THE APPLICATION OF CATIONIC FLOCCULANTS AS DECOLOURISING AGENTS IN THE SUGAR INDUSTRY

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Abstract

The use of cationic flocculants as decolourising agents in the refinery has been investigated. The results of experiments in the laboratory and from full scale plant trials are presented. The findings indicate that these chemicals can be used in the refinery to replace partially existing chemicals, thus lowering the overall chemical cost of refining, or to achieve additional decolourisation during periods of high colour loading.

Introduction

Cationic surfactants (Bennett et al., 1971) can be used to precipitate colourants and other anionic impurities from sugar liquors. They have a strongly basic centre coupled with a long chain hydrocarbon residue. The cationic centre serves only as a means of attaching the hydrocarbon to the impurity or colourant anion. It is the hydrocarbon that renders the colourant repellant to water and which causes the colour molecule to be precipitated from solution. The relationship between the molecular structure of cationic surfactants and their activity as colour precipitants have been studied extensively (Bennett *et al.*, 1971). The most active cationic surfactants were found to be the dialkyl quaternary ammonium compounds containing two C_{16} or two C_{18} hydrocarbon chains. One product that has been developed for the sugar industry is Talofloc (dioctadecyl dimethyl ammonium chloride). The mode of interaction of Talofloc (Bennett, 1982) with colourant molecules is shown in Figure 1.

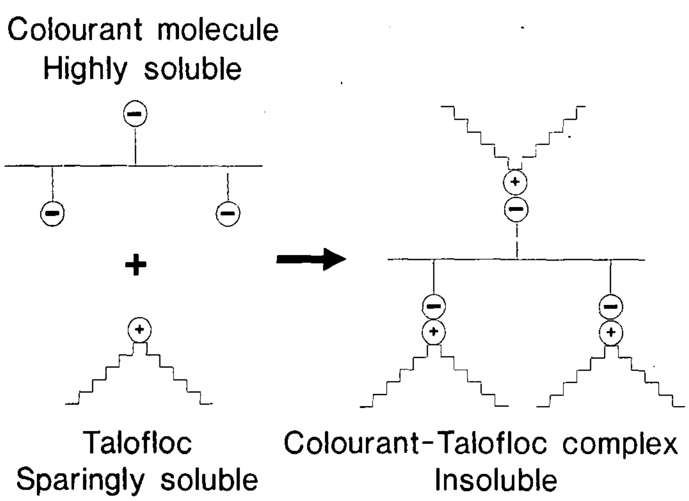

FIGURE 1 Mode of interaction of Talofloc with colourant.

Bennett *et al.* (1971) also found that colour can be precipitated from solution with the use of primary or secondary amines. The addition of 100-200 ppm (on cane) of Talomel (acyclic dimethylamine polymer) to a syrup clarifier was found to increase the decolourisation by 20-30% (Anon). Residual Talomel in final A-sugar was found to be below detectable levels.

Talocarb (dimethylamine polymer), an FDA approved colour precipitant, when dosed to final carbonatated liquor immediately before filtration at a dosage rate of about 200 ppm on liquor solids, was found to increase the decolourisation over carbonatation by 25-30% (Trot, 1988). The reaction mechanism of Talocarb has been described in the product data sheet (Anon.). According to this mechanism, Talocarb reacts with negatively charged colour molecules, neutralising their charges and causing precipitation. The precipitated colour is subsequently removed during flotation or filtration.

A full scale plant trial done at a refinery with Talocarb (Anon) has shown that the addition of the flocculant improved the colour of both the carbonatated liquor and the liquor from the secondary acrylic resin station by about 20%.

Mochtar (1989), in his pilot plant work on melt phosphatation, found that the refined sugars produced from melt treated with either polyamines or dioctadecyl dimethyl ammonium chloride were of similar quality and could meet the specifications needed for the soft drink and food industries.

In South Africa, Matic *et al.* (1977), found that the addition of cationic flocculants during melt phosphatation improved liquor decolourisation as well as phosphate and starch removals. Rein (1988) found that the addition of 10 ppm of cationic flocculant improved colour removal during refinery sweetwater clarification. Getaz and Bachan (1989), in their work on syrup sulphitation/clarification, found that the addition of a water treatment flocculant (polyacrylamide) improved the decolourisation quite significantly.

Polyamines (copolymers of dimethylamine and epichlorohydrin) and other chemicals with cationic properties are used extensively as flocculants in the clarification of potable water. In the clarification of water, according to Baxter *et al.* (1992), flocculants destabilise colloidal matter by the formation of physical bridges between two or more particles, uniting the solid particles into a random three-dimensional structure which is loose and porous. In the sugar industry these cationic chemicals do not act as flocculants as described above but behave more as decolourising agents.

In view of the encouraging results in the literature, work was initiated at the SMRI to investigate the use of these chemicals as decolourising agents in the sugar industry.

Experimental

Pilot plant work

Laboratory phosphatation of refinery melt (65° brix) was carried out in two kilogram batches. The cationic flocculant (200 ppm) was added to melt, with stirring, at 80°C and was allowed to react for five minutes. The required volume of phosphoric acid as a 10% (v/v) solution was then added, with stirring at 80°C. The pH was raised to 7,3 with milk of lime and the reaction was allowed to proceed with high speed stirring for a further three minutes. Flocculant (10 ppm of Magnafloc LT 25) was added with slow stirring, and the sample was allowed to stand (no stirring) at 80°C for flotation of scum. The clear liquor was removed and boiled in the pilot pan. A description of the SMRI pilot pan has been given previously (Lionnet, 1987).

For the melt sulphitation tests the calculated volume of lime was added and sulphur dioxide gas was bubbled into the sample (at 80°C) until the pH dropped to 7,3. The cationic flocculant (200 ppm) was added and the sample was stirred for five minutes. The liquor was then filtered and boiled to produce sugar.

Although carbonatation was not conducted on a laboratory scale, several tests were done where the cationic flocculant was added to unfiltered carbonatated liquor. The treated liquor was stirred for five minutes at 80°C, filtered and boiled to produce sugar.

Full scale tests

During the full scale tests, samples of all the refinery streams were taken before, during and after the flocculants were added. Hourly catch samples were taken and composited per shift. The samples were composited and analysed at the SMRI.

Analyses

Colour measurements were conducted at 420 nm, using 0,45 micron membranes for filtration and at pH 7. Turbidity measurements were done at 720 nm. Crystal colour determinations were conducted on sugar samples affinated according to the ICUMSA method. The sugar colours reported are on affinated sugars unless otherwise stated.

Flocculants

The cationic flocculants that were tested are given in Table 1.

Table 1

Cationic flocculants evaluated

Flocculant	Description
Bulab 5031	Polyamine
Talocarb	Dimethylamine polymer
Primco 144	Polyamine
Ultrafloc 5000	Polyamine

Results

Carbonatation

The effect of flocculant concentration on colour removal was investigated in the laboratory. Different aliquots (50 to 250 ppm on liquor) of three cationic flocculants were added to unfiltered carbonatated liquor. The results are plotted in Figure 2. The results indicate that the optimum dosage for these chemicals is between 150 and 200 ppm on liquor. At these levels the liquor colour improved by 30-40%. These initial tests were done on liquor only. Lionnet (1990) found that liquor colour is not always a good indicator of crystal colour. A crystallisation step was therefore included in the experimental work. The results are given in Table 2.

The results show that the addition of Primco 144 and Ultrafloc 5000 can improve both the liquor and crystal colours by 30-45%.

Sulphitation

Liquor decolourisation tests were done on melt. Ultrafloc 5000 was added to the sulphited liquor prior to filtration.

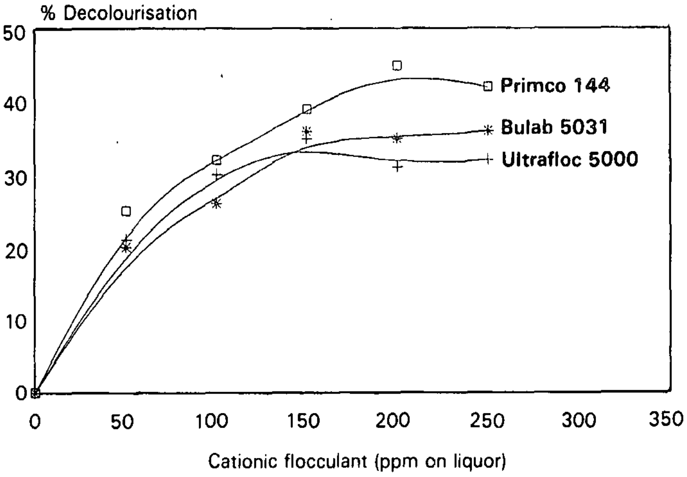

FIGURE 2 Effect of dosage levels of Primco 144, Bulab 5031 and Ultrafloc 5000 on decolourisation.

Table 2

Unfiltered carbonated liquor decolourisation with Primco 144 and Ultrafloc 5000

Chemical	ppm chemical	Untreated liquor colour	Treated liquor colour	Liquor decolourisation (%)	Sugar colour
–	–	1 043	–	–	43
Primco 144	200	–	691	34	23
Ultrafloc 5000	200	–	674	35	30

The results (Table 3) on liquor decolourisation were encouraging and so boilings were done in the SMRI pan to investigate sugar decolourisation. The results (Table 4) show that 200 ppm of either Primco 144 or Ultrafloc 5000 could replace 1 500 ppm of SO_2. This replacement would lower the overall chemical cost of refining by 28% and also produce a sugar of similar or even lower colour.

Table 3

Sulphitation tests on melt of 1685 colour at the SMRI

SO_2 (ppm)	Chemical (ppm)	Liquor colour	% Decolourisation
3 000	–	1 060	37
2 000	200	545	68
1 000	200	570	66

Table 4

Effect of replacing 1 500 ppm of SO_2 with 200 ppm polyamine, original melt colour was 1 910

Chemical	ppm chemical	Liquor colour	Liquor decolourisation (%)	Sugar colour	Run-off colour
SO_2	3 000	819	57	30	2 065
SO_2 + Primco 144	1 500 200	573	70	26	1 582
SO_2 + Ultrafloc 5000	1 500 200	616	68	30	1 628

Phosphatation

Laboratory liquor decolourisation tests were done at the SMRI. The chemicals were added either to melt or to phosphated liquor prior to flotation and the results are given in Table 5. These results tend to indicate that to achieve the maximum decolourisation, the chemical should be added to melt rather than to phosphatated liquor.

Table 5

Tests on melt of 1 919 colour where the cationic flocculant was added either before or after phosphatation

Chemical	ppm chemical	Liquor colour	Liquor decolourisation (%)	Sugar colour	Run-off colour
P_2O_5	300	1 080	44	49	2 916
Primco 144 then P_2O_5	200 300	747	61	27	2 049
P_2O_5 then Primco 144	300 200	825	57	33	2 012

Full scale tests

At a carbonatation/sulphitation refinery, 200 ppm of Ultrafloc 5000 were added to carbonatated liquor prior to filtration. The complete results are given in Table 6. The addition of 200 ppm of flocculant improved the melt decolourisation from 26% to 47%. There is also an improvement in the sugar and run-off colours.

Table 6

Full scale tests at a carbonatation/sulphitation refinery with Ultrafloc 5000

	No chemical		Chemical added		No chemical
	25/8	26/8	27–28/8	28–29/8	29–30/8
Melt colour	1 879	1 678	1 827	1 609	1 512
Carbonatated liquor colour	1 387	1 238	955	883	1 114
Number of colour units removed	492	440	872	726	398
% Decolourisation	26	26	48	45	26
Fine liquor colour	1 311	1 152	877	741	1 093
First sugar colour	25	28	16	21	23

Primco 144 (200 ppm) was continuously added to limed melt at another carbonatation/sulphitation refinery for a period of 56 hours. Samples of carbonatated liquor were taken at hourly intervals during the first six hours of the trial. These results are plotted in Figure 3. The average results (56 hours) of the sugars and liquors are shown in Table 7. The chemical was added to limed melt at 4,00 pm. From Figure 3 it can be seen that there is a marked improvement in the carbonatated liquor colour within a short time after addition.

The addition of the flocculant to limed melt has improved the decolourisation of melt from 41 to 63%, but sugar colour only improved by 17%. This seems to indicate that to achieve the maximum benefit in terms of liquor and sugar colours, the chemical should be added to unfiltered carbonatated liquor rather than to melt.

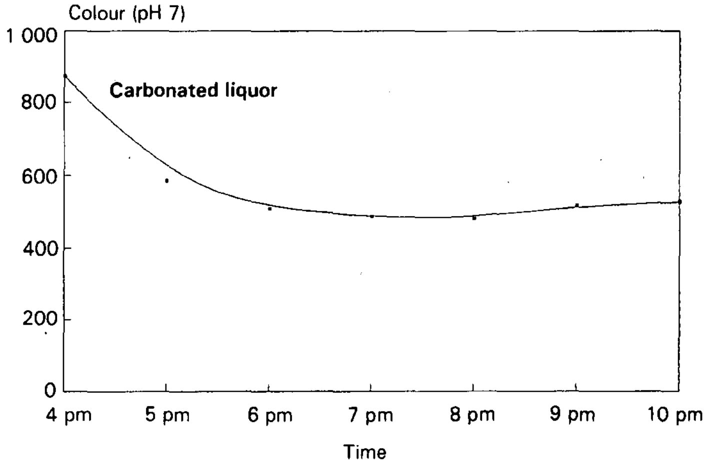

FIGURE 3 Results of flocculant dosing on carbonated liqour colours.

Table 7

Full scale tests at a carbonatation/sulphitation refinery with Primco 144

	No chemical 24 h	Chemical added 56 h
Melt colour	1 349	1 161
Carbonatated liquor colour	797	425
Number of colour units removed	552	736
% Decolourisation	41	63
Fine liquor colour	638	396
First sugar colour	12	10

In a carbonatation/ion exchange refinery, 200 ppm of Primco 144 were added to unfiltered carbonatated liquor. The average results are given in Table 8 and the fine liquor and first sugar colours are plotted in Figure 4. From the results in Table 8 it can be seen that the addition of Primco 144 improved the number of colour units removed during carbonatation by 20%. The first sugar colour improved by 29%.

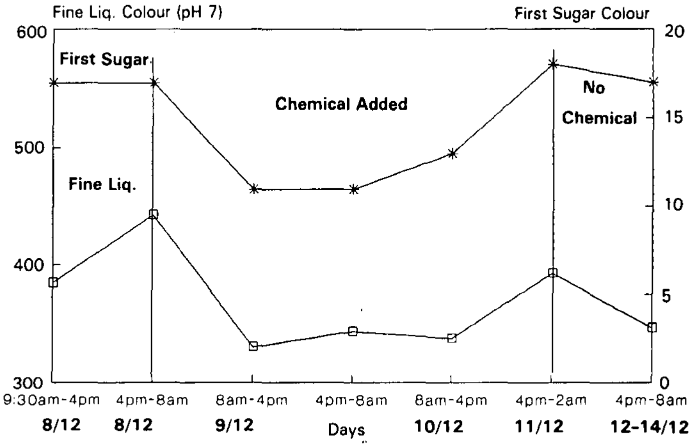

FIGURE 4 Effect of dosing and not dosing on fine liquor and first sugar colours.

Table 8

Full scale tests at a carbonatation/ion exchange refinery with Primco 144

	No chemical 24 h	Chemical added 40 h	No chemical 24 h
Melt colour	1 717	1 630	1 726
Carbonatated liquor colour	997	766	895
Number of colour units removed	720	864	831
% Decolourisation	42	53	48
Fine liquor colour	414	338	370
Number of colour units removed	583	428	525
% Decolourisation	58	56	59
First sugar colour	17	12	18

The results of analyses done by the refinery laboratory for the period of the trial are given in Table 9. Here again there seems to be a definite improvement in both fine liquor and first sugar colours.

Table 9

Colour analyses of fine liquor and first sugar by the refinery laboratory

	No chemical 24 h	Chemical added 40 h	No chemical 24 h
Fine liquor colour	373	300	331
First sugar colour (unaffinated)	28	19	27

In a sulphitation refinery, 5,2 kg of sulphur and 9,1 kg of calcium oxide are consumed per ton of refined sugar produced. During the trial 30% of the sulphur consumption was replaced with 200 ppm of Primco 144. The results are given in Table 10. The replacement of part of the sulphur consumption with Primco 144 has improved the liquor and refined sugar colours by 21 and 25% respectively. This replacement has also lowered the chemical costs in the refinery by 18%. Another advantage would be an improvement in the filter cycles due to the reduction in the quantity of cake.

Table 10

Effect of reducing SO_2 consumption and adding Primco 144 during a full scale test at a sulphitation refinery

	No chemical 24 h	Chemical added 56 h	No chemical 24 h
Melt colour	1 153	1 000	971
Fine liquor colour	618	354	452
Number of colour units removed	535	646	519
% Decolourisation	46	65	53
First sugar colour	20	13	18
First run-off colour	1 953	920	1 198
Final sugar colour	32	24	27

Due to the encouraging results obtained during the one week plant trial, in terms of both sugar quality and chemical costs, it was decided to continue using Primco 144 in the refinery for the rest of the season (10 weeks). The average results (10 day period) have shown that the liquor decolourisation has improved from around 45% to 59%. The monthly refined sugar colours analysed by the SMRI for the last 3 years are plotted in Figure 5. From this figure it can be seen that the refined sugar colours for 1990 and 1991 followed the normal seasonal trend. The sugar colours for 1992, despite being higher than the two previous years in the beginning of the season were in fact lower during the period of flocculant addition. The sugar colours remained low and did not rise as is normally expected at the end of the season. Recent results of a full scale test done at a phosphatation/ion exchange refinery have shown that the addition of 200 ppm of Primco 144 to melt has improved the decolourisation over phosphatation from 20 to 35%.

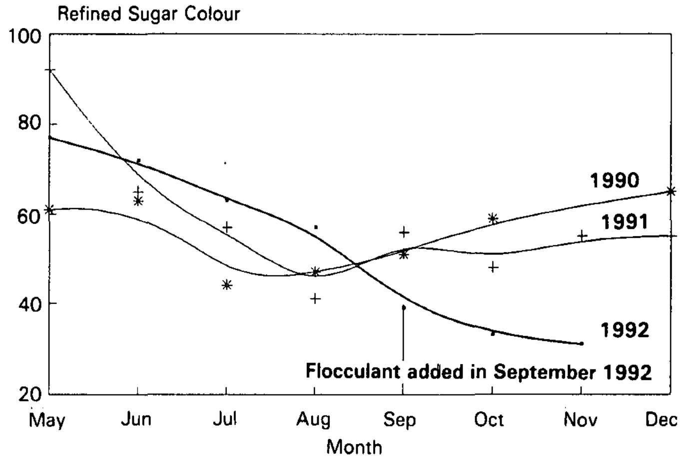

FIGURE 5 Monthly refined non-affinated sugar colours for a sulphitation refinery.

Residual levels of polyamine in final sugar

Samples of refined sugar from the first week plant trial at the sulphitation refinery were analysed for residual polyamine. The detection limit for the method is 0,05 ppm. No residual palyamine could be detected in either the untreated or treated sugars.

A sugar sample was then spiked with 2 ppm of polyamine and the residual polyamine in the sugar was found to be 1,95 ppm. This indicates that all the flocculant has reacted with the colourant molecules and the precipitant/colour complex has been removed during filtration. Some of the final sugars from the full scale tests have also been analysed. These results are given in Table 11.

Table 11

Residual polyamine in final refined sugar

Week ending	Residulal polyamine (ppm)
08/11/92	< 0,05
16/11/92	< 0,05
23/11/92	< 0,05

Conclusions

Laboratory tests on unfiltered carbonatated liquor have shown that the use of these chemicals improves both the liquor and sugar colours by 30-40%. The run-off colour also dropped by a similar margin. Full scale tests at a carbonatation/sulphitation refinery have confirmed the results obtained in the laboratory. The addition of Ultrafloc 5000 to unfiltered carbonatated liquor lowered both the liquor and crystal colours by 30%. The efficiency of these chemicals in a carbonatation/sulphitation refinery depends on the point of addition. At a carbonatation/sulphitation refinery where Primco 144 was added to limed melt rather than unfiltered carbonatated melt, the liquor colour improved by 33% but the first sugar colour only improved by 17%. It has therefore been established that in carbonatation/sulphitation refining the overall decolourisation can be increased by 30-40% by the addition of 200 ppm of polyamines. The chemical must be added to carbonatated liquor prior to filtration.

The addition of 200 ppm of Primco 144 to carbonatated liquor at a carbonatation/ion exchange refinery increased the liquor decolourisation by 20%. This was lower than was obtained from previous tests of similar melt colours (average 30%). However there was a 29% improvement in the first sugar colour.

The results also indicate that there is a lowering of the colour transfer (affinated sugar colour/fine liquor colour) when polyamines are added to a carbonatation/ion exchange refinery. This however, will have to be confirmed by pilot plant work.

Laboratory tests have shown that polyamines can be used successfully to replace 50% of the chemicals used during melt sulphitation. This replacement reduces chemical costs and improves sugar colour. Full scale tests have confirmed these laboratory findings. When 30% of the sulphur was replaced with 200 ppm of Primco 144, the liquor and refined sugar colours improved by 21 and 25% respectively.

Laboratory phosphatation tests have shown that the use of polyamines can increase the overall decolourisation by 30%. To achieve maximum decolourisation in terms of liquor and sugar colours these chemicals should be added to raw melt prior to phosphatation. Full scale tests have confirmed the laboratory findings.

Sugar samples from the full scale tests have been analysed for residual polyamine and none could be detected. This indicates that the polyamine has reacted fully with the colourant molecule and has been removed during filtration.

Some of the advantages of these chemicals are:

- They are made locally from imported raw materials and there are a number of suppliers encouraging competitive prices.
- Being liquids they can easily be dosed directly from the container to the liquor stream.
- No capital investment is necessary.
- A major advantage is the possibility of reducing chemical costs in the refinery. Firstly, additional decolourisation may be obtained during periods of high colour loading, at about R1,50 per ton of refined sugar. This is felt to be the cheapest way of producing the required sugar quality. Secondly, and more importantly, marked chemical cost reductions can be achieved when these chemicals are used as partial replacements for existing chemicals. A partial replacement of sulphur in a sulphitation refinery has lowered the cost of producing a ton of refined sugar by R1,16 while at the same time producing lower colour sugar.

A number of areas needs to be further investigated. Some preliminary work in the raw house has been done but the additions needed in the raw house are high. Full scale plant trials need to be repeated. Finally, additional chemicals are available and need to be tested.

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