

# CLARIFICATION AND MISCELLANEOUS DATA

By G. C. DYMOND.

Items of general sugar interest are classified under the following headings:

1. Preservation of juices. General.
2. Preservation with SO<sub>2</sub>.
3. Clarification. The use of aqueous SO<sub>2</sub>.
4. Aqueous SO<sub>2</sub> data.
5. Clarification. Comparison of four methods.
6. Filter Cake. Drying difficulties. Loss of organic matter and cane wax on composting.
7. Summary.

## 1. Preservation of Juices. General.

The preservation of juices over shut downs has always been a subject of economic importance. In order to combat the losses incurred, evaporation to syrup, cleanliness, temperature and pH control, together with the use of preservatives, usually Formaldehyde, are the methods employed with varying degrees of success.

The two causes of loss are chemical and bacteriological. The former is caused by the inversion of sucrose in an acid medium at high temperatures. The latter by fermentation at both high (thermophilic bacteria) and low temperatures.

The basis of the problem lies in the normal (sometimes abnormal) infection of cane juices with a multitudinous array of micro-organisms. These may be checked from multiplying abnormally by scrupulous cleanliness, by steaming and washing down the mills and by the use of germicides during shut downs, but under the best conditions they are not the complete answers to a universal problem.

## 2. Preservation with SO<sub>2</sub>.

A closer investigation into the acid pre-clarification process shows that SO<sub>2</sub> in juices below 30° Cent. and a concentration of 0.6-0.7 gms per litre, or 3.0-3.2 pH, acts as an excellent germicide and preservative.

The basis of the acid pre-clarification process lies in the precipitation of a portion of the non-sugars, principally cane wax, protein and silica at a pH of 3.0-3.2 in the cold.

Ordinary methods of comparison by apparent purities on mixed juice, supernatant liquid and clarified juice from the acid pre-clarification process are impaired by the alteration in constituents of the Brix solids. The standard of comparison in these tests is the normal weight pol.

A number of test runs using the normal wt. pol. and the standard method by tables (December and January) gave in every case a lower pol. by the standard method. A further peculiarity showed that the pol. of the supernatant liquid (first precipitation) by both methods is usually 0.1 lower than the mixed

juice. In a few cases it is the same and occasionally higher, as it should be owing to the elimination of non-sugars in the precipitate.

Example:

	Brix	Pol. by normal weight	Pol. by tables
Mixed juice ... ..	14.4	12.6	12.46
Supernatant liquid .	14.5	12.5	12.36
Slurry ... ..	—	11.7	—

Experiments were then carried out by weighing the mixed juice, supernatant liquid and slurry. Analyses by the two methods of pol., showed a disappearance of 1.4 and 1.2 per cent. pol. respectively. Apart from this unknown loss, which might be due to the occlusion of starch in the slurry, the preservation of the juices was excellent. Thus the supernatant liquid at 27.5° Cent. over twenty-four hours showed no further drop by either method of pol. determination. At 20° Cent. there was no loss after three days—the period of the test.

If, therefore, the acid pre-clarification process were introduced into our factories, with some cooling device during the hot weather if found necessary, there would be a reduction of sucrose losses during shut downs and to a smaller degree during general running from the same cause, and further, with cleaner factories, there would be easier production of sugars free from bacterial infection.

## 3. Clarification. The Use of Aqueous SO<sub>2</sub>.

The advisability of using a solution (6 per cent.) of SO<sub>2</sub> lies in the sensitivity of the acid precipitate to agitation. If the floc is repeatedly broken precipitation is seriously retarded. This rules out the use of sulphitation boxes with SO<sub>2</sub> injection. Rapid absorption by efficient towers is also impractical for controlling the fine end point. There appear to be no practical difficulties in making a 6 per cent. solution of SO<sub>2</sub> at atmospheric temperatures.

By courtesy of Messrs. African Explosives, pH curves using both phosphoric and sulphurous acids were plotted. The following shows the abbreviated average results:

	Phosphoric Acid			Sulphurous Acid		
	Solution—			Solution—		
	1 ml H <sub>3</sub> PO <sub>4</sub> = 7.78 mgs H <sub>3</sub> PO <sub>4</sub>			6 per cent. SO <sub>2</sub>		
	ml H <sub>3</sub> PO <sub>4</sub>	pH	Drop	ml H <sub>2</sub> SO <sub>4</sub>	pH	Drop
Mixed Juice	—	5.06	—	—	5.06	—
	25	4.16	0.90	3	4.22	0.84
	50	3.57	0.59	6	3.67	0.55
	75	3.11	0.46	9	3.20	0.47
	100	2.81	0.30	12	2.84	0.36

*Note.*—The possible use of phosphoric acid instead of sulphurous acid in the acid pre-clarification process is ruled out for two reasons: the comparative costs and the non-germicidal effect of phosphoric acid at low pH values.

#### 4. Aqueous SO<sub>2</sub> Data.

The desirability of a rapid and accurate mixing of SO<sub>2</sub> with cold mixed juice to a pre-determined pH, as in the acid pre-clarification process, has led to a preliminary investigation into the possibilities of making aqueous solutions of SO<sub>2</sub> in practice. I am indebted to Messrs. African Explosives for their assistance in working out the following basic figures:

1 lb. of SO <sub>2</sub> occupies . . .	= 5.65 cu. ft.
1 lb. of 12% gas occupies .	= 47 cu. ft.
1 lb. of SO <sub>2</sub> in 6% solution	= 1.67 gallons.
30,000 gallons of juice containing 0.6 gms. of SO <sub>2</sub> per litre . . . . .	= 180 lbs. SO <sub>2</sub> .
	= 306 gallons.
Sulphur burnt . . . . .	= 90 lbs.
	= 306 gallons.
Sulphur burnt . . . . .	= 90 lbs.
per week . . . . .	= 6.5 tons.
Gas to be cooled 45 × 180	= 8,100 cu. ft. per hr.

*Note.*—With water at 25° Cent. a 6 per cent. solution can be obtained by percolation through towers packed with Raschig rings. At lower temperatures higher concentrations can be achieved. The use of an aqueous solution of SO<sub>2</sub> with a low sulphur consumption, as in the acid pre-clarification process, gives a simple and positive control, without the use of expensive pH meters. There is a minimum of floc dispersion. The amount of extra water to be evaporated is less than .1 per cent. on mixed juice.

#### 5. Clarification. Comparison of Four Methods.

A comparison was made between the acid pre-clarification process, the same without separation of the first precipitate, simple defecation and sulpho-defecation as practised at Darnall.

Ten comparative juice samples were treated and analysed individually and the precipitates, together with composite sample of juice ash, kept for final analyses.

##### No. 1. The Acid Pre-clarification Process.

To the cold mixed juice sufficient phosphoric acid preparation is added to give a total P<sub>2</sub>O<sub>5</sub> content of 0.03 per cent. In these experiments 0.5 gms of phosphoric paste, containing approximately 50 per cent. soluble P<sub>2</sub>O<sub>5</sub>, was added per litre of mixed juice. This caused a reduction in pH of approximately 0.2 degrees.

SO<sub>2</sub> gas was then passed until a reaction of 3.2 pH was obtained, or 780 mg per litre. The juice is then allowed to stand for thirty minutes, when normally an ochre coloured precipitate settles out. In practice this precipitate is thickened by slow moving stirrers. The volume of precipitate normally occupies 10 per cent. of the total juice volume. With efficient slow stirring this can be reduced to 8 per cent. of the total—an important point.

In these experiments the precipitate was filtered and washed once under vacuum and the residue dried at 80° Cent.

The supernatant liquid was decanted and milk of lime of known solid content was added to give a reaction of 7.5 pH. This tempered juice was then boiled and allowed to settle. The second precipitate was then filtered and washed once under vacuum and the residue dried at 80° Cent.

##### No. 2. The same without separation of the first precipitate.

The same technique is used with the exception that the precipitates are not separated. Thus phosphoric acid is added as in No. 1, SO<sub>2</sub> gas is passed until a reaction of 3.2 pH is obtained. The juice is then immediately neutralised with milk of lime to a reaction of 7.5 pH. The tempered juice is then raised to the boiling point and allowed to settle.

The precipitate thus obtained was filtered and washed once under vacuum, dried at 80° Cent. and weighed.

##### No. 3. Simple defecation.

A comparison was made with the clarification process usually employed in other sugar countries. Phosphoric acid, which is comparatively low in Natal, was added as in No. 1 and No. 2. Milk of lime was then run in to the stirred juice until a reaction of 8.0 pH was obtained. The juice was then raised to the boiling point and allowed to settle. The precipitate was filtered as in No. 1 and No. 2.

##### No. 4. Sulpho-defecation as practised at Darnall.

The procedure is that the juice is heated to 50° Cent. and milk of lime added to give a reaction of approximately 9.5 pH. The juice is then pumped through a sulphur tower, where in this case an average SO<sub>2</sub> content of 1.69 gms per litre, were absorbed. The variations which occur under this system range from 2.14 to 1.40 gms per litre.

The juice is now tempered with milk of lime to a reaction of 8.4 pH, and a weighed quantity of phosphoric paste added, so that after boiling a reaction of approximately 7.3 pH is obtained. In these experiments the final tempered juice, comparative with the other tests, was taken from the factory and heated in the laboratory, the precipitate being collected as in the previous experiments.

### Comparisons of App. Purities and Clarity

Average 10 Samples	Juices Clarified				
	Mixed Juice	1	2	3	4
Apparent purity ...	85.7	87.2	86.8	87.4	86.7
pH ...	5.1	6.8	6.7	6.7	7.3
Clarity—Luximeter . . .	—	68	66	40	50
Kopke ...	—	50	50	27	31

*Note.*—For reasons already stated, the apparent purity variations are not considered significant, but the clarity of No. 1 and 2 is considerably better than in No. 3 and 4.

### Comparisons of Lime and Sulphur used together with Solids produced.

	1	2	3	4
Lime—gms CaO per litre ...	1.52	1.62	0.76	3.22
Sulphur—gms SO <sub>2</sub> per litre:				
Tempered . . . . .	0.78	0.85	—	1.69
Clarified ... ..	0.48	0.52	0.15	0.27
Gms solids in Precipitate per litre:				
First Precipitate ... ..	5.78	—	—	—
Second Precipitate... ..	4.70	—	—	—
Total . . . . .	10.48	11.03	8.81	13.24

*Note.*—No sulphur was used in No. 3, but the standard test with iodine showed an average figure of 0.15 gms per litre in the clarified juice. The amounts of lime and sulphur used in Nos. 1 and 2 were half that in use at Darnall this season. In the 1951 crop there would have been a saving industrially in sulphur alone of 3,400 tons.

Slightly less SO<sub>2</sub> was consumed in No. 1 than in No. 2, though both juices were brought to the same pH. This peculiarity persisted into the clarified juice.

The total solids are related to the amounts of sulphur and lime used.

### Analyses of Solids

	1		2		3		4	
	First Ppt.	Second Ppt.	Total	Total	Total	Total	Total	Total
Ash per cent. solids ... ..	16.6	40.4	26.3	27.3	28.0	41.7		
Organic matter per cent. ...	83.4	59.6	72.7	72.7	72.0	58.3		
Gms O.M. per litre ... ..	4.82	2.80	7.62	8.02	6.34	7.72		
Wax per cent....	26.45	6.60	17.5	13.65	18.70	14.09		
Gms wax per litre ... ..	1.53	0.31	1.84	1.50	1.55	1.86		

*Note.*—In No. 1 the solids in the two precipitates were 5.78 and 4.70 gms per litre. In practice this would mean that the amount of filter cake solids would be reduced from 13.24 gms per litre (No. 4) to only 4.70 gms. Expressed as lbs. solids per ton cane, the reduction would be from 26.48 to 9.40 lbs.

p.t.c., an important consideration. As the second precipitate filters readily, cloth filters could be used, a clear juice ready for the evaporators obtained, together with an appreciable saving in wash water.

As has been noted in past years the wax per cent. first precipitate varies from 25 to 35 per cent. The total weight of wax per cent. solids is the same in Nos. 1 and 4. The high figure in the latter is due to the additional wax in the bagacillo, which varies from 1 to 6 per cent.

The reduction in Nos. 2 and 3 is due to the natural emulsification of cane wax in hot water or juice. Ten per cent. of wax is easily lost in this way. Other figures of interest, not shown in the above table, show that the protein content of the first precipitate varies from 12 to 22 per cent. and that the ash contains from 74 to 86 per cent. of silica. This precipitate is a wax, protein, silica complex, containing further still unknown constituents. The rate of precipitation varies with the percentage of silica naturally present. Addition of heavy substances, clay or silica itself, increases the rate of precipitation, but these merely increase the weight of solids with no other benefit accruing. Since no losses of sucrose occur at reasonably low temperatures, time can be employed in thickening, diluting and re-thickening the precipitate, so as to obtain the highest percentage of solids in the least volume. Thereafter several methods can be adopted to utilise this valuable raw material for by-products production.

### Silica in Clarified Juice.

Analyses were carried out on the ash contents of both precipitates and ash from the clarified juices. An accurate balance of silica in particular was invalidated by the natural silica content of the lime and phosphoric acid used. This is shown in the following figures expressed as lbs. per ton cane.

Lbs. SiO <sub>2</sub> p.t.c.	Mixed Juice	1				2				3				4				
		1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	
Precipitates . . . . .	—	1.05	1.14	1.32	1.50													
Juice ... ..	1.47	0.17	0.30	0.28	0.32													
Total ... ..	1.47	1.21	1.44	1.60	1.82													

*Note.*—No. 1 contains the least amount of silica in the clarified juice, while No. 4 contains more silica in juice and precipitate than existed in the original mixed juice. This is due to the silica impurities in the increased amount of lime used.

### Lime Salts in Clarified Juice.

The amount of lime salts in the clarified juice increases progressively with increasing amount of lime used. Thus:

	3	1	2	4
Lime. gms. per litre in increasing order	0.76	1.52	1.62	3.22
Lime. lbs. CaO per ton cane ... ..	0.83	1.04	1.11	1.16
CaO per cent. Ash .	10.78	11.72	13.09	14.30

### General.

A general assessment of the four processes show that the acid pre-clarification process is better in some respects to No. 2, and better in all respects over either simple defecation or sulpho-defecation.

The principal benefits are:

1. Germicidal action of SO<sub>2</sub> in original juice.
2. Reduction in all chemicals.
3. Reduction in quantity of filter cake.
4. Better filtration. No recirculation of muddy juice.
5. Reduction in undetermined losses.
6. Better clarification, better wax retention and easier boiling.

### 6. Filter Cake Drying Difficulties. Loss of Organic Matter and Cane Wax on Composting.

The drying of filter cake is extremely difficult, as the outer layer forms an insulating cover, whereby both heat and moisture are retained for long periods.

Even the daily turning and aerating of small heaps, the passing of cold or hot air under pressure has little effect. Without such aids to drying there is no loss of moisture within the heap itself.

The following experiment illustrates this. A small heap of fresh filter cake approximately 4 cub. ft. was turned daily for twenty-eight days. A similar quantity was kept in a barrel under anaerobic conditions. The results were as follows: A

*Note.*—Under aerobic conditions the temperature rose to a peak 25° Cent. higher than under anaerobic conditions. In the former the loss of organic matter was over 20 per cent., the ash per cent. rose from 21.8 to 48.2 and there was a considerable loss of the wax complex.

### Loss of Organic Matter.

During the stacking of filter cake, the natural decomposition may be aerobic or anaerobic or both. Under aerobic conditions, there is a sweet earthy smell, temperatures rise to 75° Cent. and over a period of three months the loss of organic matter by weight ranges from 50 to 55 per cent.

Under anaerobic conditions there is a noxious smell of albuminoid putrefaction and sulphuretted hydrogen. Temperatures never exceed 55° Cent. and the loss in organic matter is negligible or comparatively low, with no loss of moisture except in the outer layers.

### Loss of Wax.

The percentage of cane wax in fresh filter cake ranges from approximately 6 to 11 per cent. depending on the variety of cane, its condition and the efficiency of the rotary filters. This efficiency covers fineness and quantity of bagacillo used and the degree of heat and recirculation, whereby part of the wax becomes emulsified and passes into fabrication. Thereafter much of the wax complex may be lost by decomposition. This depends on the nature of the fermentation (aerobic or anaerobic) and time.

In controlled experiments on the availability of P<sub>2</sub>O<sub>5</sub> in rock phosphates, the weighted controls, which were aerated by turning five times in three months, showed only 1 to 2 per cent. of wax at the completion of the tests.

Experiments were finally carried out to determine the rate of loss. The figures are curiously erratic, due possibly to the varying degrees of temperature and aeration throughout the heaps: B

A.	On Stacking	Days										
		1	2	3	4	5	6	7	8 <sup>r</sup> rain	9	20	28
<i>Aerobic</i>												
Moisture %...	73.5	72.6	72.2	68.4	67.3	64.3	61.2	58.2	—	70.2	53.1	52.2
Temperatures Centigrade .	55	50	50	62	62	65	70	75	—	55	65	42
<i>Anaerobic</i>												
Moisture %...	73.5	—	73.7	76.4	75.1	—	73.1	71.0	—	70.7	69.6	73.2
Temperatures Centigrade .	50	45	50	50	55	56	55	50	—	50	48	49

B.	On Stacking	Days										
		1	2	3	4	5	6	7	9	20	28	
<i>Aerobic</i>												
Wax per cent ...	11.7	12.1	5.9	8.5	4.5	8.0	7.3	6.3	5.1	3.5	2.3	
<i>Anaerobic</i>												
Wax per cent. ...	11.7	8.8	8.6	9.0	7.0	—	—	8.3	10.0	9.9	10.8	

*Note.*—Under aerobic conditions a whitish mycelium forms a few inches below the surface. The wax per cent. of this layer was 4.9 per cent. whereas the centre and hottest part showed 7.3 per cent.

### 7. Summary.

The undetermined loss of sucrose in the Industry is over 8,000 tons per annum. There are a number of possible reasons, but one important cause is the loss by bacterial action during shut downs. This loss may be prevented by using  $\text{SO}_2$  as a germicide in the cold mixed juice, as in the acid pre-clarification process. At  $27.5^\circ$  Cent. no loss of pol. was recorded over twenty-four hours. At  $20^\circ$  Cent. no loss was recorded over three days—in both cases the time of the trial. Slight rises and falls of pol. were recorded in the supernatant liquid immediately on settling, which thereafter remained constant. No very definite reason can be ascribed to this peculiarity as yet.

### Clarification.

Four methods of clarification were compared, the acid pre-clarification, the same without separation of the first precipitate, simple defecation and sulpho-defecation.

The acid pre-clarification is assessed the best and the reasons given. The use of aqueous  $\text{SO}_2$  is described, this method being essential in the acid pre-clarification process, in order to minimise the breaking of the sensitive floc and for accuracy.

In general the clarity of processes 1 and 2 were superior and the amount of chemicals reduced. In the 1951 crop 4,640 tons of sulphur were burnt. This would have been reduced to 1,240 tons, a saving of 3,400 tons of sulphur alone.

The amount of filter cake (second precipitate) is reduced to approximately one-third—26.5 lbs. solids p.t.c. reduced to 9.4 lbs. This would result in easier filtration, less sucrose loss with less dilution water. This saving in water would then be used for dilution of the first precipitate.

Finally the acid pre-clarification process shows the best wax retention in practice, with the least  $\text{SiO}_2$  and lime salts in the clarified juice.

### Filter Cake.

The difficulties of drying filter cake are described. The rise in temperature under aerobic conditions may be  $25^\circ$  Cent. higher than under anaerobic conditions.

The loss of organic matter under aerobic conditions is high—50 to 55 per cent. Under anaerobic conditions this loss is minimised. Among the organic materials lost is "cane wax"—a general term covering a variety of high and low boiling point fractions:

Under aerobic conditions this loss may range from 70 to 90 per cent. of the total according to the time and temperature period of decomposition. Under purely anaerobic conditions this loss is reduced, ranging normally from 10 to 20 per cent. during the first month and progressively increasing with time and slow decomposition.

**Dr. Douwes Dekker** said that, as in past years, Mr. Dymond had again given a paper dealing with his work on clarification problems. The present paper led to the question how in actual processing, the use of  $\text{SO}_2$  as suggested by Mr. Dymond could prevent the loss of sucrose in clarified juice during shut downs.

**Mr. Dymond** said that during shut downs there was a loss in clarified juice. This was veiled because on many occasions lime was added and the pH brought up on the Saturday night. He thought this was wrong because the action still went on. Those who had worked in distilleries or acetic acid plants knew that bacteria would only live in a low concentration of the product they produced. To maintain equilibrium the products were often neutralised, thereby enabling the bacteria to live under normal conditions. He suggested that experiments be carried out to test this suggestion which he thought worthy of investigation. Under present conditions it was known that a loss was incurred. He maintained that if the clarified juice was cleared off and the pH maintained at  $3.2^\circ$  in the cold mixed juice then less loss would be incurred. In reply to Dr. Douwes Dekker, Mr. Dymond said that he thought that clarifiers should be cleaned out as far as possible at the weekend.

**Dr. Douwes Dekker** said that he was satisfied that Mr. Dymond had shown that if cold mixed juice was sulphited to 3.2 pH, decomposition of sucrose was negligible within a period of about 48 hours. But he did not see how this fact could be used to prevent decomposition of sucrose in the hot juice in the clarifiers during the week-ends. A statement as made by Mr. Dymond should have been supported by the results of factory tests.

**Mr. Dymond** admitted that the figures were not final, but work would be carried on to verify whether his theory was correct or not.

**Dr. Parrish** asked about the silica in clarified juice and referred to the figures given in the tables. He asked whether the figure in Process No. 1 was for the final clarified juice or the juice after the use of  $\text{SO}_2$ . The results obtained at the S.M.R.I. with pure lime were somewhat different to those obtained by Mr. Dymond.

**Mr. Dymond** said he would very much like to see the S.M.R.I. figures with the use of pure materials. He admitted that he had worked with the ordinary substances in the mill and not with purified chemicals. The results from clarification experiments were never spectacular and further experimentation was necessary.

**Dr. Douwes Dekker** said that the question of silica removal was now a subject of investigation by the S.M.R.I. They knew already that they would have to discern between "total"  $\text{SiO}_2$  and "available"  $\text{SiO}_2$ . It had also been found that a considerable part of  $\text{SiO}_2$  in mixed juice could be removed by filtration only. To obtain a proper

flocculation of the suspended nonsugars was an important part of clarification.

**Mr. Dymond** said he had already indicated that the  $\text{SiO}_2$  could be removed from the heated juice by straight filtration and if this were the better way methods could be devised of incorporating it.

**Dr. Douwes Dekker** asked by what method CaO in juice had been determined, by the soap test or by a more perfected method.

**Mr. Dymond** replied that it was a purely analytical determination.

**Mr. Alexander** asked whether Mr. Dymond was certain that because there were fewer micro-organisms in the juices there would be fewer in the final product.

**Mr. Dymond** replied that it had been suggested that his experiments suppressed the bacteria. This could only be proved in general practice and he had merely set out ideas which could be followed by further research work. Mr. Dymond added that it had been decided to go into a pilot plant at Darnall in connection with his process. They would put in a grid of cooling tubes between the sulphur burner and the sulphur tower to bring the temperature of the gas down. The gas would then be passed through a small tower 7 ft.  $\times$  3 ft.  $\times$  3 ft. and water be allowed to percolate through. From the bottom would then be drawn off whatever aqueous  $\text{SO}_2$  was required.

**Dr. Douwes Dekker** then asked the meeting to convey to Mr. Dymond their appreciation in the usual manner.