

PRELIMINARY RESULTS ON THE DECOLOURISATION OF MELT WITH HYDROGEN PEROXIDE

By M. MOODLEY

Sugar Milling Research Institute, Durban

Abstract

The use of hydrogen peroxide as a decolourising agent in the refinery has been investigated. Experiments were done, in the laboratory and on a pilot plant scale, to investigate the effectiveness of this chemical and to establish optimum conditions, particularly in terms of pH, temperature and reaction time. The results indicate that there is a possibility of this chemical being used in the refinery.

Introduction

Hydrogen peroxide (H_2O_2) is extensively used as a bleaching agent in the textile and the pulp and paper industries. Riffer (1980) in his work on the application of hydrogen peroxide for sugar refining found the following:

- Hydrogen peroxide cleaves unsaturated sites and diketones in colourants, forming carboxylic acids, and oxidises phenolics to quinones and acyclic products.
- The reaction of hydrogen peroxide with colourants is a fast one at typical refinery operating temperatures.
- In addition to its direct bleaching action, there is some evidence that hydrogen peroxide also oxidises certain colourants to forms that are more readily removed by adsorbents.
- Both pH sensitive and insensitive colourants are reactive towards hydrogen peroxide.
- Liquor pH drops upon treatment with hydrogen peroxide as a result of acid formation.

The reaction products of hydrogen peroxide are water and oxygen. Its use does not contribute non-sugars (Madsen *et al.*, 1978).

Cordovez (1988) describes the use of hydrogen peroxide in a cane sugar mill in Venezuela which decolourised its melt with 400 ppm of H_2O_2 and 500 ppm of P_2O_5 to produce refined sugar of 50 ICUMSA colour units. Initially hydrogen peroxide was added to liquor clarified by phosphatation but the results obtained were not good. Colour removal was low and some colour reversal was experienced. When the peroxide was added to the melter prior to phosphatation the decolourisation improved.

Experimental

All the decolourisation work was done in the laboratory and the treated liquors were then boiled under standard conditions in the SMRI pilot pan. The pan has been described previously (Lionnet, 1987).

The general procedures used for the tests were as follows:

- The melt (68° brix) was well stirred and kept at a given temperature in a 2 litre vessel.
- If required the melt pH was adjusted to 7,2 with milk of lime.
- The required volume of hydrogen peroxide was then added to the stirred melt, at 80°C, and a reaction time of 3 minutes was allowed. During that period the pH was kept at 7,2 using milk of lime.

- The treated liquor was then filtered and boiled.

The above procedures yielded liquors decolourised with hydrogen peroxide only. Most of the tests, however, involved a combination of hydrogen peroxide and other decolourisation processes. These were done as follows.

Hydrogen peroxide and phosphatation

Procedures (a), (b) and (c) above were performed. This was then followed by the addition of the required amount of phosphoric acid as a 10% (v/v) solution, with stirring at 80°C. The pH was adjusted to 7,3 with milk of lime and the reaction was allowed to proceed, at high speed stirring (for aeration) for a further 3 minutes. Flocculant (10 ppm of Magnafloc LT 25) was added, with slow stirring, and the reaction mixture was allowed to stand (no stirring) at 80°C for flotation of the scum. The clear liquor was then removed and boiled.

Hydrogen peroxide and sulphitation

Again, procedures (a), (b) and (c) were followed. A calculated volume of milk of lime was added and sulphur dioxide was bubbled into the sample (at 80°C) until the pH dropped to 7,3. The liquor was then filtered and boiled.

Hydrogen peroxide and carbonatation

The procedures used here were similar to those of sulphitation, except that carbon dioxide was used to back titrate to a final pH of 8,4.

The sugar samples were affinated by the ICUMSA method. The colour analyses were done according to the ICUMSA method but at pH 4, 7 and 9 using membrane filtration. Turbidity was determined using the ICUMSA method at 420 nm and the decolourised liquors were analysed for pol and brix.

In all cases a 50% solution of hydrogen peroxide was used for decolourisation but the quantities of hydrogen peroxide quoted in this paper apply to pure hydrogen peroxide as ppm on melt at 68° brix. The quoted amounts of sulphur dioxide and carbon dioxide have been determined by stoichiometry, using the reaction with calcium hydroxide.

The costs (1991) of the various chemicals were calculated as follows:

Hydrogen peroxide: R2,60 per kg of the 50% solution.

Phosphoric acid (H_3PO_4): R1,50 per kg of the 65% solution. The conversion from H_3PO_4 (100%) to P_2O_5 is 100 ppm of $H_3PO_4 \equiv 72$ ppm of P_2O_5 .

Carbon dioxide (CO_2): No chemical cost has been attached to carbon dioxide itself as flue gas is often used as a source of carbon dioxide.

Sulphur dioxide (SO_2): The cost of sulphur dioxide in industry is affected by the efficiency of the conversion of elemental sulphur to the gas and by the efficiency of the reaction between the gas and the liquor. The cost of sulphur is R1,00 per kg. Assuming an overall efficiency of 50% (Getaz and Bachan, 1989), the cost of sulphur dioxide is R1,00 per kg.

Lime (Ca(OH)₂): An average cost (including transport) of lime to industry has been taken as R0,25 per kg, at 90% CaO. The costs used here are based on the mass of CaO added to the melt.

Results

The use of hydrogen peroxide only

Work done at the SMRI (Patel and Moodley, 1991) and elsewhere (Cordovez, 1988) has shown that decolourisation by hydrogen peroxide only has the following disadvantages:

- (a) The pH of the treated liquor drops. The drop in pH with the addition of various levels of hydrogen peroxide is given in Figure 1. Milk of lime has therefore to be added to bring the pH to above 7 (to prevent inversion) but this increases the turbidity of the decolourised liquor.
- (b) There is a tendency for some colour to return. This can be prevented by using a clarification process which removes the colour and increased turbidity after the treatment with hydrogen peroxide.
- (c) If the total decolourisation is done with hydrogen peroxide only, the amount required will be large. Tests done at the SMRI have shown that the use of hydrogen peroxide in quantities around 2 000 ppm can result in the formation of odours. This has not been investigated fully since only between 200 and 400 ppm will be used here.

In view of the above, hydrogen peroxide has been tested in conjunction with carbonatation, phosphatation and sulphitation.

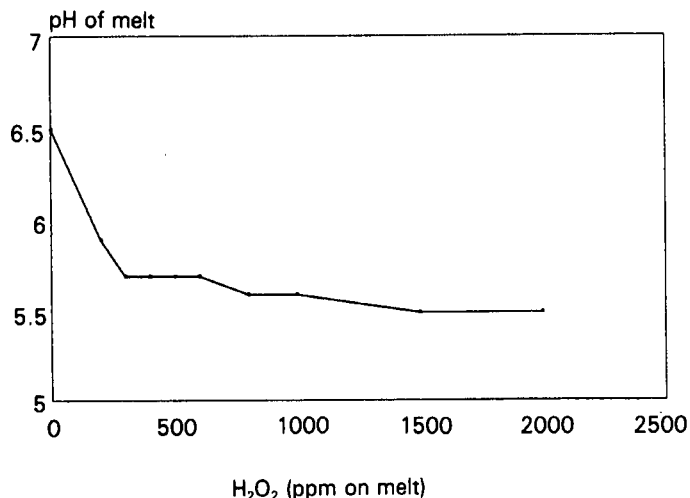


FIGURE 1 Effect of hydrogen peroxide on melt pH.

Combination of hydrogen peroxide with conventional clarification processes

Hydrogen peroxide (200 or 400 ppm) was used in conjunction with reduced amounts of carbon dioxide, phosphoric acid and sulphur dioxide. The liquor decolourisations are compared to those with the typical amounts of these chemicals in Figures 2, 3 and 4, respectively. The results in these three figures show that the same level of liquor decolourisation and turbidity removals can be achieved by replacing some of the carbon dioxide, phosphoric acid or sulphur dioxide with hydrogen peroxide.

The indications are that as far as liquor decolourisation is concerned, 200 ppm of hydrogen peroxide in combination with either 1 000 ppm of carbon dioxide, 1 000 ppm of sulphur dioxide or 100 ppm of phosphoric acid could replace 7 000 ppm of carbon dioxide, 3 000 ppm of sulphur dioxide and 350 ppm of phosphoric acid, respectively.

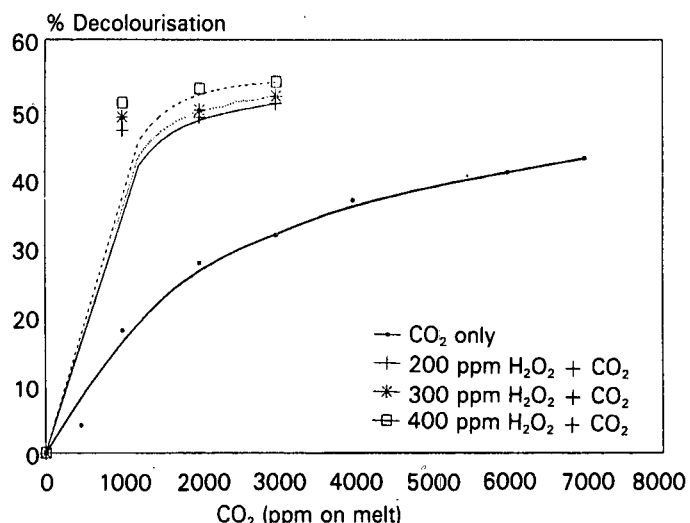


FIGURE 2 Decolourisation with carbon dioxide and hydrogen peroxide.

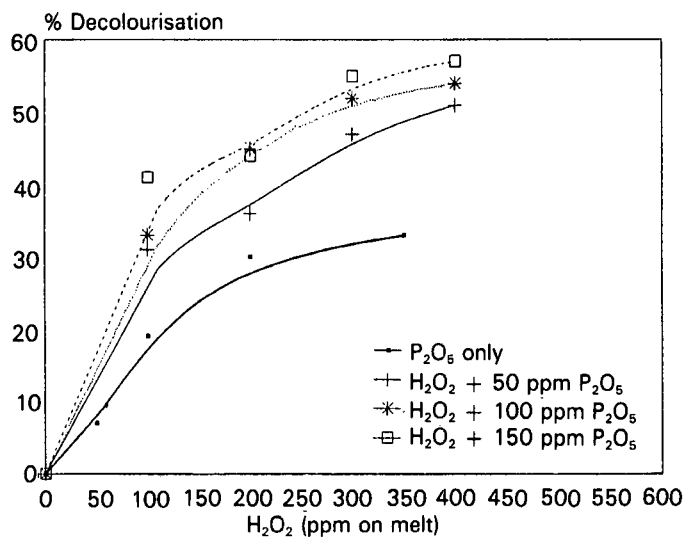


FIGURE 3 Decolourisation with hydrogen peroxide and phosphorus pentoxide.

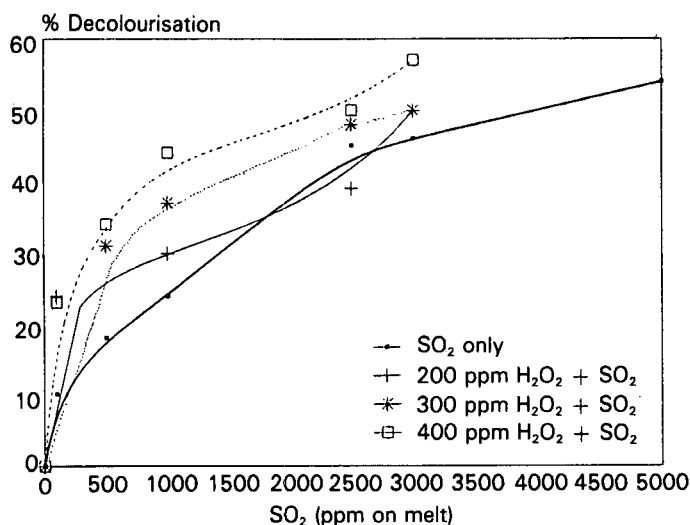


FIGURE 4 Decolourisation with sulphur dioxide and hydrogen peroxide.

The purpose of decolourisation is to produce the required sugar colour. Thus the colour transfers (crystal colour/feed colour) (Lionnet, 1991) and the crystal colours need to be examined before costs are investigated.

Crystal colour

Work at the SMRI has shown that the mother liquor film around the refined sugar crystal accounts for 20% of the sugar colour. This figure has been used to calculate the final sugar colour from the crystal colour.

Hydrogen peroxide with phosphatation

Series 1 (July 1991) Melt samples from Noodsberg (NB) and Hulett Refineries (HR) were decolourised with 350 ppm of P₂O₅ and with 150 ppm of P₂O₅ plus various levels of hydrogen peroxide. The results are given in Table 1. Melt colours were low at that time of the year. Good liquor decolourisations and low crystal and sugar colours were achieved with a combination of phosphatation and hydrogen peroxide.

Table 1

Decolourisation of melt with phosphoric acid alone and with hydrogen peroxide (first series)

Melt Sample	ppm H ₂ O ₂	ppm P ₂ O ₅	Liquor decolourisation (%)	Crystal colour	Sugar colour
NB	-	350	26	38	48
NB	400	150	63	14	18
HR	400	150	57	15	19

Series 2 (Jan./Feb.1992) These tests were done using HR melt. The results, given in Table 2, show that the required colour of sugar can be achieved with a combination of hydrogen peroxide and phosphatation. The average colour transfer for the phosphated liquors (350 ppm phosphoric acid) was 0,038. When some of the phosphoric acid was replaced with hydrogen peroxide the average colour transfer was 0,033. This indicates that hydrogen peroxide can lower the colour transfer.

Table 2

Decolourisation of melt with phosphoric acid alone and with hydrogen peroxide (second series)

Melt Sample	ppm H ₂ O ₂	ppm P ₂ O ₅	Liquor decolourisation (%)	Crystal colour	Sugar colour
HR	-	350	42	28	35
	200	100	58	22	28
	400	100	61	20	25

Hydrogen peroxide with sulphitation

The results of tests done on HR melt are given in Table 3 and show that peroxide can replace some of the sulphur dioxide to produce the same or lower sugar colours. Work done by Lionnet (1991) has shown that the colour transfers for sulphited liquors range between 0,02 and 0,04. For these tests the colour transfer for sulphited liquor was 0,025 and when some of the sulphur dioxide was replaced with hydrogen peroxide the average colour transfer was 0,020. There is once again an indication of a lowering of the colour transfer with hydrogen peroxide.

Hydrogen peroxide with carbonatation

The results of tests done on HR melt are given in Table 4 and show that hydrogen peroxide can replace some of the carbon dioxide to produce the same or lower sugar colours.

Table 3

Decolourisation of melt with sulphur dioxide alone and with hydrogen peroxide

Melt Sample	ppm H ₂ O ₂	ppm SO ₂	Liquor decolourisation (%)	Crystal colour	Sugar colour
HR	-	3 000	54	18	23
	200	1 000	45	17	21
	400	1 000	50	16	20

Table 4

Decolourisation of melt with carbon dioxide alone and with hydrogen peroxide

Melt Sample	ppm H ₂ O ₂	ppm CO ₂	Liquor decolourisation (%)	Crystal colour	Sugar colour
HR	-	7 000	47	26	33
	200	2 000	44	23	29
	400	2 000	43	24	30

Chemical costs

The costs (1991) for the various chemicals, listed in the experimental section above, were used to calculate the total chemical costs for the combinations tested. It should be noted that only the chemical costs were considered and these costs for the various processes are given in Table 5. From the cost comparisons in this table, the following conclusions can be reached with regard to the various decolourisation processes.

Table 5

Comparison of costs of phosphatation, sulphitation or carbonatation alone and with hydrogen peroxide

Conventional process chemicals (ppm)	H ₂ O ₂ ppm	Sugar colour	Cost of chemicals (R) per ton melt
Phosphatation (P₂O₅)			
350	-	48	1,28
150	400	19	2,56
350	-	35	1,28
100	200	25	1,36
100	400	28	2,40
Sulphitation (SO₂)			
3 000	-	23	3,43
1 000	200	21	2,27
1 000	400	20	3,27
Carbonatation (CO₂)			
7 000	-	33	2,23
2 000	200	29	1,67
2 000	400	29	2,72

Phosphatation The only combination that compares favourably with the cost of 350 ppm of phosphoric acid is 100 ppm of phosphoric acid and 200 ppm of hydrogen peroxide. All the other combination are more expensive.

Sulphitation The results show that the replacement of some of the sulphur dioxide with hydrogen peroxide could be profitable in terms of chemical costs.

Carbonatation Replacing some of the carbon dioxide with hydrogen peroxide (200 ppm) seems to produce similar sugar colours but at a reduced cost.

Discussion

The use of hydrogen peroxide, on its own, for the decolourisation of melt does not appear to be feasible because of costs and of processing problems such as turbidity increases. This chemical has therefore been used in conjunction with other decolourisation processes, such as phosphatation, sulphitation and carbonatation.

The objective of this work was to investigate the costs of replacing some of the phosphoric acid, sulphur dioxide or carbon dioxide with hydrogen peroxide. Obviously the process must yield the required sugar quality at a comparable cost. At this stage only 200-400 ppm of hydrogen peroxide can be considered, to keep the costs within usual levels.

Procedures for decolourisation using hydrogen peroxide have been established. The chemical is added as a 50% solution, with stirring at 80°C. Milk of lime must be added to keep the pH of the melt above 7. A reaction time of around 3 minutes has been found necessary. This process has been followed by traditional phosphatation, sulphitation or carbonatation, but with reduced levels of phosphoric acid, sulphur dioxide or carbon dioxide.

The results obtained show that the required sugar quality has been achieved. Only the cost of chemicals is considered here and, on this basis, hydrogen peroxide appears to be most cost effective when it is used to replace some sulphur dioxide. It can also replace part of the phosphoric acid and carbon dioxide. In both these cases the costs of the combinations are not much lower, but the sugar colours appear slightly better.

The above results are based only on chemical costs. The handling and dosing costs for hydrogen peroxide should be relatively low. The chemical must be stored in a covered stainless steel tank and only a metering pump is required. It can be kept for 6 months (50% solution) in a clean closed vessel.

Finally, it must be stressed that this work is very preliminary. Decolourisation performances and colour transfers (Lionnet, 1988) vary with raw sugar quality and time of year, so that many tests are required to obtain average results. Full scale tests would also be valuable. Future work must therefore consider these two aspects. Furthermore, the possibility of using hydrogen peroxide in raw house syrup needs to be investigated.

Acknowledgments

The author would like to thank Messrs C Rungasamy, R Ramsamer, P Ramsuraj and B Padayachee for carrying out all the experimental work. Thanks are also due to the Analytical Services Division for all the analyses and Mr M N Patel for doing the initial experimental work. The help and guidance received from Mr GRE Lionnet is also appreciated.

REFERENCES

- Cordovez, F, Mendoza, JJ *et al.* (1991). A simplified sugar refining process. *Proc Sug Ind Technol* 50: 133-140.
- Getaz, MA and Bachan, L (1989). Chemical methods for lowering the colour of A-sugar. Part 2: Some preliminary experimental work. *SMRI Technical Report* No. 1534: 22 pp.
- Lionnet, GRE (1987). Impurity transfer during A massecuite boiling. *Proc S Afr Sug Technol Ass* 61: 70-75.
- Lionnet, GRE (1988). The effect of some operational factors on colour transfer during pan boiling. *Proc S Afr Sug Technol Ass* 62: 39-41.
- Lionnet, GRE (1990). The use of ion exchange and of sulphitation in the refining of cane raws. *SMRI Technical Report* No. 1570: 25 pp.
- Lionnet, GRE (1991). Colour transfer, from liquor to crystal, during the refining of South African raw sugar. *Proc CITS* 19: 15-30.
- Madsen, RF, Kofod Nielson, W, Winstrom-Olsen, B and Nielson, TE (1978). Formation of colour compounds in the production of sugar from beet. *Sugar Technol Reviews*, 6(1): 49-116.
- Patel, MN and Moodley, M (1990). Decolourisation with hydrogen peroxide, ozone and other chemicals. *SMRI Technical Report* No. 1598: 30 pp.
- Riffer, R (1981). A study of chemical additives for use in sugar refining. *Proc 1980 Tech Sess Cane Sugar Refining Res* 84-102.