AIR PURIFICATION BY HYPOCHLOROUS ACID GAS

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(With 1 figure in the text)

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SYNOPSIS OF WORK UP TO 1939

THE employment of hypochlorites for purification of the air was tried out as early as 1918, when humidifiers in Lancashire cotton mills were dosed with hypochlorites during the influenza epidemic of that year. Since that date, the subject has been investigated by me from time to time and reports made to a Proprietary Company. Later, the subject was explored on more definite scientific lines.

With permission I reproduce a short report made to the Company concerned in January 1925:

For the purpose of the experiment a well-ventilated room was employed having the following dimensions:

Length	...	...	...	...	...	16 ft.
Breadth	...	...	...	...	...	15 ft.
Height	...	...	...	...	...	11 ft.
Cubic content	...	...	...	...	...	2640 ft.

This room was thoroughly sprayed with an aqueous mixture of 1% hypochlorite diluted to 1 in 80, for a period of 3 min., during which a total quantity of 1280 c.c. of the mixture was used. So far as possible the spray was evenly distributed over the room up to a height of 8 ft.

According to Petri the bacteria present in 10 l. of air are deposited on 100 sq. cm. of a gelatine plate in the course of 5 min. Following this method, I tested the air before and after the experiment by a series of Petri dishes, their contained growth medium being freely exposed to the air. After such exposure for a fixed period of 3 min. the plates were incubated

for 3 days and the colonies were counted. No distinction was made between pathogenic and other bacteria. The result was as follows:

Before spraying	...	...	...	...	627
After spraying (5 min.)	...	...	...	...	51
After spraying (30 min.)	...	...	...	...	90

A control was carried out under similar conditions, except for the use of distilled water instead of hypochlorite, giving the following results:

Average number of bacteria per sq. ft.

Before spraying	...	...	...	...	648
After spraying (5 min.)	...	...	...	...	1764
After spraying (30 min.)	...	...	...	...	525

The average bacterial content of the air was much the same in each case. Spraying resulted in the deposition of large quantities of bacteria, but whereas in the case of hypochlorite the greater portion were killed, in that of water only they survived to form fresh colonies. After the lapse of 30 min., whereas the air sprayed with water only had regained nearly its normal content of bacteria, the air sprayed with hypochlorite still retained a very reduced quantity (14.3%). These facts indicate clearly that spraying with 1% hypochlorite in a dilution of 1 in 80 has a marked effect on the disinfection of air, not only by mechanical deposition of the bacteria as in the case of sprays with water only, but by germicidal action, the effects of which remain for some time as shown by a reduced bacterial content.

It will be noticed that large quantities of very dilute hypochlorite (1 part of available chlorine in 8000) were used. The destruction of 81% of the bacteria 5 min. after spraying was noteworthy.

From then onwards the matter received constant investigation into the most suitable methods and into the reactions involved in the results which were attained. Evidence showed that there was a production of hypochlorous acid gas set free by the carbonic acid gas in the air, especially by the gas used for producing the spray. The major part of the disinfection, if not the whole, appears to be due to the hypochlorous acid gas.

It was found at an early stage that the method of atomization played a very important part in the results obtained and numerous attempts were made to devise a suitable form of atomizer, which would not only deliver a sufficient quantity of finely divided "spray", but would avoid trouble with corrosion of metals, splashing with large drops, etc. Difficulty was experienced with oil drops from the motor compression, which was finally overcome by the use of a diaphragm compressor. The amount of noise was also taken into consideration and reduced to a minimum.

In 1928 an experiment was published by Douglas, Hill and Smith¹ in which the air in a closed room was charged with *B. coli* and sprayed with sodium hypochlorite solution (1%). The authors found that considerable reductions in bacterial content were obtained, in some cases with indication of complete sterility. They made a cautious suggestion for the use of antiseptic sprays in crowded workrooms, offices and theatres.

¹ I am indebted to Prof. E. L. Collis for recently (1937) calling my attention to this work.

During 1930-5 the treatment of inhabited rooms was undertaken on an extensive scale. Details of some of this work and the results are given in *Journal of Industrial Hygiene* (Masterman, 1938).

Dilute solutions of 1-2 g./l. of available chlorine were employed and satisfactory results were obtained, with over 90% reduction in the bacterial content of the air.

In some instances atomizers were installed in office premises for daily use.

It was felt that, for further progress, especially for therapeutic application, it was necessary to obtain confirmation by medical authorities, more especially those qualified in bacteriology.

In a conjoint paper Tanner-Hewlett and J. Eyre (1935)¹ reported that "the original observations of Dr Masterman were confirmed".

The type of atomizer they employed has been fully described in my report (1938), and hypochlorite of various strengths was used. Table 1 condenses their results.

Table 1. *Available chlorine, g./l.*

No. of count ...	2	5	5	10	10
Hours after spraying					
0	31	21	12	39	73
1	9	7	8	3	3
2	5	7	8	1	1
3	6	4	2	0	0

They reported:

The filtration method confirms and perhaps still more strikingly demonstrates, the reduction in the number of aerial bacteria brought about by Hypochlorite sprays. In the first experiment 20 cu. ft. of air gave a count of 233 aerial bacteria. After 15 min. spraying with hypochlorite (10 g./l.) and sampling 30 min. later, the count was nil, i.e. a 100% reduction.

In the second experiment 20 cu. ft. of air yielded a count of 40 aerial bacteria, and after spraying with hypochlorite (5 g./l.) say, 5 germs remained alive, a reduction of 87%. After 1 hr. 100% reduction was obtained.

As regards pathogenic germs, experiments with cultures of *Streptococcus*, *B. coli* and *S. aureus* in a room of 1800 cu. ft. spraying with hypochlorite of 5 g./l. showed complete destruction in 4 hr. Masses of cultured bacteria, far greater than would ever occur naturally in the air, were submitted to the action of the spray, consequently the test was a severe one.

It is noteworthy that even with 10 g./l. hypochlorite the air was quite respirable, and there is no indication that free chlorine gas is present even in traces.

The conclusion seems to be definite that hypochlorite spraying does exert a germicidal or killing effect upon the aerial bacteria including, if they are present, disease germs.

Further research (Masterman, 1940*a*) was subsequently made on improvements in the atomizer, and these have been more than justified in the resulting efficiency of the spraying. The atomizer ("Dynalysor"), which was eventually adopted as standard, has a constant level automatic feed, diaphragm pump

¹ This report has not been published but was made at the request of a Proprietary Company under this condition. It is, however, accessible to technical and professional workers.

with no oil and delivers spray drops from 10μ radius downwards. Its operation for 3 or 4 min. gives results comparable with those for much longer periods in the older type.

The apparatus consists of a carrying case containing an electric motor *A*, to which is bolted a diaphragm-type air compressor *B*. Air from this compressor is led through a receiver *D* to a compound jet or atomizer *E*. This atomizer is carried by a container *G*, the floor of which carries the charge of liquid. Above this is suspended an inner chamber *H* which carries a pair of cones *F*, *F*, on the action of which the efficiency of the apparatus depends.

Fig. 1. Vertical section of Dynalysor.

The upward blast from the atomizer induces a strong current of air through the "Dynalysor" via the slot *K*, and is assisted in doing this by the centrifugal fan *C* mounted on the end of the motor shaft. This fan also delivers a strong blast of air through the opening *J*, whence it is deflected horizontally across the top *L* of the "Dynalysor" and so effectively distributes the vapour throughout the room.

Experiments with spraying fluid led to an early reduction in the salt content from 16.5 to 5% with consequent prevention of any perceptible mist and very little salt deposit.

Numerous tests have been made with this "Dynalysor", which has been in general service for many months.

In February 1939, Pulvertaft, Lemon & Walker gave a concise and popular résumé of the "Aerosol" theory followed by a description of their research on the production and testing of aerosols produced from various organic agents and from mercury chloride.

In November 1939, another report by Pulvertaft & Walker appeared, in which the subject of hypochlorites was discussed, and certain experiments were

described. Reference to these will be made later, but I may state here that the low results at first obtained for aerial disinfection have since been refuted by subsequent work of Pulvertaft.

In 1939, Pulvertaft (Westminster Hospital) with a somewhat similar type of atomizer carried out some tests. A summary of his results has been given by Masterman (1940*a*, p. 14). Pulvertaft found that "the maximum concentration (1% NaOCl) devoid of all inconvenience is 1 part in 10,000,000 parts of air. The effective concentration is less than 1 part in 40,000,000 parts of air."

More recently Spitta (St George's Hospital) carried out research on much the same lines and confirmed Pulvertaft's work. He also obtained sterility with a heavy culture of *M. catarrhalis* in 15 min. with a concentration of 1:8,500,000. This research was conducted in occupied and furnished rooms with the usual ventilation.

For many months the Dynalysor has been successfully employed for hypochlorite spraying in hospitals, offices and other inhabited rooms, and air purification by hypochlorites is not a scheme "with definite possibilities" but a successful *fait accompli* (Masterman, 1940*b*).

MORE RECENT WORK

Early last year Twort, Baker, Finn & Powell (1940) published a paper on disinfection by germicidal aerosols. Phenolic compounds and mixtures were mostly dealt with and hypochlorites were dismissed as of little value. In September 1940 a report, by Baker, Finn & Twort, on the application of hypochlorites to air purification appeared. I propose to deal with this report in some detail. From one aspect it may be regarded as an attempt to apply the "Aerosol" theory to aqueous solutions of hypochlorite.

(a) "Nebulizers"

The work of Baker, Finn & Twort (1940), later called the authors, was carried out by the use of two different types of "nebulizers", the "Atmozon" and the "Aerograph".

"Atmozon."

A diagram and short description of the "Atmozon" has been given by Twort *et al.* (1940, p. 294). It consists of a small metal container terminating in a conical bulb. Down the centre is a column which carries two suction jets. Compressed air passes down the centre of the column and emerges as a mist from the main cavity of the container. There are no data given as to the size of charge, the rate of vaporization, the pressure of intake air, compressor power, etc. There are no baffle plates and nothing to maintain constant liquid level.

The crude design of this apparatus would hardly promise satisfactory results, and "certain anomalies in the results soon became apparent" (p. 295). It was soon discovered that the fault was inherent in the method of atomiza-

tion and was due to the passage of considerable volumes of air through the nebulizer having a "distillation effect" on the water.

Baker, who is responsible for the section on "bacteriological aspects", insists that dried air must always be used with the "Atmozon" and that "the solution should be renewed before any appreciable concentration occurs". This, of course, makes the use of this apparatus prohibitive for practical purposes.

Without apparently any modification, this "Atmozon" has been used to obtain certain data on hypochlorites (Baker *et al.* 1940). They are so remarkable that they are quoted here:

Table 2. *Data extracted from the authors' tables giving results obtained by the "Atmozon"*

Table		Mist Conc. (7×10^8) ⁻¹	% survivors		
			5 min.	15 min.	30 min.
1 (a)	NaOCl (12)	$y=20$	105	100	71
		$y=13$	100	100	83
		$y=5$	100	75	60
1 (c)	NaOCl + CO ₂	$y=20$	103	60	77
		$y=13$	75	57	65
		$y=5$	75	79	100
1 (e)	NaOCl + HA	$y=12$	35	47	24
		$y=5$	107	113	168
4	NaCl	$y=10$	86	79	67
		$y=5$	108	100	97
6	NaOCl + 10% glycerol	$y=25.6$	110	89	77
		$y=13.3$	100	60	25
		$y=2.2$	62	17	0.4

The greatest reduction with NaOCl only is 40%, which requires a concentration of 1:5,000,000 and half an hour's contact. An equivalent result might easily be obtained with distilled water alone if an efficient nebulizer were employed.

The addition of weak acids to hypochlorites is known to set free HOCl and thereby increase germicidal activity, but this is not shown here. On the contrary, the addition of acetic acid, while improving the dilute solution ($y=12$) appears to destroy all germicidal action whatever in the stronger. There is a positive increase in the bacterial index up to the half-hour, by which time the percentage has risen to 168! The authors, with commendable reserve, describe this as a "No kill". In the case of NaCl solution, the stronger solution again has the lesser bacterial reduction, practically none at all.

Glycerol is known to decompose hypochlorite and rapidly reduce the strength of available chlorine, yet No. 6 (10% glycerol) gives by far the best results of the whole series—in fact the only germicidal results which can be regarded as of any practical value.

This machine tends to produce droplets of small size, and this is offered as an explanation of the anomalous results. In point of fact, the average size

(p. 561) runs about 0.5μ on either side to 0.2 and 1.7μ , closely coinciding with 0.4 – 1μ , which is given as the most efficient size for “aerosol” production! (p. 573).

These inconsistent and, in some instances, contradictory results obtained by the “Atmozon” lead to the inevitable conclusion that it is impossible to draw any correct conclusions from them. So far as hypochlorite is concerned, the “Atmozon” appears to be incapable of efficient nebulization.

It is stated that the mist concentrations calculated for this machine are “grossly in error” (and may be so by as much as 900 %), yet throughout the report the figures for the two types of nebulizer are contrasted as being due to difference in average size of the droplets only. If the results are accepted as “grossly in error” it is difficult to justify their use as typical of “small droplets”.

“*Aerograph.*”

There remain the results obtained by the use of the “Aerograph” nebulizer.

In the previous work Baker (Twort *et al.* 1940, p. 295) refers to this apparatus as an “Aerograph” air brush, A.E. Model. No details of this apparatus are given, but it is remarked that “a measured quantity of fluid can be put into the cup of the brush”, and the whole volume expelled by compressed air.

Apparently the atomization of a given quantity of fluid is effected so rapidly as to avoid any “distillation effect”.

The results obtained by this “Aerograph” are superior to those of the Atmozon in consistency and in quality. They present a rational sequence which can possibly be employed for drawing certain inferences *inter se*. The figures for effective mist concentration, however, compare very unfavourably with those obtained by other nebulizers such as the “Dynalysor.”

As an approximation one can say that the “Aerograph” will give a reduction of 99% in bacterial content in 15 min. in a concentration (nominal) of 1 : 5,000,000. This result is obtained in a small and closed empty air space with still air.

This may be compared with the results from another type of nebulizer given in table form (Masterman, 1940*a*, p. 14). Here a reduction of 99.75% up to 99.9% was obtained in concentration from 1 : 40,000,000 to 1 : 10,000,000. These experiments were conducted, under practical working conditions, in an ordinary furnished room of 1600 cu. ft. with doors and windows and with occupants.

Even an early form of nebulizer (long since discarded) which was used in my (1938) experiments in inhabited rooms from 1930 to 1935 gave over 90% reduction of bacteria with 1 : 27,000,000, and when ordinary hand sprays were used the same degree was attained with a concentration of 1 : 16,000,000.

It is evident that the “Aerograph” is incapable of developing even an approximation to the full germicidal possibilities of hypochlorites.

(b) Review of results with "Aerograph"

For a general survey I have drawn up Table 3. This gives the authors' figures in each case for a concentration of one part by weight of fluid in 5,000,000 parts of air volume (designated as $y=5$). At this strength the bracket is usually obtained showing the minimum lethal dose.

Table 3. *Percentage of survivors*

Ref. no. in following comments	Reference to authors' tables	Spray fluid	Time of exposure		
			5 min.	15 min.	30 min.
1	(1)(c)	NaOCl (1 %)	4.8	0.1	0
2	(1)(d)	NaOCl + (CO ₂ (1 %))	0.4	0	0
3	(1)(f)	NaOCl + HA	0	0	0
4	(2)	HOCl in solution	3.1	2	7
5	(2a)	HOCl (gas)	1.8	0.9	0
6	(7)	NaOCl (free from CO ₂)	2.5	0.37	0
7	(5)	NaOCl + NaOH	70	47	21
8	(6)	NaOCl + (10 % glycerol)	50	36	20
9	(4)	NaCl only	100	38	27
10	(3)	Chlorine gas	66	45	43

(1) NaOCl (1 %).

A concentration of 1 in 5,000,000 (w/v) is shown to give from 95.2 to 100 % bacterial reduction according to time of contact (5 min. to $\frac{1}{2}$ hr.). It should be pointed out that a result of a similar test of NaOCl (1 %) is given in Table 9:

		5 min.	15 min.	30 min.
Table 1: (c)	$y=5$	4.8	0.1	0
Table 9:	$y=5$	14.8	11.1	4.6

The margin of difference here greatly exceeds that between the various data shown in the first six given in Table 3. This casts considerable doubt on the validity of any conclusion based on comparisons made between the different items of Table 3.

(2) and (3). The addition of weak acids.

CO₂ gas up to 1 % by volume was introduced into the sealed chamber and the experiment repeated as in (1). Results show a very substantial and marked increase of germicidal potency. In 5 min. there was obtained 99.6 % reduction and thereafter complete sterility. The authors agree that the result "seems to be beneficial"!

On the addition of acetic acid to the solution, complete sterility was obtained in 5 min. and onwards. The minimum lethal dose was therefore not reached, but sterility was also obtained with 1 : 13,000,000 dilution.

Both these acids are known to set free HOCl when added to hypochlorites, and I have already shown (Masterman, 1938, p. 280) that the action of acetic acid is complete without any loss through formation of chlorate.

The part taken by the carbonic acid added to the air is specially marked, and the inference, from the figures as they stand, is fully justified not only that

hypochlorous acid gas is the "lethal agent" but that CO_2 gas plays an important role in its production.

(4) and (5). HOCl gas.

The three experiments recorded in the authors' Tables 2, 2*a* and 2*b* were designed to elicit the part, if any, played by HOCl gas in hypochlorite spraying.

In Table 2 an attempt is made to charge the chambers with HOCl gas by spraying with HOCl solution.

Although the "Aerograph" delivers "large" droplets of mist, the assumption is made that all the mist is evaporated before bacterial contact, leaving only HOCl gas. This is, of course, totally incompatible with the "Aerosol" theory, and does not agree with the later statement (p. 574) that CaCl_2 present "caused retention of some HOCl in the mist". The readings do not differ materially from those for NaOCl (Table 1(c)).

In 2*a*, the HOCl gas is generated by passing CO_2 gas through NaOCl solution and thence into the chambers. The figures show a considerable improvement over those for NaOCl with a mean of 0.9 against 1.63. They also show a much better result (2*a*) when HOCl is introduced in the gaseous form rather than in solution (2). Even so, it is certain that the concentration of the HOCl has been grossly overestimated.

This has been determined by the difference in titrations for available chlorine of the NaOCl solution in the nebulizer before and after passage of CO_2 . There are here at least three serious sources of error:

(a) The germicidal mist carried over is intentionally trapped before entering the chamber.

(b) The method of HOCl gas production by passage of CO_2 gas under no circumstances can deliver its equimolecular quantity of HOCl .

I have already given (Masterman, 1938) tabular details of the different conditions under which NaOCl decomposes into HOCl and NaClO_3 respectively. The proportions are seen to vary according to conditions from 100% NaClO_3 to 100% HOCl . The following experiments throw further light upon this subject.

100 c.c. of 1% hypochlorite were treated with CO_2 gas, passed through it with a diffuser at ordinary laboratory temperature. Analysis before and after the experiment gave the following results:

	Before experiment	After experiment	Diff.
	g.	g.	g.
NaOCl	1.19	0.80	-0.39
NaO_3Cl	0.128	0.245	+0.117

There was a loss of hypochlorite of 0.39 g., whilst the chlorate had increased by 0.117 g. The amount of hypochlorite consumed in formation of this is 0.245 g. The amount available for production of HOCl gas is therefore 0.145 g.

or roughly about 37%. The gases were led through sodium arsenite which absorbed the equivalent of 0.114 g.

Another experiment on similar lines but with different strengths of hypochlorite and salt gave the following result:

	Before experiment g.	After experiment g.	Diff. g.
Available Cl	1.433	0.675	-0.77
NaO ₃ Cl	0.96	1.19	+0.23

0.23 g. of chlorate represents 0.46 g. of available chlorine, and this remains in solution. The balance is 0.298 g. of available chlorine or 39.3%.

These results appear to indicate a reaction somewhat as follows:

in which 40% of the available chlorine is set free as HOCl.

It is clear that on this count alone the concentrations of HOCl present in Table 2a are overestimated to the extent of 5 : 2. The real concentration should be $y = 11.5$.

(c) In their technique the authors do not appear to have made themselves sufficiently acquainted with the properties of HOCl, especially in the gaseous state. In some ways this gas is even more reactive to decomposition by contact with metals or organic materials than ozone. But we find them presumably using metal nebulizers, experimental chambers lined with sheet lead and furnished with other metal parts, and rubber bungs. They also employ wool filters (Twort *et al.* 1940). Losses of HOCl gas under these conditions must be high.

On these grounds the indications are that the effective concentrations of HOCl were many times lower than those estimated.

This test (2a) appears to be of remarkable significance. The above errors justify the assumption that the figure of 4.6 should in reality be nearer 12, and may be compared with the series ($y = 13$) in Table 1(c). For example, we have:

		y	5 min.	15 min.	30 min.	Mean
1(c)	NaOCl	13	20	3.2	1.8	8.2
1(d)	NaOCl + CO ₂	13	13	7.3	8.7	9.7
1(f)	NaOCl + HA	13	7.1	4.5	0	3.9
2(a)	HOCl gas	12	1.8	0.9	0	0.9

According to these figures, it is evident that the results for HOCl gas indicate the highest germicidal power of any shown by the authors.

This experiment was particularly designed to ensure that there was no mist whatever in the chambers. "There was no possibility of germicidal mist entering the chamber" (p. 564). The result was therefore obtained solely by the action of hypochlorous acid gas, and there can be no question of an aerosol.

(6) NaOCl in CO₂-free air.

It is known that, at normal pressure and temperature, CO₂ gas reacts with NaOCl in aqueous solution, setting free HOCl as one product. The intensity of such reaction will be determined by (a) the surface of contact and (b) the time of contact.

In atomizing into and by means of the ordinary atmosphere, its contained CO₂ has two opportunities for reaction: (1) in the air used for atomizing and spraying (spray CO₂), and (2) in the air space of the experiment (space CO₂).

If the process of atomizing be (a) prolonged, (b) under high pressure or (c) carried out with very fine jets, then the spray CO₂ will have a maximum effect.

If the droplets are (a) small, (b) numerous and (c) long-lived and (d) the concentration of the CO₂ high, the space CO₂ will have its maximum effect.

In the experiment with NaOCl (Table 3, 1(c)) with the "Aerograph", the space CO₂ must have its normal operation, but it is probable that the low result compared with other atomizers may be largely due to a restricted operation of spray CO₂. The "Aerograph" was selected, we are told (Twort *et al.* 1940, p. 295), because its rapidity of action eliminated or greatly reduced the "distillation effect", or loss of water due to evaporation. A similar restriction, and for the same reason, should operate on the contact action of the spray CO₂.

In this view the result with NaOCl (1(c)) includes the production of HOCl by space CO₂ only, the spray CO₂ being inhibited by the rapid atomization. This production is considerably enhanced by the artificial increase in the space CO₂ (1(d)).

When the CO₂ is apparently excluded (Table 7) the effect only differs slightly from that of NaOCl by the loss of space CO₂, the spray CO₂ being inhibited in both cases.

On the other hand, with an efficient atomizer both stages of CO₂ absorption can come into full operation, and the efficiency is very considerably increased. These facts may be illustrated in tabular form.

Table 4. *Active agents producing HOCl*

		Hydrolysis	Spray CO ₂	Space CO ₂
(1)	NaOCl ("Dyna lysor")	+	+	+
(2)	NaOCl + CO ₂ ("Aerograph")	+	-	++
(3)	NaOCl ("Aerograph")	+	-	+
(4)	NaOCl - CO ₂ ("Aerograph")	+	-	-

Finally, in order to put the matter to a practical test,¹ the following experiment was carried out:

Experiment to determine effect of using (1) air and (2) CO₂ in "Dyna lysor"

Emulsion of *B. prodigiosus* in 0.9% saline. 20 c.c. sprayed into air by hand spray.

Capacity of room: 950 cu. ft.

Concentration: (1) 50 × 10⁶ per cu. ft. (2) 200 × 10⁶ per cu. ft.

¹ I am indebted to Mr E. A. R. Bousfield, B.Sc., A.I.C., for carrying out this experiment.

"Dynalysor" operated for 2 min., spraying 2 c.c. of 1% NaOCl.
Concentration (*w/v*) = approximately 1 : 13,500,000.

	No. of colonies (24 hr.)			
	(1) Air spray		(2) CO ₂ spray	
Before spraying	5278	(100)	18,300	(100)
After spraying:				
5 min.	42	(0.7)	344	(0.18)
25 min.	8	(0.14)	38	(0.02)
45 min.	18	(0.3)	6	(0.003)
Mean		(0.38)		(0.068)

It is seen that when CO₂ gas was used for spraying the hypochlorite, there was a great increase in the germicidal efficiency though a much greater concentration of bacteria was present. The experiment confirms our previous experience that the spray CO₂ increases the efficiency by setting free HOCl. The same phenomenon has been shown for the space CO₂ from the authors' own figures (Table 1(*d*)).

The authors claim to have "finally established" that CO₂ gas plays little part in hypochlorite disinfection, although this gas is present in the spray and in the air and is known to decompose NaOCl on contact. As a matter of fact they rely upon this reaction taking place at every turn in the interpretation of their results.

The following quotations illustrate this point:

p. 565: "...until some HOCl is liberated by CO₂ absorbed from the air...."

p. 571: "...the older the mist, the greater the proportion of HOCl gas liberated and available...."

p. 574: "...the former having a proportionately smaller surface area available for the absorption of CO₂...."

p. 574: "...the rate of absorption of CO₂ by the droplets is slow compared with their rate of loss of water...."

(7) *Addition of NaOH.*

The addition of NaOH has an obvious result of greatly reducing the lethal effect.

On the assumption that HOCl is the main lethal agent, the presence of the NaOH, counteracting the hydrolysis of the hypochlorite and screening it from the chemical action of the CO₂, would be expected to give this result.

On the other hand, the presence of the alkali should not materially inhibit the germicidal action of NaOCl. The result here obtained seems to point to the very small part which NaOCl in solution (as aerosol) plays in air sterilization.

NaOCl (1%) has been shown to contain approximately 18% of HOCl, and under the conditions of air spraying one can only rely on the CO₂ reaction to increase this quantity.

(8) *Addition of 10% glycerol.*

The use of glycerol is much favoured by adherents of the "Aerosol" theory, owing to its hygroscopic properties with a consequent delay in evaporation of

the droplets. Pulvertaft *et al.* (1939) were inclined to the view that great increase in the germicidal index was obtained by this means. He has since obtained results with far less concentrations of hypochlorite, but without glycerine. Pulvertaft & Walker (1939) added sulphonated oleic acid to hypochlorite as a "surface tension producer", but found that it also "greatly reduced the efficiency of a hypochlorite preparation".

The authors' Table 6, quoted in Table 3, shows that the use of glycerol entails a great inhibition of lethal properties, bringing the NaOCl solution down to the level (approximately) of NaCl and of alkalinized NaOCl.

In retarding evaporation, the glycerol would also retard the liberation of HOCl gas. Any effect it may be expected to have in prolonging the life of the droplets is certainly not reflected in these figures.

Both glycerol and lissapol are incompatible with hypochlorites, and it appears that some other non-reactive agent is required to adapt hypochlorites for aerosol production.

(9) NaCl solution.

On these experiments the authors remark: "The sodium chloride experiments can be disregarded because the salt in the hypochlorite solution is of no practical value as a germicide in comparison with the other constituents."

In point of fact NaCl in solution has a considerable lethal and inhibitory action on bacteria. A comparison of the figures in Table 3 shows that though slightly slower in action, NaCl is superior to chlorine gas, and is quite comparable with alkalinized NaOCl and with NaOCl containing 10% of glycerol.

(10) Chlorine gas.

Confirmation is made of the well-known fact that chlorine gas as an air germicide is not to be compared in potency with HOCl.

It may be remarked that the suggestion is put forward by the authors (p. 575 and 581) that "nascent chlorine" gas is set free in hypochlorite spraying and forms an objection to the process. No shade of evidence for this view has ever been provided.

(c) *Stability of hypochlorite solution*

The facts described in this section are already well known. The subject was dealt with in 1938 in my report, where the conditions under which sodium hypochlorite decomposes and its method of decomposition are set out in some detail. As already pointed out, the authors were apparently unaware that there is a reaction of glycerol with hypochlorites, and that in decomposition of hypochlorites an important but varying amount is not set free as HOCl but produces NaClO₃ which is not reactive as available chlorine, a point dealt with above.

(d) Effect of concentration of NaOCl and NaCl

In experiments on the effect of dilute hypochlorite solutions the authors find an optimum in lethal effect at a strength of about 2 g./l.

They appear not to have observed that the majority of my bulk experiments (Masterman, 1938, Table 2), besides the preceding ones, were conducted with 2 g./l. dilution or a one-fifth dilution of the 1% hypochlorite. It had already been found that the action of hypochlorite is greatly enhanced by the addition of water. The proprietary solution of 1% hypochlorite gives the following effect by hydrolysis:

Hydrolysis of hypochlorite

100 c.c. of NaOCl (1% available chlorine)

Dilutions	Available chlorine as HOCl (g.) Increasing kill	Concentration of available chlorine* as HOCl (g./l.) Decreasing kill
0	0.17	1.7
50	0.25	1.25
75	0.34	0.85
90	0.48	0.48

* Strictly speaking, the effective concentration will be HOCl/water vapour.

If we accept the view that HOCl is the main lethal agent, then as dilution proceeds the increasing quantities will give an increased "kill". At the same time, the actual concentration of HOCl will decrease and give a decreased kill. If these two columns be plotted against the dilutions, the combined curve will give an optimum germicidal effect at their intersection, from which the two curves will diverge in opposite directions to lower germicidal levels. In other words, the curve will closely resemble that given by the authors in Fig. 3.

Such a result tends to confirm the predominant part played by HOCl in the germicidal function. This appears to be a more rational explanation than an appeal to the size of the droplets.

Where the experiment was repeated by the authors with NaCl only, it was found that no such optimum was obtained. As the size of the droplets should be determined by the concentration of NaCl in the same way as that of NaOCl it appears that the size of droplet cannot be the determining cause of the phenomenon.

(e) Persistence of hypochlorite mists

In the figures obtained under this section the authors (p. 571) find discrepancies with their previous results and indicate some possible sources of error. To these I might venture to add the reactivity of HOCl gas to contact, prolonged as it is, with metallic lead. The older the mist the greater the loss of HOCl due to this factor.

If the "falling off" in efficiency of the mists is, however, accepted, the most

obvious explanation in the case of 1 % NaOCl is the "settling out" of its heavy and large particles.

The HOCl in a sodium hypochlorite solution does not "evaporate" so long as the hypochlorite is protected from the action of CO₂.

(f) *Discussion*

(a) *Hypochlorous acid as the germicidal agent.*

This review has necessarily been very brief, but I am of the opinion that it is sufficient to show that all those phenomena described, which are obviously not the result of deficient technique, can be simply and effectively interpreted by an appeal to the known chemical and physical reactions of HOCl.

It has been possible to show, from the available figures, that:

(1) The highest germicidal efficiency was obtained by the use of HOCl gas.
(2) The next highest were obtained when the addition of water or of weak acids had increased the quantity of HOCl, acetic acid and carbonic acid falling in their right order as expected from their chemical reactions.

(3) The least efficient were cases in which glycerine or NaOH was added to the hypochlorite. The former decomposes HOCl and the latter inhibits its liberation.

Since my initial employment of hypochlorites for air purification, a considerable body of research work on their method of action has been carried out. This pointed to the conclusion that the lethal agent concerned was hypochlorous acid (HOCl) and that the sodium hypochlorite played only a subsidiary part other than acting as a source of supply of the more active hypochlorous acid (see Masterman, 1940).

The authors are led to the same conclusion, viz., "hypochlorous acid in solution and not the molecularly dispersed gas was the form in which the germicide being considered was lethal" (p. 574) and "It would appear that the most effective agent is hypochlorous acid in solution or nascent chlorine resulting therefrom" (p. 575).

This conclusion was reached in spite of the statement that there "is strong support for the conclusion that it is the hypochlorite in the mist-form which acts upon the suspended bacteria" (p. 573). Figures are quoted to show that HOCl in solution is not nearly so lethal as NaOCl (e.g. Table 10 (1) and (2)). Either the conclusions of the authors or their working results are incorrect, and I have given evidence to show that the latter is probably the case.

(b) *The function of hypochlorous acid gas.*

HOCl has, of course, only been isolated in the gaseous state though readily soluble in water. The question arises as to how far, if at all, HOCl gas as such takes part in the germicidal process.

On this point the authors remark: "The claim that NaOCl sprayed into the

air is bactericidal by virtue of the HOCl liberated has not been substantiated by the two nebulization methods we have employed."

In Table 1(c) and 2 and 2(a) we have the following figures for ($y=5$):

				Mean
NaOCl (1%)	4.8	0.1	0	1.62
HOCl in solution	3.1	2	7	4.03
HOCl (gas)	1.8	0.9	0	0.9

The only possible inference, if the results are reliable, is that HOCl in gaseous form is the most potent germicide at the dilution named.

In addition, I have already pointed out there is reason to believe that in these experiments the effective concentrations of HOCl gas have been grossly overestimated.

The authors themselves remark that in "tests in which no mists were utilized it will be seen that hypochlorous acid gas is effective, and rapidly so when in sufficient concentration. The mechanism of its rapid action appears to be due to its high rate of absorption by the moist bacteria" (p. 574).

They are at some pains to show that dry HOCl in contact with dry bacteria has very little lethal action and suggest that by this means they are combating some claim put forward to this effect. It would have clarified the position had they given the reference to such a claim, which is contrary to all experience of hypochlorites and even of chlorine gas.

In comparing the relative potency of NaOCl mists and HOCl vapour they state (p. 574) "the hypochlorite mist equivalent to $(100 \times 10^6)^{-1}$ of 1% NaOCl, obtained for the proprietary product diluted 5 times with water, allowed of only 0.92 per cent survivors". This result was obtained (p. 569) "over the half-hour period".

It is claimed to be equivalent to that of the HOCl gas in Table 2a with a concentration of $(4.6 \times 10^6)^{-1}$ though in point of fact this concentration "over the half-hour period" gave complete sterility, the "equivalent" figure being in half the time period, viz. 15 min. The 15 min. figure for the NaOCl solution is not given. The deduction made as to relative germicidal value of NaOCl and HOCl gas in vapour is therefore based on an error.

As regards the germicidal potency of HOCl gas it may be added here that, as a bacterial reduction of 99.75% can be obtained with a concentration of 1:40,000,000, of 1% NaOCl, the concentration *w/v* of the active agent, NaOCl, is 1:4,000,000,000. Assuming that all the NaOCl is decomposed, this represents a maximum concentration of HOCl gas to air, volume to volume, of 1 part in 3500 millions. This is by the CO_2 reaction and, as confirmed by the authors, still greater effective dilution can be obtained by hydrolysis.

(c) "*Aerosol*" theory.

The attempted explanation of the authors' results by the "Aerosol" theory, however ingenious, is not convincing.

An appeal is made as required, to size of droplet, rate of evaporation, rate of "settling out", mobility, for each case as it arises, leading, in general, to conflict of conclusions.

As one instance, the authors produce HOCl "gas" by spraying the solution and assuming that the mist is completely evaporated, though the droplets are of the large type. As the experiment is designed to determine the relative germicidal merits of HOCl gas and HOCl solution, some definite proof seems required that the solution was completely vaporized. As a matter of fact it is stated (p. 574) that "CaCl₂ present caused retention of some HOCl in the mist". Other phenomena are "explained" by the greater evaporation rate of the smaller droplets giving no time for formation of HOCl.

Compare also: "We were not altogether convinced that all the HOCl present was in the gaseous form (a small quantity of CaCl₂ was also present)."

In spraying with hypochlorites, it is naturally suggested to interpret the results in the light of Bechhold and Trillat's "Aerosol" theory. In other words, does the sprayed hypochlorite act germicidally by contact between particulate droplets of a suitable size and the suspended bacteria?

A very strong case has been made out that this is so for many organic compounds. If one attempts to apply the reasoning employed in the case of, e.g., phenolic compounds to that of inorganic solutions of hypochlorites greatly diluted with water, a series of new conditions arises.

A successful "Aerosol" requires extremely minute droplets which must be sufficiently long-lived to conduct an effective contact with the bacteria.

It has been stated definitely by Twort *et al.* (1940) that "to give the best results, the size of mist droplets of the 1% sodium hypochlorite solution should be from 0.4 to 1 μ radius".

Whytlaw-Gray & Patterson (1932, p. 176) have calculated that "in an unsaturated and still atmosphere a water-drop of radius 1 mm. will take about 11 min. to evaporate completely at 18°, but that if the radius is $\frac{1}{100}$ mm. its duration will hardly exceed 0.06 sec."

In this proportion a drop of 1 μ in radius would have a life of 0.0006 sec. Doubtless a 1% sodium hypochlorite solution (say 94% water) would have a much longer life than this, but even if it be multiplied by 10³ it is evident that the droplet would have little enough length of life to carry out its work.

In the practical conditions of rooms with natural draughts and other means of keeping the air in motion, a further shortening of life must take place, and reflect itself in reduced germicidal efficiency.

Pulvertaft & Walker (1939, p. 698) specially note the markedly beneficial results of a fan in, it is assumed, assisting contact between the bacteria and the aerosol droplets, but this was in respect of a mixture of glycol and resorcinol (52%), and water.

The effect of a fan in promoting evaporation of droplets of over 90% water and no hygroscopic ingredient can easily be conjectured.

Imbued with the "Aerosol" theory, Pulvertaft, and Baker *et al.* have recognized the necessity for prolonging the life of hypochlorite droplets by adding some hygroscopic agent, such as glycerol, with very mixed results—partly due to the incompatibility of the ingredients.

Whytlaw-Gray & Patterson (1932, p. 177) found that "with aqueous solutions of glycerine...the water evaporated so rapidly that no quantitative results could be obtained".

Further light could be obtained by an actual determination of the droplet life of 1% hypochlorite. Meanwhile, its duration is under suspicion of being so short as to preclude the formation of a functional aerosol.

Failing more concise and detailed information, I have carried out the following experiment:

The "Dynalysor" was put into operation and plates carrying a film of moist potassium iodide and starch were placed in a horizontal position in the path of the ascending mist. They were each exposed for a period of 5 min., during which the droplets were collected on the film and produced dark disks. These disks were, probably through flattening, of slightly larger radius than the droplets.

At a distance of 2 in. from the outlet, the droplets were of different sizes, but none exceeded 10μ in radius.

At 4 and 6 in. the droplets showed a progressive decrease in numbers and in size, whilst the whole surface of the film became evenly tinted.

At 20 in. there was no trace of any droplets under magnifications which were capable of recognizing those exceeding 0.1μ in radius.

Nothing remained but an even dark tint over the whole film, caused by the action of the gas.

This experiment may well be repeated with closer checking, capable of giving quantitative results, but the inference appears to be that at a distance of less than 2 ft. from the outlet of the "Dynalysor", all droplets had evaporated leaving behind only gas (HOCl) and solid nuclei, both of which were then distributed throughout the room.

PRACTICAL APPLICATION OF HYPOCHLORITES FOR AIR PURIFICATION

The conclusion of the authors, based on their investigations, is "That there are definite possibilities for the use of hypochlorite mists for combating aerial infections".

Although a large amount of research has already been done on this subject by medical and bacteriological authorities, confirming and extending my previous work, and although the completed apparatus and process have been in successful operation in hospitals, offices, and other inhabited rooms for many months, it is always welcome to receive confirmation from others working

later in the same field, even if such confirmation is qualified as in the present instance.

By way of such qualification they proceed to add: "...but that the odour, irritant effects, opacity of the mist and corrosion of metals, etc., will limit the sphere of 'utility'."

This definite statement made about a process in daily commercial operation should, of course, be based upon definite evidence. On reference to the report it is found that the mere opinions and impressions of the authors, stated as probabilities and possibilities, have later been converted into "conclusions". These opinions are based upon their own work conducted with their own nebulizers which have been shown to require enormously stronger concentrations of antiseptic to obtain the required germicidal results. On their own statement they require a concentration of a 1% solution of sodium hypochlorite $(1 \times 10^6)^{-1}$ or 1 : 1,000,000. No proposal has ever been made—apart from the authors—that such a strength as 1 : 1,000,000 should be used for air purification.

My early results with an atomizer, which has been abandoned in favour of an improved model, required a concentration of 1 : 27,000,000. The operation of the "Dynalysor" requires a standard concentration of 1 : 40,000,000 to 1 : 50,000,000.

Pulvertaft¹ remarks:

the maximum concentration of mist tested was obtained by running the nebulizer for 5 min. in a room of 1200 cu. ft. capacity, i.e. 10 c.c. of antiseptic to this volume of air (1 : 3,000,000)... the smell was definite but quite tolerable and completely non-irritant. Concentration of $\frac{1}{10}$ th, $\frac{1}{5}$ th and $\frac{2}{3}$ th of this were tested. (1 : 40,000,000; 1 : 20,000,000 and 1 : 10,000,000.)

These produced no visible mist and in each case a slight odour only, completely non-irritant, and, as a personal observation, rather pleasant. In my opinion, there is no possible menace to the health or convenience of anyone submitted to the mist in efficient concentration.

As regards irritant properties, it may be added that for many years the general public have been using hand sprays for the nose and throat in many thousands with a recommended dilution of 1 : 200. No trouble or inconvenience has been reported, except for one or two idiosyncratics. It is to be borne in mind that hypochlorite in contact with organic tissue acts in the majority of cases as an oxidizing agent and rapidly disintegrates into NaCl and oxygen. In others, it may act as a chlorinating agent with a residue of water (Masterman, 1939). In either case there is no danger of an accumulative effect, such as is a marked feature of some organic compounds.

Apart from the very small concentrations of spray fluid which are found to be effective, as regards opacity of the mist due to evaporated salt it is to be repeated that the spray solution in use has approximately one-third of the salt content found in the standard proprietary product used by the authors.

¹ See footnote, p. 46.

As regards corrosion of metals it is true that damp salt, not the hypochlorite, tends to promote rust on cast iron and affects certain other metals by tarnishing. Bronze and brass are unaffected. In a dose of 1 : 40,000,000 sprayed into a room of 2000 cu. ft. of a height of, say, 10 ft., there would eventually be deposited 0.002 mg. of salt in each square inch of floor space!

The authors raise another "contingency for serious consideration" in "the bleaching and rotting effects of the free chlorine". No proof whatever is offered that "free chlorine" is produced from the hypochlorite. It is well known that this can only be the case when "strong" acids are used (e.g. HCl) and the H—O—Cl linkage is disrupted.

The whole system of hypochlorite air disinfection, as now in operation, is based upon the fact that HOCl gas is released into the air, and that this gas differs fundamentally from "chlorine" in odour and in irritant and corrosive effects.

Lastly (Masterman, 1940) this system of air purification has been tried out during 1930–5 in extended experiments under the practical conditions of inhabited and furnished rooms, without experiencing any of the "objections" raised by the authors. The same applies to the practical and rapidly extending use up to the present date.

SUMMARY

1. A short synopsis of research upon application of hypochlorites to air-purification is given.

2. A short review of the most recent work on this subject shows that:

(a) Of the "nebulizers" employed by Baker, Finn & Twort (1940) the "Atmozon" is incapable of consistent atomizing of hypochlorites, whilst the "Aerograph" has an efficiency much below that of modern atomizers.

(b) The data obtained by them, after due allowance for defective technique, can be interpreted as fully confirming the view that HOCl gas is the active germicide in hypochlorite spraying. Sterility can be approximately attained (99.75% reduction) by HOCl gas with a volumetric concentration in air, of not more than $(3.5 \times 10^9)^{-1}$.

(c) The application of the "Aerosol" theory is discussed and reasons given for its non-applicability to hypochlorite spraying.

(d) Alleged drawbacks to this practical application of hypochlorite air disinfection are discussed and shown to be of no practical importance.

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ERRATUM

p. 54, line 8: *for* the experiment (spray CO₂)
read the experiment (space CO₂).