ELECTROLYTIC CHLORINE.—ITS VALUE AS A DISINFECTANT.

By G. C. DYMOND

Mr. G. C. Dymond read the following paper:—

E.C., or Electrolytic Chlorine, is the name given to a solution of Sodium Hypochlorite made electrolytically from brine in a specially designed electrolyser. Its manufacture is simple and consists merely of passing a direct electric current through a solution of common salt in water. Hydrogen is given off at the negative electrode and sodium hypochlorite is formed in the solution.

In 1927 Dr. Haldane reported in the International Sugar Journal on the value of E.C. as a cheap and efficient disinfectant specially suited to sugar mills. Dr. Haldane shows that E.C. is equal to Formalin in preserving juices. The object of this investigation was to ascertain what value E.C. had under our local conditions, bearing in mind the opinion of some chemists that E.C. had a marked deteriorating effect on juices.

Despite adverse reports from other factories the Company decided to buy the apparatus for manufacturing E.C. on the reports and results received from the manufacturers. The experiments carried out by the Chemical Staff at Empangeni would seem to verify the reports received from them.

The initial series of experiments confirmed the "apparent" deterioration observed by some chemists. This is however, only apparent, being due to the dilution factor of E.C., which dilutes the sucrose present but not the total solids. E.C. has a brix of from 18—19°, so that, on addition of E.C. in increasing quantities, the density rises slightly in juices below the density of E.C., but the Sucrose % is diminished. This effect is demonstrated in the following experiments.

Available Chlorine in E.C. used = 1.1%.

	Brix.	Sucrose.	Apparent Purity.	Drop in Sucrose.
Control. No preservative	17.40	14.05	80.7	Control
2 ml. of E.C. per litre (1 : 500)	17.40	14.05	80.7	Nil
4 ,, ,, ,, (1 : 250)	17.45	14.05	80.5	Nil
6 ,, ,, ,, (1 : 167)	17.45	14.00	80.2	0.05
8 ,, ,, ,, (1 : 125)	17.45	13.95	79.9	0.10
10 ,, ,, ,, (1 : 100)	17.45	13.95	79.9	0.10
15 ,, ,, ,, (1 : 67)	17.50	13.80	78.8	0.25
20 ,, ,, ,, (1 : 50)	17.55	13.80	78.6	0.25
0.2 ,, Formalin (1 : 5000)	17.40	14.05	80.7	Nil

Repeat Experiment.—Available Chlorine in E.C. used = 1.2%.

	Brix.	Sucrose.	Apparent Purity.	Drop in Sucrose.
Control. No preservative	15.00	12.70	84.7	Control
5 ml. of E.C. per litre (1 : 200)	15.00	12.65	84.3	0.05
10 ,, ,, ,, (1 : 100)	15.00	12.60	84.0	0.10
15 ,, ,, ,, (1 : 67)	15.05	12.50	83.0	0.20
20 ,, ,, ,, (1 : 50)	15.05	12.45	82.7	0.25
30 ,, ,, ,, (1 : 33)	15.10	12.30	81.4	0.40
0.2 ,, Formalin (1 : 5000)	15.00	12.70	84.7	Nil

The Sucrose in these series was determined by weighing out the Normal Weight, the 100–110 method being found to be inaccurate owing to the dilution factor. In the same way, the use of the refractometer was found unsuitable, while the determination of reducing sugars was invalidated to a progressive extent on account of the reducing effect, though slight in dilute solutions, of E.C. on Fehling's solution.

The sucrose, determined by weighing out the normal weight and corrected for dilution, was then adopted as the basis for comparisons, and not the Purity, which is greatly influenced by dilution factors.

In all the experiments E.C. was used having a strength of from 1.0 to 1.2% Available Chlorine. Haldane used a 2% concentration, and it is noticeable that where he obtained practical sterilization with 5 ml. per litre our experiments required, as was to be expected, more than twice that amount to obtain the same result.

First Experiment.

A sample of Mixed Juice fresh from the mills was contaminated with a small quantity of partially fermented juice, and treated as follows :— Available Chlorine in E.C. used = 1.2%.

	On Sampling.		6 Hours later.		6 Hours later.		24 Hours.
	Sucrose.	Drop in Sucrose.	Sucrose.	Corr. Sucrose.	Sucrose.	Corr. Sucrose.	General Condition.
Control. No preservative	14.05	Control	13.90	13.90	12.90	12.90	Fermenting rapidly
2 ml. of E.C. per litre ..	14.05	Nil	13.95	13.95	12.90	12.90	,,
4 ,, ,, ,, ..	14.05	Nil	13.95	13.95	13.00	12.90	,,
6 ,, ,, ,, ..	14.00	0.05	13.95	14.00	13.10	12.95	,,
8 ,, ,, ,, ..	13.95	0.10	13.85	13.95	13.10	13.20	,,
10 ,, ,, ,, ..	13·95	0.10	13.90	14.00	13.20	13.30	Slightly less rapidly
15 ,, ,, ,, ..	13·80	0.25	13.90	14.15	13.40	13.65	
20 ,, ,, ,, ..	13.80	0.25	13.90	14.15	13.50	13.75	,,
0.2 ,, Formalin ..	14.05	Nil	14.00	14.05	12.20	12.20	Rapid

From the results of this experiment it will be noted that the Control kept fairly well for 6 hours. Small amounts of E.C. from 2—4 ml. per litre had practically no effect, while amounts over 10 ml. per litre preserved the juice equally with Formalin, which was used (1 : 5000) in the quantity generally recommended for factory practice.

After 12 hours the juice had rapidly deteriorated, but the preservative action of E.C. with amounts over 6 ml. per litre is noticeable by a progressively decreasing loss. In this experiment the sample with Formalin had deteriorated more rapidly even than the control.

Second Experiment.

A sample of Mixed Juice was infected with slime from the mill gutters. The day was excessively hot, maximum temperature 90° F., and conditions were thus eminently suitable for rapid deterioration of the juice.
Available Chlorine in E.C. used = 1.1%.

	On Sampling.		6 Hours later.		6 Hours later.	
	Sucrose.	Drop in Sucrose.	Sucrose.	Corr. Sucrose.	Sucrose.	Corr. Sucrose.
Control. No preservative ..	12.70	Control.	12.25	12.25	10.45	10.45
5 ml. of E.C. per litre ..	12.65	0.05	12.35	12.40	10.40	10.45
10 ,, ,, ,, ..	12.60	0.10	12.40	12.50	10.60	10.70
15 ,, ,, ,, ..	12.50	0.20	12.40	12.60	11.10	11.30
20 ,, ,, ,, ..	12.45	0.25	12.30	12.55	11.30	11.55
30 ,, ,, ,, ..	12.30	0.40	12.30	12.70	11.70	12.10
0.2 ,, Formalin ..	12.70	Nil	12.50	12.50	11.00	11.00

The Reducing Sugar Ratios were also indicative of the rapid fermentation.
Available Chlorine in E.C. used = 1.2%.

	On Sampling. Red Sugar Ratio	6 Hrs. Later. Red Sugar Ratio	6 Hrs. Later. Red Sugar Ratio
Control. No preservative	1.26	4.41	13.97
5 ml. of E.C. per litre	1.26	4.37	—
10 ,, ,, ,,	1.27	3.64	—
15 ,, ,, ,,	1.28	3.48	—
20 ,, ,, ,,	1.29	3.40	—
30 ,, ,, ,,	1.30	3.17	6.75
0.2 ,, Formalin	1.26	3.84	11.72

Third Experiment.

Having proved that E.C. has certain preservative abilities under exceptionally adverse conditions, the next step was to discover what amount is necessary under normal conditions.

A sample of Mixed Juice was taken from the mills at mid-week, when the mill housings, gutters, etc., are normally infected with bacterial slime. Available Chlorine in E.C. used = 1.2%.

	On Sampling.		6 Hours later.		24 Hours later.	
	Sucrose.	Drop in Sucrose.	Sucrose.	Corr. Sucrose.	Sucrose.	Corr. Sucrose.
Control. No preservative ..	16.00	Control.	15.70	15.70	13.90	13.90
1 ml. of E.C. per litre ..	16.00	Nil	15.70	15.70	14.00	14.00
3 ,, ,, ,, ..	16.00	Nil	15.65	15.65	14.00	14.00
5 ,, ,, ,, ..	15.95	0.05	15.65	15.70	13.95	14.00
7 ,, ,, ,, ..	15.90	0.10	15.65	15.75	13.90	14.00
10 ,, ,, ,, ..	15.85	0.15	15.70	15.85	14.00	14.15
12 ,, ,, ,, ..	15.85	0.15	15.70	15.85	14.00	14.15
14 ,, ,, ,, ..	15.80	0.20	15.70	15.90	14.10	14.30
16 ,, ,, ,, ..	15.70	0.30	15.60	15.90	14.20	14.50
20 ,, ,, ,, ..	15.60	0.40	15.50	15.90	14.20	14.60
0.5 ml. of Formalin per litre..	16.00	Nil	15.85	15.85	14.95	14.95
0.2 ,, ,, ,, ..	16.00	Nil	15.80	15.80	15.50	15.50

The weather was cold during this period and conditions were not favourable for rapid fermentation.

From this experiment and confirmatory data it was found that for any practical result, E.C. must be used at the rate of from 10 to 16 ml. per litre. The curious result obtained with varying quantities of Formalin is unaccounted for, though such variations have been noted on other occasions.

Fourth Experiment.

This experiment was designed to determine the effect of temperature on the rate of deterioration. A sample of mixed juice, four hours after sampling, was divided into two series, one being kept at a temperature varying from 17° C. to 21° C. and the other series from 30 °C. to 35° C.

	On Sampling		4 Hours later		4 Hours later		4 Hours later		24 Hours later	
17—21° C.	Sucr.	Drop in Sucr.	Sucr.	Corr. Sucr.	Sucr.	Corr. Sucr.	Sucr.	Corr. Sucr.	Sucr.	Corr. Sucr.
Control. No preservative	11.15	Cont.	10.80	Cont.	10.55	Cont.	10.25	Cont.	8.80	Cont.
10 ml. of E.C. per litre ..	11.10	0.05	10.75	10.80	10.60	10.65	10.60	10.65	9.70	9.75
15 ,, ,, ,, ..	11.05	0.10	10.80	10.90	10.65	10.75	10.65	10.75	10.10	10.20
20 ,, ,, ,, ..	10.90	0.25	10.75	11.00	10.55	10.80	10.55	10.80	10.10	10.35
0.2 ,, Formalin ,, ..	11.10	0.05	10.90	10.95	10.85	10.90	10.75	10.80	10.40	10.45
30—35° C.										
Control. No preservative	11.15	Cont.	10.50	Cont.	9.75	Cont.	9.15	Cont.	6.80	Cont.
10 ml. of E.C. per litre ..	11.10	0.05	10.60	10.65	10.00	10.05	9.50	9.55	7. 5	7.55
15 ,, ,, ,, ..	11.05	0.10	Spoilt.		—	..	—	..	—	..
20 ,, ,, ,, ..	10.90	0.25	10.60	10.85	10.30	10.55	10.10	10.35	9.00	9.25
0.2 ,, Formalin ,, ..	11.10	0.05	10.80	10.85	10.70	10.75	10.40	10.45	9.50	9.55

This experiment demonstrates the following points :—

1. That in amounts less than 20 ml. per litre 1% E.C. does not compare favourably with Formalin (1 : 5000).

2. That, as was to be expected, temperature plays a big part in the rate of deterioration, the second series, which were kept at from 30–35° C. showing in every instance a greater loss of sucrose than in those maintained at a lower temperature. Dr. Haldane says that "although the inverting activity of micro-organisms can be suppressed by the addition of E.C. or Formalin, a loss of sucrose dependent upon acidity, concentration and temperature will generally be recorded."

3. A further important point was noted in this series, and that is the effect of temperature on the selectivity of the predominant organisms. At low temperatures, the gum-forming bacteria develop most rapidly, but this development was apparently suppressed by E.C. After 24 hours the control filtered with great difficulty, whereas those treated with E.C. filtered easily. At the high temperatures the control after 24 hours still filtered comparatively readily, though the loss in sucrose was considerably increased. The predominance of gum-forming micro-organisms and filtering troubles usually occurring during the cold spells associated with rain and the occurrence of Leuconostoc from frosted canes may here be noted.

4. E.C. improves the keeping qualities of a juice, its action increasing with the percentage of E.C. added. The amount required for practical preservation is about 20 ml. per litre when the concentration of available Chlorine is 1%.

Fifth Experiment.

Sample of fresh Mixed Juice from mills a few hours after a wash-down.

	Ml. E.C. added 1.2% Available Chlorine.												
	Nil	6	8	10	12	14	16	18	20	25	30	35	40
Control ..	15.95	Corrected Sucrose.											
After 6 hrs.	15.80	15.85	15.80	15.80	15.80	15.80	15.80	15.80	15.80	15.80	15.90	15.90	15.90
„ 24 „	13.70	14.20	14.50	14.50	14.60	14.85	14.90	15.30	15.40	15.70	15.70	15.70	15.80

In this experiment the amount of infection was apparently very small, as the sample kept comparatively well without E.C. for six hours. In studying the value of any preservatives, one must always bear in mind the variable factors at work such as temperature, degree of infection, specific micro-organisms predominating, etc., which influence the result. Further, bacterial infection in sugar mills is distinctively a cumulative one, and the practical utility of a disinfectant such as E.C. should not be one of attempting to rectify a bad condition of active fermentation but to prevent such a condition from arising.

Effect of E.C. as a Spray.

A number of Petri dishes were prepared with Nutrient Gelatine and infected with diluted samples of juice. After a few hours the dishes were exposed and sprayed with E.C. in varying intensities. The plates only remained sterile when the E.C. was effectively applied, so that the whole surface came in contact with the liquid.

Effect of E.C. in Clarified Juice.

A sample of Clarified Juice was divided into two series, one was allowed to get cold and the other was maintained at approximately 40°C. for 48 hours. The result was as follows:—

			After 48 Hours (Cold)			After 48 Hours 40°C.		
	Sucrose.	Drop in Sucrose.	Sucrose.	Corr. Sucrose.	pH	Sucrose.	Corr. Sucrose.	pH
Control..	14.90	Cont.	14.90	Cont.	6.9	14.00	Cont.	6.3
5 ml. of E.C. per litre ..	14.90	Nil	14.80	14.8	6.8	13.50	13.50	6.0
10 „ „ „ ..	14.75	0.15	14.85	15.0	6.8	14.50	14.65	6.3
20 „ „ „ ..	14.60	0.30	14.90	15.2	6.8	13.75	14.05	6.0
0.2 „ Formalin per litre..	14.90	Nil	14.90	14.90	7.6	14.50	14.50	6.3

The results of this experiment show that the deterioration of clarified juice is not primarily due to micro-organisms, but to a heat and acid inversion. The irregular losses in sucrose in the series kept at 40°C. are confirmed by the pH values and are due to irregular heating of the individual samples. The two showing the highest loss were inadvertently kept at a higher temperature.

Effect of E.C. on the SO_2 Content of Clarified Juice.

The effect of E.C. on the SO_2 content is of interest, though its application to practice is out of the question.

Clarified Juice SO_2 parts per million :—

	On application	1 hour later	24 hours later
Control	46	49	24
2 ml. of E.C. per litre..	44	42	26
5 ,, ,, ,, ..	36	36	18
10 ,, ,, ,, ..	26	25	12
20 ,, ,, ,, ..	12	12	8
30 ,, ,, ,, ..	10	9	6

Repeat Experiment.

	On application	2 hours later
Control..	72	72
2 ml. of E.C. per litre	72	64
4 ,, ,, ,, ...	64	56
6 ,, ,, ,, ...	56	48
8 ,, ,, ,, ...	44	40
10 ,, ,, ,, ...	40	32
14 ,, ,, ,, ...	28	20
18 ,, ,, ,, ...	16	12
20 ,, ,, ,, ...	16	12
25 ,, ,, ,, ...	12	12
30 ,, ,, ,, ...	12	10
35 ,, ,, ,, ...	12	10
40 ,, ,, ,, ...	8	8
50 ,, ,, ,, ...	6	6

These experiments demonstrate the immediate oxidising effect of E.C., but the amount required to reduce the SO_2 to a low figure is large and therefore impracticable. Thus at the rate of 10 ml. per litre, 15 gallons of E.C. would be required for one 1,500 gallon tank in order to reduce the SO_2 content to one-half. The use of E.C. as a purging agent on Treacle Sugar was tried out, but very little reduction in the SO_2 content resulted, showing that the SO_2 is present chiefly in the grain itself.

Cost of E.C. as against Formalin.

E.C.—Cost of producing 24 gallons of E.C. per diem :—

30 lbs. of Salt	1	0
Wages, Current, etc.	1	6
Total	2	6

Formalin.—42 gallons and railage cost £13/11/-.

If Formalin be used at the rate of 1 part to 10,000 parts water and be used to perform the same work as 24 gallons of E.C., the cost would be approximately £2/18/- per diem.

Conclusions.

It is apparent from the foregoing experiments that E.C. has valuable antiseptic properties which, when considered in conjunction with its extremely low cost of production, makes its wide application desirable. Its use has been so far more or less restricted to intermittent application to the Maceration water, which is of doubtful value on account of the great dilution.

The best method of application is in the form of a spray round the mills, etc,. by which means its maximum disinfectant properties are exerted.

E.C. has been criticised as a molasses former. This is quite true, since 1 part of ash will prevent 5 parts of sucrose from crystallising. If 2,600 lbs. of salt are used in one crop, 6 tons of sucrose will be lost through extra molasses formation. On the other hand, if the use of E.C. has prevented the loss of even 0.1 degrees in Purity, approximately 50 tons of Sucrose will have been gained on the same basis.

CHAIRMAN: Mr. Dymond has given us a study of a method of meeting one of our very big problems—the problem of sanitation in the sugar factory, keeping the mills and juices free from fermentation. In this climate it is one of the big problems which affect almost everything we do, and the effects of fermentation at the mills are felt, as you know, at almost every subsequent station, so that this method of treating the mills with chlorine is one which should have very far reaching effects not only at the mill station but the filtration and other places. Can Mr. Dymond give us any details about the cost of the plant, size of it, and staff needed to work it, and how big an undertaking it is to instal, and whether it is within the reach of the smaller factories?

Mr. DYMOND: I am afraid I am unable to give you exact costs on introduction of this plant. It is very simple and its cost of upkeep very reasonable. One Native boy is quite capable of looking after it. As you will note the cost, wages and current, is 1/6 a day. There is no extra cost except the cost of the salt, which for 24 hours is only 1/-.

Mr. RAULT: Mr. Dymond is to be congratulated on his work because he has been able to show us one method by which we can keep our scums free from fermentation, and indirectly it will have a great effect. You will not have to do hourly samples of juice. We are only doing that extra amount of work now on account of a few mills who have not found means of keeping their mills in a proper state of sanitation. So if we can have this it will be a means of doing away with a lot of work in our laboratories.

Mr. FOSTER: I would like to ask Mr. Dymond if he has used this E.C. for any length of time in his factory? If so, in what manner he applies it and in what manner he considers it best to apply?

Mr. DYMOND: We first used this substance about a month after the crop had started, and it was quite a problem to us to know exactly how to apply it. I would not like Mr. Rault to get away with the idea that he is going to keep his mills clean by the use of E.C. only. I still consider that is a problem which should be tackled by the use of high pressure steam and washing down wherever possible. E.C. has a definite value after such a con-

dition has been reached. It is more a stage of keeping the mills clean rather than attempting to destroy a bad condition of fermentation which has become cumulative through the non-washing down of mills. We used E.C. first of all on Dr. Haldane's recommendations, small quantities at a time in the juices and in the maceration water, but from the results of these experiments we soon found that if you dilute the E.C. beyond a certain amount the value of that E.C. as a disinfectant becomes negligible; in fact, if you read up authorities on Drugs and Poisons, as you all know in minute amounts they are not poisons any longer but are actually stimulants, and it has been shown that small quantities of chloride of lime actually exert a stimulative effect on the growth of bacteria if in diluted amounts. So that the addition of E.C. to the maceration water is a very dangerous operation I consider. We stopped using it in small proportions and in place of that added it in bulk every four or six hours, about 8 or 10 gallons, thereby passing it through the mills, and with the return of juices it took probably a quarter of an hour before it was finally pumped out. But I still think the best means of application would be in the form of a spray round about the premises and mill floorings where, being more concentrated, it would exert its maximum effect.

CHAIRMAN: In that connection its use in the imbibition water would not touch the first mill or first two mills, and you would still have the difficulty of the rollers, etc., which would need to be disinfected.

Mr. DYMOND: I might also say that taking the drop in purity from the crusher juice to mixed juice, in the first month of working the drop appeared to be rather high, about 3.2, and soon after that we used E.C., and for about six weeks it dropped to a normal 2.8 or 2.9. There was another break after that just for a few weeks and it rose again. Thereafter we used it continuously in maceration water and had efficient means for steaming the mills, and it dropped back again to 2.8. I always consider that drop in purity is a very good indication of the sterilisation of the fermentative conditions and cleanliness of mills and mill-houses.

Mr. RAULT: I am very glad Mr. Dymond also said something about the molasses fermentation with the use of E.C. Molasses fermentation depends a lot on the amount of ash present in the liquid we are boiling, but specially on the nature of that ash, and if I am not mistaken I think de Lynden in Java has made extensive experiments to find out which of the elements that make up the ash are the most detrimental, and among them chlorine has been found to be the worst, so that we ought to be extremely careful when we are adding chlorine to our juices, and in that probably is the explanation why our South African molasses do not exhaust as well as the molasses from other sugar lands, because if you make a complete analysis of the ash of the molasses in South Africa one peculiarity comes out immediately, that whereas in Java the chlorine in ash may be about 9 to 10 per cent., in South Africa it is anything from 17 per cent. to 25 per cent. Therefore, as I say, this may be one of the explanations, apart from the glucose ash ratio, of the non-exhaustibility of our molasses, and we therefore must be very careful before adding chlorine.

Mr. BLACKLOCK: With regard to the cost of the E.C. against Formalin, are we to understand that the cost of E.C. per day would be 2/6, and the cost of Formalin for an equal amount of work to be £2/18/– ?

Mr. DYMOND: Yes.

Mr. BLACKLOCK: According to your experiments 0.2 ml. of Formalin gives better results than 20 ml. of E.C. Therefore 1 gallon of Formalin is equal to 100 gallons of E.C.

Mr. DYMOND: I take it that you based your calculations on 20 ml. of E.C. This calculation was based on about 10 to 12 ml.

Mr. BLACKLOCK: In all your experiments your maximum amount added is 20 ml. per litre and you always finish up with Formalin 1 in 5,000, a ratio of 100/1 and both give equal results. I think Formalin seems cheaper to us and less dangerous, as Mr. Rault remarks.

Mr. DODDS: There is one rather curious little chemical point in this interesting paper, that is on the first page, where the reducing effect of E.C. is mentioned. Is this a case of mutual de-oxidation such as one finds, for example, between hydrogen peroxide and certain other oxidising agents, and that the chlorine acts on the cupric sulphate with the mutual loss of oxygen from each? In any case, one would have expected in the presence of reducing sugars the tendency would be for the E.C. to oxidise the glucose and thereby lessen the amount of indicated reducing sugars instead of increasing it as is shown in the paper.

Mr. DYMOND: The amount of reduction as noted is very small, but when used in concentrated amount it did have quite an appreciable effect, and consequently it was cut out of the experiments as a definite basis for arriving at the value of E.C., the whole of these experiments being based on sucrose only. In the actual effect of E.C. on Fehling's solution I could not account for it.

Mr. GOLDING: If Mr. Dymond proceeds to spray round his mill with this E.C. mixture, is he not rather concerned with pollution problems?

Mr. DYMOND: No, the pollution problem would rather be by the addition of E.C. in maceration water. Also having chlorine in that form if it is

going to combine with anything it will be with iron, and that is not a thing we want to encourage in our juice. That is one of the points where we felt that the application of spray round the mills would be best. These housings and parts are of immense thickness, and it is to prevent the filth and dirt on the curves and pillars where the juice does not normally get access to, and allow the steaming and washing down to do the rest of the job.

CHAIRMAN: I would like to move a special vote of thanks to Mr. Dymond because we owe him a lot from this Association. In all the Committees of which he is a member he has always done a great deal of work, and has produced reports on any particular subject which we happen to be discussing, and has carried out experiments at Empangeni to verify points in doubt, and in addition to all that work on the Committees he has now produced two interesting and valuable papers for us, and but for certain circumstances he would have produced a third one. I think we should appreciate the work Mr. Dymond is always ready to do and does. (Hear, hear, and enthusiastic applause.)