

UNITED STATES PATENT OFFICE

2,463,677

PROCESS FOR THE REMOVAL OF REDUCING
SUGAR FROM POLYHYDRIC ALCOHOL
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Serial No. 699,077

4 Claims. (Cl. 260—637)

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The present invention relates to the removal of reducing sugars from compositions comprising polyhydric alcohol and reducing sugar.

An object of the present invention is the production, from compositions comprising polyhydric alcohol and reducing sugar, of compositions which have a very low reducing sugar content.

Another object of the invention is the provision of a method which is particularly useful in the removal of residual reducing sugar from polyhydric alcohol compositions prepared by the reduction of reducible sugar.

Still another object of the invention is the provision of an economical method of removing reducing sugars from polyhydric alcohol compositions to produce compositions which contain the polyhydric alcohol in substantially its original condition, that is, without substantial conversion to other products as by oxidation or internal or external etherification.

Other objects of the invention will hereinafter more fully appear.

Polyhydric alcohol compositions frequently contain substantial amounts of reducing sugar. By reducing sugar is meant a sugar that will reduce Fehling's solution at the boiling point, as for example a triose such as glyceraldehyde, a pentose such as xylose, rhamnose, and the like, a hexose such as glucose, fructose, mannose, galactose, and the like, or a reducing dissacharide such as lactose, maltose, or the like.

Polyhydric alcohol compositions are often used in industrial processes under conditions in which the presence of any substantial quantity of reducing sugar is objectionable. Thus, for example, the polyhydric alcohol composition may be employed in chemical reactions under temperature conditions which tend to decompose any reducing sugar present with resultant discoloration or other objectionable performance, either physical or chemical, or both. Consequently, the provision of a method for the ready and economical removal of reducing sugar from polyhydric alcohol compositions containing the same is highly desirable.

The polyhydric alcohol of the compositions from which reducing sugar is removed in accordance with the method of the present invention may be any of the water-soluble polyhydric

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alcohols, such as glycol, polyglycol, glycerine, polyglycerine, erythritol, pentaerythritol, sorbitol, mannitol, dulcitol, and the like. As above indicated, the method of the present invention is particularly applicable to the treatment of polyhydric alcohol compositions derived from reducible sugar and containing residual reducing sugar, as for example, sorbitol solutions prepared by the reduction of glucose.

In the production of such polyhydric alcohol compositions by the reduction of reducible sugar it is seldom practical to carry the reduction beyond 99.9% completion. Moreover, in many such processes, the rate of sugar reduction decreases very rapidly after about 90% of the sugar has been reduced. The method of the present invention is sufficiently economical to make it advantageous in such processes to terminate the hydrogenation when further hydrogenation could only be accomplished at a very low rate and to thereafter treat the polyhydric alcohol composition in accordance with the method to bring the reducing sugar down to a very low level. However, the method of the present invention is not to be considered as limited to the treatment of compositions produced by the reduction of reducible sugar as it is applicable to polyhydric alcohols containing reducing sugar irrespective of the manner in which the reducing sugar became mixed with the polyhydric alcohol.

In accordance with the method of the present invention, the polyhydric alcohol composition which contains reducing sugar is heated with a basic substance to effect substantial alkaline degradation of the reducing sugar and the reacted mixture is then passed through a cation exchanger and then through an anion exchanger to effect removal of the basic substance and of organic acid degradation products of the reducing sugar. The method is readily capable of removing over 75% of the reducing sugar from such compositions and is particularly useful when applied to compositions having small amounts such as 2%, or even 0.5% or less, of reducing sugar present, to lower the reducing sugar content to less than 0.1%. If desired, the method may be repeatedly applied to the polyhydric alcohol solution with resultant further lowering of the reducing sugar content.

Any basic substance may be employed in the

alkaline degradation step which is sufficiently strong to effect the alkaline degradation and be absorbed in the cation exchanger. Preferably, a basic substance selected from the group consisting of alkali and alkaline earth metal (including magnesium) hydroxide is employed and of these the alkali metal hydroxides such as potassium and sodium hydroxide are preferred. Such a base may be provided by adding alkali or alkaline earth metal oxide to an aqueous solution of the polyhydric alcohol composition or by the addition to such an aqueous solution of a water-soluble alkali metal salt whose aqueous solution is alkaline, as for example, sodium carbonate. However, the invention is not to be considered as limited to the use of alkali or alkaline earth metal hydroxides as the bases of other metals, ammonium hydroxide, or organic bases may be employed if desired.

In carrying out the alkaline degradation an aqueous solution of the reducing sugar containing polyhydric alcohol composition and the basic substance is heated to degrade the reducing sugar. While the temperature at which the alkaline degradation of the reducing sugar is conducted is not critical, the rate of degradation increases with increase in the temperature at which the degradation is conducted, and in order to accomplish the degradation at a reasonable rate the alkaline composition should be heated, generally at a temperature above 60° C. When heated in this manner, an equilibrium condition at which substantially no further loss of reducing power occurs will usually be reached within a few hours. The degradation is preferably conducted by heating the alkaline solution under atmospheric pressure at or about its boiling temperature.

The exact nature of the degradation products of the reducing sugar is not known, but these products are principally organic acids obtained presumably by rearrangement of the reducing sugar molecule due to internal oxidation-reduction, as for example, saccharinic acid, and by fragmentation or splitting of the reducing sugar molecule and the formation of lower acids such as pentonic, lactic, and formic acids. In the presence of the basic substance these acids consume a portion of the alkaline material and appear in the form of their salts.

If desired, the alkaline degradation of the reducing sugar may be conducted in the presence of air or oxygen, but it has been found that the alkaline degradation can be carried out in an inert atmosphere with almost equal ease and that the treatment in the presence of air results in a higher consumption of alkaline material per unit weight of reducing sugar consumed. Consequently, the alkaline degradation is preferably carried out in an atmosphere essentially free of oxygen, as for example, by boiling the alkaline solution under a reflux condenser. The use of strong oxidizing agents in the alkaline degradation step tends to result in the oxidation of the polyhydric alcohol as well as the reducing sugar and hence is generally to be avoided.

The basic substance is employed in a concentration such that at the beginning of the degradation, the aqueous solution of polyhydric alcohol has a pH above 8.5. As the pH of the solution at the commencement of the alkaline degradation is not critical as long as the solution has sufficient alkalinity, the pH of the solution is preferably adjusted to 10 or 11 to insure sufficient alkalinity.

The degradation products of the reducing sugar formed during the alkaline degradation consume

from 1 to about 4 equivalents of base per mol of reducing sugar degraded to non-reducing compounds during the alkaline degradation depending upon the composition and the conditions under which the alkaline degradation is conducted. Preferably, the basic substance is present in an excess of from about 5 to about 50% over the amount actually consumed by the alkaline degradation products of the sugar as such excess seems to cause a more complete degradation of the sugar. The excess of basic substance over the amount actually consumed by the alkaline degradation products remains in the solution upon completion of the degradation, and while proportions of base greater than an excess of 50% over the amount actually consumed by the degradation products do not interfere with the degradation, such greater proportions are not preferred because they result in an increased load on the cation exchanger in the subsequent cation exchange step.

Thus, where the alkaline degradation is conducted for one-half hour under atmospheric pressure and at the boiling temperature of the solution in the absence of substantial amounts of air, the basic material will generally be consumed in a proportion of from about 1.6 to 2.0 equivalents per mol of reducing sugar converted to non-reducing compounds during the degradation. Assuming that the actual consumption of basic substance during alkaline degradation of a particular composition under these conditions is 1.6 equivalents per mol of reducing sugar converted to non-reducing compounds, the alkaline degradation will preferably be conducted with basic substance present somewhat in excess of this proportion, as for example, up to about 2.5 equivalents per mol of reducing sugar so converted. If a deficiency below 1.6 equivalents of base per mol of converted reducing sugar be used under these conditions, essentially all of the basic material will be combined with degradation products and when an excess of basic material is employed, a portion of the base remains at the conclusion of the alkaline degradation.

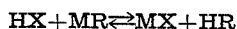
If the alkaline degradation is conducted similarly except that oxygen be present (as by blowing with air) throughout the degradation, two or more equivalents of base will generally be consumed per mol of reducing sugar converted to non-reducing compounds during the degradation and as in the case of the alkaline degradation in the absence of oxygen, it is preferable to provide an excess of the basic material to assist in the complete degradation of the reducing sugar.

Consequently, while degradation of the reducing sugar can be effected with amounts of basic substance varying over a considerable range, it is preferred to include a proportion of basic substance somewhat in excess of the amount consumed by the degradation products under the particular conditions of the alkaline degradation. If it is desired to conduct the process with such preferred proportions, the proportion of reducing sugar converted to non-reducing compounds and the amount of basic substance consumed under particular degradation conditions can readily be determined by degrading a sample of the composition under such conditions with basic substance present in a proportion somewhat in excess of 4 equivalents per mol of reducing sugar present in the original composition and determining the quantity of reducing compounds and basic substance remaining after the degradation. Such a proportion of basic sub-

stance based upon the original sugar content will assure the presence of an excess of base because 4 equivalents of base per mol of reducing sugar converted to non-reducing substance is about the maximum that can be consumed. In practicing the preferred method, the proportion of basic substance may then be adjusted to an amount somewhat in excess of that actually consumed by the degradation products under the particular conditions. Such preferred amounts will generally fall within the range of from 1.05 to 6.00 equivalents of basic substance per mol of reducing sugar converted to non-reducing compounds during the degradation.

It will be understood that the equivalents of base referred to are exclusive of base that may be utilized to neutralize other compounds that may be present in the original polyhydric alcohol composition such as metallic salts capable of forming metal hydroxides in the presence of the base, organic acid, or compounds which yield organic acid upon hydrolysis as, for example, lactones. However, such other compounds will be removed from polyhydric alcohol compositions containing them when such compositions are treated in accordance with the process of the present invention.

Following the alkaline degradation, the composition is passed through a cation exchange material capable of removing metal cations and replacing them with hydrogen. In this manner the metal cations of the salts of the acids formed during the alkaline degradation and the metal cations of any excess base remaining in the composition after the degradation are replaced with hydrogen. As the cation exchanger material any of the carbonaceous or resinous types which are capable of operating on the hydrogen cycle



where X is the structure of the cation exchanger, M is the cation and R is the anion, may be employed. As exemplary are the carbonaceous cation exchange materials produced by the treatment of lignite or coal with sulfuric acid or equivalent, and the resinous cation exchange materials of the phenol-formaldehyde type. The cation exchanger materials sold under the trade-mark Zeokarb, Catex, and Amberlite IR-1 are exemplary of commercially available cation exchange materials that are suitable for use.

When the effluent from the cation exchanger fails to show the reduction in pH which normally occurs in the passage of a salt-containing solution therethrough the exchanger has become exhausted through the replacement of all of the readily available hydrogen ions with metal ions. The cation exchange material may thereupon be regenerated by passing acid through the bed to replace the metal ions with hydrogen ions. The use and regeneration of cation exchange material can go on indefinitely as long as the ion exchanging material is not destroyed.

After the cation exchange treatment, the composition is passed through an anion exchanger capable either of adsorbing whole acid molecules or anions of acid molecules to thereby remove the acids or the anions of the acids resulting from the degradation of the reducing sugar and the cation exchange. In the case where the acid anion alone is adsorbed, the anion exchanger gives up a hydroxyl in exchange. Where the anion exchanger operates by adsorbing the whole acid molecule, it does not involve a true "exchange," but the action is generally referred to an anion exchange

and the term as used herein is intended to include regenerables of this type.

As the anion exchange material either the inorganic types such as the dolomite or heavy metal silicates or the organic types such as those containing basic groups such as amine, quaternary ammonium or other nitrogen base groups may be employed. The resinous anion exchangers such as the amine-formaldehyde resin exchangers are excellently suited for use. Anion exchange materials sold under the trade-marks Anex, Amberlite IR-4 and Deacidite are exemplary of commercially available anion exchangers which may be employed.

When the effluent from the anion exchanger fails to show the proper high pH value indicative of operation of the exchanger, the exchanger is approaching exhaustion and may thereupon be regenerated by treatment with an alkali solution which either removes the acid molecules previously adsorbed or exchanges hydroxyl ions for acid anions depending upon the way the anion exchanger operates.

The alkaline degradation is capable of converting most of the reducing sugar present in the original composition to non-reducing compounds without substantial effect upon the non-reducing polyhydric alcohol. Moreover, it has been found that a substantial proportion of the reducing compounds remaining after the alkaline degradation are usually converted to a form such that they are removed by the subsequent cation-anion exchange treatment. As the cation-anion exchangers have substantially no effect upon the polyhydric alcohol present, it can be seen that the method utilizes alkaline degradation and cation-anion exchange for the ready and economical removal of reducing sugar from polyhydric alcohol compositions without substantial conversion of the polyhydric alcohol content to other chemical compounds.

Non-limiting examples of the method of the present invention are as follows:

Example I

Commercial sorbitol solution prepared by the catalytic pressure hydrogenation of glucose and which had been filtered and cation exchanged by resinous cation exchanger to remove residual nickel catalyst and iron, was found to contain 0.56% residual reducing sugar on a dry basis and small proportions of free organic acid or lactones. This commercial sorbitol solution was made up into the following composition:

Sorbitol solution (28% H ₂ O)	grams	2,200
Water	do	1,579
One-half normal KOH	cc	165

This solution, which contained 60% water, was boiled (104° C.) at atmospheric pressure in an atmosphere substantially free of oxygen and with reflux of condensate for thirty minutes.

The reducing compounds present after the alkaline degradation amounted to 0.14% on a dry basis. In addition to the KOH required to neutralize the free organic acid or lactones which were present in the original sorbitol solution, the alkaline degradation consumed 0.56 gram of KOH per gram or about 1.8 mol of KOH per mol of sugar converted to non-reducing compounds.

This alkaline treated solution having a pH of 10.25 was passed through a cation exchange (Amberlite IR-1) column operating in the hydrogen cycle. The collected solution had a pH of 3.25. This solution was then passed through an anion

exchange (Deacidite) column resulting in a collected solution of pH 6.55. This solution was evaporated to a water content of 26.3%. An analysis of the product, which had a very low color value, showed that reducing compounds present amounted to only 0.07% (dry basis) and that the sorbitol remained substantially unchanged.

Example II

Commercial sorbitol solution prepared by the catalytic pressure hydrogenation of glucose and which had been filtered and freed of acids by passage through an anion exchanger was analyzed and observed to contain 0.91% reducing sugar on a dry basis. This sorbitol solution was used in making the following composition:

Dilute sorbitol solution containing 83.9%	Grams
water and 0.11% reducing sugar "as is"	12,214
43% NaOH -----	25

The composition so prepared was heated for two hours at a temperature of 75 to 87° C. under nitrogen. At the end of this time the pH dropped to 8.8 and the reducing sugar content was .099% "as is."

25 grams of 43% NaOH were added and the heating continued for 1¼ hours at a temperature of 87-97° C. At the end of this period the solution had a pH of 9.7 and the reducing sugar content was .044% "as is." 25 grams of 43% NaOH were added and the heating continued for one hour at 100° C. The product was cooled and was found to have a pH of 10.65 and a reducing sugar content of .023% "as is" or 0.12% dry basis.

The alkali solution was then passed through a cation exchange (Zeokarb) column operating in the hydrogen cycle and then through an anion exchange (Deacidite) column. After partial evaporation to 82.3% water the solution was found to contain .085% reducing sugar dry basis.

The solution was further evaporated to approximately 50% solids, treated with three grams of sodium hydroxide pellets and the evaporation continued for two hours until the water content was 37.6%.

This solution which contained .038% reducing sugar dry basis was again passed through a cation exchange (Zeokarb) column operating in the hydrogen cycle and through an anion exchange (Deacidite) column. After evaporation and treatment with activated carbon 1918 grams of a practically water white solution was obtained which contained 30.9% water and .020% reducing sugar dry basis. The sorbitol in this solution was unaffected by the treatment.

Example III

30 cc. of one-half normal KOH were added to 1,000 grams of glycerol solution containing 84.3% water, 0.63% of reducing sugar believed to be glycerose, the per cent of reducing sugar being reported as glucose, dry basis, and a small proportion of impurities hydrolyzable in the cold to acid. By "per cent of reducing sugar reported as glucose" is meant that the reducing sugar, which was believed to be glycerose, reduced Fehling's solution to the extent that it would have been reduced by the stated per cent of glucose. The alkali solution was refluxed at about 100° C. for three hours, additional one-half normal KOH being added in two 10 cc. increments during the last two hours of refluxing. Of the KOH added approximately 32 cc. of the one-half normal solu-

tion were required to neutralize impurities hydrolyzable in the cold to acid.

The resulting solution contained 84.1% water and 0.101% reducing sugar reported as glucose, dry basis.

This solution was passed through a cation (Zeokarb) exchange column operating in the hydrogen cycle and then through an anion (Deacidite) exchange column, after which water was removed by evaporation, the final glycerol containing 0.6% water and 0.061% reducing sugar reported as glucose, dry basis.

An advantage of the method of the present invention is that it is capable of removing metal cations and acid anions that may be present in the original composition in addition to removing reducing sugar. Thus, while as utilized in Examples I and II above the method is supplemental to prior demineralization by filtering and cation exchange, the method is also excellently suited for the direct treatment of undemineralized sorbitol solution as it is received from the hydrogenation equipment, the only difference being that a somewhat larger proportion of base is consumed in the alkaline degradation step due to the alkali consumed in the formation of the hydroxides of the metals. Where the method of the present invention is applied to undemineralized solutions, it will remove the metal cations in the cation exchange step and any free acid, such as gluconic, will be removed with the acidic degradation products of the reducing sugar in the anion exchange step.

It is to be understood that the method of the present invention may be utilized in conjunction with other treatments if so desired. For example, a portion of the reducing sugar present may first be removed by fermentation and the method of the present invention utilized to remove reducing sugar which remains after the fermentation treatment. Also, while the cation-anion exchange steps have been found to be quite effective in the removal of color bodies, it may be advantageous in the treatment of certain polyhydric alcohol solutions to supplement the method of the present invention with one or more activated carbon treatments. Such activated carbon treatments may be given the composition prior to the alkaline degradation, between the cation exchange and anion exchange steps or after the anion exchange. Other such modifications of the method of the present invention will be readily apparent to those skilled in the art.

Having described the invention what I claim is:

1. The method of removing reducing sugar from an aqueous polyhydric alcohol solution containing reducing sugar which comprises heating under non-hydrogenating conditions the said aqueous solution with a basic substance until reducing sugar is degraded, passing the reacted mixture through a cation exchanger operating in the hydrogen cycle and through an anion exchanger.

2. The method of removing reducing sugar from an aqueous polyhydric alcohol solution containing reducing sugar which comprises heating under non-hydrogenating conditions the said aqueous solution with a basic substance selected from the group consisting of alkali and alkaline earth metal hydroxides at a temperature above 60° C. until reducing sugar is degraded, said basic substance being initially present in amount of from 5 to 50% in excess of the amount of basic substance consumed during degradation, said

amount being within the range of from 1.05 to 6.00 equivalents of base per mol of reducing sugar converted to non-reducing compounds during the degradation and said amount being sufficient to provide an initial pH above 8.5, passing the reacted mixture through a cation exchanger operating in the hydrogen cycle and through an anion exchanger.

3. The method of claim 1 and wherein the polyhydric alcohol is a polyhydric alcohol prepared by the reduction of reducible sugar.

4. The method of claim 2 and wherein the polyhydric alcohol is a polyhydric alcohol prepared by the reduction of reducible sugar.

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