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PURIFICATION OF SUGAR CONTAINING LIQUIDS

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In addition to the existing methods to purify sugar containing liquids, e. g. sugar juices, whereby frequently lime, whether or not used in excess, is applied, which lime is later on precipitated and removed with the aid of carbonic or sulphurous acid, of late also other purification agents like infusorial earth, activated carbon, colloidal humic substances, etc. are applied.

However, the ideal of a good purification, viz. the removal of practically all non-sugar substances, like inorganic and organic salts etc., even has not yet been approached.

In the cane and beet sugar industry after an intensive purification, the juice still contains on 100 parts of solid matter besides 90–93% of saccharose, 7–10% of the so-called non-sugars. It needs no explanation how harmful this is, because: *a*. The liquid can only be freed from sugar by repeated crystallization *b*. Finally a sugar liquid, blackstrap, is left, which still contains about 50% of sugar, which will not crystallize out, because the non-sugars hinder this and which thus remains in this blackstrap and gets lost for consumption, at least is only of value as forage or for manufacturing alcohol.

Now, according to my invention, the sugar containing liquid is wholly or partially freed from non-sugars by bringing the liquid successively into contact with substances of contrary polar binding and adsorptive power. Thus the acid reacting substances (anions) and the substances with negative electric load on the one side are removed by the positive polar substances and the basic reacting substances (cations) and the substances with positive electric load on the other by the negative polar substance. The substances having polar binding and adsorptive power, which are applied according to my invention, are under the circumstances of their application practically insoluble and also form practically insoluble components. They are of micellar structure. Certain equilibriums occur at the binding or adsorption, which obey generally known principles and have frequently been the subject of scientific study.

Not only substances having a certain electric load are isolated in this way, but also the substances having not a noticeable load or being of amphoter character. According to my new method besides the electrolytes, also the non-electrolytes can be removed from the sugar solution to a rather large extent, as will be shown by the examples.

From the electrolytes not only the strongly dissociated ones are removed, but especially rather easily the weakly dissociated, organic acids or substances the acid character of which may hardly be observed or is available in latent condition.

This is especially evident, if blackstrap is subjected to the treatment, in which liquid, as is known, all non-sugars are accumulated, so that the contents amount to 30–40% of the solid weight. In fact strong alkalis occur in same, about 15% of K_2O of the non-sugar weight, 2½% of Na_2O and still some percents of the weaker inorganic bases and also 1%–2% of strong organic acids, but about 75% consist of weak organic acids and non electrolytical organic matter, esters, albumines, etc. By the new method all these substances can be removed for the greater part in a simple way, which will appear from the examples. The most striking feature hereby is, that the organic acids or bases and non-electrolytes can be removed as well as or even better than the strong dissociated inorganic substances, having a very large affinity to the polar adsorbents. It might be expected that in presence of these strong dissociated inorganic substances they could not be removed practically, but this is still possible, whereas the capacity of the material for eliminating the strong dissociated inorganic substances is only very little influenced by them. The elimination of these substances must thus probably be of a complicated nature, double binding and condensation phenomenons certainly occur.

Some investigators consider this phenomenon as a normal chemical binding, but in any case it must then be taken for granted, that the reaction is very reversible, which e. g. is shown by the fact, that anions are much more strongly adsorbed from a very strong acid milieu.

Other investigators wish to see in the binding of the substances by the products, which are applied according to the present invention, a normal adsorption and declare the ion-exchange to be a result of the slight solubility, which also practically insoluble substances possess, whereas the large exchange capacity of some materials is a result of their micellar structure. It is a matter of fact, that the binding phenomenons sometimes may be declared much more easily by chemical binding, sometimes by physical adsorption. However, it is important, that one is practically able to remove the desired impurities from the sugar-solutions, provided this can take place under the right circumstances.

In order to demonstrate this with an example: according to the new working method it would practically not be possible to remove the salt from seawater, viz. because by percolation over the negative polar adsorbent, the slightest cation-binding would cause such low a pH, that further binding becomes only possible, after the acid has been removed. Thus a very large number of cycles must be applied, which practically is impossible, whereas furthermore for the regeneration of the substances with polar binding power

more leaching water is needed than the process yields. When, however, purifying a sugar solution, the salt can be removed for the greater part in one single cycle, because when binding cations a low pH only occurs after a very large removal, viz. the freed organic acids do not cause a strong decrease of pH. It also is of no importance how much leaching water is required for the regeneration. The cost of same is minimal with regard to the one of the sugar solution.

With regard to the foregoing it is also practically possible to free the strongly acidified sugar solutions, e. g. those, which are obtained by the conversion of flour, from acid by a treatment with the positive polar substances. The treatment with the negative polar substance then needs only take place to a very small extent.

When proceeding according to my invention, the decolouration especially when applying the positive polar adsorbent, is enormous and larger than may be obtained with any known decolourizing agent. Also as a result of this, the invention gets technically very important, because there are no decolourizing agents, which are able to remove similar substances.

There are many substances known which have polar binding power, which under the required circumstances are practically insoluble and may be applied when working according to my new method.

From the inorganic substances the zeolithes, which can bind cations, are known. However, owing to their large solubility, especially at a lower pH, they are unsuitable. As negative polar adsorbents, however, such materials, as are obtained by the reaction of sulphuric acid and equivalent dehydrating agents on carbonaceous material, e. g. coal, are excellently suitable.

These materials resist a treatment with the strongest chemicals. For the elimination of acid-radicals, various metal-oxide-gels are known, e. g. iron-oxide-gels and gels of copper-oxide, manganese-oxide, chrome-oxide, aluminium-oxide etc. Frequently these gels are precipitated on bearers. Natural bauxite, which contains much iron-oxide, is also often suitable. The suitability frequently lies between a certain pH-range, for fresh aluminium-oxide-gel e. g between 4.8 and 8. By drying the material, this range can be increased. However, it is a matter of fact that the application of this kind of substances does not lead to practical results as per the present invention.

As positive polar substances further since years ago many of the so called bases of Schiff are known and other insoluble resinous condensation products or dye stuffs of alkaline character, provided they meet the requirements of practical insolubility when used in my process.

Raikow found already in 1896 (Berichte 1896) that a condensation product from formalin and anilin has a basic character, is practically insoluble and also forms insoluble salts. This refers to all condensation products from aldehydes and cyclic compounds with amin-groups or imin-groups, if condensation takes place in the right way. Like the above- and hereunder mentioned resins, they have a micellar structure.

A very cheap positive substance, however mostly less active, is the reaction product of sulphuric acid and the like on carbonaceous material, sawdust etc., which product is a kind of humic acid and in which ammonia has been incorporated.

As a negative polar substance at present also synthetical resins on phenol basis are known and also some practically insoluble organic acids. For binding acid radicals, various natural nitrogenous organic products, wool etc. are known. Technically their importance is little.

However, applicant has found that many of these synthetical resins are of amphoter character. Thus a resin being negatively polar, also under the right circumstances may act as positive polar adsorbent and this reversion frequently also takes place with positive polar substances. To a still larger extent, this refers to the substances with a weak electric load, or if they themselves are of amphoter character.

The process may be applied in various stages of the treatment of sugar extracts. Sometimes it is advisable to apply the process immediately after the extraction, in order to avoid other expensive purification methods in the sugar industry, as a large excess of lime, which is later precipitated with carbonic acid or sulphurous acid.

It is known, that by this lime treatment many valuable substances are destroyed, vitamines etc. According to the new process one is able to separate these. However, when treating raw materials of inferior quality, the binding capacity of the polar adsorbents is influenced unfavourably.

Technically it is of importance that blackstrap, being a waste product as has already been explained above, may be gathered from different factories and can be subjected to the new process. As a result thereof one succeeds in crystallizing the sugar which is present in the blackstrap for the greater part. It is also possible to sell this treated backstrap as a syrup for human consumption. This syrup excels in a low non sugar content and fine aromatic taste, even if the raw material is the very badly tasting blackstrap of beet.

It goes without saying that the method is also very suitable for the treatment of already purified extracts, whether concentrated or not.

In glucose manufacture a fine result may be obtained, if the converted juice is first treated with a positive polar substance and thereafter with a negative polar one.

The application of the working method takes place in a simple way by percolation of the liquid over thick layers of the polar substances, which in this case have to be of granular structure. However, a treatment with powdery substances, which are filtered-off afterwards also leads to proper results, but this way of application is more expensive and requires much labour.

By applying substances of granular structure one is also better able to use the principle of counter current. The application of this principle is always of advantage in case of reactions of equilibrium, with which one has to do in this case.

For preference the liquid to be treated be first percolated over the negative polar substance and thereafter over the positive polar substance. As soon as important quantities of substances to be removed break through one of the contact filters, this filter must be cut out. According to the principle of counter current, finally a greater quantity of liquid can be treated if one does not apply one filter of each kind consecutively but more. Hereby care must be taken that the liquid by turns passes a filter containing negative polar contactmass, one containing positive polar contactmass, one containing negative polar contact-

mass etc. By turns, a filter, viz. the one which has been into contact with the fresh liquid, must be prepared for a new purification of the liquid by treating it with a suitable solution of electrolytes. Then this filter comes into contact with the liquid, which has already passed all the other filters.

The principle of counter current is also applied, if one uses one filter of each kind, but keeps operating some time after the liquid has broken through and pumps the liquid—which has passed thereafter—over the contactmass again after this has been regenerated.

One acts also according to this principle, if one carries the regenerating-liquid through the contactmass in opposite direction to the liquid to be purified. Whether the principle of counter-current can be applied to advantage, depends on the price of the chemicals, which are used for the regeneration and whether the chute in neutralizing power of the contactmass occurs rapidly or slowly, that is to say whether the breaking through of the substances to be removed, increases rapidly or slowly. In the latter case a more or less complete application of the principle of counter current is of advantage. When making use of synthetical resins this is the case to a large extent, the load becomes much greater, e. g. in case of higher acidity of the liquid.

In some eases a contactmass, consisting of a mixture of the negative and positive polar substances may be applied, viz. if the regeneration of the substances can take place in the same way, or with chemicals which regenerate one of the substances without disturbing the capacity of the other.

If e. g. sulphuric acid is used as regenerating agent, such as mentioned in Example 2, one can proceed in this way. Sulphurous acid is also very suitable as a regenerating agent, especially for the positive polar substance. The sulphurous acid applied in excess pushes away the impurities absorbed and may be driven out of the acid-binding resin by steaming or heating.

If the substances are introduced into a liquid, in which certain ions prevail, these ions are incorporated in the substance. As well the removal of the substances from the liquids to be treated as the regeneration of the polar adsorbents is based on this principle.

Applicant has found, that when making use of synthetical resins, which bind acids a. o. polarly, the loading is much higher if these acids are present in a milieu of low pH. Practically this is the only right method to remove a large quantity of the acids from the sugar solutions, at least it offers big advantages. Only if this low pH meets with objections, one may derogate from it. On that account one will not carry thick juice in sugar factories over two percolators, but over various ones, which by turns contain the different substances with polar binding power.

The chemicals which can serve for the regeneration, principally sulphuric acid, hydrochloric acid, soda, caustic soda, lime and sodium chloride, are cheap, but frequently have to be applied in a large excess, for which reason the solutions are often systematically used repeatedly. In sugar factories, in which one disposes very often of strong alcaline condensed water from the evaporation plant, this is a cheap regenerating liquid, especially for the alcaline contactmass.

For the regeneration of the negative polar substance a treatment with acid is best, as applicant has found. A modification of this working method is the use of sulphurous acid, which has sterilizing capacities and which besides by washing can also be removed in a simple way by steaming or heating.

Also for the regeneration of the positive polar substance, this regeneration method with sulphurous acid is extremely suitable, as applicant has found. The sulphuric acid can be applied in excess, because it may be easily recuperated out of the liquid by heating and consequently all substances adsorbed can be driven out of the mass to be regenerated.

When regenerating the positive polar substance according to the present working method, also a good result may be obtained—if much water is available—by washing the mass to be regenerated during a long time. The impurities absorbed are then carried way. The process can be accelerated if hot water is used.

If an alkali treatment for the regeneration of the positive polar substance is applied, a diluted lime solution is better and cheaper than a solution of soda or caustic soda. Furthermore a solution of lime is much easier to be removed from the mass by rinsing.

It may be that in the long run on the polar adsorbents substances accumulate, which are not removed by the above mentioned regenerating method. In this case a treatment of the positive polar substanee with strong solutions of caustic soda and of strong sulphuric acid, to which eventually oxidation agents have been added, is advisable. The negative polar substance is treated in the most suitable way with strong sulphuric acid. It is also possible to get rid of the strongly adsorbed organic substances in the biological way, especially of the albuminous compounds. This method has formerly also been suggested for the regeneration of bone char, but here almost the same result could be obtained by glowing the bone char.

However, the present polar substances cannot be glown, because they then would lose their activity.

At this biological purification of the substances in question, micro-organisms of different nature play part. These micro-organisms can also be cultivated separately; they are present nearly everywhere in the nature. The cultivation of these microorganisms and the destruction of the impurities adsorbed are furthered in a weak acid milieu and at moderate increased temperature (30–40° C). It is also desirable that air can get admittance, because the fermentation which occurs is principally of an oxidative nature.

It goes without saying, that, if one wants to gather the substances accumulated in the contactmass on account of their value, regenerating liquids of suitable composition and concentration should be applied. Mostly strongly concentrated solutions will be applied in order not to obtain the liquids to be gathered in a too dilute condition.

An advantage not to be underestimated of the present method is this, that mostly the liquid can be filtered over the contactmass in cold condition or at moderate temperatures. Decomposing losses of sugars and albumines then do not occur, whereas still the colloids which hinder filtration are removed and which, when applying the old methods, could only be made harmless by a thorough heating and with the aid of chemicals. Moreover the substances to be gained with the contactmasses are not decomposed or coagulated.

I give hereunder the following examples:

Example 1

Blackstrap of beet with a sugar content of 51%, water-content 18%, ash content 9.8%, is diluted to 65 Brix with the aid of a sugar containing liquid to be mentioned later on, the pH=7.9.

This liquid is treated wth 5% of an active humus, made of sawdust with the aid of sulphuric acid, heated to 80° C and filtered, on account of which the pH decreases to 7 and the Brix to 60.

This liquid is successively filtered over a contactmass of a substance, obtained by the reaction of gaseous SO_3 on coal at a tempertaure of about 100° C, and over a contactmass of synthetical resin obtained by the reaction of formalin on metaphenylendiamin.

The negative polar contactmass has a size of grain of 0.25–1 mm. and is stored in an iron container, which is covered with ebonite. This container has a net content of 6000 L. and contains 2900 kg of the substance. The positive polar contactmass has an equal size of grain and is also stored in an iron container covered with ebonite with a net content of 7500 L. containing 2500 kg of the substance. The substances are put on layers of sand. Both containers are filled with water up to the surface (level) of the mass; a suitable overflow tube takes care that the mass cannot become dry.

Now over both masses, respectively 2500 L. of water, which contains 320 kg of HCl, and 3750 L., which contains 350 kg of caustic soda, are introduced from the top downward, thereafter respectively 4000 L. and 8000 L. of water.

Then 4000 L. of the dilute blackstrap are carried over the negative polar substance, afterwards 3000 L. of water and finally the regenerating liquid and the leaching water.

The liquid running first out of the filter is water, only at 3 Brix concentration one gathers separately, viz. successively:

1000 L. of liquid, concentration 10.2 Brix
1000 L. of liquid, concentration 25.1 Brix
1000 L. of liquid, concentration 40.4 Brix
1000 L. of liquid, concentration 39.2 Brix
1000 L. of liquid, concentration 35.– Brix
1000 L. of liquid, concentration 29.2 Brix
1000 L. of liquid, concentration 22.2 Brix
1000 L. of liquid, concentration 14.1 Brix
1000 L. of liquid, concentration 7.3 Brix
1000 L. of liquid, concentration 4.– Brix

The then following liquid is thrown away.

The sugar solutions collected are carried successively over the positive polar contactmass, then 3000 L. of water and finally also the regenerating liquid and the leaching water.

The liquid running first out of the filter is water, only at 3 Brix concentration the liquid is gathered viz.

1000 L. of liquid, concentration 5.– Brix
1000 L. of liquid, concentration 10.4 Brix
1000 L. of liquid, concentration 18.9 Brix
1000 L' of liquid, concentration 25.4 Brix
1000 L. of liquid, concentration 28.3 Brix
1000 L. of liquid, concentration 27.4 Brix
1000 L. of liquid, concentration 25.6 Brix
1000 L. of liquid, concentration 20.0 Brix
1000 L. of liquid, concentration 13.4 Brix
1000 L. of liquid, conceneration 7.6 Brix
1000 L. of liquid, concentration 4.– Brix

The then following liquid is thrown away.

The pH of the liquid, which has passed the negative polar substance, has decreased considerably, to abt. 2.8, that of the liquid, which has passed the positive polar substance, is normal again and practically neutral. Only the last running-off sugar solution shows a low pH again.

From the solid matter introduced abt. 87% passes the negative polar contactmass, abt. 72% the positive polar contact mass. This last filtrate as far as the colour, purity and crystallizing power are concerned, does not yield to purified thick juice.

The largest removal of colour is to be attributed to the positive polar substance, after having passed this mass the liquid still contains about 15% of the original coloring matter. The negative polar contactmass removes only 10% of the coloring matter.

The dilute first running and running-off of the filtrates are used for diluting the original blackstrap.

In the regenerating liquid of the negative polar contactmass all potassium be accumulated, also betaine, in the one of the positive polar mass all organic acids, the valuable glutaminacid e. g. and other organic matter. These liquids may be worked on these products.

The positive polar contactmass has often a tendency to disperse originally and to give off colour. In this case it is desirable to carry the first running of the positive polar mass over the negative polar mass, as a result of which this dispersion is separated.

Example 2

The polar adsorbents are mixed or placed in layers on each other in a container, having a net contents of 13.000 liters. Through this container the blackstrap diluted as per Example 1 in the same quantity is filtered. The regeneration takes place with 600 kilos of sulphuric acid. On account of this the working method is very much simplified, although the removal of non-sugars, particularly of colour takes place to a less extent. Finally the liquid is strongly acid, owing to the sulphuric acid, which has to be precipitated with baryt and filtered off. If a negative polar contactmass, proof against lye, is used, regeneration with a lye- or soda-solution is also possible.

Example 3

The regeneration of the positive polar mass from Example 1, takes place by carrying through water, in which sulphurous gas is blown.

As soon as the running-off rinsing water is almost freed from the impurities rinsed from the positive polar substance, the mass is steamed out.

The free sulphurous acid can be gathered.

Example 4

In Example 3 exclusively hot town water is used for rinsing purposes till in the running-off water practically no more impurities occur. Then the mass is sterilized by steaming out.

Example 5

In Example 4 water saturated with lime is used and this is rinsed out with town water, as soon as there are practically no more impurities present in the running-off liquid.

Example 6

Over the same apparatus as applied in Example 1, unheated diffusion juice obtained from beets or press juice from sugar cane, can be carried.

The regeneration takes place in the same way. From the regenerating liquids pectin-substances etc. can be gained.

It is desirable to sterilize the filters from time to time e. g. by steaming or boiling out with hot water.

Example 7

As per Example 1 liquors from refineries can be treated, principally in view of decolouration to replace the bone-char-treatment. The decolourizing expenses are much lower.

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