate is 1.8 and 2.3 times higher than that of ammonium chloride. This phenomenon opens up new opportunities of using the catalysts concerned for curing low-toxic resins containing insignificant quantities of formaldehyde and not curing with ammonium chloride.

The action mechanism of these catalysts may be related either with the hydrolysis of salts in aqueous medium, leading to acidifying the medium, or with the complexation reaction between the ions of salts and electron-donor groups of the oligomers ($=NH$ and $-NO$ groups). To ascertain the features concerned the changes in the pH of the adhesive composition immediately after adding the catalysts salts and 10–320 min later have been studied (Table 3).

Ammonium chloride has little effect on the acidity of the adhesive composition. Thus, within

the first 10 min the pH decreases by 0.2 units and then does not change. When using aluminammonium alum containing both ammonium ions and aluminum ones, the pH decreases by 0.5 for ten minutes, for the first hour it is 0.8, for the second hour by 0.85, for the third hour by 0.15, for the fourth hour – by 0.15, at the fifth hour – by 0.15.

Similar change in the acidity of the adhesive is observed when using PMC with the consumption of 0.25% by weight of the resin. By increasing the consumption of PMC to 0.5% the rate of acidifying the adhesive composition increases 1.5 times.

When selecting adhesive compositions special attention should be paid to their viability – the time during which the composition retains the required viscosity. Table 4 reveals the results of measuring dynamic viscosity of the adhesive with the addition of various catalysts at the temperature of 20°C. For comparison it also contains the data obtained when using ammonium chloride. If ammonium chloride is used, the viability lasts for more than 4 hours. During this time the viscosity increases 1.3 times.

During the first 3 hours after adding aluminammonium alum the trends of the change in viscosity is almost equal to the figures obtained with the introduction of ammonium chloride as a curing agent. During the fourth hour noticeable increase of viscosity (from 135 to 210 s) begins. Adding PMC in the amount of 0.25% by weight of the resin, it was possible to observe the trends of change in the viscosity of the adhesive composition, which was close to that obtained using ammonium chloride. By increasing the amount of PMC to 0.5% by weight of the resin viscosity began to increase noticeably after 2 hours from the time of its manufacture.

Thus, the viability of the adhesive composition is about 4 hours when PMC with the consumption of 0.25% and aluminum silicate alum of 1% by weight of the resin are used as a curing catalyst, and 2.0–2.5 hours – when using PMC in the amount of 0.5%.

Table 3

Change in the pH of the adhesive composition with the addition of various catalysts

Time, min	Catalyst type and its consumption			
	NH ₄ Cl, 1.0%	AlNH ₄ (SO ₄) ₂ , 1.0%	PMC, 0.25%	PMC, 0.5%
0	6.55	6.57	6.55	6.55
10	6.38	6.05	6.20	6.20
60	6.35	5.75	5.60	5.45
120	6.45	4.90	4.95	4.75
180	6.40	4.85	4.90	4.70
240	6.40	4.70	4.80	4.65
320	6.35	4.55	4.75	4.60

Table 4

**Change in the viscosity of the adhesive composition
with the addition of various catalysts**

Time, min	Catalyst type and its consumption			
	NH ₄ Cl, 1.0%	AlNH ₄ (SO ₄) ₂ , 1.0%	PMC, 0.25%	PMC, 0.5%
0	105	105	105	105
10	105	115	102	102
60	115	115	115	115
120	125	125	130	165
180	128	135	150	210
240	135	210	160	300

Conclusion. The fillers adding into the adhesive composition reduces their consumption by 10–20%. Usage fillers of aluminum-silicate type is not convenient: at the first stage balling of the filler occurs, followed by its swelling and hydration, whereby the viscosity of the adhesive increases considerably.

Usage of sulfate and carbonate types fillers is more preferable as in this case there is no balling and noticeable thickening of the adhesive. The addition of filler of silicate type reduces the viscosity of the adhesive composition.

The combination of fillers of different types permits to control the rheological properties of the adhesive composition.

Effective catalysts for curing UFR are compounds containing ions of trivalent metals. When using these catalysts the resin curing time is reduced by 1.8–2.3 times, which opens up additional possibilities for the usage of low-toxic resins with low formaldehyde content. The gelling time of the adhesive prepared using new catalysts remains for 2–4 hours.

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