

UNITED STATES PATENT OFFICE

2,240,734

PROCESS FOR THE PREPARATION OF
PENTAERYTHRITOLJoseph A. Wyler, Allentown, Pa., assignor to
Trojan Powder Company, Allentown, Pa.No Drawing. Application March 28, 1940,
Serial No. 326,377

7 Claims. (Cl. 260-635)

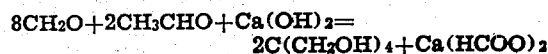
This invention relates to a process for the alkaline condensation of formaldehyde and acetaldehyde to pentaerythritol through the use of certain catalytic agents.

It is well-known that pentaerythritol is formed by the condensation of four molecules of formaldehyde with one molecule of acetaldehyde in the presence of such alkalis as NaOH, KOH, Ca(OH)₂, or Ba(OH)₂, and although many such processes are described in the literature, the yields are usually low—approximately 50-60% of theory. In addition to the low yields, further unfavorable factors in these processes are the length of time required to complete the reaction and the formation of a relatively large amount of a dark colored resinous syrup.

It is an object of my invention to increase the yield of pentaerythritol received from a given amount of aldehydes. A further object is to prevent the formation of colored products during the condensation of the CH₂O and the CH₃CHO. Still further objects are to speed up the reaction in the cold and to obtain more uniform and consistent results for this condensation.

In general, the commercial condensation of CH₂O and CH₃CHO is based upon the use of 4 to 5 molecules of formaldehyde for each molecule of acetaldehyde in alkaline media, at temperatures not exceeding 50° C., and in such a volume of water as to provide a solution to contain less than 20% of aldehydes at the beginning of the reaction.

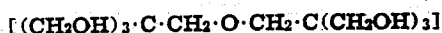
Although the general reaction for the formation of pentaerythritol is as follows:



the pentaerythritol is generally believed to be the result of the following reactions:

1. $2\text{CH}_3\text{CHO} + 6\text{CH}_2\text{O} = 2(\text{CH}_2\text{OH})_3\text{C}\cdot\text{CHO}$
2. $2\text{CH}_2\text{O} + \text{Ca}(\text{OH})_2 = \text{Ca}(\text{OOCH})_2 + 2\text{H}_2$
3. $2(\text{CH}_2\text{OH})_3\text{C}\cdot\text{CHO} + 4\text{H} = 2\text{C}(\text{CH}_2\text{OH})_4$

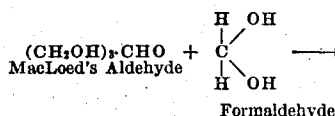
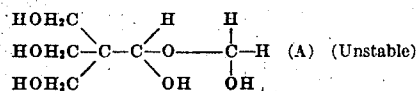
However, in addition to these reactions others, producing dipentaerythritol, and sugary, syrupy products also take place, but as is readily observed, the reactions above do not explain the formation of dipentaerythritol



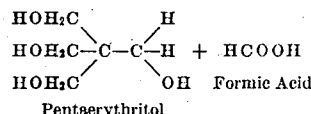
which usually forms to the extent of about 10-15% of the pentaerythritol.

It is possible that some of the pentaerythritol

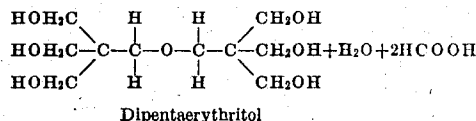
and the dipentaerythritol is formed in accordance with the following reactions:



and that one molecule of "A" undergoes decomposition into



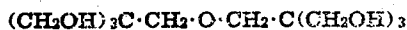
and that two molecules of "A" undergo decomposition into:



I wish to emphasize that the theory just given is not intended to limit my invention in any way and that it has been presented in order to convey a better understanding of the possible function of my catalytic agents and of the principles upon which the action of my catalytic agents may be based.

In my previous applications, S. N. 200,683, and S. N. 270,340 I have disclosed the use of oxalates of Fe, Co, Cr, Mn, Ni and Cu as well as of Cu₂O and Pt as catalytic agents.

I have now discovered that certain acid amides are effective catalysts in the condensation of CH₂O and CH₃CHO to C(CH₂OH)₄ and



and that these acid amides may also be used in combination with the agents disclosed in the applications mentioned above to obtain an additional advantage.

In order to point out my invention more clearly, the following examples, in which all parts are by weight, are given.

Example #1

396 parts of 30% formaldehyde and 45 parts of acetaldehyde (99%) are mixed with 955 parts of water in a suitable container provided with a stirrer. To this is slowly added, with continued stir-

ring, 53 parts of hydrated lime (low in magnesium) made into a slurry by means of about 100 parts of water. This slurry is added over a period of three to five hours and the reaction mixture is maintained at approximately 20-30° C. throughout the period of addition.

Just before the beginning of the addition of the lime slurry, about 2 parts of formamide are added to the condensation mixture.

After all of the lime has been added the stirring is continued at 20-30° C. until an iodine titration indicates less than, say, 0.10% of aldehydes, calculated to CH_2O . The time to arrive at this point varies considerably with the quality of the lime used and other factors. In general 48-72 hours is considered an average length of time for the completion of the reaction at the temperature indicated above.

The reaction mixture, at completion, is treated in the cold with about 10% less sulfuric acid than is theoretically equivalent to the lime used. This precipitates most of the lime as calcium sulfate. In order to precipitate all of the calcium out of solution, a small amount of oxalic acid is added, in portions, until tests indicate a slight excess present in the mixture. At this stage there will be some sulfate ions in the solution. These are removed by the addition, in small portions, of barium hydrate or barium carbonate, until tests indicate the absence of sulfate ions. This mixture, after a short period of stirring is allowed to settle for several hours or more when the clear supernatant liquor is decanted and the residue filtered. The clear liquors are vacuum evaporated and the pentaerythritol recovered by crystallization. The yield of pentaerythritol plus dipentaerythritol is over 80% of theory and the mother liquors usually have a yellow-brownish color.

Example #2

Using the same reactants and procedure as given in Example #1, except that 0.25 part of copper oxalate are added at a stage in the reaction corresponding to 2½ hours after the beginning of the lime addition, the time of reaction is considerably reduced. Also, the pentaerythritol and dipentaerythritol obtained as original crystals from this reaction mixture are essentially colorless. The mother liquor obtained from these crystals is usually practically colorless and is more stable toward heat and oxidizing influences than is the mother liquor made in accordance with Example #1. The yields of pentaerythritol plus dipentaerythritol are, in this case, also above 80% of theory.

Example #3

Using the same reactants and procedure as given in Example #2 and adding about 1 part of precipitated Cu after the condensation reaction had proceeded for a few hours, the time of reaction is still further reduced and good yields of pentaerythritol and dipentaerythritol obtained. The product is usually white and the mother liquor obtained is more stable toward heat and oxidative effects than that obtained in either of the previous examples. The greatest single effect of the metallic copper is to speed up the reaction for a given temperature, particularly at the final stages of the condensation. In this respect it is more effective than copper oxalate or cuprous oxide.

In the examples, mention was made of formamide, copper oxalate and metallic copper. How-

ever, in place of the formamide I may use such water soluble amides as acetamide, propionamide, butyramide, and valeramide; in place of copper oxalate I may use oxalates of Fe, Co, Cr, Mn, or Ni, which are metals of the first long period Mendelejeff's Periodic System, and in place of metallic copper I may use Cu_2O or Pt. Also, I may use a larger or a smaller proportion of the acid amide, the oxalate, the oxide, or metal in relation to the aldehydes; or I may use a lower or higher temperature for the reaction, a higher or lower concentration of the reactants, or I may vary the stage at which the various catalysts are added. In short, I may use such operative conditions or details as would occur to a workman skilled in this art, without departing from the essence of this invention.

I claim:

1. The process for the preparation of pentaerythritol comprising the condensation in aqueous media of formaldehyde and acetaldehyde to pentaerythritol in the presence of a fixed alkali and an aliphatic acid amide containing not more than 5 carbon atoms.

2. The process for the preparation of pentaerythritol comprising the condensation in aqueous media of formaldehyde and acetaldehyde to pentaerythritol in the presence of a fixed alkali, an aliphatic acid amide containing not more than 5 carbon atoms, and an oxalate of a metal of the first long period of Mendelejeff's Periodic System having an atomic weight between 52 and 63.6.

3. The process for the preparation of pentaerythritol comprising the condensation in aqueous media of formaldehyde and acetaldehyde to pentaerythritol in the presence of a fixed alkali, an aliphatic acid amide containing not more than 5 carbon atoms, an oxalate of a metal of the first long period of Mendelejeff's Periodic System having an atomic weight between 52 and 63.6, and a member of the group consisting of cuprous oxide and copper.

4. The process for the preparation of pentaerythritol comprising the condensation in aqueous media of formaldehyde and acetaldehyde to pentaerythritol in the presence of a fixed alkali, an aliphatic acid amide containing not more than 5 carbon atoms, and an oxalate of a metal of the first long period of Mendelejeff's Periodic System having an atomic weight between 52 and 63.6; the molecular ratio of formaldehyde to acetaldehyde being approximately four to one and the total aldehyde content of the solution being less than 20% by weight.

5. The process for the preparation of pentaerythritol comprising the condensation in aqueous media of formaldehyde and acetaldehyde to pentaerythritol in the presence of a fixed alkali, an aliphatic acid amide containing not more than 5 carbon atoms, an oxalate of a metal of the first long period of Mendelejeff's Periodic System having an atomic weight between 52 and 63.6, and a member of the group consisting of cuprous oxide and copper; the molecular ratio of the formaldehyde to acetaldehyde being approximately four to one and the total aldehyde content of the solution being less than 20% by weight.

6. The process for the preparation of pentaerythritol comprising the condensation in aqueous media of formaldehyde and acetaldehyde to pentaerythritol in the presence of calcium hydroxide, an aliphatic acid amide containing not more than 5 carbon atoms and an oxalate of a metal of the first long period of Mendelejeff's

Periodic System having an atomic weight between 52 and 63.6; the molecular ratio of the formaldehyde to the acetaldehyde being approximately four to one and the total aldehyde content of the solution being less than 20% by weight; the proportion, by weight, of the metal oxalate to formaldehyde being approximately 0.25 to 119, and that of the acid amide being 2 to 119.

7. The process for the preparation of pentaerythritol comprising the condensation in aqueous media of formaldehyde and acetaldehyde to

pentaerythritol in the presence of calcium hydroxide, formamide and copper oxalate; the molecular ratio of the formaldehyde to the acetaldehyde being approximately four to one and the total aldehyde content of the solution being less than 20% by weight; the proportion, by weight, of the copper oxalate to formaldehyde being approximately 0.25 to 119 and that of the formamide being 2 to 119.

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