

THE USE OF SULPHITATION AND OF ION-EXCHANGE IN THE REFINING OF CANE RAWS

By G. R. E. LIONNET

Sugar Milling Research Institute, Durban

Abstract

Decolourisation by sulphitation and ion-exchange was investigated. The efficiencies of the processes were assessed on the basis of colours of affinated crystals boiled from the different liquors. This crystallisation step was necessary for colour studies, since it is well established that the colour transfer from liquor to crystal is influenced by the nature of the colourant. Industrial liquors from refineries using different decolourisation processes were boiled under standard conditions in the Sugar Milling Research Institute pilot pan. The results showed significant differences in the colours of the affinated crystals obtained, and a clear indication of higher colour transfer from the non-sulphitation liquors. When a given liquor was treated by sulphitation or ion exchange in the laboratory, sulphitation removed 35% of the colour from the liquor whereas resin removed 60%. After crystallisation, however, the crystal colour from the resin-treated liquor was only marginally lower than that of the sulphited liquor. Under strictly comparable conditions, colour transfer from resin-treated liquors was about 20% higher than that from sulphitation liquors. It is shown that a combination of the resin and sulphitation processes offers possibilities of reducing the cost of achieving the required crystal colour.

Introduction

Colour in commercial sugar is found both on the surface and within the crystal. The external colour can be controlled by the washing process in centrifugals but the internal colour, which is associated with the crystal itself, cannot be eliminated and therefore determines the lower limit to sugar colour. Two main groups of factors determine the quantity of internal colour. The first comprises the physical conditions under which crystallisation takes place and includes supersaturation and thus the rate of crystallisation (Broughton *et al.*,³ Lionnet¹²), crystal size (Lionnet¹²) and other aspects such as the use of stirrers. The second group involves the impurities themselves. There is no doubt that such properties as molecular weight and electrical charge distribution together with type and quantity can affect the adsorption, inclusion or co-crystallisation of the impurity in the crystal. This indicates that even low coloured syrups can contain colourants which will have a greater than normal affinity for the sucrose crystal.

Evidence of colourants having different affinities for the crystal is well documented. Godshall and Clarke⁹ show that 66% of the affinated crystal colour is associated with high molecular weight colourant. Gel permeating chromatography has been used (Anon¹) to show that a high molecular weight fraction of colourants, which contains plant derived polysaccharides and phenolics, has the more pronounced effect on sugar colour. Broughton *et al.*,³ using beet liquors and artificial colourants, show that caramellisation products, alkaline degradation products of fructose and glucose and fructose/glycine Maillard reaction products gave transfers (colour of crystal/colour of feed) of 0,04; 0,01 and 0,03 respectively, whereas factory data showed transfers around 0,008.

There are significant differences in the behaviour of colourants in the beet and cane industries. Rein¹³ reports that in cane sugar refineries only 95% colour removal is normally achieved by crystallisation whereas the beet industry achieves over 99%. Colour formation during boiling is around 7% in beet but 19% in cane refineries (Cox personal communication; Rein¹³), but a stirrer in a cane refinery pan reduced the colour formation to 8-10%. An explanation might be given by the results of Broughton *et al.*³ In cane, glucose and fructose are much more abundant than in beet and could produce those colourants that were found to have the higher transfers. Lionnet¹¹ reports colour transfers, for raw cane syrups in a pilot pan, of 0,012. This compares with values of 0,008 given by Broughton, using beet liquors.

Williams (personal communication) investigated raw syrups and affinated sugars boiled from these syrups in a pilot pan at the Sugar Milling Research Institute (SMRI). Higher transfers were found for the low and high molecular weights, which is at variance with beet sugar experience.

Another area of possible differences between cane and beet is the higher levels of phenolics in cane. A number of workers (Clarke *et al.*,⁴ Getaz,⁶ Godshall and Legendre,⁸ Lionnet¹⁰) have stressed the importance of phenolics as far as colour is concerned. Godshall and Legendre⁸ show that the cane plant is rich in phenolics and that their concentration correlates with fungal, bacterial and insect resistance. Mechanical and chemical injury, borer damage, bacterial and viral diseases induce tissue reddening and it is possible that the increase in phenolic concentration may be a general stress response in cane. Phenolic concentration in cane increases as the cane matures. There is a significant varietal effect but the maturing trend was found to be more important. Indicator value (Lionnet¹¹) or IV, (colour at pH 9/colour at pH 4) is an important parameter as far as phenolics are concerned, values of 5 to 14 being characteristic of these colourants.

Lionnet¹¹ measured phenolics in raw syrups and in affinated sugar boiled from those syrups. The level of phenolics in the syrup correlated positively with colour in the crystals. The same author (Lionnet¹⁰) found that the phenolic content was 143% and 70% higher in rind and nodes respectively than in internodes. Drought stressed cane showed a doubling up of phenolic content, as expressed on brix, with respect to similar but not stressed cane. This increase was due firstly to higher levels of phenolics and secondly to the increase in the proportion of rind and nodes in the stressed stalks.

Getaz⁶ reviewed the application of ion exchange resins in sugar refining. Although there can be conflicting results, there is no doubt that there are colourants that resin removes poorly (Delaney⁵) or is incapable of removing.

The use of sulphitation is reviewed by Getaz and Bachan⁷ and by Jullienne (personal communication). Rein¹⁴ looked at the possibility of having a sulphoflotation process for the treatment of melt. Encouraging results were obtained.

In the beet industry (Bourlet and Lescure,² Vaccari *et al.*¹⁶) sulphurous acid salts are used for colour reduction and inhibition. Shore *et al.*¹⁵ show that sulphur dioxide inhibits

non-enzymatic browning reactions forming products less reactive with respect to Maillard reactions and to the degradation of reducing sugars. Sulphur dioxide also inhibits enzymatic colour formation, which can affect phenolics. It is noteworthy that the colourants affected here were those mentioned earlier as possible causes of high transfer factors.

Two conclusions may be made from this brief literature survey. Firstly there appear to be significant differences in the behaviour of the colourants found in the beet and cane industries. There is evidence that the different levels of reducing sugars and of phenolics found in these industries could be involved. Many results from work with beet liquors may therefore not be directly applicable to cane products. Secondly it is clear that the colour of a liquor may not always be a good indicator of the colour of the sugar to be crystallised from that liquor. It is therefore important to include a crystallisation step in decolourisation experiments.

For the past two years the SMRI has been investigating the use of ion exchange and of sulphitation for the decolourisation of refinery liquors originating from cane raws. A pan boiling stage, using the Institute's pilot pan (Lionnet^{11, 12}) has been included in view of the comments made earlier. This paper presents some of the results obtained.

Experimental

Colour was measured at 420 nm, using a 0,45 µm membrane for filtration, according to the ICUMSA method but at pH values of 4, 7 and 9.

The laboratory sulphitation involved the simultaneous addition of milk of lime and sulphur dioxide gas. The amount of gas to be used was controlled by stoichiometry, using the mass of calcium hydroxide added. The liquor pH was not changed by the sulphitation process.

The pilot pan has been described previously. It is well instrumented and is operationally very flexible. Tests were conducted to compare its performance with that of industrial pans in a number of South African refineries. These tests showed very clearly that the pilot pan yields results, particularly in terms of colour transfers, which are directly applicable to industrial conditions. The reproducibility of the boiling procedures was also checked and found to be good.

General survey

Liquors from every South African refinery were boiled in the pilot pan under standard boiling conditions. The liquors and affinated sugars were analysed for colour at pH's of 4, 7 and 9, which allowed indicator values (IV, colour at pH 9/colour at pH 4) to be calculated.

Two conclusions were immediately apparent. Firstly the liquor colours were lower for the non-sulphitation refineries, and secondly, when the affinated sugars were compared, the situation was now reversed with the crystals from the sulphitation process showing lower colours. These findings are summarised in Table 1.

These results show clearly that different purification processes can have marked effects on impurity transfers. It is also evident that sulphitation, although not yielding the lower liquor colours, appears to be a more efficient decolourisation process when the crystal colour is considered.

Carbonatation/sulphitation compared to phosphotation/ion exchange

Liquors from Gledhow (carbonatation/sulphitation) and from Noodsberg (phosphotation/ion exchange), were sampled and boiled under standard conditions in the pilot pan. The liquors and affinated sugars were then analysed for colour (pH 4, 7 and 9).

The liquors sampled from GH consisted of the melt, the liquor after carbonatation (carb), the sulphited liquor (sulph), the fine liquor (after evaporation) and the four jets. Melt, liquor after phosphotation (clear), filtered liquor (filt), fine liquor and the four jets were obtained from NB, where the fine liquor has been treated with ion exchange.

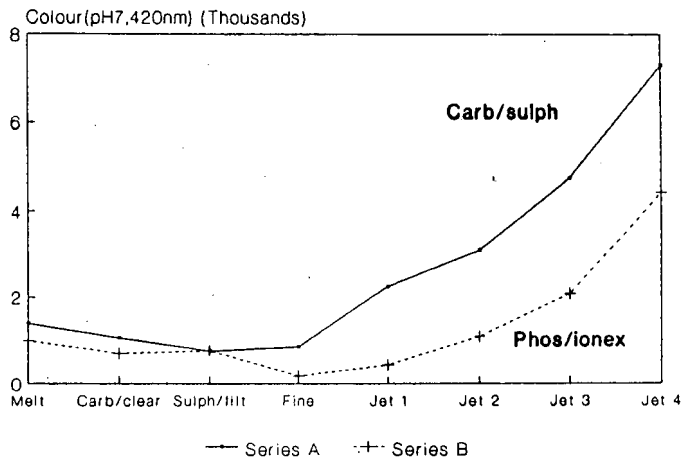


FIGURE 1 Comparison of feed liquor colours

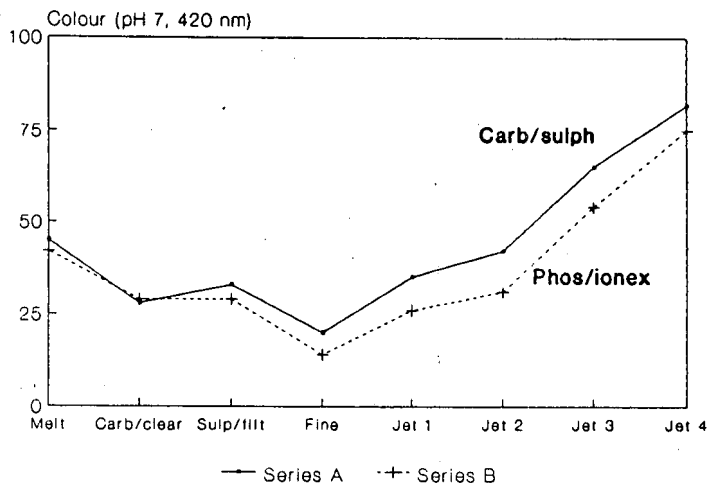


FIGURE 2 Comparison of affinated sugar colours

Table 1
Comparison of liquors and crystals from sulphitation and non-sulphitation processes

	Liquor		Crystal	
	Sulphited	Non-sulphited	Sulphited	Non-sulphited
Colour pH 7	566	323	18	28
IV	5,1	4,8	4,3	3,7
Colour transfer pH 7			Sulphited 0,032	Non-sulphited 0,087

Large differences were found between the liquors from the two refineries. The colours although not very different for the first three liquors, differed from the fine liquors onwards with the phosphotation/ion exchange refinery showing values lower by about 50%, as shown in Figure 1. The indicator values were also different from the fine liquors. The colours obtained for the affinated sugars boiled from these liquors are shown in Figure 2.

The sugar colours are now different by about 14% only which is less than would have been expected from the feed colours. It is also noted that the indicator values show significant differences which appear to be more pronounced in the sugars than in the liquors.

The difference between the two sets of results is made very evident in Figure 3 which shows the colour transfers (averaged for pH's 4, 7 and 9) obtained for these boilings. As can be seen in Figure 3 there is a fairly smooth trend in colour transfers for the carbonatation/sulphitation liquors with values ranging from 0,035 to 0,012. There is however a marked increase in colour transfer for the liquor treated with ion exchange resin and the higher values appear to persist in down stream liquors.

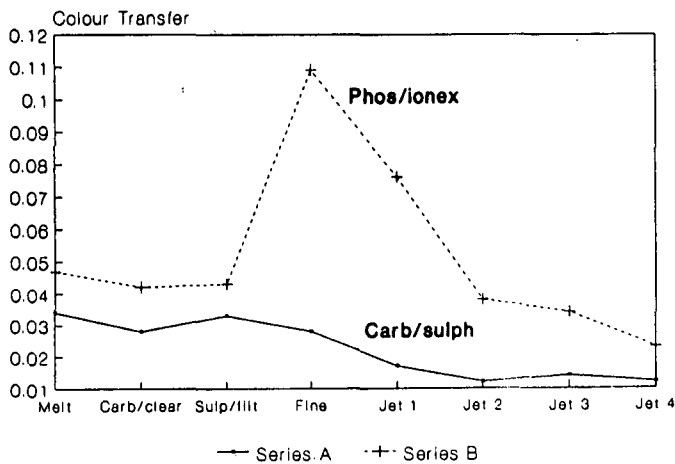


FIGURE 3 Comparison of colour transfers

Comparison of sulphitation and ion exchange

In view of the results reported in the previous section it was decided to investigate the differences between the effects of sulphitation and ion exchange in more detail.

Laboratory sulphitation and ion-exchange treatment of refinery liquors.

The experimental approach consisted essentially of splitting samples of filtered liquors from two different refineries into three parts. The first subsample was boiled as is, the second was submitted to a laboratory sulphitation, filtered and boiled, while the third was fed through a pilot plant resin column, using an anion exchange, strong base, macroreticular resin, and boiled as were the other two subsamples under standard conditions in the SMRI pilot pan. The average liquor quality, from about 10 sets of data, is shown in Table 2.

Table 2
The effect of sulphitation and of ion exchange on liquor quality

	Filtered liquor	Resin treated	Percent change	Sulphited liquor	Percent change
Colour pH 7	768	302	-61	506	-34
IV	3,0	4,2		3,8	

The percent changes in Table 2 are expressed on the filtered liquor value. The results show that resin removes larger quantities of colour from the original liquors when compared to sulphitation. It is however more significant to look at the changes in the affinated crystals, obtained from the boilings. This is done in Table 3. The effects of ion exchange and of sulphitation are now much closer. This contrasts with the results shown in Table 2 where ion exchange showed significantly higher removals for colour in the liquors.

Table 3
The effect of sulphitation and of ion exchange on affinated crystal quality

Affinated crystal	Colour pH 7	IV
From original liquor boiling	35	3,0
From resin liquor boiling	20	3,8
Percent change	-42	
From sulphited liquor boiling	23	3,4
Percent change	-34	

Average values for the colour transfers are shown in Table 4. These results which were obtained with the same liquors, boiled under standard conditions of temperature, stirring, time, final crystal size etc., confirm the earlier findings. It is thus apparent that ion exchange resins could leave in the liquor colour bodies that have a high affinity for the sugar crystal.

Table 4
The effect of sulphitation and of ion exchange on colour transfer

	Original liquor boiling	Resin liquor boiling	Sulphited liquor boiling
Colour pH 7	0,045	0,067	0,045

The use of colour transfers.

The use of colour transfer can be misleading if the liquor colours are not always in similar ranges. If it is assumed that the sucrose crystal has a measurable colour and that the

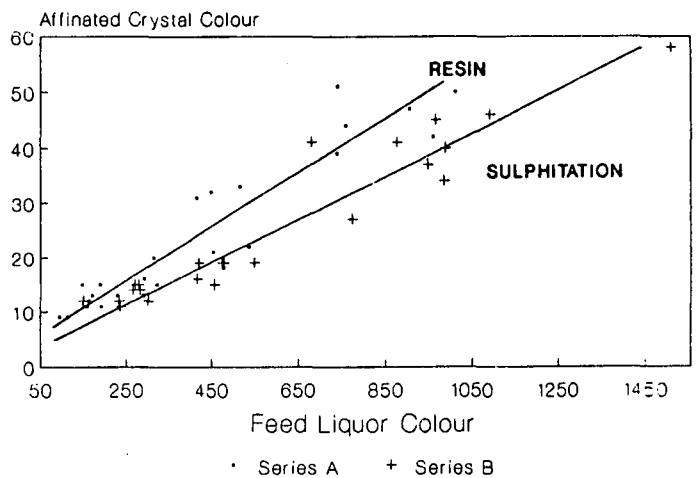


FIGURE 4 Crystal colour versus feed liquor colour, laboratory boilings of resin treated and sulphited liquors

relation between feed and crystal colour is linear, then the slope of the line will represent a true transfer. This has been done with the results obtained from the laboratory boilings of filtered liquors (from the two refineries mentioned earlier) and of the laboratory sulphited and ion exchange treated liquors. The plot of crystal against feed colour for the resin treated and sulphited liquors, both liquors being from the same original stock of filtered liquor, is shown in Figure 4.

Equations 1 and 2 were obtained for the lines in Figure 4 for the sulphited and resin treated liquors respectively.

$$\text{Crystal colour} = 2,90 + 0,0376 \times \text{Feed colour} \dots\dots (1)$$

(n = 27; r = 0,96)

$$\text{Crystal colour} = 3,74 + 0,0474 \times \text{Feed colour} \dots\dots (2)$$

(n = 24; r = 0,94)

Equation 3 was obtained for the regression concerning the boiling of the original brown liquor.

$$\text{Crystal colour} = -3,08 + 0,0446 \times \text{Feed colour} \dots\dots (3)$$

(n = 21; r = 0,95)

In all cases the fits are excellent confirming the linearity of the relationship between feed and crystal colours. The slope, and therefore the real colour transfer, for the resin treated liquor is about 20% higher than that for the sulphited liquor. This contrasts with the average transfer for ion exchange being about 50% higher than that for sulphitation in Table 4. It is also interesting to note that the real transfer for the sulphitation treatment is about 15% lower than that found for the original liquor boilings. This indicates that sulphitation preferentially removes a small quantity of colourants which have a higher than average affinity for the sucrose crystal. Ion exchange resin on the other hand appears to leave colourants with higher than average affinities for the crystal in the liquor. The mechanism through which this difference occurs is unknown at this stage.

Investigating combinations of resin and sulphitation.

Since the above results indicate that there are significant differences between the performances of resin and of sulphitation, a combination of the two treatments could have beneficial effects. This possibility was therefore tested in the laboratory.

A large sample of brown liquor from Huletts Refineries was taken and treated as follows:

Subsample 1 was not treated in any way and was boiled in the pilot pan under standard conditions.

Subsample 2 was sulphited in the laboratory, using 3000 ppm of sulphur dioxide, filtered and boiled. The feed to the pan was therefore sulphited liquor.

Subsample 3 was fed through the SMRI pilot resin columns. The pan feed in this case was resin treated liquor.

Subsample 4 consisted of a mixture of resin treated liquor and brown liquor, in the ratio of 67:33 (m/m). This mixture was then sulphited, using 150 ppm (as opposed to 3000 ppm) of sulphur dioxide, filtered and then boiled in the pan. The feed in this case was therefore a liquor having been treated with both resin and sulphur dioxide.

Subsample 5 was treated in exactly the same way as subsample 4 except that the mixture of resin treated liquor to brown liquor was in the ratio of 33:67.

The liquor and affinated crystal colours are given in Table 5.

It evident from the results in Table 5 that it is possible to get low crystal colours in a number of different ways. The use of sulphitation as the sole decolourising process requires about 4000 ppm of sulphur dioxide. This should result in liquor decolourisations of 30–40% which have been shown by Getaz and Bachan⁷ to be the maximum that can be expected. Resin on the other hand can achieve liquor decolourisations in excess of 60% but results in higher colour transfers. Both processes thus appear to have limitations, particularly if low colour sugars are required. A combination of the two processes would offer more flexibility. The financial aspect which needs to be investigated is whether a reduced load on the resin, for example a 30% decolourisation, followed by a light sulphitation with 150 ppm of sulphur dioxide, would reduce the cost of achieving the required sugar colour.

Discussion

Detailed comparisons between the SMRI pilot pan and industrial pans have shown that, although there are differences such as hydraulic head and boiling times, the results in terms of massecuite and crystal qualities agree remarkably well. It can therefore be concluded that the results obtained with this pan will be meaningful industrially.

The boilings of fine liquors from a number of South African refineries showed clearly that non-sulphitation liquors were of lower colour than sulphitation ones, but that the situation was actually reversed when the affinated crystals were compared. A detailed study involving the boiling of liquors from a phosphotation/ ion exchange and from a carbonation/sulphitation refinery showed that the liquors before the resin treatment gave similar results but major differences were found between the two fine liquors, namely the sulphited and ion exchange treated liquors. The colour (pH 7, 420 nm) of the sulphited fine liquor was 847 units while that of the resin liquor was 179 units, but the affinated sugars were 20 and 14 units respectively, resulting in a marked difference in the colour transfer. The difference in transfer was highest for fine liquor but persisted in the jet boilings.

Differences between the two decolourisation processes were investigated further by using subsamples of the same brown or filtered liquors for all the tests. Since the same liquor was now sulphited or treated with ion exchange, the results can be compared directly. It was found that sulphitation removed 34% of the colour in the original liquor while ion exchange removed 61%. Where the affinated crystals were concerned, however, it was found that, when compared with the crystals of the untreated liquor, colour removal was now 34% and 42% for sulphitation and ion exchange, respectively.

The use of colour transfers can be misleading if the feed colours are very different. If the crystal colour is plotted against the feed colour, however, the slope of the line represents a true transfer. When this is done it is found that the averaged colour transfers for untreated, sulphited and ion exchange liquors are 0,046; 0,038 and 0,047 respectively.

Table 5

The liquor and crystal colours obtained from the resin/sulphitation experiments

Sub-sample	Material boiled	Colours					
		Liquors			Crystals		
		pH 4	pH 7	pH 9	pH 4	pH 7	pH 9
1	Brown liquor	416	744	1696	19	27	74
2	Sulphited liquor	198	423	1130	10	15	49
3	Resin liquor	217	405	1077	13	18	55
4	R/S liquor	182	396	1052	11	16	52
5	R/S liquor	239	482	1237	13	19	54

This result indicates that sulphitation could remove or change the nature of some colourants which have a higher than average affinity for the sucrose crystal, since the transfer for sulphited liquors is about 15% lower than that for the untreated liquor.

Results of experiments involving a combination of ion exchange and sulphitation show that it is possible to obtain the required low crystal colours in a number of ways. For example the decolourisation by the resin could be reduced by 50%, thus increasing resin life, reducing effluent etc., if the liquor is then sulphited. This sulphitation would require about 150 ppm of sulphur dioxide, which is a level currently used in industry. This approach could present the possibility of optimising the decolourisation with respect to cost.

Conclusions

This work has shown clearly that the decolourisation process used can have a marked effect on the colour transfer. The results obtained indicate that a combination of ion exchange and sulphitation is worth considering as it could provide financial benefits.

A number of areas need further investigations. Thus laboratory phosphotation and carbonation processes should be developed. This will allow all the traditional decolourisation processes to be available on a laboratory or pilot plant scale. An area which needs urgent attention is the chemical categorisation of the various colourants. This is important for a deeper understanding of the colour transfer process itself and for the planning of further work.

Acknowledgements

Many people have been involved with this project and the author is indebted to all of them. In particular the author would like to thank Mr M.A. Getaz, the Technicians of the

Processing Division and the Analysts of the Analytical Services Division of the SMRI for their help in the planning, experimental and analytical aspects of the work; and the process staff at Huletts Refineries and at a number of factories with back-end refineries, for all the samples.

REFERENCES

1. Anon, (1988). Report on high molecular weight colorants in refining. *Sugar Proc Res Inc Conf* Preprint.
2. Bourlet, P and Lescure, JP (1989). Tentatives pour optimiser la sulphitation. *Suc Fr* (April): 117-126.
3. Broughton, NW, Houghton, BJ and Sissons, A (1986). Factors affecting white sugar colour. *Zuckerind* 111 (11): 1039-1046.
4. Clarke, MA, Godshall, MA, Tsang, WSC and Roberts, EJ (1987). Cane sugar colourants in processing operations. *Com Int Tech Suc Conf* 67-79.
5. Delaney, HR (1980). Experience in decolourisation alternatives, CSR experience with ion exchange resin decolourisation. *Proc Cane Sugar Ref Res Conf* 1-7.
6. Getaz, MA (1988). The application of ion exchange resins in cane sugar refining. *Communications from the SMRI* (146): 77 pp.
7. Getaz, MA and Bachan, L (1989). Some ideas on the use of chemical methods for improving the colour of A sugar. *Proc S Afr Sug Technol Ass* 63: 76-80.
8. Godshall, MA and Legendre, BL (1988). Phenolic content of maturing sugar cane. *Int Sugar J* 90 (1069): 16-19.
9. Godshall, MA and Clarke, MA (1988). High molecular weight colour in raw and refined sugars. *Sug Ind Tech Inc Conf* 47: 180-193.
10. Lionnet, GRE (1986). An analytical approach for the determination of colour and other impurities in cane. *Proc S Afr Sug Technol Ass* 60: 62-65.
11. Lionnet, GRE (1987). Impurity transfer during A massecuite boiling. *Proc S Afr Sug Technol Ass* 61: 70-75.
12. Lionnet, GRE (1988). The effect of some operational factors on colour transfer during pan boiling. *Proc S Afr Sug Technol Ass* 62: 39-41.
13. Rein, PW (1988). The effect of pan design and operation on white sugar quality. *Sug Proc Res Inc Conf* 32-40.
14. Rein, PW (1988). The application of flotation clarification in sugar processing. *Sug Proc Res Inc Conf* Preprint.
15. Shore, M, Broughton, NV and Sissons, A (1984). Factors affecting white sugar colour. *Conf British Sugar plc* 27 (June): 1-15.
16. Vaccari, G, Sgualdino, G and Vignali, A (1987). L'action du bisulphate de sodium sur les sirops. *Ind Agric Alim* (Dec.): 1117-1180.