

1

3,489,718

PROCESS FOR THE MANUFACTURE OF UREA FORMALDEHYDE CONDENSATION PRODUCTS

Rudolf Goullon, Grossburgwedel, über Hannover, and Kurt Rehne, Düsseldorf-Holthausen, Germany, assignors to Bohme Fettchemie GmbH, Düsseldorf, Germany

No Drawing. Continuation-in-part of application Ser. No. 321,400, Nov. 5, 1963. This application Apr. 19, 1967, Ser. No. 631,899

Int. Cl. C08g 9/34, 9/10

U.S. Cl. 260—70

9 Claims

ABSTRACT OF THE DISCLOSURE

A process for the manufacture of water-clear etherified alkoxylated urea-formaldehyde resins which are resistant to aging and to discoloration. The process is carried out by a precondensation of a larger part of the formaldehyde with urea, followed by alkoxylation, etherification, and postcondensation with the remainder of the formaldehyde. It has been established that the postcondensation step leads to the properties named. All steps are carried out in a single reaction zone, and intermediate products need not be isolated.

This application is a continuation-in-part of our co-pending application Ser. No. 321,400, filed Nov. 5, 1963, and now abandoned.

The invention relates to the manufacture of ethers of alkoxylated urea-formaldehyde condensates and, more particularly, to their manufacture in the presence of complex boron fluorides and without the need for isolating intermediary products.

It has been established that waterclear etherified alkoxylated urea-formaldehyde condensates, stable upon prolonged storage, can be produced in a single reaction zone avoiding the need for isolation of intermediary products by precondensing 23 mols urea with substantially 7 to 10 mols formaldehyde in weakly alkaline medium and in presence of sodium borotetrafluoride; alkoxylation of the precondensate with an alkylene oxide in an inert gas atmosphere; etherifying with a low-molecular monovalent aliphatic alcohol in weakly acid medium; and postcondensing with substantially 2 to 3 mols formaldehyde in weakly alkaline medium.

The products obtained in this manner are of resinous character and are useful for finishing of textiles, as stabilizer for aminoplastic resins in aqueous solution, and for other purposes. They are especially distinguished, on contrast to the customary urea condensates, by the property of being stable in the presence of chlorine or agents emitting chlorine and particularly by the fact that they do not discolor thereby. Textiles finished with the materials according to the invention do not yellow during washing-, rinsing- or cleansing-operations or when in contact with chlorine-containing liquors during textile finishing. Moreover, the novel condensates can be stored for great lengths of time without incurring disintegration.

In the process according to the invention, the precondensation step of urea with formaldehyde is effected in the customary manner in a weakly alkaline medium in a pH range of approximately 8.0 to 9.0 and at a temperature of approximately 80° C. The duration of the precondensation step preferably is 2 to 6 hours.

For the alkoxylation, ethylene oxide preferably is used, which, however, may be replaced totally or in part by other alkylene oxides, e.g., propylene oxide. As a rule, 0.3 to 0.8 mol alkylene oxide are used per mol urea. The resistance to chlorine is not impaired, however, when larger amounts of alkylene oxide are employed. To avoid

2

local overheating during the alkoxylation, it is expedient to dilute the alkylene oxide by a gas which is inert in the alkaline reaction medium. Such gases are substantially the so-called noble gases and nitrogen, the latter being preferred by reason of its economy only.

As alcohols suited for the etherification methanol, ethanol, n-propanol and isopropanol are named, methanol being the preferred embodiment. Approximately 0.5 to 1.3 mols alcohol are used per mol urea. After the addition of the alcohol, the mixture opportunely is agitated for approximately 30 minutes at approximately 80° C., as is customary in etherifications and esterifications. This part of the reaction is carried out in a weakly acidic range, i.e., a pH of 6.0 to 6.5. Organic acids, such as formic or acetic acid, serve as catalysts.

After readjustment of the pH-value by addition of sodium hydroxide to weakly alkaline, i.e., 8.0 to 9.0, the alkoxylated and partially etherified product is postcondensed without its isolation with substantially 2 to 3 mols formaldehyde. During the postcondensation step, the temperature may be the same as in the etherification step, i.e., substantially about 80° C.

The postcondensation step of the inventive process is important with regard to the light-fastness of the novel condensates. The duration of the postcondensation may be 5 to 60 minutes, but a time of 10 minutes is preferred leading to products combining very good results in textile finishing with optimal quality in storage.

The invention now will be further explained by the following examples. However, it should be understood that these are given merely by way of illustration, not of limitation, and that changes may be made in the details without departing from the spirit and the scope of the invention as hereinafter claimed.

EXAMPLE 1

700 g. Formalin (30%; 7 mols), 155 g. urea (2.6 mols) and 8 g. sodium borotetrafluoride were precondensed at a pH of 8.0 to 9.0 under addition of NaOH for 4 hours at approximately 80° C. The mixture then was cooled to 60° C., and 50 ml. ethylene oxide introduced within the course of 1 hour while providing a nitrogen atmosphere. Thereafter, the temperature of 80° C. was restored and the pH adjusted to 6.0–6.5 by addition of formic acid, 55 g. methanol (1.7 mols) added, and etherification carried out within 30 minutes. The pH then again was raised to 8.0–9.0, 270 g. formalin (2.7 mols) added, and postcondensation carried out at that pH for approximately 10 minutes at substantially 80° C. After cooling to 20° C. (substantially room temperature), a water-clear condensate was obtained which did not exhibit any changes physically or chemically after a 10 months storage period.

EXAMPLE 1A

A cotton poplin, shirt quality, was immersed in an aqueous solution containing per liter water 150 g. of the condensation product obtained according to Example 1 and 15 g. magnesium chloride. The textile, after immersion, was squeezed free of excess solution, dried at 90° C. and then heated for 2 minutes at 160° C. to harden or set the resin. The textile thus finished after adjustment to 60 percent relative humidity and 20° C. had a crease angle of 105°.

A sample of the same cotton finished under like conditions with dimethylolurea and 4 g./l. ammonium nitrate had a crease angle of 106°. The tear resistance of the cotton treated according to the invention, after treatment with sodium hypochlorate, was 80 percent of the original value. The textile finished with dimethylolurea exhibited a tear strength loss of 86 percent, after a like treatment.

3

EXAMPLE 2

700 g. Formalin (30%; 7 mols) and 155 g. urea (2.6 mols) were precondensed in the presence of 8 g. sodium borotetrafluoride for 2 hours at 80° C. at a pH of 8.0 to 9.0. After cooling to 60° C., 100 ml. (2 mols) ethylene oxide were introduced together with nitrogen in the course of 2-3 hours. The temperature then again was raised to 80° C. and the pH changed to 6.0-6.5, and 55 g. methanol (1.7 mols) added. The etherification time was 30 minutes. After readjustment of the pH to 8.0-9.0, 270 g. (2.7 mols) Formalin were added, and a 10 minute postcondensation carried out at 80° C. After cooling to 20° C. again a product was obtained which did not exhibit any changes after 10 months of storage.

EXAMPLE 3

700 g. Formalin (30%; 7 mols), 120 g. urea (2 mols) and 8 g. sodium borotetrafluoride were adjusted to a pH of 8.0 to 9.0 with NaOH and precondensed for 4 hours at 80° C. After cooling to 60° C., 50 ml. ethylene oxide (1 mol) were introduced in a nitrogen atmosphere within the course of 1 hour. The temperature again was raised to 80° C. and the pH adjusted to 6.0-6.5 by addition of formic acid, 55 g. methanol (1.7 mols) added, and etherified within 30 minutes. After changing the pH to 8.0-9.0, 270 g. formalin (2.7 mols) were added, and postcondensation carried out for 10 minutes at the same pH and at 80° C. After cooling to 20° C. a waterclear product was obtained.

EXAMPLE 3A

A cotton poplin was finished as described in Example 1A with an aqueous solution containing per liter 150 g. of the condensation product from Example 3 and 15 g. magnesium chloride. The textile thus treated exhibited a tear strength loss of 18 percent after a sodium hypochlorite treatment.

A cotton poplin chlorine-treated in the same manner which had been finished with dimethylolurea, as described in Example 1A, had a tear strength loss of 86 percent.

EXAMPLE 4

700 g. Formalin (30%; 7 mols), 180 g. urea (mols) and 9 g. sodium borotetrafluoride were adjusted with NaOH to a pH of 8.0 to 9.0 and precondensed for 4 hours at 80° C. After cooling to 60° C., 50 ml. ethylene oxide (1 mol) were introduced with one hour in a nitrogen atmosphere. The temperature then again was raised to 80° C., the pH adjusted with formic acid to 6.0-6.5, 55 g. methanol (1.7 mols) added, and etherified within 30 minutes. After restoring the pH to 8.0 to 9.0, 270 g. Formalin (2.7 mols) were added, and postcondensed at like pH for approximately 10 minutes at 80° C. After cooling to 20° C. a water-clear product was obtained.

EXAMPLE 4A

A cotton poplin was finished as described in Example 1A with an aqueous solution containing 150 g. of the product obtained according to Example 4 and 15 g. zinc nitrate per liter. The textile thus treated had a tear strength loss of 30 percent after washing five times with 2 g./l. soap and 2 g./l. soda at 100° C. and chlorine treatment after each wash with a sodium hypochlorite solution. A textile finished with dimethylolurea, as shown in Example 1A, after the same wash and chlorine treatment conditions, had a tear resistance loss of 60 percent

EXAMPLE 5

The proportions of the ingredients were the same as in Example 1, except that etherification was carried out with 110 g. methanol (3.4 mols). After termination of the reaction and cooling, a water-clear condensate of excellent storage resistance was obtained.

4

EXAMPLE 6

In a 2 liter round-bottom flask, equipped with agitator, reflux condenser, thermometer, dropping funnel and single-rod electrode, 155 g. urea (2.6 mols), 700 g. formaldehyde (30%; 7.0 mols) and 8 g. NaBF₄ were precondensed at a pH of 8.0-8.5 (adjusted with NaOH) for 4 hours at 80° C. After cooling to 60° C., 73.0 ml. propylene oxide (1 mol) were dropped in within 2-3 hours while providing a nitrogen atmosphere, whereby 0.85 mols were reacted. The temperature then was restored to 80° C., the pH lowered to 6.0-6.5 by addition of formic acid, 55 g. methanol added (1.7 mols), and etherified within 30 minutes. By addition of NaOH the pH again was raised to 8.0-8.5, 270 g. 30% formaldehyde (2.7 mols) added, and postcondensed at that pH for 10 minutes at substantially 80° C. The reaction then was stopped by cooling to 20° C. A water-clear and stable condensate solution resulted.

EXAMPLE 7

The conditions were the same as in Example 6 except that 145 g. propylene oxide (2.0 mols) were reacted and the precondensation was limited to 2 hours. Again a water-clear, stable solution of the condensate was obtained.

EXAMPLE 8

The same conditions were employed as in Example 6, with the following exceptions: 2 mols urea were reacted with a total of 9.7 mols formaldehyde, 1 mol propylene oxide and 1.7 mols methanol. The resulting condensate was very stable.

The conditions of Example 6 were varied concerning the time of postcondensation to demonstrate in the following table its influence on color-stability of the condensate based on "Cibacron türkischblau G" (registered trademark) (turquoise blue) in the xenon-test according to DIN 53 952 ("DIN" is a German Industrial Standard comparable to ASTM standards). The test material was an unfinished cotton poplin of shirt quality colored with "Cibacron türkischblau G" having the optimal test value of 6. A cotton poplin finished with an aqueous solution of formaldehyde showed no change in the sensitivity value of 6.

Time of post condensation (min.):	Sensitivity value according to DIN 53 952
0	1
10	1-2
20	2-3
30	3
40	2
50	1
60	1

Although a postcondensation time of 30 minutes leads to condensates giving the best results in the xenon-test, it is preferred to use condensates which are postcondensed for only 10 minutes because they have better stability on storage.

EXAMPLE 9

Under the same conditions as described in Example 6, 3 mols urea were reacted with a total of 9.7 mols formaldehyde, 1 mol propylene oxide and 1.7 mols methanol. The condensate obtained was very stable.

EXAMPLE 10

Under the same conditions as in Example 6, 2.6 mols urea were reacted with a total of 9.7 mols formaldehyde, 1 mol propylene oxide and 3.4 mols methanol. A stable condensate was obtained.

EXAMPLE 11

700 g. Formalin (30%; 7.0 mols), 120 g. urea (2.0 mols) and 6 g. sodium borotetrafluoride were adjusted to a pH of 8.0 to 9.0 with NaOH and precondensed for 4 hours at 80° C. After cooling to 60° C., 1 mol propylene

oxide was added within the course of 2 to 3 hours while providing a nitrogen atmosphere. The temperature then again was raised to 80° C., the pH adjusted to 6.0–6.5 with formic acid, 1.7 mols ethanol added, and etherified during approximately 30 minutes. After raising the pH again to 8.0–9.0, 270 g. Formalin (2.7 mols) were added, and postcondensation carried out for approximately 10 minutes at 80° C. After cooling to approximately 20° C., a water-clear, stable compound resulted.

EXAMPLE 12

700 g. Formalin (30%; 7.0 mols) and 155 g. urea (2.6 mols) were precondensed in the presence of 8 g. sodium borotetrafluoride at a pH of 8.0–9.0 for 6 hours at 80° C. After cooling to 60° C., 1 mol propylene oxide was introduced in a nitrogen atmosphere within the course of 2–3 hours. The temperature again was raised to 80° C., the pH adjusted to 6.0–6.5, 1.7 mols n-propanol added, and etherified for 30 minutes. The pH then was adjusted to 8.0–9.0, and postcondensed under addition of 270 g. (2.7 mols) Formalin at substantially 80° C. After cooling to 20° C., a clear and stable condensate resulted.

Although in the foregoing examples either propylene oxide or ethylene oxide have been used singly, the use of mixtures of these alkylene oxides within the limits given and in all proportions is not precluded thereby and is entirely possible.

We claim as our invention:

1. A process for the manufacture of etherified alkoxy-ated urea-formaldehyde condensates in a single reaction zone and while avoiding the need for isolation of intermediary products, which comprises precondensing 2 to 3 mols urea with substantially 7 to 10 mols formaldehyde in weakly alkaline medium and in the presence of sodium borotetrafluoride; alkoxy-ating the precondensate with substantially 0.3 to 0.8 mols, per mol urea, of an alkylene oxide selected from the group consisting of ethylene oxide, propylene oxide and mixtures thereof in an inert gas atmosphere; etherifying with approximately 0.5 to 1.3 mols, per mol urea, of a low-molecular monovalent aliphatic alcohol in weakly acidic medium; and postcondensing with substantially 3 mols formaldehyde in weakly alkaline medium; thereby obtaining a water-clear product, stable against discoloration and aging.

2. The process as defined in claim 1, wherein said alkylene oxide is selected from the group consisting of ethylene oxide, propylene oxide and mixtures thereof.

3. The process as defined in claim 1, wherein said alcohol is selected from the group consisting of methanol, ethanol, n-propanol and isopropanol.

4. The process as defined in claim 1, wherein said weakly alkaline medium for precondensation and postcondensation is at a pH range of substantially 8.0–9.0.

5. The process as defined in claim 1, wherein said weakly acidic medium is at a pH range of substantially 6.0–6.5.

6. The process as defined in claim 1, wherein precondensation is carried out for substantially 2 to 6 hours at substantially 80° C.

7. The process as defined in claim 1, wherein alkoxylation is carried out at substantially 60° C. within essentially 1 to 3 hours.

8. The process as defined in claim 1, wherein postcondensation is carried out within 5 to 60 minutes at substantially 80° C.

9. A process for the manufacture of etherified alkoxy-ated urea-formaldehyde condensates in a single reaction zone and while avoiding the need for isolation of intermediate products, which comprises precondensing 2–3 mols urea with 7 to 10 mols formaldehyde at a pH of essentially 8.0–9.0 for approximately 2–6 hours at substantially 80° C., in the presence of sodium borotetrafluoride; alkoxy-ating the precondensate in an inert gas atmosphere with substantially 0.3–0.8 mol per mol of urea of a substance selected from the group consisting of ethylene oxide, propylene oxide, or mixtures thereof, within approximately 1–3 hours at substantially 60° C.; etherifying with approximately 0.5–1.3 mols, per mol urea, of an alcohol selected from the group consisting of methanol, ethanol, n-propanol and isopropanol, at a pH of substantially 6.0–6.5; and postcondensing with essentially 3 mols formaldehyde at a pH of essentially 8.0–9.0 at substantially 80° C. for approximately 5–60 minutes; thereby obtaining a water-clear product, stable against discoloration and aging.

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WILLIAM H. SHORT, Primary Examiner

T. PERTILLA, Assistant Examiner