Urea-Formaldehyde Resin

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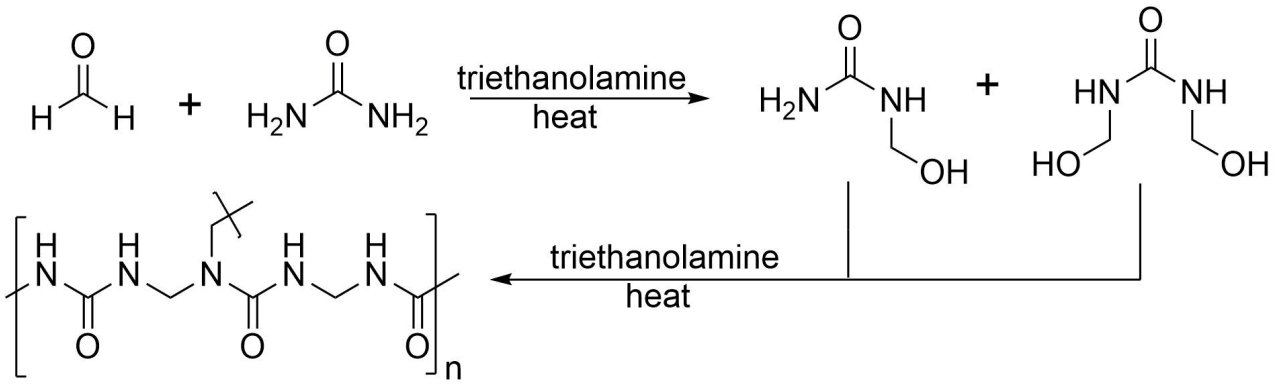

1. Procedure

Low methanol-37% formalin (2840 g, 35 mol, Note 1), 2 g of 80% triethanolamine, and urea (1133 g, 18.9 mol) are charged with agitation into a 5 L, three-necked flask equipped with stirrer, reflux condenser, and thermometer. The urea is dissolved while the temperature of the solution is maintained between 20° and 25°C (Note 2). When the urea is in solution, the pH is adjusted to 7.2-7.4 with triethanolamine or 5 *N* formic acid (Note 3). The reaction mixture is heated to reflux in 30-40 min, maintaining a uniform temperature rise, using a heating mantle attached to a 1KVA variable transformer at 110 volts. The batch is refluxed 1-2 h between 98° and 102°C with vigorous agitation until the reaction is complete.

After 5 min of reflux, a sample is obtained and cooled to 25°C for Ph and viscosity tests (Note 4). The Ph should be 6.4-6.8. The viscosity is checked every 10 min and the readings plotted against time until a value of 17-19 cp is anticipated by extrapolation. When this viscosity is reached, heat is removed, the batch cooled with a cold water or ice bath, and about 2 g of triethanolamine is added to raise the Ph to 7.5-7.7. The resin is concentrated under vacuum (Note 5) until a viscosity of 150-250 cp (Note 6) is reached; the pH should be 7.8-8.0 (Note 7).

2. Characterization

The resin-solids content of the syrup obtained by the described procedure is about 60% (Note 8), and the free formaldehyde in the syrup is between 2% and 4% (Note 9). The composition of the resin is $UF_{1.7}$. This means that, because of the equilibrium between the combined and unreacted formaldehyde, about 2.5 mol of the 35 mol of CH_2O charged is not reacted and is lost during concentration. Less than 50% of the combined formaldehyde is converted into methylene bridges during resinification. It can be assumed that the resin is a blend of mono- and dimethylol ureas, partially crosslinked, forming linear or branched units, or both. These units are probably dimers and trimers; however, no molecular weight data are available.

3. Notes

1. The formalin should contain less than 2% methanol. If methanol-stabilized formalin (6-7% methanol) is used, the resinification is carried out at a somewhat lower pH level.

2. The urea is added slowly to maintain the desired temperature. The checker found that, if the total urea charge is added at one time, the temperature drops to 5-10°C because of the negative heat of solution, necessitating rapid external heating back to 20-25°C. The resultant syrup is slightly opaque and, although it has the required pH and solids content, the viscosity is higher than desired.
3. If the temperature is allowed to rise above 25°C, a rapid reaction starts with constantly changing pH. The pH is measured on a 25-50 g sample with a glass electrode at 25°C.
4. A Brookfield LVF viscometer with No. 1 spindle is used at 60 rpm.
5. The temperature of the syrup should not exceed 50°C. About 910 g of condensate should be collected.
6. A Brookfield LVF viscometer with No. 2 spindle is used at 60 rpm.
7. The equipment is cleaned with hot water immediately.
8. A 5 g sample, weighed in a 3 in diameter aluminum dish, is dried in an oven at 115°C for 5 h to determine solids content.
9. The free formaldehyde is determined by the sodium sulfite method. A 5.0 g sample of the resin is weighed into a 250 ml beaker and dissolved in 100 ml of distilled water. Thymolphthalein solution (10-15 drops) is added and the solution is neutralized with 0.5 *N* NaOH. Exactly 5.0 ml of 0.5 *N* HCl is added from a buret with stirring. A saturated sodium sulfite solution (25 ml) is added, the mixture is stirred for a few seconds and titrated with 0.5 *N* NaOH to the endpoint. A blank is run by diluting 25 ml of saturated sodium sulfite solution with 100 ml of distilled water. Thymolphthalein indicator (10 drops) is added and the solution is titrated to the endpoint with 0.5 *N* HCl. The % free formaldehyde is calculated as:

$$\frac{[(5.0 - \textit{blank}) \times 1\ N\ HCl] - [\textit{ml NaOH} \times 1\ N\ NaOH]}{\textit{grams of sample}} \times 3.003$$

4. Method of Preparation

The condensation of urea and formaldehyde has been widely investigated, and numerous review articles have been published.[3,4,5,6,7,8,9] The resin syrup as described above has a shelf life of at least 6 months. When properly catalyzed with acids or acid salts, it can be used in many binder applications, especially as wood adhesives.

5. References

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