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RESOURCE-SAVING TECHNOLOGY OF CASTING RESINS MANUFACTURE

Carbamidfuran and carbamiddianfuran pitches the technology of reception is developed for foundry manufacture resource-saving. As a source of formaldehyde and partially a carbamide it is used carbamidformaldehyd a concentrate. Concentrate use allows to receive pitch with the high maintenance of solids, to exclude a stage evaporation ready pitch, to reduce time of synthesis of pitch and to lower the expense of heat on its reception. The conducted tests of pre-production models of pitch in industrial conditions have shown its suitability for reception sand pitch mixes which apply to manufacturing casting from aluminium.

Introduction. During the manufacture of carbamide-formaldehyde, phenol-formaldehyde, carbamid-formaldehyde-furan and other adhesive resins, formaldehyde is used as a “linking” agent. Traditional technological schemes of the manufacture of adhesive resins provide usage of formalin – water solution containing 36–38% of formaldehyde as a source of formaldehyde.

As a stabilizer commercial formalin contains 3–11% of methanol [1]. During the shelf life of formalin formaldehyde polymerization takes place with formation of polyoxymethylene glycol (paroform) hardly soluble in cold water and capitated. Due to this reason dehomogenization of commercial formalin takes place with changing of formaldehyde concentration in different parts of storage container. This phenomenon results to considerable difficulties in providing of formalin dosage accuracy into the reactor and, consequently, to obtaining of low-quality product [2]. For avoiding of this phenomenon commercial formalin are kept in heated containers made of corrosion-resistant materials [3]. This results to excessive formation of highly toxic formaldehyde from hot solutions and considerable expense on manufacture and heated containers and on catching of gaseous formaldehyde.

In order to receive resin with concentration of dry substances of 60–70% technological operation of dehydration (evaporation) of resin under vacuum takes place. During this operation sewage water is generated containing up to 3% of formaldehyde and up to 5% of methanol. The number of this highly toxic waste product reaches 20–30% out of commercial resin mass [4]. Neutralization of evaporated condensate is very power-intensive and expensive operation.

During the manufacture of phenol-formaldehyde adhesive resins there are considerable ecological problems. This is connected with the usage of formaldehyde as well as phenol having melting temperature of 40–42°C and demanding special equipment for its storage, dosing and providing manufacturing factory with melted phenol [5].

Forconcentrates are being used lately during the manufacture of amino-formaldehyde resin. Forconcentrates are initial condensation product of carbamide and formaldehyde [6]. Manufacture of several kinds of forconcentrates exists in enterprises of the Russian Federation [7]. According to technical standard documentation concentrates contain 40-60% of total formaldehyde and 20–30% of carbamide.

To our point of view, usage of forconcentrates for manufacture of resins is perspective. However, there are no any data on usage of concentrates for manufacture of casting resins including the most perspective - carbamidefuran [8, 9].

Main part. For manufacture of casting resins the following reagents have been used:

– carbamide NSS 2081-86;
– diphenylol propane NSS 12138-86;
– furfuryl alcohol NSS 28960-91;
– sodium hydroxide NSS 4328-77;
– acidum citricum NSS 3652-79;
– carbamideformaldehyde concentrate (CFC) TOR RF 2494-002-1518536-2006.

CFC used for studies contained 60.2% of total formaldehyde and 25.3% of carbamide. Relative viscosity of CFC made 75 s according to viscosity meter B3-246 with nozzle diameter of 4 mm, pH was equal to 8.2, density – 1.32 g/cm^3.

Routine of experiment included: 100 g of CFC was put into three-neck flask with capacity of 500 cm^3. Then mixer was switched on, heating of flask and refrigerator was supplied with water. Acidity of reaction medium was regulated with the help of 10% sodium hydroxide solutions or citric acid. After reaching of specified temperature carbamide, diphenylolpropane (DPP) and furfuryl alcohol (FA) were put into the flask in the specific order. In the course of synthetic reaction of resin samples of resin by volume of 2–5 cm^3 have been chosen for the analysis. Upon the expiry of the specified time ready-made pitch was poured into the container and after cooling till 20–25°C was analyzed.

Changes in composition of reaction medium during the synthesis of carbamidefuran resin at the temperature of 80°C without pH are shown in Fig. 1. Mole ratio of carbamide : formaldehyde : FA in reaction medium made 1 : 2 : 1. pH correction was not carried out. Under such conditions formaldehyde has high reaction capacity and quickly enters into a condensation reaction. In 20 minutes after the beginning of the reaction its content makes 15.3% out of the initial, in 40 min – 3.9%, in 60 min – 0.4%. FA is less reactive substance and considerably slower consumed. Its number made 64.2; 52.2; 44.8% out of the initial content in 20, 40 and 60 min from the beginning of the experiment correspondently.

During the fusion reaction formation of oligomers and their further condensation with trivariate fragments can be observed. This can lead to the considerable increase of pitch viscosity. Under the conditions of the reaction during the first 50 minutes relative viscosity slightly increases from 22 to 36 s. During the next step of the reaction quick increase of viscosity can be observed and in 70 minutes it makes 88 s.

From the experience of casting shops it is known that accuracy of dosage of binding substance and obtaining of homogeneous quartz-resin mixture can be implemented in case of using resin with relative viscosity not more than 90–100 s. Taking into account increase of viscosity in the process of storage, resin viscosity after the fusion reaction have to make not more than 60–70 s. Thus, under such conditions time of the reaction should not be over 60 minutes.

pH phases of resin fusion reaction and ready-made resin have a considerable influence on the quality of carbamidefuran resins. Earlier we have established that during the process of resins manufacture with the usage of formalin, resin of better quality can be obtained at pH phase of fusion reaction, equal 4.5–5.0 [10].

Fig.2 shows changing of composition of the reaction medium at fusion reaction of carbamidefuran resin at pH of 5,0. Citric acid was used as pH regulator. Other parameters were on conformity with the above mentioned ones. Under such conditions the speed of consumption of the initial components and, consequently, speed of condensation reaction is considerably higher.

In 10 minutes of synthesis content of formaldehyde decreases to 41.1%, and FA – to 53.1% out of the initial content, in 20 minutes – to 25.3 and 17.4%, and in 40 minutes – to 2.1 and 5.4% correspondently. In 60 minutes of synthesis the content of free formaldehyde in resin makes 0.15% and content of FA – 1.4%. During the reaction of polycondensation increase of oligomer molecular mass takes place and as a consequence -increase of resin viscosity. However, under such conditions at pH 5.0 viscosity grows slower, in spite of the fact that initial components are consumed faster. During the first 40 minutes gradual increase of viscosity takes place from 26 to 34 s. At further heating viscosity grows on faster and in 50, 60 and 70 minutes makes 43, 61 and 99 s correspondently. Under such conditions time of synthesis should not exceed 50–60 minutes.

Fig. 3 shows changing of composition of carbamidefuran resins, obtained from CFC and FA at different initial value of pH reaction medium.

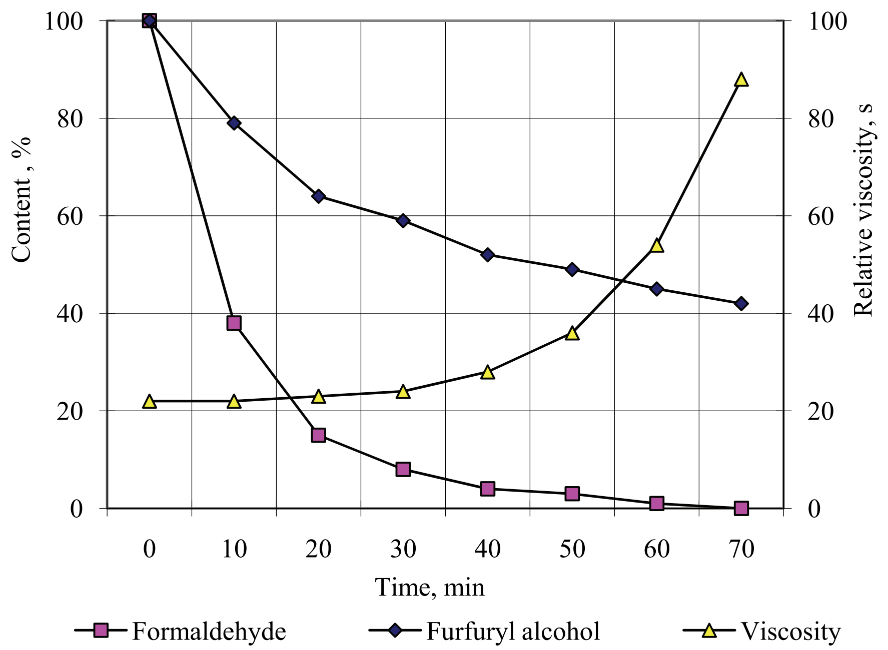

Fig. 1. Changing of reaction medium composition during the manufacture of carbamidefuran resin without pH regulator

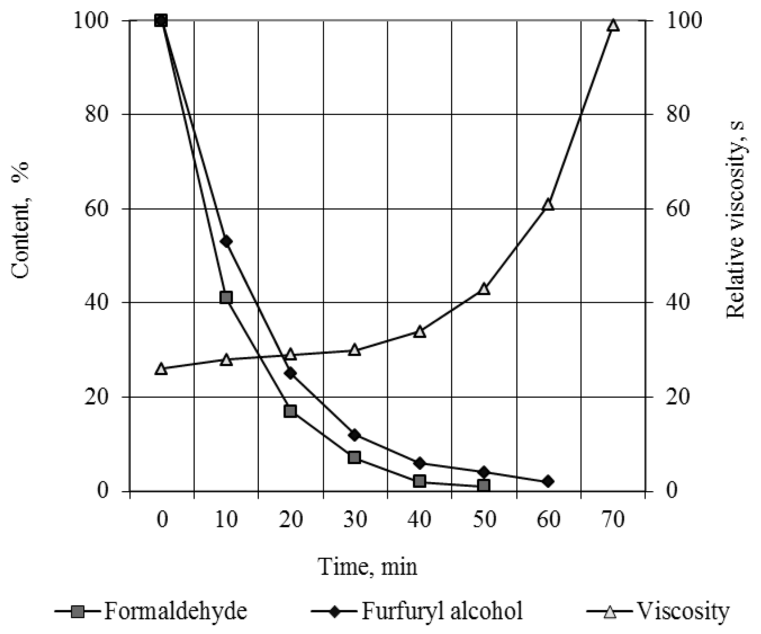

Fig. 2. Changing of composition of reaction medium at manufacture of carbamidefuran resin at pH of 5,0

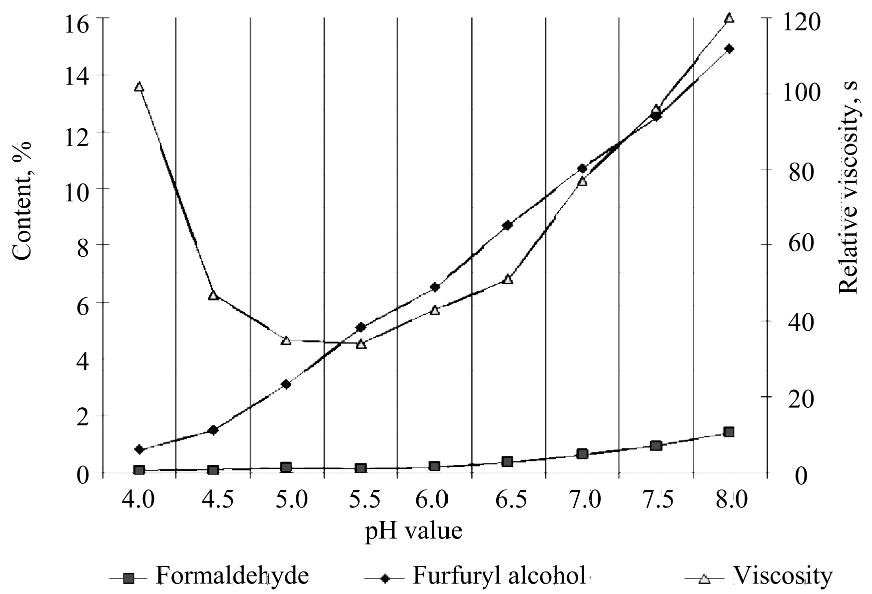

Fig. 3. Influence of pH reaction medium on synthesis phases on composition of carbamidefuran resin

In all the cases time of reaction has made 60 minutes, temperature – 70°C. In the examined range of pH (4–8) minimal content of formaldehyde and FA in the ready-made resin is observed at minimal pH value. At the increase of pH synthesis phase content of free FA and formaldehyde increases. Viscosity of the obtained resin has extreme dependence. Minimal viscosity value, equal 35–40 s, has been obtained at pH reaction medium of 4.5–5.5.

Polycondensation may also take place during the shelf life of the ready-made resin. Studies have shown that this process happens the quickest in acid medium at pH lower than 5.5. Additional neutralization of the obtained resin to neutral pH value considerably slows down this process.

Thus, it is possible to make a conclusion that synthesis of carbamidefuran resins from CFC, carbamide and FA have to be carried out at pH equals 4.5–5.5. In this case we can obtain resin with low viscosity and minimal content of toxic substances. It is necessary to stabilize ready-made resin by adding of alkaline agent into it and reaching pH level to 6.5–7.5 for increasing of shelf life.

Based on obtained experimental data experimental samples of carbamidefuran resins for additional testing have been received. The best samples of resins had 65–67% of dry substances, 0.1–0.2% of free formaldehyde, 3–8% of free FA and 3.2–9.6% of nitrogen.

Testing of resin CKF was carried out in aluminum foundry of JSC "Minsk engine plant" according to the technology "HOT-BOX"-process.

For this, dry molding sand at the amount of 10 kg was put into laboratory blender (grinding-mill) of core area. Then a portion of resin (180–200 g) was put into working grinding-mills and the mixture was stirred during 2.5–3 minutes till even distribution of resin on sand particles. Then 50–70 g of catalyst LK was added into the sand-resin blend and the blend was stirred again during 1.5–2.0 minutes. Ready-made core blend was poured into the bucket and put into a bunker of the core machine (model 4749A1T2) by hand. Under the action of pneumatic air the sand-resin blend was blown into preliminary heated core box (model 50-1307044-B "Branch pipe"). Temperature of the box was regulated with the help of electric heating and during the testing was 187–240°C.

The blend was kept in the heated box during 35–99 s. Then the box was opened and partially harden core was taken out of the box with the help of pushers. In connection with the fact that there was not any experience in usage of new composition in commercial conditions it took some time to choose the time and temperature necessary for the core machine functioning. During the experiment it became possible to establish all the necessary parameters: temperature 230–235°C, time – 75–85 s. Received, under above mentioned parameters, cores had thick filling. Surface of cores was smooth and even with slight surface friability. By the time of withdrawal of the cores from the box a hard "crust" as thick as 10–15 mm had been formed. Final hardening of the core took place during the shelf life due to the accumulated heat. Received cores were cooling down till the temperature of the foundry and were kept for 1.5–2.0 hours for stabilization and then were taken to the external chill sector to the technological operation "Casting". Casting was carried out in accordance with operating technological mode. Temperature of molten aluminium was 680–690°C. Casting was carried out as a routine operation without violation of technological mode. After cooling down, foundry goods were exposed to used-core shaking with the help of the machine 3748B2K2. Used-cores were easily removed and shaking time did not exceed the standard. After removal of the core visual examination of inside surface of foundry goods took place. Roughness of inside surface was the same as surface of foundry goods received in accordance with the present technological mode. There was not any burning-in or rest of sand on surface of foundry goods. For revealing of possible inner defects of foundry goods they were exposed to lengthwise sawing with the help of cutting band. Analysis of cut surface revealed that holes, pinholes, clinks, scabs and other hidden defects were not discovered.

According to the studies, the committee consisting of specialists from JSC "Minsk engine plant" concluded that experimental sample of resin and catalyst are able to provide necessary quality of intricate aluminum castings. At the same time, it is necessary to reduce hardening time of cores to 30–50 s at the temperature of 180–220°C and decrease volatile organic emissions during the production of cores and casting.

Based on the studies, technical standards TS 100354659.081-2010 "Resin carbamidefuran RCF" were developed. Guaranteed shelf life of resin makes 4 months.

At present formula of carbamidedianfuran resins based on CFC and bisphenol A is being developed. These resins have advanced heat-resistance, low nitrogen content, absence of phenol and can be used for production of steel and iron foundry goods.

Conclusion. According to the fulfilled studies it is possible to make the following conclusion:

1. It is necessary to carry out synthesis of carbamidefuran resins from CFC, carbamide and FA at pH 4.5–5.5. In this case we obtain resin with low viscosity and minimal content of toxic substances: content of free formaldehyde – 0.1–0.2%, free furfuryl alcohol – 1–3%, free phenol – absent.

2. For increase of shelf life, it is necessary to stabilize ready-made resin by adding alkaline agent and making pH of ready-made resin to 6.5–7.5.

3. Experimental samples of carbamidefuran resins are suitable for manufacture of qualitative aluminum castings.

4. For wide commercial introduction of new resins it is necessary to choose effective resin curing agent providing hardening of quartz-resin mixture during 30–50 s. at temperature of 180–220°C.

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