A NEW ION EXCHANGE PROCESS FOR REMOVING COLOUR BODIES AND COLLOIDAL IMPURITIES FROM CANE SUGAR

By R. A. GRANT

Ion exchange resins have been employed in the sugar refining industry to a limited extent as decolourizing agents and for absorbing ash constituents. However, in spite of much research in this field, an ion exchange process capable of replacing established techniques such as carbonatation, sulphitation and bone char treatment, has not been developed for application in the cane sugar industry. Ion exchange resins are used mainly for the removal of ash and residual colour remaining after bone char treatment and find their principal use in the production of high grade liquid sugars.

The work reported in this communication was initiated with the object of developing a comprehensive ion exchange process which could be applied to cane sugar solutions containing high concentrations of colour and other impurities, e.g. solutions of third crop crystals and liquors from the early stages of the refining process. The colour bodies present in raw cane sugar appear to be comprised of several molecular species of widely different properties. In order to simplify the problem, it was assumed that these fell into two main groups. A high molecular weight type giving the solution a brown colour and a low molecular weight species behaving as a weak organic acid and imparting a yellow colour to the solution at neutral or alkaline pH values. Although the chemical properties of these colour bodies have not been studied in detail, the foregoing division has proved convenient. It was found that available ion exchange resins were virtually useless in dealing with the high M.W. type of colour body. The reason for this appears to be connected with the porosity of the resin. For an ion to be easily adsorbed and subsequently eluted from an ion exchange resin it must be small enough to diffuse readily into and out of the resin particles. For ions above a certain limiting size, the capacity of the resin is extremely low. This has been known for some time and resins with low degrees of cross linking have been developed for decolourizing sugar solutions. However, even these special resins are strictly limited in their application.

In order to eliminate diffusion within the resin particle as a limiting factor, a new type of resin has been developed in which the active groups are situated on or near the surface of the resin particles. Preparative details of this type of resin will be published elsewhere. Resins prepared in accordance with this principle have proved very effective in removing high M.W. colour bodies and colloidal impurities from cane sugar solutions, and are stable enough to withstand several hundred cycles of operation. Regeneration is very rapid, probably because all the active sites are readily accessible to the regenerating ions. Figure 1 shows a typical operating curve for this type of resin (curve A). The test solution contained 40 per cent sucrose and was highly coloured (optical density 1.4 at 420 mμ) The solution was passed through a 2 gram bed of the resin having a depth of 3 cm. and the effluent was collected in 250 ml. fractions. The optical density was determined in a Zeiss spectrophotometer type PMQ II at a wavelength of 420 mμ using 1 cm. cells. A total of 1500 ml. was passed through the bed, this being equivalent to 600 g. sucrose giving a sugar/resin ratio of 300:1. This bed was considered to be exhausted when the optical density of the effluent reached 50 per cent of the initial value. The original solution was dark brown and almost opaque, the effluent was a clear yellow. By this simple treatment more than half of the total colour was removed from the solution.

The yellow effluent was then treated with a new type of porous anion exchange resin (Figure 1, curve B). This type of resin has proved effective in removing the low M.W. yellow colour bodies. Again, a high uptake of colour was achieved, the final effluent having a pale straw colour.

Tests have also been made on refinery liquors (Table I). Since the colour of these solutions is known to vary with pH, this was adjusted to be within the range 6.5–7.0 prior to and after treatment with the resin. Liquor 1, or "settled juice" (O.D. 2.0 at pH7) was passed through a 2 g. bed of the surface active resin. The effluent had an optical density of 0.27, giving a colour uptake of 86 per cent. Liquor 2 (remelted raw sugar), having an initial colour density of 0.61, gave an effluent having a colour density of 0.10 corresponding to a colour uptake of 83 per cent. Liquor 3 had been subjected to the carbonatation process and had an initial colour density of 0.52 at pH 7.9, adjustment of the pH to 6.5 with hydrochloric acid resulted in a drop in colour to 0.185. This may be compared with the colour change produced by sulphitation to 0.17 at pH 6.7 which indicates that the decrease in colour following sulphitation results mainly from the pH change. After passing through the resin, this liquor gave an effluent with a colour density of 0.03 corresponding to a colour uptake of 84 per cent. Liquor 4

(after sulphitation) was also greatly impoved by the resin treatment.

A concentrated clarified syrup having a sugar content of 65 per cent and a colour density of 0.3 (deep yellow) could not be successfully treated with this type of resin. However, passage through the porous anion exchanger removed virtually all the colour giving an almost water clear effluent (O.D. 0.01–0.02). With a load of 50 bed volumes, the resin appeared to be only partly exhausted (Figure 2). In this case the resin bed was operated at a temperature of 60°C maintained by pumping thermostat water through a water jacket.

Between them, these two types of resin appear capable of removing virtually all the colour bodies found in the cane sugar liquors examined. A detailed analysis of the economic factors has not been made, but it would appear that the ion exchange syst could compete favourably with the existing processes.

TABLE I

Liquor	*Initial Colour and pH*	*Colour at pH 6.5–7.0*	*Colour after resin Treatment*
1	1.34 pH 6.0	2.00 pH 7.0	0.27 pH 6.9
2	1.06 pH 7.5	0.61 pH 6.5	0.10 pH 7.0
3	0.52 pH 7.9	0.185 pH 6.5	0.03 pH 6.9
4	0.17 pH 6.7	0.17 pH 6.7	0.02 pH 6.7

1. Settled juice
2. Raw remelted sugar
3. After carbonatation
4. After sulphitation

Colour measured at 420 mμ in 1 cm. cells.

FIG. 1

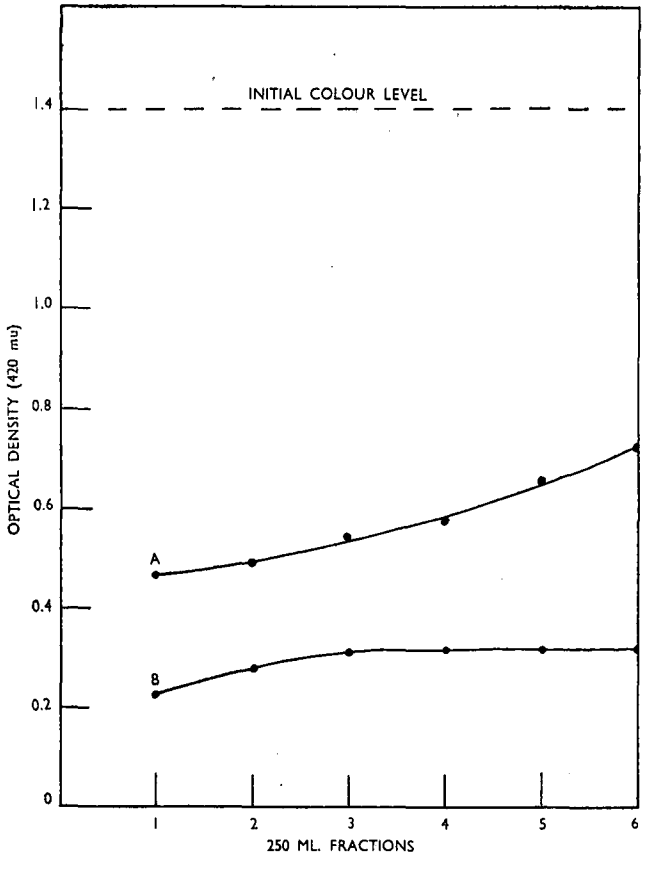

FIGURE 1.

A. Surface active resin (2 g. dry weight) operating with 40 per cent sucrose (colour density 1.4). Effluent volume 1,500 ml. equivalent to 600 g. sugar. Sugar/resin ratio 300:1, bed depth 3 cm.

B. Porous anion exchange resin (10 g.) operating with effluent from A. Bed depth 5 cm. working temperature 60°C.

FIG. 2

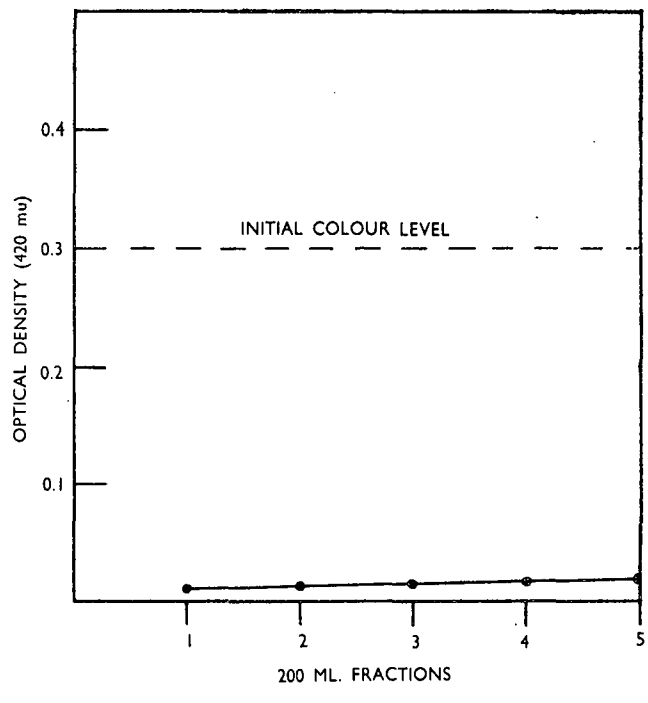

FIGURE 2.

Porous anion exchange resin (10 g.) operating with concentrated clarified syrup containing 65 per cent sugar, colour density 0.3, working temperature 60°C, load 1,000 ml., bed depth 5 cm. Sugar/resin ratio 65:1.

Mr. Bentley asked Dr. Grant whether he could give the probable costs of using resins of these types on a practical scale.

Dr. Grant replied that it was difficult to give any exact idea of the economics of the process. Naturally, the more colour in the sugar, the more expensive it was to remove it. For a colour density of 1.4 at 40 per cent sucrose concentration he had worked out that the cost of treating one pound of sugar would be about 0.1d. He said he had done some tests at Hulett's refinery and had got quite good results with greens and third crop crystals.

Mr. Boyes said that on a practical scale one would have to use many tons of resin and quite a lot of sucrose would be held in the resin bed, so a considerable quantity of water would have to be used to remove the sugar before one could tackle the colour bodies.

Dr. Grant said that when the resin was exhausted one could rinse with one or two bed volumes of water to remove the sugar. The colour bodies would not be removed until the regenerating solution was used.

Mr. Boyes said that the amount of water used to rinse off the regenerative substance would mean a considerable amount of evaporation in the factory.

Dr. Grant said that he had worked with a sugar to resin ratio of 300–1 with a solution colour density of 1.4. Some resins, such as Amberlite 401 were recommended only for taking up residual colour. Supposing in the case of a 2 gram bed with a volume of 20 ml., one used one bed volume of water for rinsing to remove the sugar, then with a 50 bed volume load of syrup the increase in total volume would be only 2 per cent.

Dr. van der Pol asked whether the surface absorption resin was commercially available. He suggested that either bone char or vegetable carbon could be used for the second step instead of the resin used by the author, as only the lower molecular weight type of coloured material was left at this stage.

Dr. Grant said that there was no commercially available resin of the type he had described for dealing with high M.W. colour bodies. He agreed that bone char could be used for the second stage of colour removal, but he had endeavoured to develop an ion exchange process which could, in principle, replace bone char.

Dr. Douwes-Dekker said he found the properties of the surface reacting resins particularly interesting. He asked if Dr. Grant could give, in simple terms, the composition of the resin, give some information on the removal of ash from the sugar liquor and, thirdly, if Dr. Grant could give some information on the poisoning of resins by those impurities in the sugar liquors which were not easily removed from the resins by regeration.

Dr. Grant said that the resins could be prepared in a large number of ways, for example, they could be deposited on substances like keiselguhr having large surface areas. The actual preparation and manufacture of these resins was, however, still in the experimental stage. With regard to ash removal, the number of active groups per unit weight of resin was not very high and these would not greatly affect the ash constituents, such as would the conventional ion exchange resins. There was a certain amount of ash removal however, and phosphate and sulphate would be taken up, but not chloride to any marked extent. With regard to poisoning of the resins he could not easily see how poisoning could occur. In the case of commercial porous resins, the resins could be blocked by large ions and this could be said to be a type of poisoning. With surface active type resins this was unlikely. He had not encountered in his experience anything which could be called poisoning of the resins.

Dr. Graham said that in uranium plants it took a very long time for resins to be poisoned. They could be used 20 or 30 times before poisoning was apparent. He would like to know if Dr. Grant had tried to use the resins as a mixed bed. If it were necessary to use different regenerative agents the resins could be separated by an airstream, for instance. He asked what pH was used, because this could be very important, especially at high temperatures. Evaporating the effluent after resin treatment would be dangerous if the acidity was high. He asked what the composition was of the impurities left after the second resin treatment and wondered if using a slower flow rate would improve removal of colour.

Dr. Grant said, in his experiments, he had studied substances such as egg albumen as well as colour bodies but poisoning did not occur. He thought that in the uranium industry they probably used very drastic chemicals, this might account for the resin poisoning in this industry.

Dr. Graham said that the poisoning in the uranium process was mostly due to cobalt.

Dr. Grant said that the type of resin used would depend upon the substance one wished to remove. For the removal of different types of colour bodies one required different types of ion exchange resins. He had not tried to use mixed beds, but this could be conceivably done, because both resins would be basic. In regard to the pH of the effluent, it could not be, as far as the bulk was concerned, very different from that of the intake material. With regard to the apparent residual colour remaining after the second stage, he thought that this was in part due to a slight haze in this particular solution which was measured as colour by the spectrophotometer. In general, varying the flow rate did not greatly affect the colour uptake.

Mr. Dedekind asked if any attempt was made to crystallize the liquor. In tests at Sezela they got the liquor absolutely colourless but could not get this water-white liquor to grain.

Mr. Alexander said the refinery had used these resins for treating greens and boiled sugar from the effluent. Instead of a greyish product, the treated liquor gave an attractive yellow-coloured one.

Dr. Grant pointed out that the experiments Mr. Alexander was referring to, only went as far as the removal of the higher molecular weight colour bodies and the sugar made from the resulting yellow-coloured liquor was yellow in consequence. He could not see why it should be harder to crystallise the liquor after coming from the ion exchange beds, than that coming from bone char, provided there was no marked change in the pH.

Mr. Walsh asked Dr. Grant if he could give the time of the cycle.

Dr. Grant replied that that would depend upon the volume of effluent and the size of the resin bed and also on the amount of colour in the material to be treated.