

UNITED STATES PATENT OFFICE

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PROCESS FOR THE PREPARATION OF
PENTAERYTHRITOLJoseph A. Wyler, Allentown, Pa., assignor to
Trojan Powder Company, Allentown, Pa.No Drawing. Application April 7, 1938,
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9 Claims. (Cl. 260-635)

This invention relates to a process for the preparation of pentaerythritol and more particularly to a process for condensing formaldehyde and acetaldehyde to pentaerythritol through the use of certain modifying and directive 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 alkalies as NaOH, KOH, $\text{Ca}(\text{OH})_2$ or $\text{Ba}(\text{OH})_2$, and although many such processes are described in the literature, the yields are usually low—approximately 60% of theory. In addition to the low yields, a further unfavorable factor in these processes is the formation of a relatively large amount of a dark colored, resinous syrup. The elimination of this syrup from the pentaerythritol is a rather difficult operation and increases the cost of the pentaerythritol considerably.

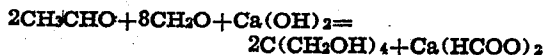
Now, it is an object of my invention to increase the yield of pentaerythritol received from a given amount of aldehydes.

It is a further object to prevent the formation of colored products during the condensation of the CH_2O and the CH_3CHO .

A still further object is to retard or prevent the formation of brownish colored products during the evaporation of the condensation liquors containing the pentaerythritol.

Other and further objects will become apparent upon a perusal of the remainder of this specification.

The theoretical reaction for the condensation of formaldehyde and acetaldehyde to pentaerythritol is as follows:



although in all known processes, this reaction is accompanied by several side reactions which produce sugars and other products. These side reactions lower the yield of pentaerythritol.

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

I have discovered that if this condensation is carried out in the presence of an oxalate of a metal of the 1st long period, of Mendelyev's Periodic System, having an atomic weight between 52 and 63.6, a distinct improvement in the

color and the yield of pentaerythritol is obtained, and the condensation liquors are either free from or contain only an insignificant amount of a resinous product. The absence of the latter product has an important bearing upon the usefulness of my process.

In order more clearly to point out my invention it is necessary to deal with certain theoretical aspects of the condensation of CH_2O with CH_3CHO in the presence of alkali. Consequently, although certain parts of my theories may later be found to be in error, I do not limit myself by these theories; I am exposing these theories merely to explain my invention.

All known processes for the condensation of CH_2O and CH_3CHO to $\text{C}(\text{CH}_2\text{OH})_4$ are conducted in alkaline solutions. If, for purposes of illustration we choose $\text{Ca}(\text{OH})_2$ as the alkali, the general reaction given above shows how the pentaerythritol is formed, and as previously indicated, this equation does not give a complete picture of the condensation.

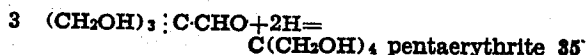
It is well known that pentaerythrose (MacLeod's) is an intermediate product. The latter may be considered as forming according to the following equation:



A simultaneous reaction is as follows:



The next reaction may then be considered to be as follows:



In addition to these reactions, others producing sugary, syrupy products also take place. It is evident, however, that the more perfect is the balance between Reactions 1 and 2, the greater is the yield of pentaerythritol and the less is the yield of syrupy products.

Now, I have discovered that there are agents which promote Reaction 2 and consequently Reaction 3, while at the same time not materially affecting Reaction 1.

I have also discovered that these agents prevent the formation of certain colored intermediate products of unknown composition. The presence or absence of these colored materials can readily be detected in the manner to be explained later.

I wish to emphasize that a very significant part of my invention is the discovery that it is possible to alter the course of the reaction between

formaldehyde and alkali in such a manner as to produce reactive or atomic hydrogen in relatively larger amounts and sugars in relatively smaller amounts—and this through the agency of certain materials present only in very minor proportions. In other words, I have discovered that oxalates of metals of the 1st long period of Mendelyev's Periodic System having atomic weights between 52 and 63.6 act as agents which cause formaldehyde to react with alkali, in the presence of acetaldehyde, to form formate and atomic hydrogen, in preference to sugars. For convenience I call these agents "formate-hydrogen" catalysts.

The following example illustrates my invention.

Example

396 parts (by weight) of 30.34% formaldehyde and 79.5 parts (by weight) of 52.8% of commercial acetaldehyde are mixed with 966 parts (by weight) of water in a suitable container provided with a stirrer. To this is slowly added, with stirring, a mixture of 35 parts (by weight) of CaO and 100 parts (by weight) of water. This slurry is added over a period of four to six hours and the reaction mixture is kept at approximately 20–30° C. throughout the period of addition.

Just before the addition of the lime slurry, 0.25 parts of finely powdered copper oxalate is added to the mixture of aldehydes.

After all the lime has been added, the stirring is continued until an iodine titration indicates less than, say, 0.10% total aldehydes, calculated to % CH_2O . The time required to arrive at this point varies with conditions but is usually not over 20 hours.

The reaction mixture, at completion, generally is colorless or of a slight greenish cast. It is then treated with slightly less sulphuric acid than is theoretically equivalent to the lime used. This precipitates the lime as calcium sulfate. In order to precipitate all of the lime out of solution, a small amount of oxalic acid is added in the form of a water solution and the mixture stirred for an hour or more. The mixture is then filtered. The filtrate is evaporated and the pentaerythritol recovered by crystallization. This pentaerythritol is almost pure white. The weight of dry crystals readily obtainable is 96 parts. By further treatment it is possible to obtain 10–15 parts more of pentaerythritol making a total yield of about 80% of theory. The remaining material is a syrup of a cream to almost white color.

In the embodiment of my invention mentioned above I have given certain specific details. I have not mentioned these for the purpose of limiting my invention, but to show the preferred mode in which I contemplate applying my invention.

In place of the lime, I may use any water soluble fixed alkali as $\text{Ba}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, NaOH , KOH , K_2CO_3 , Na_2CO_3 , $(\text{CH}_3)_4\text{N}(\text{OH})$, $(\text{C}_2\text{H}_5)_4\text{N}(\text{OH})$, etc., and in place of the copper oxalate, I may use an oxalate of such metals as Fe, Co, Cr, Mn and Ni. I may also use a mixture of two or more of these oxalates in place of the copper oxalate alone.

I may vary the temperature at which the reaction is carried out, the proportion of CH_2O to CH_3CHO , the concentration of these aldehydes, the rate of addition of the fixed alkali, the amount of alkali used, the amount of "formate-hydrogen" catalyst and such other operative details as would occur to a workman skilled in this art.

In regard to the stage in the condensation reaction at which to add the "formate-hydrogen" catalyst, I wish to mention that the best results are usually gotten when the catalyst is added after about 60% of the condensation (as determined with iodine) is over. However, this varies with the nature of the fixed alkali used. A simple test to determine if the "formate-hydrogen" catalyst has been added early enough, is to remove a small sample of the alkaline condensation liquor and to acidify carefully. At the point at which the liquor just becomes acid a dark green to blue coloration will make its appearance if the "formate-hydrogen" catalyst has not been added early enough.

In the case of certain commercial hydrated limes, difficulty is at times experienced in inducing the condensation to complete itself. In such cases it is advantageous to heat the mixture up to 40–50° C. This usually completes the reaction within a few hours after the addition of the lime.

Under certain conditions it is advisable to use a mixture of say $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$, of $\text{Ca}(\text{OH})_2$ and KOH , of copper oxalate and iron oxalate, of manganese oxalate and chromium oxalate, or etc., in order to carry out the condensation.

Persons skilled in the commercial preparation of pentaerythritol are aware that a small percentage of dipentaerythrite is always formed along with the pentaerythritol, and such is the case in my process.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that no limitations are to be made upon my invention, except as defined in the appended claims.

I claim:

1. The condensation of formaldehyde and acetaldehyde to pentaerythritol in the presence of a fixed alkali and an oxalate of a metal of the 1st long period, of Mendelyev's Periodic System, having an atomic weight between 52 and 63.6.

2. The condensation of formaldehyde and acetaldehyde to pentaerythritol in the presence of an alkaline earth metal hydroxide and an oxalate of a metal of the 1st long period, of Mendelyev's Periodic System, having an atomic weight between 52 and 63.6.

3. The condensation of formaldehyde and acetaldehyde to pentaerythritol in the presence of an alkaline earth metal hydroxide and an oxalate of copper.

4. The condensation of formaldehyde and acetaldehyde to pentaerythritol in the presence of an alkaline earth metal hydroxide and an oxalate of nickel.

5. The process of condensing formaldehyde and acetaldehyde to pentaerythritol which comprises the addition of a fixed alkali to an aqueous mixture containing an oxalate of a metal of the 1st long period, of Mendelyev's Periodic System, having an atomic weight between 52 and 63.6, formaldehyde and acetaldehyde, the molar ratio of formaldehyde to acetaldehyde being approximately four to one.

6. The process of condensing formaldehyde and acetaldehyde to pentaerythritol which comprises the addition of an alkaline earth metal hydroxide to an aqueous mixture containing an oxalate of a metal of the 1st long period of Mendelyev's Periodic System, having an atomic weight between 52 and 63.6, formaldehyde and acetaldehyde

hyde, the molar ratio of formaldehyde to acetaldehyde being approximately four to one.

7. The process of condensing formaldehyde and acetaldehyde to pentaerythritol which comprises
5 the addition of an alkali metal hydroxide to an aqueous mixture containing an oxalate of a metal of the 1st long period of Mendelyev's Periodic System, having an atomic weight between 52 and 63.6, formaldehyde and acetaldehyde, the
10 molar ratio of formaldehyde to acetaldehyde being approximately four to one.

8. The process of condensing formaldehyde and acetaldehyde to pentaerythritol which comprises the addition of calcium hydroxide to an aqueous
15 mixture containing an oxalate of a metal of the 1st long period of Mendelyev's Periodic Sys-

tem, having an atomic weight between 52 and 63.6, formaldehyde and acetaldehyde, the molar ratio of formaldehyde to acetaldehyde being approximately four to one.

9. The process of condensing formaldehyde and
5 acetaldehyde to pentaerythritol which comprises the addition of a fixed alkali to an aqueous mixture containing an oxalate of a metal of the 1st long period of Mendelyev's Periodic System, having an atomic weight between 52 and 63.6, form-
10 aldehyde and acetaldehyde, the molar ratio of formaldehyde to acetaldehyde being approximately four to one and the total aldehyde content of the solution being less than 20% by weight.

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