XCII.—*The Action of Carbon Dioxide in the Bleaching Process.*

By SYDNEY HERBERT HIGGINS.

IT is well known that the carbon dioxide of the air plays a part in the bleaching of vegetable fibres by hypochlorite solutions, but the nature of this part has not hitherto been thoroughly explained. A number of observations have been made which have a bearing on this matter: Williamson (*Mem. Chem. Soc.*, 1850, **2**, 234) passed chlorine into water containing calcium carbonate in suspension, when he found carbon dioxide was driven off. Dreyfuss (*Bull. Soc. chim.*, 1884, [ii], **41**, 600) showed that carbon dioxide acted on calcium chloride in the presence of hypochlorous acid to produce chlorine. Lunge and Schäppi (*Dingl. Polyt. J.*, 1889, **273**, 63) pointed out that nearly the whole of the chlorine is expelled from bleaching powder by the action of carbon dioxide. von Tiesenholt

(*J. pr. Chem.*, 1901, [ii], **63**, 30; 1902, [ii], **65**, 512; 1906, [ii], **73**, 301) stated that the action of chlorine on alkalis is a reversible one. He explained the production of chlorine by the action of carbon dioxide on bleaching powder as being due to (1) the production of hypochlorous acid by the action of the carbon dioxide on the calcium hypochlorite, and (2) the action of this hypochlorous acid on the calcium chloride; thus:

$$CaCl_2 + 2HOCl = Ca(OH)_2 + 2Cl_2.$$

Taylor (Trans., 1910, **97**, 2541) confirms von Tiesenholt's conclusion as to the reversibility of the action of chlorine on alkalis, but does not support him as regards the explanation of the production of chlorine from bleaching powder by the action of carbon dioxide. He points out that, if von Tiesenholt's view is right, hypochlorous acid cannot exist in the presence of a chloride, whereas it is known that hypochlorous acid and calcium chloride exist together in bleaching powder solution. Taylor states that the action of carbon dioxide on bleaching powder is the same as the action of any other acid, the carbon dioxide decomposing both the chloride and the hypochlorite contained in the bleaching powder. His experiments in proof of this contention, however, are not conclusive, and an explanation will be given later which better conforms with the facts. According to Taylor, when ordinary air acts on bleaching powder the free lime is removed by the action of the carbon dioxide contained in the air, and then the direction of the reversible action:

$$2Ca(OH)_2 + 2Cl_2 \rightleftharpoons Ca(OCl)_2 + CaCl_2 + 2H_2O$$

is determined; the action proceeds from right to left, the free chlorine produced being a very active bleaching agent. As is shown later, however, it is not so much the removal of the free lime from the solution of bleaching powder as the action of the carbon dioxide of the air on the solution after the free lime has been removed that increases the bleaching efficiency of the bleaching powder solution.

If the free lime be removed from the bleaching powder solution, and if an excess of calcium chloride be then added to the solution, Taylor states that the bleaching action of the resulting solution will be extremely rapid, because the two factors mentioned will both tend to make the equation given proceed from right to left. In actual bleaching, however, the present author has not found this to be the case. In support of his conclusion, Taylor mentions the experiment of breathing on to a piece of litmus paper which has been moistened with bleaching powder solution, when the rate of bleaching of the litmus is thereby greatly increased. In this case, however, the heat of the breath greatly accelerates the bleaching action, and the excess of carbon dioxide in the breath, after precipitating the free lime, acts further on the bleaching powder solution as described later. In the reaction

$$2NaOH + Cl_2 \rightleftharpoons NaCl + NaOCl + H_2O,$$

Taylor states that an excess of common salt, on being added to a solution of sodium hypochlorite, causes that solution to have an increased bleaching efficiency, because it tends to make the action proceed from right to left of the equation; but the present author has shown that other neutral salts of sodium have an effect similar to that of the chloride, so that this explanation of the increased bleaching effect is untenable. Again, Taylor assumes that bleaching solutions prepared by the electrolysis of common salt solution are more active than solutions of sodium hypochlorite prepared from bleaching powder solution, whereas this has been shown (*J. Soc. Chem. Ind.*, 1911, **30**, 185) not to be the case. The explanation of the activity of old bleaching vats as being due to their exposure to air seems to have been put forward because Taylor confounded bleaching powder solutions which had been kept exposed to the air with solutions which had previously been used for bleaching (see Higgins, *loc. cit.*). The action of pure carbon dioxide on bleaching powder is attributed by Taylor entirely to the carbon dioxide, but in the action of air on bleaching powder, either in the solid state or in solution, he has no part for the carbon dioxide of the air to play except to remove the free lime from the solution, whereas it is known that the carbon dioxide of the air plays a part in actual bleaching.

The action of common salt in increasing the bleaching efficiency of hypochlorite solutions has been explained (*loc. cit.*) as being due to the increased attraction of the carbon dioxide of the air by the salt solution, and it has now been shown that this increased attraction exists in the case of lime water and calcium chloride. Taylor (*loc. cit.*) pointed out that carbon dioxide bubbled through water containing common salt, and methyl-orange caused a pink coloration, and that this coloration was produced in pure water when the carbon dioxide was at a pressure of five atmospheres. In the case of the salt solution Taylor attributed the pink colour to the liberation of hydrochloric acid from the salt by the carbon dioxide; but this explanation does not suffice for the pure water experiment. In the present author's opinion these facts are best explained as being due to the carbon dioxide being more soluble in dilute salt solutions than in pure water, although as to the state in which the carbon dioxide exists in solution no definite statement can be made. In the discussion on Taylor's paper, Senter accounted for the increased action of the carbon dioxide in the presence of common salt by the so-called "neutral salt action":

as it is shown later that neutral salts have a similar action on hypochlorite solutions, it is possible that these salts act catalytically on the hypochlorites, decreasing their stability and increasing their bleaching effect.

EXPERIMENTAL.

Absorption of Carbon Dioxide from Air by Lime Water.

The effect of adding calcium chloride to lime water on its rate of attracting carbon dioxide when exposed to air was determined in the following manner. Two equal quantities of lime water, to one of which a quantity of calcium chloride was added and the solution filtered, were exposed to air in Jena-glass beakers. After remaining for a certain time, and being periodically stirred, the solutions were filtered through weighed filter papers to collect the calcium carbonate, which had been precipitated from the solutions by the action of the carbon dioxide of the air. The filter papers were again dried and weighed. The following results were obtained:

1. 220 c.c. of lime water. A quantity of calcium chloride added to similar sample. Both solutions contained in 2-litre Jena-glass beakers.

	Calcium carbonate in grams.	
	After 18 hours.	After 42 hours.
Lime water alone	0·1601	0·3210
,, ,, and $CaCl_2$	0·2311	0·3607
	After 22 hours.	
2. 100 c.c. Lime water	0·1847	
,, ,, ,, +20 grams of $CaCl_3$	0·1906	
	After 24 hours.	
3. 200 c.c. Lime water	0·2209	
,, ,, ,, +15 grams of $CaCl_2$	0·2878	
	After 22 hours.	
4. 200 c.c. Lime water	0·2035	
,, ,, ,, +15 grams of $CaCl_2$	0·2857	

Experiment 4 was a repetition of 3, but under different atmospheric conditions. In case 2 it is evident that all the lime is precipitated during the time of exposure, hence the figures obtained are practically the same for the two solutions. The figures show that the addition of calcium chloride to lime water increases the rapidity of the attraction of carbon dioxide from the atmosphere. This estimation is, of course, complicated by the slight solubility of calcium carbonate in water and its unknown solubility in calcium chloride solution. It was noticed that in the case of the pure lime water the precipitate was coarser than the other precipitate, and that it formed mostly at the surface of the solution, thus tending to shield the lime water from the further action of the air. The beaker containing the lime water and calcium chloride showed a thick deposit of calcium carbonate at the bottom, and very little of the precipitate as a scum at the surface of the solution. It was also noticed that the pure lime water showed signs of precipitation sooner than the other solution.

Knecht has shown that the addition of calcium chloride to bleaching powder solution accelerates the bleaching action of that solution, but it has been shown (Higgins, *loc. cit.*) that under the conditions of actual bleaching this effect is very slight. The increased attraction of the carbon dioxide caused by the addition of calcium chloride, as mentioned above, causes an increased deposition of the free lime from the bleaching powder solution, and hence slightly increases the bleaching effect of that solution.

Absorption of Carbon Dioxide by Bleaching Powder Solution.

Bleaching powder solution (170 c.c. of D 1·08) was exposed to air for a number of days in a 2-litre beaker. After two days the solution had deposited 0·8 gram of calcium carbonate, and towards the end of the fifth day it was found to have lost almost all its chlorine, as it did not react with potassium iodide solution. It was noticed that the deposit of calcium carbonate was much greater than that from the same volume of lime water when exposed for a similar time (p. 861). This indicates that the calcium carbonate precipitated from the bleaching powder solution is not entirely produced from the free lime contained in that solution, but also from the other calcium salts in solution; in short, the carbon dioxide from the air, after removing the free lime, reacts with the other calcium salts. This conclusion is supported by further observations. Another sample of bleaching powder solution (400 c.c.) was now exposed to the air, and the precipitated calcium carbonate filtered off each day. After each filtration 50 c.c. of the filtrate were made up to 500 c.c., and 10 c.c. titrated with *N*/10-sodium thiosulphate (after adding potassium iodide and acidifying) to give the following results:

(*a*). Original solution. 10 c.c. = 16·5 c.c. thiosulphate.
(*b*). After 1 day's exposure. ,, = 16·4 ,, ,,
(*c*). ,, 2 days' ,, ,, = 13·7 ,, ,,
(*d*). ,, 3 ,, ,, ,, = 2·6 ,, ,,

The solution was alkaline to litmus paper after two days' exposure, but after the third day the alkalinity could not be discerned. After two days' exposure the solution was greenish, but on the third day it became colourless, and decomposed rapidly, as shown by the figures.

The bleaching effects of the solutions *a*, *b*, *c*, and *d* were now compared. Water was added in each case to make 400 c.c. of solution of the same chlorine content, and a further solution (*e*) was obtained by adding 17 grams of pure calcium chloride to 400 c.c. of (*d*). Into each solution 15 grams of boiled linen were placed, and the solutions titrated at intervals as before to give the following results; 10 c.c. of solution = c.c. of thiosulphate.

	a.	*b.*	*c.*	*d.*	*e.*
Original	8·1	8·0	7·9	8·0	7·8
After ½ hour	7·4	7·2	6·9	6·5	6·2
,, 1 ,, ...	7·3	7·0	6·7	6·1	5·9
,, 2 hours	6·9	6·7	6·3		
,, 4 ,, ...	6·7	6·5	6·1		

It is noticed that the efficiency of the bleaching liquor is only slightly increased by an exposure of two days, but after the third day this increase is very marked. Thus in the case of (*d*) the bleaching was performed in one hour, whereas it took four hours to bring (*c*) to the same point; the colours of the linen samples after bleaching confirmed the results given, yet (*c*) contained little or no free lime. It is therefore evident that the increased efficiency is not so much due to the removal of the free lime as to the further effect of the carbon dioxide of the air on the solution after the free lime has been eliminated. The addition of calcium chloride to the solution after the removal of the free lime as represented by (*e*) is seen to have no measurable effect on the bleaching efficiency, although in this case it must be remembered that (*d*) also contains some calcium chloride in solution, which it has retained from the original bleaching powder solution. To ascertain the effect of adding common salt to the bleaching solutions, 30 grams were added to 400 c.c. of (*b*) and (*c*) to give samples (*f*) and (*g*). Titrations were made as before.

	f.	*g.*
Original solution.........................	7·6	7·6
After ½ hour	6·8	6·7
,, 2 hours	6·3	6·2
,, 4 ,, ...	6·0	5·7

Comparing these results with those obtained in the case of (*b*) and (*c*) it is seen that the addition of common salt to bleaching powder solution has only a very slight effect on the bleaching efficiency, even when the free lime has been removed from that solution.

The results recorded above clearly prove that there is no advantage to be gained by leaving bleaching powder solution exposed to air in order to get rid of the free lime, as suggested by Taylor (*loc. cit.*). In another case, where a larger volume of solution was exposed and consequently proportionally less surface was under the action of the carbon dioxide of the atmosphere, a week's exposure was required in order to separate the free lime. This practice of exposing powder solution was common at one time with bleachers because their liquors were thus made more active, but the results show that by the time the liquor is made very active it has also lost a large proportion of its chlorine.

The Effect of Neutral Sodium Salts on the Bleaching Efficiency of Sodium Hypochlorite.

It has been shown (Higgins, *loc. cit.*) that varying amounts of common salt have different effects on the bleaching efficiency of sodium hypochlorite. The effects of other neutral salts of sodium were tried, these salts being used in equivalent proportions. Solutions containing 50 grams of sodium chloride, 140 grams of crystallised sodium sulphate, and 73 grams of sodium nitrate per litre were prepared, and kept until of the same temperature. To 475 c.c. of each of these solutions and also of pure water, 25 c.c. of sodium hypochlorite solution were added, and into each solution 30·8 grams of boiled linen were placed, the solutions being tested periodically as before.

	Water.	NaCl.	Na_2SO_4.	$NaNO_3$.
Original	12·7	12·8	12·8	12·8
After 2 hours	7·9	7·1	6·9	7·3
,, 4 ,, ...	6·4	5·4	5·4	5·6

It is seen that, like common salt, other neutral salts of sodium have the effect of increasing the bleaching efficiency of sodium hypochlorite solution, and that this effect is approximately the same when equivalent proportions of the salts are used. In the above experiment the proportions of cloth, chlorine, and solution were not those used on the large scale, but were chosen to emphasise the effects of the salts.

Effect of Neutral Salts on the Bleaching Efficiency of Bleaching Powder Solution which has been Exposed to Air.

A quantity of strong bleaching powder solution was exposed to the air for four days, and the precipitate of calcium chloride filtered off. After the filtrate had remained for five days in the dark in a stoppered bottle it was used for the following experiments, which were performed to confirm previously formed conclusions.

Fifty c.c. of the solution were added to:

(*a*) 450 c.c. of water.

(*b*) 450 c.c. of the sodium chloride solution used in the previous experiment.

(*c*) 450 c.c. of calcium chloride solution containing 47·5 grams of the salt per litre.

The solutions of common salt and calcium chloride contained equivalent proportions of the two salts.

30·3 Grams of boiled linen were placed in these solutions, and titrations of 25 c.c. of the solutions were made as before.

	Water.	NaCl.	$CaCl_2$.
Original........	18·3	18·3	18·2
After 1 hour.................	11·8	11·2	11·2

It is noticed that equivalent amounts of calcium chloride and common salt cause approximately the same increase in the efficiency of the bleaching powder solution. Moreover, this increased efficiency is only slight under the prevailing conditions, which are somewhat similar to those used in bleaching cisterns on the large scale, and is similar to the effect produced in bleaching powder solution which has not been exposed to the action of the carbon dioxide in the air (compare Taylor, *loc. cit.*).

Considering the whole of these results, it would appear that the following equations represent the action of carbon dioxide, and therefore the action of air on bleaching powder solution:

(1) $Ca(OCl)_2 + H_2O + CO_2 = CaCO_3 + 2HOCl.$

(2) $2HOCl + CaCl_2 + CO_2 = CaCO_3 + H_2O + 2Cl_2.$

These equations explain all the facts. Thus Dreyfuss (*loc. cit.*) found that calcium chloride, carbon dioxide, and hypochlorous acid yield chlorine.

Williamson (*loc. cit.*) passed chlorine into water containing calcium carbonate in suspension, when the following reaction took place:

(3) $CaCO_3 + 2Cl_2 + H_2O = 2HOCl + CaCl_2 + CO_2.$

It is seen that equation (3) is the reverse of (2), so that we have a reversible action:

$$2HOCl + CaCl_2 + CO_2 \rightleftharpoons CaCO_3 + H_2O + 2Cl_2.$$

An excess of carbon dioxide causes the reaction to proceed from left to right, and produces pure chlorine; this is what Taylor observed on passing pure carbon dioxide through bleaching powder solution. When air containing carbon dioxide is passed through the bleaching powder solution some of the hypochlorous acid present in the solution and produced in equation (1) is swept out by the current of air, and some chlorine is produced according to equation (2). The current of air rapidly sweeps out the chlorine, and hence causes the reversible action shown to tend to proceed from left to right. On exposing bleaching powder solution to air, the carbon dioxide first precipitates the free lime and then produces hypochlorous acid and some chlorine according to the equations given. Hence a stream of air free from carbon dioxide on being led through the solution, sweeps out chlorine and hypochlorous acid. The presence of these substances accounts for the instability of the solution after exposure (p. 864). In the case of bleaching with hypochlorite solutions in ordinary air it is therefore evident that hypochlorous acid enters into the bleaching action, and as much nascent chlorine as can be produced by the equation given.

The reason that sodium chloride and calcium chloride do not assist the action of the bleaching powder to any great extent is because the carbon dioxide can only be supplied from the air at a slow rate, and this rate determines the rate of production of chlorine. In Taylor's case, where he had excess of calcium chloride and pure carbon dioxide, the chlorine would be produced at a greater rate because of the mass action:

$$2HOCl + CaCl_2 + CO_2 \rightleftharpoons CaCO_3 + 2Cl_2 + H_2O.$$

It has been shown (p. 861) that calcium chloride assists the attraction of carbon dioxide from the air by solutions containing lime; the addition of this salt therefore assists the bleaching action of bleaching powder solution according to the equation given.

In bleaching cisterns one notices that a large amount of calcium carbonate is produced during the bleaching process; this arises from the action of the carbon dioxide of the air on the free lime of the bleaching powder solution, and also according to equations (1) and (2).

The free chlorine liberated in reaction (2) is quickly used up in oxidising the colouring matters of the textile fabrics which are immersed in the solution, and this elimination of one constituent of the reversible reaction determines the direction of this action:

$$2HOCl + CaCl_2 + CO_2 = CaCO_3 + H_2O + 2Cl_2.$$