THE INVESTIGATION OF THE EFFECT OF PRE-TREATMENT OF CANE JUICE WITH ZEO-KARB 215, AND THE SUCCESSFUL ELIMINATION OF INVERSION LOSSES DURING TREATMENT

I. INTRODUCTION

One of the most interesting subjects for research workers in the sugar industry to study is the recent development of Ion Exchange - the most important new sugar development in many decades - the mysteries of how it works, what it will do, and the general economics of it.

Sugar refining is comprised of two main types of operations. The first is a series of steps to remove a maximum amount of dissolved non-sugar solids. The second involves the separation of maximum yields of pure sugar from the remaining dissolved impurities by evaporation and crystallisation. The success of the second step is dependent on the first, since the major factor limiting the crystallisation of sugar is the presence of non-sugar solids in the solution (134) (141) (142) (161). Prinsen Geerligs (140) published a boiling house recovery formula well known as Winter's factor based on Winter's observations of actual results in Java which showed that 1 part of non-sucrose held 0.4 parts of sucrose in the final molasses.

There have been many papers and treatises published on the application of the ion exchange process to the treatment of defecated beet and cane sugar juices. It is claimed (86) (151) that with the proper use of these exchangers 95-98% ash and 60-75% organic non-sugar eliminations are possible permitting recoveries of 83.5 - 85%. Processes for the manufacture of refined sugar direct from cane and beet juices involving an ion exchange operation for purifying the raw liquors have recently been the subject of several interesting patents (22) (59) (74) (152) ([illegible]) (184) (185) (186) (187).

Large scale trials both in a pilot plant (26) (86) (139) (151) and in a commercial beet factory (57) (125) (171) (194) have been carried out in the United States to purify second carbonatation juice, green syrups and molasses. The results indicate that the method is technically feasible and that the production of refined beet sugar from second carbonatation juice is more economical than the conventional refining technique (57) (67) (86)(151). Several advantages often claimed for the ion exchange purification of beet juices include greater recovery of white sugar "in the bag" rather than in the molasses with extractions up to 93%; better color removal; production of low ash white sugar; elimination of evaporator and pan boil-outs; production of edible molasses and greater potentiality for by-products development.

In working with sugar cane and sugar beet juices most of the early efforts were directed toward introducing the ion exchange process after defecation (86) (148) (171) (194). Definite advantages (125) (138) (151) would accrue to the sugar maker if the raw cane or beet juice was purified before defecation as (a) defecation with lime actually increases the ash content (151) and therefore decreases the capacity of the ion exchange unit; (b) purification of the juice before defecation minimises or even eliminates the need of any further defecation; (c) elimination of the need for Steffens house treatment where beet sugar is recovered from straight-house molasses.

In order to remove all the ionisable impurities (cations as well as anions) the ion exchange process must be operated in single or multiple pairs (pair = cation - anion exchanger) working in parallel or in series. If this operation could be performed in a "Universal adsorbent" (100) capable of effecting the simultaneous removal of cations and anions

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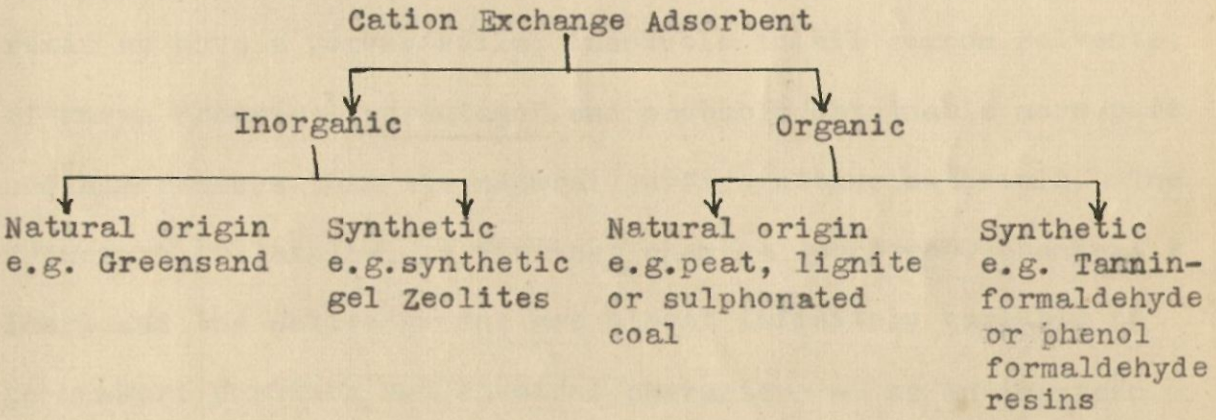
from impure solutions (e.g. sugar juices) great advantages are possible. The hope for a "Universal adsorbent" has not yet materialised. Since the cation exchanger is claimed to remove the metallic cations and most of the complex nitrogenous products from the sugar juices, an attempt was made to investigate the effect of pre-treatment of raw cane juice with a cation exchanger (Zeo-karb 215) as a one-step unit on the quantity and quality of the sugar produced.

Ion exchange substances may be either cation or anion exchangers. Carleton Ellis (48) suggested that the term "organolites" be applied to all base-exchange substances of organic origin, while Bird (29) classified exchange adsorbents on a cation and anion basis. Myers and Eastes (128) classified them as follows :-



Cation Exchange Adsorbent

Inorganic

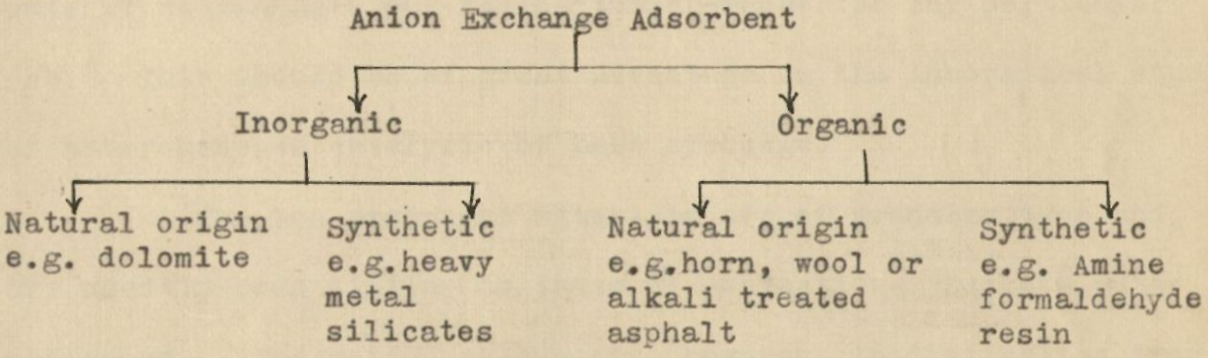
Natural origin e.g. Greensand

Synthetic e.g. synthetic gel Zeolites

Organic

Natural origin e.g. peat, lignite or sulphonated coal

Synthetic e.g. Tannin-formaldehyde or phenol formaldehyde resins



Anion Exchange Adsorbent

Inorganic

Natural origin e.g. dolomite

Synthetic e.g. heavy metal silicates

Organic

Natural origin e.g. horn, wool or alkali treated asphalt

Synthetic e.g. Amine formaldehyde resin

Most important in today's ion exchange operations are the organic ion exchangers. These fall in two classes: (1) The "carbonaceous Zeolites" which are cation exchangers obtained by the sulphonation of coal or other natural organic materials and (2) synthetic resins for both cation and anion exchange.

Cation exchange resins are phenol-formaldehyde, sulphonic acid derivatives. Anion exchangers are amine derivatives of either aromatic or aliphatic resins. The cation exchangers utilise ion active groups ([illegible]) such as Sulphonic ($-SO_3H$, nuclear), Sulphonic acid hardened, carboxylic ($-COOH$), phenolic ($-OH$) and methylene sulphonic ($-CH_2SO_3H$). While all anion exchangers depend on the anions ($-NH_2$) or imino ($>NH$, aromatic or aliphatic) group. Characteristically these newer materials have high capacities for removing ions from solution and are relatively stable under a fairly wide range of operating conditions. Zeo-karb 215 is a strong acid resin claimed to be extremely efficient for removing metal cations.

That ion exchange resins are valuable tools both in large scale work and in the laboratory will be generally agreed and new uses are continually being proposed. In an exchange resin we have a porous soild, insoluble in all common solvents, of known "chemical parentage" and probably obtainable more pure and homogeneous than the natural surface active materials. The framework or lattice, is for most chemical purposes, chemically inert and the active groups are almost infinitely variable as to number, position and chemical character - as an American puts it we can have our resin "tailor-made" for any particular job. This should be of great advantage in the theoretical study of heterogeneous catalysis of base exchange.

The ion exchanger materials are of granular type and are used in beds similar to those of conventional Zeolite water softeners. The cation exchangers, however, in distinction from Zeolites and Natural Zeolitic green-sands, have the property of exchanging hydrogen ions (H^+) or sodium ions (Na^+) for the cations such as sodium (Na^+), potassium (K^+), Calcium (Ca^{++}), Magnesium (Mg^{++}), organic cations etc., in a solution of these salts if operated in the hydrogen or sodium cycle respectively.

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This action results in the formation of the acids of the various anions in solution. The resulting solution is acidic. The anion exchangers are similar granular materials employed in bed form and have the property of removing these acids. The resulting solution is essentially free of ionising solutes.

The exact nature of anion exchange is not fully understood. It appears to take place as an additional reaction where the acid molecule as a whole is adsorbed in which case the term "acid adsorbent" is preferable to "anion exchange". True ion exchange may take place with an acid exhausted resin. Kunin and Myers (108) have concluded that acid adsorption on an anion exchange resin is actually an exchange of anions rather than a molecular adsorption.

The exchangers are capable of repeated regeneration and re-use to perform the same function of ion removal again and again. The cation exchanger resins are regenerated by passing a solution of strong acid (such as Sulphuric or hydrochloric acid) over them, whereby, due to mass action effects, the cations are removed from the exchanger and replaced by Hydrogen ions (H^+) again, so that the exchanger is ready for re-use. The anion exchanger is regenerated with an alkali, usually sodium carbonate (Na_2CO_3) though certain of the newer synthetic resins may be regenerated with caustic soda ($NaOH$) or ammonium hydroxide (NH_4OH).

Typical reactions of these resins are as follows:-

Cation Exchangers:

$R....Na + \frac{1}{2}Ca^{++} \rightleftharpoons R....\frac{1}{2}Ca + Na^{+}$ (Cation Exchange or Sodium cycle)

$R...H + NaCl \rightleftharpoons R..Na + HCl$ (Hydrogen Exchange or Hydrogen cycle)

$2R...H + Na_2CO_3 \rightleftharpoons 2R...Na + H_2O + CO_2$ (Hydrogen Exchange or Hydrogen cycle)

$R...Na + HCl \rightleftharpoons R...H + NaCl$ (Regeneration)

In the case of Zeo-Karb 215 and cane juice :-

$$R\text{-}SO_3^{-}..H^{+} + NH_3^{+}X\ COO^{-} \rightleftharpoons R\text{-}SO_3' \ldots NH_3^{+}X\ COOH$$

$$R\text{-}SO_3^{-}..H^{+} + \tfrac{1}{2}Ca^{++} \rightleftharpoons R\text{-}SO_3\ldots\tfrac{1}{2}Ca + H^{+}$$

Where R = Cation Exchange resin

Anion Exchangers:

$$R_1 \equiv N + HCl \longrightarrow R_1 \equiv NH^{+} \ldots Cl \quad \text{(Acid adsorption)}$$

$$R_1 \equiv NH^{+} \ldots Cl^{-} + \tfrac{1}{2} Na_2SO_4 \rightleftharpoons R_1 \equiv NH^{+} \ldots \tfrac{1}{2}SO_4^{=} + NaCl \quad \text{(Anion Exchange)}$$

$$R_1 \equiv NH^{+} \ldots Cl^{-} + NaOH \rightleftharpoons R_1 \equiv N + NaCl + H_2O \quad \text{(Regeneration)}$$

Where R_1 = Anion "exchange" resin

Although the word "demineralisation" has often been used to designate an operation involving successive treatment of a solution with cation and anion resins, the removal of organic substances, notably nitrogen compounds, is a highly important function of the ion exchange operation in sugar juice processing. Therefore the term "deionisation" is preferred. It is ions, actually, and not minerals as a class, that are being removed.

With the production of organic resin adsorbents, several investigations of ion exchange reaction mechanisims have been completed. For a series of cations the exchange capacity usually follows the Hofmeister or ~~the~~ Lyotropic series, e.g.

$$Li^{+} < Na^{+} < K^{+} < NH_4^{+} < Rb^{+} < Cs^{+}$$

or

$$Mg^{++} < Ca^{++} < Sr^{++} < Ba^{++}$$

this being the order of decreasing size in the hydrated state. Thus in the ion exchange process "leakage" of ions at "break - through" point is possible. Boyd and co-workers (36), Bauman and Eichorn (17), Kunin and Myers (108), and Wiklander (196), are among those who recently have made significant contributions to the theoretical aspects of the ion exchange process. The elucidation of basic exchange functions has involved many physico-chemical principles including the law of mass action (17) (36), Donnan membrane equilibria (17), heat transfer theory (6), Freundlich and Langmuir adsorption isotherms (36), ion diffusion (17), ion hydration, reaction rates, and other phenomena which are outside the scope of this paper.