(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 020 124**
B1

(12) # EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **16.02.83**

(51) Int. Cl.³: **C 13 D 3/14**

(21) Application number: **80301751.6**

(22) Date of filing: **28.05.80**

(54) **Decationisation of aqueous sugar solutions.**

(30) Priority: **30.05.79 GB 7918716**

(43) Date of publication of application:
10.12.80 Bulletin 80/25

(45) Publication of the grant of the patent:
16.02.83 Bulletin 83/7

(84) Designated Contracting States:
BE DE FR GB IT NL

(56) References cited:
IT - A - 641 205
NL - B - 146 576
US - A - 2 402 960
US - A - 2 578 938
US - A - 2 926 110

CHEMICAL ABSTRACTS, vol. 53, no. 21, ref. 20852 e,f (1939) Columbus, Ohio, US L. CAVALLARO: "The inversion of sucrose by ion-exchange resins"
F. SCHNEIDER: "Technologie des Zuckers", 1968, pages 624—625, Verlag Schaper, Hannover DE

(73) Proprietor: **ROHM AND HAAS FRANCE, S.A.**
La Tour de Lyon 185 Rue de Bercy
F-75579 Paris, Cedex 12 (FR)

(73) Proprietor: **GENERALE SUCRIERE, S.A.**
23-25 Avenue Franklin D. Roosevelt
F-75008 Paris (FR)

(72) Inventor: **Rousseau, Gérard**
Avenue Sole Melee
Eppeville F-80400, Ham (FR)
Inventor: **Lamotte, Claude**
Eden Parc Batiment 7 Vieux Chemin de la Colle
F-06160 Juan les Pins (FR)

(74) Representative: **Angell, David Whilton et al,**
Rohm and Haas Company Patent Department
Chesterfield House Barter Street
London WC1A 2TP (GB)

Courier Press, Leamington Spa, England.

EP 0 020 124 B1

Decationisation of aqueous sugar solutions

This invention is concerned with the purification of (i.e. complete or partial removal of ions and colour bodies from) aqueous sugar solutions.

The field to which the invention relates is the purification of solutions in sugar refineries or mills by removal of some or all cations, anions and colour bodies using ion exchange resins.

In conventional ion exchange processes for the deionisation of aqueous sugar solutions, the solution is passed in a fixed bed process, through a bed of ion exchange resin containing at least one strong ion exchange resin in order satisfactorily to split the impurity salts. However, it has been necessary when a strong cation resin in the hydrogen form is used to cool the sugar to minimise inversion which takes place when sugar is subjected to a low pH, as is inevitable at the exchange sites in a strong acid cation exchange resin, for the time required for the sugar solution to pass through the bed within acceptable hydraulic parameters, that is to say without an unacceptable pressure drop. Since cooling down to about 10°C is needed, this significantly increases the viscosity of the sugar solution and so the problem is compounded, and the sugar solution has usually been diluted to offset this effect, at least in part. The diluted solution has eventually to be reconcentrated and this, of course, is wasteful in power consumption.

It is known from Italian Patent 641205 to treat sugar solutions in a batch process with ion exchange resins. Batch treatment, wherein sugar solution and ion exchange resins are mechanically agitated together does not demand that the sugar solution be as low in viscosity as in a process wherein the sugar solution must flow through a fixed bed of resin. This specification, however, does not teach that weak electrolyte resins may be used.

U.S. Patent 2926110 discloses the use of a mixture of weak anion and cation resins to partly desalt and decolourise sugar solutions in a continuous column operation. However this patent teaches the necessity for this purification to be completed by subsequently contacting the partly purified solution with a strong resin. Nowhere is there any teaching that the mixture of weak resins can alone split the impurity salts and satisfactorily purify the solution without inverting the sugar if used in a batch process with a long contact time.

We have now unexpectedly found that inversion can be kept within acceptable limits and deionisation and some decolouration can be achieved by using, in a batch operation, weak cation exchange resins in a mixed bed with weak anion exchange resin, usually in the free base form, at quite high temperatures and contact times.

Accordingly this invention provides a process for the decationisation of an aqueous sugar solution wherein the solution is passed into contact with ion exchange resin in a batch reaction, agitated therewith and separated therefrom and wherein the resin comprises a mixture of weak acid cation exchange resin in the hydrogen form and a weak base anion exchange resin, the temperature is 20 to 90°C, preferably 40 to 90°C, most preferably 50 to 65°C, and the contact time between the resin and the sugar solution is at most 90 minutes.

Any weak acid cation exchange resin can be used in admixture with the weak base anion exchange resin in the deionisation and decolourisation process of the invention. The most preferred are acrylic acid/divinylbenzene resins such as Amberlite IRC-84 or methacrylic acid/divinylbenzene resins such as Amberlite IRC-50 also commercially available from Rohm and Haas Company.

The weak acid cation exchange resins are used in the process of the invention in a mixed bed of resins containing weak base anion exchange resins whereupon deionisation and removal of some colour bodies can be achieved. Any weak base anion exchange resin can be used for this purpose. However, it is preferred to use acrylic anion exchange resins such as the macroreticular resin Amberlite IRA-35 and the gel resin Amberlite IRA-68 (both commercially available from Rohm and Haas Company) since these afford minimal regenerant requirement and optimal decolourisation efficiency.

The sugar solutions capable of being treated by the process of the invention may be any aqueous solution of sugar (including molasses) to be found, or which can be made up, in a sugar mill or refinery operation. The impurities generally contained in such solutions are those organic and mineral salts found in the sugar beet and sugar cane, such as betaine, pyrrolidone carboxylic acid, amino acids and sodium and potassium salts.

On contacting the cation exchange resin, either alone or in the mixed bed, the cations in these impurities will be exchanged for hydrogen ions and the exhausted resin will consequently need to be regenerated to remove the cations with which it is loaded.

It is surprising that a weak acid cation exchange resin in combination with a weak anion exchange resin can remove the indicated cations within the time and temperature constraints defined.

The anion exchange resin, will partially or completely deionise the solution by removing the mineral and/or organic acids resulting from the cation exchange to liberate water, the anion exchange resin being in the free base form. The exhausted ion exchange resin will therefore need to be regenerated to remove the exchanged ions and reconvert it to free base form.

Additionally, the anion exchange resin will remove colour bodies usually present in the sugar solution and these can be eluted from the resin along with the exchanged ions during regeneration.

Regeneration of the cation exchange resin can be effected in known manner by contacting the exhausted resin with strong mineral acid.

Regeneration of the anion exchange resin, and removal of colour bodies therefrom, can conveniently be achieved by contacting the resin with ammonia or a solution of a strong base.

The concentrations of solutions which can be treated by the process of this invention may be as high as 88 Brix. This is of course much higher than the concentrations treatable by prior art fixed bed processes. The solutions treated may already be present in the sugar mills or refineries at the indicated concentration or any existing refinery or mill streams which have lower Brix values can be concentrated, for example by evaporation or mixing to increase their Brix values. Thus, the invention can be used to treat standard syrup, poor strike machine syrups and molasses.

The proportions of resin to sugar which would effectively decationise and deionise the sugar solution depend, amongst other things, on the level and nature of the impurities, the resin chosen, the temperature, concentration and time of contact and will be optimised by trial-and-error experimentation in any particular case. The ratio may be expressed as a ratio of resin volume (mls) to weight of non-sugar (grams) impurities. Depending on the operating conditions, this ratio would generally be 1.0 to 3.0, most usually 1.2 to 1.6, for decationisation alone.

For deionisation in a mixed bed of weak electrolyte resins, from 35 to 75 grams of non-sugar per litre of mixed resin can be removed from the sugar solution in a bed containing a ratio of cationic to anionic resin of 1:1.5 to 1:5, in 0.5 to 1.5 hours.

For deionisation using the mixed bed of weak electrolyte resins we prefer to use temperatures from 20 to 90°C, more preferably 40 to 90°C, most preferably 50 to 65°C, and a contact time of 60 to 90 minutes. Under these conditions solutions up to 88 Brix can be treated.

Some preferred embodiments of the invention will now be described for the purposes of illustration only, in the following Examples in which all percentages are by weight unless otherwise specified.

Example 1

Deionisation using a weak acid/weak base monobed

250 grams of a mixture of sugar syrup and poor strike machine syrup were stirred for 90 minutes at 60°C and in a 500 ml beaker with a mixed bed of resin comprising 41 ml of Amberlite IRC-84 and 78 ml of Amberlite IRA-35, in the H^+ and free base form respectively. The mixture was then transferred to a sintered glass filter and the treated syrup analysed, giving the following results:

	Mixture of syrups	Treated syrups
Brix	68.6	64.7
Sugar %	61.7	61.1
Purity	90.0	94.4
Non sugar (%)	6.9	3.6
pH	8.7	6.6
Colour (% Brix)	2420	310
K^+ (%)	0.61	0.13
Na^+ (%)	0.24	0.05
Percent inversion	—	none

Example 2

Deionisation using weak acid/weak base monobed

Into a column 5.1 m high and 0.3 m diameter were placed a mixture of 28.5 l of Amberlite IRC-84 and 57.01 of Amberlite IRA-35 accounting for 40 cm and 88 cm of bed height respectively. 53 cycles of loading and regeneration were carried out treating a 69.7 Brix sugar solution containing 91.5% by weight sucrose and 8.5% by weight non-sucrose on a solids basis. The non-sucrose was predominantly amino acids, other acids, colour bodies, sodium and potassium salts. In each loading cycle the resin was agitated (by passage upflow of preheated air) for 80 minutes at a temperature of 65°C with the sugar solution. After loading the resins were separated by upflow of very dilute sugar solution, rinsed with deionised water and regenerated with dilute sulphuric acid and ammonium hydroxide by standard procedures. Before the next loading cycle the resins were re-mixed.

The purity of the treated sugar was increased to 94.5% (from 91.5%) and 75% of the colour bodies were removed as was 62% of the potassium. The sucrose yield is increased by 1.5 times the weight of non-sucrose removed.

Comparative calculation

Extrapolating these results to compare a conventional system (fixed bed with strong sulfonic acid resin and weak carboxylic resin) with a system operated according to Example 2 gives the following comparison. In order to obtain a direct comparison certain fundamental assumptions common to both systems have to be made. In this case we have assumed that sugar solution (syrup) to be treated is the

product of the processing of 9,500 Tonnes per day of beet and that it has been decided to remove 44.2 Tonnes per day of non-sucrose from the solution.

	Conventional IER system	System operated according to Example 3
Percent total syrup treated	30—40	100
Influent syrup purity (sucrose content)	91.5%	91.5%
Total resin volume (M^3)	253	105
Cation resin volume (M^3)	143	35
Anion resin volume	110	70
Total no. of columns	24	8
Total vol. spent regenerant (M^3/day) (sulphuric acid and ammonia)	1523	820
Water used and to be evaporated in reconcentration of syrup (Tonnes/day)	888	473
Sulphuric acid regenerant (Tonnes/day)	30.586	17.857
Ammonia regenerant (Tonnes/day)	6.718	7.514
Percent decolourisation	20—24	75

It can be seen therefore that capital and operating costs using the system of the invention can be much reduced over those of the prior art, and there is an additional advantage in the decolourisation achieved. Of course if the basic assumptions are changed the benefit may be obtained in terms of greater non-sucrose removal, and therefore sucrose yield, at the expense of some of the capital and operating cost savings.

"Amberlite" and "Monobed" are trademarks of Rohm and Haas Co., Philadelphia, United States of America.

Amberlite IRA-35 is a macroreticular acrylic weak base anion exchange resin.

Amberlite IRA-68 is a gel acrylic weak base anion exchange resin.

Amberlite IRC-84 is a gel acrylic acid weak cation exchange resin.

Claims

1. A process for the decationisation of an aqueous sugar solution wherein the solution is passed into contact with ion exchange resin in a batch reaction, agitated therewith and separated therefrom and wherein the resin comprises a mixture of weak acid cation exchange resin in the hydrogen form and weak base anion exchange resin, the temperature is from 20 to 90°C and the contact time between the resin and the sugar solution is at most 90 minutes.

2. A process as claimed in Claim 1 wherein the sugar solution has a concentration of up to 88 Brix.

3. A process as claimed in Claim 2 wherein the temperature is 40 to 90°C.

4. A process as claimed in Claim 1, 2 or 3 wherein the contact time is 60 to 90 minutes.

5. A process as claimed in Claim 1, 2 or 3 wherein the cation to anion resin volume ratio is 1:1 to 1:5 and the contact time is 30 to 90 minutes.

6. A process as claimed in any preceding claim, wherein agitation is effected, at least in part, by passing air through the resin bed in contact with the sugar solution.

Patentansprüche

1. Verfahren zur Dekationisierung einer wäßrigen Zuckerlösung, bei welchem die Lösung in Kontakt mit einem Ionenaustauscherharz in eine Chargenreaktion eingeführt, damit verrührt und davon abgetrennt wird, wobei das Harz aus einer Mischung aus einem schwachen Kationenaustauscherharz in der Wasserstofform und einem schwachen Basenanionenaustauscherharz besteht und die Temperatur 20 bis 90°C und die Kontaktzeit zwischen dem Harz und der Zuckerlösung höchstens 90 Minuten betragen.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die eingesetzte Zuckerlösung eine Konzentration von bis zu 88 Brix besitzt.

3. Verfahren nach Anspruch 2, dadurch gekennzeichent, daß eine Temperatur von 40 bis 90°C eingehalten wird.

4. Verfahren nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, daß eine Kontaktzeit von 60 bis 90 Minuten eingehalten wird.

5. Verfahren nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, daß ein Volumenverhältnis des Kationen- zu dem Anionenharz von 1:1 bis 1:5 une eine Kontaktzeit von 30 bis 90 Minuten eingehalten wird.

6. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Rühren wenigstens teilweise in der Weise bewirkt wird, daß Luft durch das Harzbett in Kontakt mit der Zuckerlösung geleitet wird. .

Revendications

1. Un procédé pour la décationisation d'une solution aqueuse de sucre dans lequel on fait passer la solution en contact avec une résine échangeuse d'ions selon une réaction discontinue, on l'agite avec elle et on l'en sépare et dans lequel la résine comprend un mélange d'une résine échangeuse de cations faiblement acide sous la forme hydrogène et d'une résine échangeuse d'anions faiblement basique, la température est de 20 à 90°C et la durée de contact entre la résine et la solution de sucre est d'au plus 90 minutes.

2. Procédé selon la revendication 1 dans lequel la solution de sucre a une concentration d'au plus 88° Brix.

3. Procédé selon la revendication 2 dans lequel la température est de 40 à 90°C.

4. Procédé selon l'une des revendications 1, 2 ou 3 dans lequel la durée de contact est de 60 à 90 minutes.

5. Procédé selon l'une quelconque des revendications 1, 2 ou 3 dans lequel le rapport en volume de la résine cationique à la résine anionique est de 1/1 à 1/5 et la durée de contact est de 30 à 90 minutes.

6. Procédé selon l'une quelconque des revendications précédentes dans lequel l'agitation est effectuée, au moins en partie, par passage d'air à travers le lit de résine et contact avec la solution de sucre.