

THE CHEMISTRY OF COLOUR REMOVAL: A PROCESSING PERSPECTIVE

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Abstract

Numerous processes have been developed over the years to achieve efficient and cost-effective removal of colour in order to produce low colour white sugars. Appreciation of the types of colour present in raw sugar is important when choosing and operating refinery processes, as different processes may remove different types of colour bodies. Therefore, combinations of processes are usually required to produce the best quality refined sugar. This paper reviews the mechanisms of colour removal of the major processes in the cane sugar refining industry, in terms of physical and chemical properties relating to the different colour bodies present. Suggestions for optimum process combinations are presented.

Introduction

With increasing customer demands for higher quality, sugar mills and refineries are being forced to produce lower colour sugar more cost effectively. A number of both traditional and new processes and chemicals are available to process managers to achieve good colour removal at a reasonable cost, and with minimum downstream disadvantages. Each process or chemical acts via a different mechanism or pathway on the various types of colour present in sugar liquors. Some of these processes complement each other, while others may either duplicate or even counteract each other.

This paper, which is based on a recent communication on the topic (Davis, 2001), will review the mechanisms of colour removal in sugar processing, and draw conclusions about which colour removal processes are compatible, and which combinations should be avoided.

Review of colour types

Extensive international research has been performed into the characterisation of sugar colour. Numerous comprehensive reviews have been presented (e.g. Riffer, 1988, Clarke *et al.*, 1985 and Kennedy and Smith, 1976), and only a summary will be given here. There are generally recognised to be four types of colour present in sugar: plant pigments, melanoidins, caramels and alkaline degradation products of fructose (ADF). The last three are factory produced colour pigments.

Plant pigments

The plant pigments are principally phenolics and flavonoids, which make up about two thirds of the colour in raw sugar (Smith and Paton, 1985). The phenolics are generally uncoloured, but are oxidised or react with amines or iron to form colourants during processing. Flavonoids are polyphenols that exist in the cane plant and are involved in enzymic browning reactions.

The plant pigments tend to have low to medium molecular weights ($MW < 1000$), but are highly ionised, particularly at high pH values. Hence they have high indicator values (IV = colour at pH 9 divided by colour at pH 4), but are generally readily removed in the refinery. However, they are readily incorporated into the sucrose crystal in the refinery.

Melanoidins

These are factory produced pigments that result from Maillard type reactions of amino acids with reducing sugars (non-enzymic browning). They are only produced with the application of heat at high brix and low purity, but can also form with low heat over long periods. They are slightly negatively charged at neutral pH, but positive under acidic conditions. A sub-division of melanoidins is melanins, produced from phenol-amine reactions. These have a medium MW (> 2500) and are difficult to remove in processing. Melanoidins are insensitive to pH and hence have low IVs.

Caramels

Caramels form as thermal degradation products of sucrose, with high MWs that increase with time and temperature as a result of increasing polymerisation. They have only a slight charge and are not pH sensitive.

Alkaline degradation products of fructose (ADFs)

These are formed, as their name suggests, from thermal decomposition of fructose mainly, and glucose to a lesser extent, under alkaline conditions. The reaction products are brown-coloured and acidic in nature, leading to inversion of sucrose and further colour formation. The exact mechanisms are unclear, but amines are known to be involved (Carpenter and Roberts, 1976). These compounds are usually uncharged and of medium to high MW.

Colour precursors

These are compounds which, while not coloured themselves, undergo reactions that form colour during processing. They include amino acids, simple phenolic compounds, and 5-hydroxy-2-methyl furfural (HMF), the last being formed from acidic decomposition of fructose.

Effect of pH and ionisation

The degree of ionisation of the unwanted colour bodies is critical in determining the efficiency of removal by a particular process. One of the most significant factors affecting ionisation is the solution pH. Riffer (1988) states that, at pH 7.2¹, caramels

¹Note that all pH values in this paper are quoted at 25°C.

are 99.7% ionised while flavonoids are 0.6% ionised. In contrast, phenolics are ionised to a degree of 66% at pH 9.7. Liquor pH also affects the size and shape of high MW polymers, further influencing the effectiveness of colour removal.

Polarity

Polarity is the property of partial charges being induced at opposite ends of the molecule by the arrangement and different electronegativities of the atoms. As an example, water is polar because the hydrogen atoms are joined close together (δ^+) opposing the oxygen atom (δ^-). However, carbon dioxide is non polar as the molecule is linear, and the two oxygen atoms balance each other. This property, which can be extrapolated to functional groups within large molecules, can lead to non-ionised but polar molecules being held by ionic adsorbents.

A concise summary of the properties discussed so far in terms of polymeric characters is given in Smith *et al* (1981), and Table 1 is adapted from this work.

Carbonatation

Bennett (1972) performed extensive experiments on carbonatation and phosphatation in the laboratory, coupled with X-ray diffraction (XRD) studies, to determine the mechanisms of colour removal. He showed that the impurities are trapped within the growing calcium carbonate crystals, often distorting the crystals, rather than being adsorbed onto the surface after precipitation. Any kind of colour body that has some acidic (anionic) character and is capable of forming a weak linkage with calcium (i.e. a sparingly soluble calcium salt) will get incorporated into the precipitate.

The extent of colour removal is therefore not particularly sensitive to the surface area of the precipitated calcium carbonate. It is more a function of the rate of growth to enable the impurities

to be incorporated. However, the state of agglomeration of the precipitate, which directly influences the filterability, depends upon the nature of the impurity. Some impurities will prevent agglomeration and hence lead to poor filterabilities, but these were not identified in Bennett's work.

Thus, the data in Table 1 can be used to predict what colour components should be removed by carbonatation. Kennedy and Smith (1976) stated that carbonatation has a high affinity for polymeric colourants, which are anionic at the high carbonatation pH, and amino nitrogen, which is polar. They also found that little plant pigment of low MW is removed, but cautioned that ADFs are consistently formed, as expected under the conditions of carbonatation.

From a survey of five refineries, Clarke *et al* (1985) found that carbonatation generally removed more phenolics and amine colourants than did phosphatation, although it was also stated that phenolics can be formed during carbonatation.

Sulphitation

Substantial research has been performed to determine the mechanism of sulphitation. Carruthers *et al* (1955) found that sulphur dioxide is more effective at suppressing colour formation than reducing colour already formed. They state that if the sulphur dioxide is added before colour is produced, it must be in excess of a certain minimum quantity, but that there is also a maximum quantity beyond which no further effect is noticeable (about 200 ppm added). This work was carried out at pH values between 7.8 and 8.7, where the sulphite ion is stable. At lower pH values, the bisulphite ion is formed and other reactions are possible.

Riffer (1988) states that sulphite ions react with unsaturated carbonyl groups and some flavonoids, which shifts the light absorption out of visible wavelengths. However, Vercellotti

Table 1. Summary of properties of cane sugar colourants.

Property	Monomeric	Intermediate	Polymeric
Composition	Mainly flavonoids	Factory colourants, eg. ADF	Factory colourants, eg. caramels, melanoidins
Molecular weight (MW)	< 1000	1000 - 2500	> 2500
Ion	Neutral at low pH	Cationic below pH 5, Anionic above pH 6	Cationic below pH 5, Anionic above pH 6
Polarity	Least polar	Intermediate	Polar
Indicator value (IV)	5 - 40 Sensitive	3 -4 Intermediate	1 - 2 Insensitive

and Clarke (1997) explain further that these new compounds remain in the liquors and can later polymerise and undergo condensation reactions to form highly coloured aromatics. Thus, although sulphitation is often erroneously regarded as a 'reversible' process, some colour is in fact destroyed but new colour is later formed from the breakdown products.

The inhibition of colour formation is reportedly (Vercellotti and Clarke, 1997; and Chen, 1971) brought about by the combination of the sulphite group with reducing sugars, thereby blocking the carbonyl function which is necessary for caramel and melanoidin formation. It is well-established (Getaz, 1989) that sulphitation will inhibit Maillard-type reactions, also by combining with carbonyl groups, although this reaction is reversible.

In particular, sulphited carbonyls are prone to losing the sulphite groups over time, as these compounds are slightly unstable. Hence, as the sulphite is released as sulphur dioxide, the colour may return, as has been found when mill white sugar from a sulphitation process is stored.

There are also permanent effects of sulphitation (Chen, 1971), among them decomposition, modification or polymerisation of colour compounds such as polyphenols, melanins, melanoidins and pigments. Riffer (1988) states that dithionite (Blankite) acts by reduction of diketones, quinones and iron complexes. In particular, the reduction of quinones prevents their oxidative polymerisation, which would result in dark brown pigments. In addition, organic compounds that form sparingly soluble calcium salts will get incorporated into the calcium sulphite and calcium sulphate precipitate, as in carbonatation.

Phosphatation

A thorough review of the phosphatation process was done by Saranin (1972), and this work should be consulted for further details on operation of the process. Saranin concluded that the tricalcium phosphate precipitate occludes and absorbs fine colloidal solids and soluble colour. Most colloids in sugar liquors have negative charges, and so the addition of a cation such as calcium neutralises these charges and allows flocculation to take place. Accordingly, the anionic colour bodies are most effectively removed by this process, and some soluble colours are absorbed by the precipitate.

Bardwell *et al* (1985) found that the Talo process had a lower capacity for flavonoids than had other processes, and should therefore be coupled with granular activated carbon for best effect.

Colour precipitants and flocculants

Detailed descriptions of various chemicals tested and their structures are presented by Bennett *et al* (1971) and Elvin (1996), and these papers should be consulted for exact formulae. However, colour precipitants must have three properties for effective colour removal (Bennett, 1971):

- a strongly basic (cationic) centre which can attach to weakly acidic (anionic) centres on colour molecules. This basic centre is normally an amino nitrogen group. The ease of precipi-

tation increases with the anionic charge on the colour molecule.

- a long chain or cyclic hydrocarbon, often with a fatty acid component, which is hydrophobic.
- a balance between the above two components such that the precipitant is readily dispersible in sugar solutions.

On addition to the sugar liquor, the basic centre is rapidly attracted to and binds with the acidic centres of the soluble colour molecules, leaving the hydrocarbon portion projecting away from the colour body. This creates a hydrophobic layer around the complex (see Figure 1), rendering the colour body insoluble and it precipitates out of solution forming small black particles about 0.5 μm in size.

These particles are too small to be easily removed by conventional filtration, but are effectively scavenged by carbonatation and phosphatation precipitates. Mochtar (1989) mentions three stages in decolourisation by the Talo process.

- The cationic surfactant reacts with the anionic colour to form an insoluble precipitate.
- This precipitate is scavenged by the calcium phosphate to form a primary floc.
- The addition of an anionic polyacrylamide polymer then increases the effective size of these flocs by bridging (secondary flocculation).

Bennett (1971) mentions further that the fatty acid chains reduce the interfacial tension between air and liquor at the surface of the flocculated particles, and hence improve adherence of bubbles to the precipitate during aeration. Hence, Talofloc has a greater benefit with phosphatation than with carbonatation.

It should be noted that over-addition of the colour precipitant may cause the hydrophobic groups of the excess precipitant to attach to those already complexed with the colour bodies. This results in a further layer with ionic centres in contact with the solution, rendering the complex soluble once again.

Hence, there is an optimum dosage of the precipitant that should not be exceeded for maximum effectiveness. Bennett *et al* (1971) give extensive results in this regard for a number of chemicals, with the optimum addition rate being in the range 200-500 ppm. The range of the optimum dosage is relatively narrow, and it is recommended that periodic testing be carried out in factories to ensure best performance and efficient utilisation of the rela-

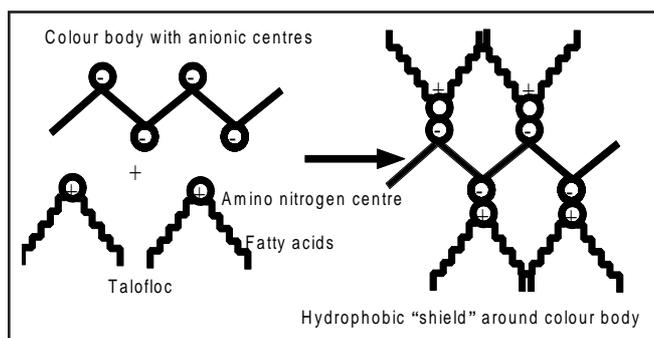


Figure 1. Reaction of Talofloc with colourant.

tively expensive chemicals. Note, though, that Talofloc does not show such an optimum, and colour removal increases with increasing dosage up to 2000 ppm.

Comments on specific precipitants

Talofloc: Talofloc produces a very fine precipitate, and hence its use is confined to the phosphatation process. The maximum permitted dosage under US FDA regulations is 700 ppm.

Talocarb and 'polyamines': Talocarb's performance is similar to that of Talofloc up to 300 ppm, but above this it interferes with the phosphatation reaction, resulting in poor clarification.

Talocarb is also used in combination with carbonatation. A dosage of 400 ppm was shown (Runggas and Shephard, 1977) to produce up to 300 units extra colour removal when dosed before carbonatation filtration.

Moodley (1993) tested some locally supplied polyamines on various clarification processes. He found that 200 ppm on liquor of these polyamines could decrease liquor and sugar colours by 20-30%. He concluded that the polyamine should be added to carbonated or sulphited liquors before filtration, or to raw melt before phosphatation, confirming the findings of other workers.

Talomel: Talomel is most often used in the production of mill white sugars in conjunction with syrup clarification, but is best added to clear juice. A dosage of 1500 ppm on Brix typically reduced the sugar colour by about 20%. However, this chemical is the most expensive of the precipitants and it should be noted that it does not have FDA approval.

Anionic flocculants

These flocculants bridge between calcium ions in previously formed precipitates. They provide the secondary flocculation to increase the effective size of precipitates such as calcium carbonate and calcium phosphate, and improve the removal of these precipitates in the clarification process.

In general, the carbonatation process works well enough that flocculation of the precipitate is not required, but this is not the case with phosphatation. Hence the use of an anionic flocculant such as Talofloc is necessary to improve the floatability of the calcium phosphate precipitate. This enables phosphatation to be run at lower temperatures (80°C instead of 95°C) and with shorter retention times (8 minutes instead of 15 minutes) (Bennett, 1971). However, Runggas and Shephard (1977) found that the addition of Talofloc tended to lower the residual phosphate in the clarified liquor at a cost of reducing the filterability of the liquor.

Oxidative decolourants

Oxidative decolourants include any strongly oxidising chemicals that may be used for colour removal. Hydrogen peroxide and ozone are the principal chemicals of interest here, and hypochlorites will be briefly mentioned.

The oxidative decolourants work by producing active free radicals in solution, and these free radicals readily attack susceptible functional groups. The exact nature of the radical depends

to some extent on the solution characteristics, particularly the pH. For instance, ozone acts via an oxygen radical in neutral or acidic media, while in alkaline media the hydroxyl radical predominates. Each of these radicals may act through a different pathway, and so different reactions will result. The oxygen radical does not appear to attack the sucrose molecule, while the hydroxyl radical does.

Jadhav *et al* (1988) mention four reaction mechanisms: ionic reactions, oxygen transfer via peroxygen compounds, electron transfer and free radical reactions, but give no further details about which mechanisms operate in sugar processing. Riffer (1988) states that oxidants cleave conjugated unsaturated bonds creating carboxylic acids and oxidise phenolics to quinones and acyclic products. These reactions have the direct effect of destroying colour.

Hydrogen peroxide

Shore *et al* (1984) found in their review of white sugar colour that several reactions of hydrogen peroxide with colour had been described. These include the oxidation of intermediate products of enzymic reactions to melanins which can be removed during carbonatation. The oxidation of invert sugar to unreactive intermediates which are unable to form colour was also described from the beet industry, where juice pH is much higher than in the cane industry. Polyphenols were also reportedly reduced to 10% of the untreated value.

Vercellotti and Clarke (1997) refer to the temporary bleaching effect of peroxide by free radical addition at allylic sites and double bonds, with eventual decomposition to acids and alcohols. In an investigation of the use of peroxide for raw juice treatment, Mane *et al* (1992) found that polyphenol and reducing sugar levels were also lowered by peroxide addition, even at pH 7.

Ozone

Ozone behaves in a similar way to peroxide, but its higher oxidation potential² results in fewer reversible reactions, and a greater range of oxidation reactions is possible. Several reactions with colour bodies are described by Davis *et al* (1998) based on an extensive investigation by Razumovskii and Zaikov (1974). These are:

- Oxidation of double bond systems and cleavage to carboxylic acids, alcohols and aldehydes
- Opening of the aromatic rings of phenols, which may be further oxidised as above.
- Oxidation of other aromatic groups to form quinones and polymeric ozonides.
- Oxidation of primary amines to nitro compounds.
- Oxidation of secondary amines via intermediate radicals to separate substituents.
- Oxidation of tertiary amines to amine oxides.

² The standard redox potential of ozone in acid media is +2.076 V, while that of hydrogen peroxide is +1.776 V.

Patel and Moodley (1991) state that the reaction rate of phenolics with ozone is dependent on the nature and size of the substituents. They also mention that the reaction rate increases with the number of aromatic rings in the colour body. However, this is not likely to have a significant effect in factory decolourisation, where most ozonation reaction rates are probably limited by diffusion processes.

These reactions show that ozone is not only capable of destroying colour directly, but also destroys the colour precursors such as amines and phenolics. However, some of the reaction products that are created may themselves be able to undergo reactions that form colour later in the process. Hence it is desirable to remove them by a precipitation and filtration process.

The oxidation process also increases the ionic character to some extent, and thus improves the effectiveness of carbonatation in colour removal. The work of Davis *et al* (1998) also showed a substantial decrease in liquor colours measured at pH 9 across ozonation, indicating that the pH sensitive plant pigments such as flavonoids and phenolics were strongly attacked. This is of great benefit in a refinery as most colour in raw sugar originates from plant pigments, and these are the colour bodies that are more readily transferred to the crystal.

Such a powerful oxidant might be expected to have some effect on the sugars present, but the work of Davis *et al* and that of Gomez *et al* (1980) showed that sugars were not attacked under neutral or slightly acidic conditions, and only above pH 8.5 was appreciable attack noted. This results from the change of mechanism from the oxygen to the hydroxyl radical at high pH as discussed earlier.

Hypochlorite

Riffer (1980) postulated a two step sequence for destruction of phenolics by hypochlorites: they are firstly oxidised to ortho-quinones, and then these cyclic rings are cleaved to acyclic products. He further stated that hypochlorite treated liquors are poorly decolourised by resins and cationic colour precipitants. He surmised that the highly polar reaction products are preferentially taken up by the resins and precipitants, thereby excluding polar colour bodies. However, there should not be such an effect if activated carbon was used after hypochlorite.

Conclusions on oxidants

Oxidative decolourants have three main effects:

- Direct destruction of colour bodies (bleaching effect), particularly those easily transferred to the crystal.
- Destruction of colour precursors to limit later colour formation.
- Increasing the ionic character of impurities to improve colour removal across carbonatation or phosphatation.

From the work surveyed, it seems essential to follow oxidation with carbonatation or phosphatation in order to remove the oxidised products and prevent colour reforming or further colour formation. The effect is thus to directly lower liquor col-

ours and to reduce colour increases across pan boilings. Furthermore, there appears to be no danger of destroying sugars as long as the pH of the liquors is held at neutral or below during the oxidation.

Activated carbons

The most important characteristic of activated carbon in determining the mechanism is the non-polar nature of the surface. The surface forces (van der Waal's or London forces) create a stronger attraction between the carbon surface and the colour molecules than between the colour molecules and the sugar liquor (Dominguez and Hyndshaw, 1977). The large colour molecules can be held against the surface at numerous points, and are thus strongly adsorbed. The enormous surface area (500 - 2000 m²/g) available as a result of the porous structure means that large quantities of colour may be adsorbed before the carbon is exhausted.

This is physical adsorption, and is responsible for most of the colour removal from sugar liquors. However, the carbon still contains some oxygenated functional groups and these cause chemisorption, which allows some polar molecules to be adsorbed. The percentage of oxygenated functional groups is controlled by the activation procedure, and is generally small. However, any given colour body may be held by physical and chemical adsorption simultaneously.

As a result, carbon is not specific for any type of colour, but gives high overall colour removal (typically 80%). It is very effective for removing flavonoid and phenolic colourants and Bardwell *et al* (1985) reported that granular activated carbon (GAC) removed virtually all the flavonoid colourants from raw liquor. It should be noted that with plant pigments the degree of ionisation increases with pH, and so it is expected that removal of the flavonoids would decrease with increasing pH. Hence, liquors passing through carbon should be at neutral pH for best results.

Riffer's 1988 review reports that GAC does not work as well as resins for removal of iron compounds or amino-nitrogen derivatives. Some colourless components of ADF products are not removed by carbon, while caramels and melanoidins are well-removed.

Before a colourant can be adsorbed onto the carbon, it must reach an appropriate surface by diffusion into the carbon pores and orientate itself correctly. Hence, the very large polymeric molecules may not diffuse far into the carbon, and limited sites are available for their adsorption, while the smaller phenolics can reach further into the carbon and will have more suitable sites available. Hence, the pore size distribution is vitally important in determining the relative quantities and the rates of removal of different types of colour bodies.

Ion exchange

A thorough review of the chemistry and operation of ion exchange decolourisation has been written by Getaz (1988), and so this paper will summarise his work and more recent publications.

Resin characteristics

Ion exchange resins are synthetically produced fine beads (0.5 - 1 mm diameter), which consist of high molecular weight polymers with a degree of cross-linking to create a porous structure. Within this porous structure are a large number of immobile but active cationic or anionic sites, coupled with mobile counter-ions. These sites are capable of exchanging anions or cations respectively from a solution according to the equilibrium constants for the ions concerned. These constants depend upon the temperature and the nature of the ions, and the equilibrium can be shifted by changes in the concentrations of the ionic species. A representation of a strong acid cation resin is shown in Figure 2 (after Kunin in Appelbaum (1968)).

A wide range of resins is available with different polymer backbones and different functional groups, leading to strong and weak cationic and anionic resins for different applications. In addition, the gross structure can be gel-like (micro-reticular) or macro-reticular, depending on the degree of cross-linking and porosity. However, due to the nature of the colour bodies in sugar liquors (generally high molecular weight and anionic), macro-reticular strong base anionic resins have proved to be most suitable for sugar refining, and the following discussion will be confined to this type.

The resins employed in the sugar industry have a quaternary ammonium functional group, and are supplied in a chloride form. The polymer backbone is either styrene-divinylbenzene or acrylic, the former having aromatic groups in the structure, while the latter is mostly aliphatic. As a result, the polystyrenic resins tend to be more selective for aromatic groups, such as are found in colour bodies, but this selectivity means that it is harder to remove the colourant molecules, and hence regeneration is less efficient. Polyacrylic resins are less selective, but regeneration is easier and more complete, so slower rates of resin deterioration are experienced.

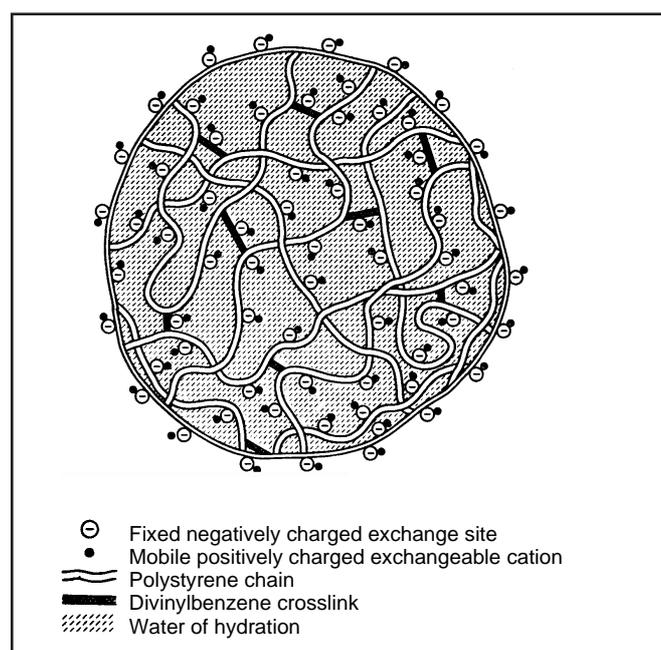


Figure 2. A strong acid cation resin.

Mechanism

Clearly, one of the principal mechanisms is that of ion exchange: anionic groups on colour bodies displace the chloride ions in the resin matrix. There are also competing reactions for the ion exchange sites, with non-coloured organic and inorganic molecules being able to occupy the sites to the exclusion of the colour bodies. The size of the molecules also has an influence in that the molecules must diffuse into the pores, and smaller ones will get there faster. Hence, if equilibrium is not reached, the smaller ions will be preferentially exchanged. Vender (1977) maintains that there is not a direct exchange of chloride with colour bodies, but that chloride ions are first exchanged with inorganic and small organic anions, which are then displaced by the large anionic colour bodies.

However, it has also been demonstrated that physical adsorption is a significant mechanism. Fries (1982) maintains that the mechanism of colour removal is predominantly by adsorption onto the polymer, with hydrophobic bonding and van der Waals' forces being responsible, much as with activated carbon. He believes that the ionic functional groups simply make the resin hydrophilic, allowing the aqueous liquor to penetrate the resin, where adsorption takes place.

The selectivity for certain compounds is thus a function of the ionic charge and the aromatic character of both the resins and the colourants, with acrylic resins being less susceptible to adsorption phenomena. Nevertheless, both mechanisms take part in the removal of colour from sugar liquors.

Bento (1992) showed that amphiphilic anionic colourants can switch between the two mechanisms, depending on their ionic form. This in turn depends on the pH of the liquor and the other inorganic and organic compounds present in the liquor. For this reason it has been recommended (Getaz, 1988) that liquor pH should be between 8 and 9 for increased ionisation of colourants and hence more complete removal via ion exchange. Bento also concluded that acrylic resins decolourise mainly by ion exchange, in contrast to styrenic resins.

In a later work, Bento (1997) stated that both mechanisms may work on a single molecule, and that carboxylic acid and phenolic groups of low molecular weight compounds are fixed by chemical reaction and molecular interactions. High molecular weight colourants can be fixed at more than one site, which makes removal difficult. He also stated that it was possible that colourants fixed to a resin can switch from one mechanism to another during regeneration.

His work further showed that resins do not remove the majority of flavonoids, and caramels are not well retained by styrenic resins, while melanoidins and ADF products are. Melanoidins are well removed from the resin during regeneration, but only half of the ADF products are, with caramels intermediate between the two.

Conclusions on ion exchange resins

Resins do not remove as broad a range of colourants as activated carbons, but are more specific. However, the colour removed is not that which is preferentially transferred to crystal.

Resin fouling can be a problem, but the process is generally robust and easy to operate.

Comparison of processes

It is evident from the findings presented here that the varied processes and mechanisms of colour removal have a number of overlapping areas and several differences. Seven different processes have been described, and a multitude of process combinations is possible. To better visualise the relative strengths and weaknesses of the processes, Table 2 has been drawn up, in which the effect of each process on each type of colour has been tabulated. In the table, each block indicates whether a certain process removes a certain type of colour well or poorly. Some interactions are not well known, and so these cells are left blank.

Based on this information and knowledge of the synergies between various processes, a table of process combinations can be synthesised, in terms of what processes should complement each other. This table (Table 3) considers the order of each process, with the first process applied listed across the top row, and the second applied listed down the first column. Several annotations have been used as follows:

- **C** denotes a benefit in terms of colour removal, in that the different processes remove different types of colour.
- **P** denotes a process benefit, in that the pH of the liquor leaving the first process is ideal for the second process, or there is a synergistic effect in that the result of the first process improves the performance of the second process.
- **X** denotes a combination that is not ideal, and should preferably be avoided.
- Diagonal lines (lower left to upper right) indicate that these combinations would normally not be considered.
- Blank cells have been left where insufficient knowledge is available on the interactions.

One particular interaction deserves special comment: the combination of oxidants and colour precipitants. From the description of the reactions of ozone and the structures of the colour precipitants, it may be expected that ozone will attack the amino nitrogen of the precipitants that is central to their function. It could well also attack fatty acid groups and the cyclic group of Talomel. In the case of ozonation ahead of the Talo process, it is very likely that Talofloc will be adversely affected. If no colour precipitant is used with phosphatation, ozonation may be

Table 2. Effect of decolourisation processes on colour types.

Colour Process	Phenolics	Flavonoids	Melanoidins	Caramels	ADF products	Colour precursors
Carbonatation	✓!	X	✓	✓	!	
Sulphitation	✓	✓	✓			✓
Phosphatation	X	X	✓	✓	✓	
Colour precipitants			✓	✓	✓	
Oxidative decolourants	✓	✓				✓
Activated carbon	✓	✓	✓	✓	X	
Ion exchange	X	X	✓	X	✓	

✓ - well removed X - poorly removed ! - formed in process

Table 3. Process combinations.

Process		First						
		Carb.	Sulp.	Phos.	Precip.	Oxid.	Act. carbon	Ion. Exch.
Second	Carbonatation					CP		
	Sulphitation	P				X		
	Phosphatation	X			CP	C		
	Precipitants	C	C	C		X		
	Oxidants	X	X	X	X			
	Activated carbon	C	CP	CP		C		
	Ion exchange	P		X		X	C	

used, but further work would have to be carried out to determine the extent of the interactions.

Based on Tables 2 and 3, there are two process combinations which stand out as highly attractive in terms of colour removal and process compatibility. These are:

- Oxidation followed by carbonatation followed by activated carbon.
- Phosphatation with a colour precipitant followed by activated carbon.

It is interesting to note that ion exchange is not one of the better options from a point of view of efficient colour removal, the reasons for which have already been explained, but it may be a good option if capital and operating costs are considered.

Regarding this point, this review has not taken into account equipment capital and process operating costs, but has simply considered the colour removal mechanisms involved. Any investigation for adding extra colour removal processes to an existing refinery or for planning a new refinery would of necessity have to consider the cost factors, and a different process combination may be found to be optimal.

For example, the capital costs for phosphatation are lower than those for carbonatation, but the operating costs are higher. By contrast, the capital costs for ion exchange and granular activated carbon are similar, but the operating costs can vary greatly depending on the regeneration method and costs for the activated carbon.

Conclusions

This review has focussed on the chemical and physical characteristics of the various types of colour bodies in cane sugar processing, and their interactions with the different clarification and decolourisation processes. It is clear that the topic is a complex one, and although most of the processes are reasonably well understood, many of the interactions between processes have not been well studied.

However, recent advances in chemical and instrumental analyses should allow the industry to further investigate these interactions and improve process selection and optimisation. Nevertheless, the information provided here gives guidelines as to which process combinations should be avoided, due to either a process incompatibility (such as oxidants and sulphitation) or because the two processes remove similar types of colour.

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