SODIUM CHLORITE

PROPERTIES AND REACTIONS

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Sodium chlorite, a new commercial chemical, is now being used for bleaching textiles and paper pulp. It is a moderately strong oxidizing agent whose use does not introduce the possibility of heavy metal contamination. The solid sodium chlorite is stable and very soluble. Its solutions are stable in the presence of a trace of alkalinity if light is excluded. They decompose but slowly if boiled. In the storage and handling of chlorite many of the same precautions should be observed as with hypochlorite and chlorate.

The oxidizing properties of chlorite are accentuated in acid solution. Such solutions are employed in bleaching. When acidified in the absence of oxidizable material, chlorite yields mainly chlorine dioxide and chlorate but not chlorine.

Chlorite reacts with hypochlorite. In alkaline solutions chlorate is produced. As the alkalinity is reduced, some chlorine dioxide is formed. This reaction with hypochlorite can be used to bleach cellulosic materials. In more acid solution the proportionate formation of chlorine dioxide is increased. The addition of chlorine to chlorite solution produces chlorine dioxide efficiently so that it can serve as a practical source for this useful gas.

CHLORITE was first identified by Millon (*23*) 100 years ago. He obtained it by alkaline absorption of the greenish-yellow gas formed by the partial reduction of chlorate. Millon believed this gas contained chlorine trioxide of formula Cl_2O_3. However, Millon's formulation was not generally accepted, and in 1881 Garzarolli-Thurnlackh (*8*) showed that the gas which had become known as Millon's gas was really a mixture of chlorine dioxide and chlorine. The chlorite resulted from the hydrolysis of chlorine dioxide and gave an equimolar mixture of chlorite and chlorate. In chemical literature (compare Gmelin and Mellor, *9*, *22*), references to chlorite are few in number and desultory prior to about 1915, when Bruni and Levi (*3*) started an investigation which has been carried on by Levi up to the present time. This work includes descriptions of various metallic salts of chlorite, laboratory methods for their preparation, and a few of their characteristic reactions. Little information is given of practical importance as to the commercial usefulness of chlorite.

The work of the present authors and their associates started about 1927 and has been concerned with the production and use of chlorite. This work has resulted in the commercial use of sodium chlorite for bleaching kraft and other types of paper pulp to a high white without loss of strength. Sodium chlorite is also finding application in textile mills in connection with the bleaching and finishing of cotton fabrics. This summary has been prepared in the belief that this new commercial chemical, sodium chlorite, is of interest to many chemists. It covers that part of the work which concerns the general application of chlorite in industry.

The property of chlorite which forms the basis of the more important uses so far developed is its oxidizing power. In cold alkaline solutions it has only a mild oxidizing action. Heating or acidification or both develop in chlorite solutions a strong oxidizing condition even at temperatures only slightly above normal and at pH values of 3 to 5 under which conditions most materials requiring bleaching resist deleterious attack.

Some preliminary determinations of oxidation potential have been made. The values were obtained for 1/142 *M* sodium chlorite solutions (1 gram per liter of available chlorine) and are referred to the normal hydrogen electrode. The oxidation potential of sodium chlorite was found to be 0.79 volt at pH 4 and 0.66 volt at pH 9. Levi (*16*) gives a value of 0.70 volt which indicates that his solution was very slightly alkaline.

It is of interest to compare these values with those for the oxidizing potential of sodium hypochlorite at the same concentration of available chlorine which are 1.2 to 0.95 volt through its normal bleaching range of pH 7 to 10. The exact values for sodium hypochlorite are uncertain although there is approximate agreement between our own results and those obtained by Remington and Trimble (*26*) and Hisey and Koon (*11*). The above values show that hypochlorite is a stronger oxidizing agent under alkaline conditions than chlorite is at pH 4. This is important and is the basis for the demonstrated superior ability of chlorite to bleach cellulose to a high white without loss of strength properties which existed prior to bleaching. This has been discussed before the American Association of Textile Chemists and Colorists (*7*) and the Technical Association of the Pulp and Paper Industry (*32*).

Chlorite is a much stronger oxidizing agent than peroxide. It is also stronger than chlorate in dilute acid solutions. Chlorite should be of value in organic oxidations where it is desired to operate in slightly acid aqueous solutions with careful control—for instance, by adjusting the temperature or pH.

Properties of Solid Chlorite

Sodium chlorite may exist in two solid forms, the anhydrous ($NaClO_2$) and the trihydrate ($NaClO_2.3H_2O$). Both were prepared by Levi (*17*) and described as to crystallographic properties by Artini (*1*). The trihydrate is the stable phase in aqueous systems at room temperature. The anhydrous material is not hygroscopic, does not seriously cake in storage, and also has the higher content of active oxygen per unit of shipping weight. Since it is the more practical material, further consideration will be limited to anhydrous sodium chlorite.

The storage stability of sodium chlorite is excellent, as the representative stability tests of Table I indicate. Samples kept for ten years show slight losses. Variations in the data may represent instability but are in part due to analytical difficulties and to the method of sampling. No stability tests extending over ten years are yet available for the commercial product. The one-year test indicates that it is very stable. Purification of the commercial product yields the grade designated "analytical" which is also stable.

TABLE I. STABILITY OF SOLID SODIUM CHLORITE (IN PER CENT BY WEIGHT)

	Date of Test:				
Sample 5	7/23/29	2/14/30	1/29/31	2/6/40	Stored in lab. cupboard
$NaClO_2$	75.97	76.85	76.24	72.40	
NaCl	6.02	5.85	5.55	7.06	
NaClO	....	0.00	0.45	0.00	
$NaClO_3$	4.79	3.60	3.51	4.98	
Na_2CO_3	15.53	13.62	11.98	12.08	
Total	102.31	99.92	97.73	96.52	
Sample 24	3/21/29	7/19/29	1/29/31	2/6/40	Stored in lab. cupboard
$NaClO_2$	84.90	87.00	87.59	86.63	
NaCl	2.40	2.28	2.05	2.77	
NaClO	....	0.00	0.11	0.00	
$NaClO_3$	2.96	1.76	1.35	1.97	
Na_2CO_3	13.52	10.12	7.47	9.17	
Total	103.78	101.16	98.57	100.54	
Sample PD 3	12/18/28	2/20/29	2/15/30	1/28/31	Stored in desiccator
$NaClO_2$	97.54	97.88	97.31	97.36	
Technical $NaClO_2$	...	1 yr.	...	...	Stored on shelf
In drum	82.40	82.40	...	...	
In glass	81.78	81.02	...	...	
Analytical $NaClO_2$	Oct.-Nov., 1937		4/15/38	4/3/39	Stored on shelf
Lot 1	97.90		98.51	96.90	
Lot 2	98.76		98.78	97.00	
Lot 3	99.16		98.20	97.60	

In order to study the effect of elevated temperatures on the stability of solid sodium chlorite, portions of a product containing 68 per cent sodium chlorite were heated in an iron crucible, placed in an oil bath previously brought to the desired temperature. Thirty minutes at temperatures up to 150° C. did not cause decomposition. Less than half the chlorite was decomposed by heating at 200° C. for 30 minutes. A sample containing 79 per cent sodium chlorite by weight was rapidly heated in a porcelain crucible. The temperature was raised by heating the surrounding oil bath. A thermocouple in the chlorite showed that decomposition started at 175° C. Within a few seconds it heated to 340° C., and then the temperature commenced to fall. Analyses showed that the decomposition had taken place mainly according to the equation:

$$3NaClO_2 \longrightarrow 2NaClO_3 + NaCl \qquad (1)$$

Less than 5 per cent of the sodium chlorite decomposing evolved oxygen in accord with the equation:

$$NaClO_2 \longrightarrow NaCl + O_2 \qquad (2)$$

These results agree with those obtained by Levi (*15*). In the presence of organic matter the balance between these two reactions is disturbed, and copious evolution of oxygen takes place so that the chlorite aids combustion. A mixture of sugar and sodium chlorite in a crucible burst into flame at about 200° C.

Levi (*17*) stated that sodium chlorite explodes upon percussion or impact. This has been investigated by placing a portion of sodium chlorite upon an anvil and striking it with a hammer. Explosion will result unless the face of the hammer and anvil have been freed from the film of grease usually present on such tools. When both the hammer and anvil are clean, there is no explosion when the chlorite is struck. The addition of a trace of oil or grease will ensure explosion. Less adherent organic matter will probably, but not always, cause explosion when the mixture is struck.

Properties of Chlorite Solutions

Data on the solubility of sodium chlorite in water are as follows:

Temp., ° C.	Moles H_2O/Mole Total Solute	Wt. % $NaClO_2$
5	9.6	34
17	7.8	39
30	5.8	46
45	4.5	53
60	4.1	55

The determination of temperature while cooling a saturated solution of sodium chlorite shows that the transition point between the trihydrate and anhydrous forms is 38° C.

Levi (*18*) and Jackson and Parsons (*12*) showed that dilute solutions of sodium chlorite containing 0.5 per cent sodium hydroxide are stable for several days if protected from the light of the laboratory. Longer tests showed that no decomposition occurs in 23 months when sodium chlorite is stored in amber glass bottles. The chlorite concentration ranged from 0.25 to 1 *M* (0.1 to 4 *N*), and the sodium hydroxide was varied from 0.1 to 4 *M* at the different chlorite concentrations used. The same solutions stored in clear glass bottles and standing beside these on the laboratory shelf decomposed somewhat, as Table II shows. In general, increase in alkalinity rendered the solutions in the clear glass bottles more stable. Assuming that chlorate can be formed only by the reaction of Equation 1, complete analysis of these solutions shows that oxygen may also be evolved in accord with Equation 2.

TABLE II. NATURE OF CHLORITE DECOMPOSITION[a]

	Concn., Moles/Liter		
	Sample 1a	Sample 3a	Sample 5a
Original			
$NaClO_2$	0.0250	0.0252	0.0253
$NaClO_3$	0.0003	0.0002	0.0003
NaCl	0.0022	0.0035	0.0044
Total	0.0275	0.0289	0.0300
NaOH	0.1034	0.5062	1.0090
Final			
$NaClO_2$	0.0199	0.0233	0.0246
$NaClO_3$	0.0016	0.0009	0.0006
NaCl	0.0062	0.0043	0.0051
Total	0.0277	0.0285	0.0303
NaOH	0.1128	0.5204	1.0158
$NaClO_2$ loss	0.0051	0.0019	0.0007
$NaClO_3$ gain	0.0013	0.0007	0.0003
NaCl gain	0.0040	0.0008	0.0007
Assuming $3NaClO_2 \rightarrow 2NaClO_3 + NaCl$ Leaves Unaccounted for:			
$NaClO_2$ loss	0.0031	0.0008	0.0002
NaCl gain	0.0033	0.0004	0.0005

[a] Solutions stood 23 months in clear glass bottles.

When boiled under atmospheric pressure, dilute solutions of sodium chlorite are stable (compare Levi, *18*). Strong solutions, however, do decompose to some extent. Table III shows the effect of boiling for 50 hours in glass flasks with reflux condensers. During the first 2 hours there was considerable change in titratable alkalinity. The first 2 hours are therefore omitted from consideration of stability in order that alkalinity may be constant. Other experiments show that lowering the boiling temperature by reducing the pressure improves the stability of the solutions.

Precautions in Handling Chlorite

Chlorite is the intermediate member in the series hypochlorite-chlorite-chlorate. In many respects its properties are intermediate. For instance, chlorite is more stable than hypochlorite but less stable than chlorate.

A serious fire hazard is known to arise when chlorate solutions are allowed to dry on clothing. Similar hazards exist in the case of chlorite. Timing the burning of measured strips

TABLE III. EFFECT OF BOILING CHLORITE SOLUTIONS IN GLASS FLASKS WITH REFLUX CONDENSERS

	Concn. of Sample 1, Moles/Liter			Concn. of Sample 2, Moles/Liter			Concn. of Sample 3, Moles/Liter			Concn. of Sample 4, Moles/Liter		
	2 hr.	52 hr.	Change	2 hr.	52 hr.	Change	2 hr.	52 hr.	Change	2 hr.	52 hr.	Change
$NaClO_2$	0.777	0.792	+0.015	2.285	2.087	−0.198	3.324	2.655	−0.669	4.356	2.838	−1.518
$NaClO_3$	0.109	0.105	−0.004	0.271	0.436	+0.165	0.405	0.882	+0.377	0.585	1.643	+1.058
NaCl	0.183	0.199	+0.016	0.531	0.603	+0.072	0.725	1.040	+0.315	1.073	1.570	+0.497
Total	1.069	1.096	...	3.087	3.126	...	4.454	4.577	...	6.014	6.051	...
NaOH	0.091	0.086	...	0.303	0.273	...	0.356	0.365	...	0.501	0.499	...

of tape showed that impregnation with low concentrations of chlorite followed by drying caused slower burning than equal quantities of oxygen from chlorate. Stronger solutions caused the chlorite-impregnated samples to burn more rapidly than comparable impregnation with chlorate. The use of cotton gloves in handling chlorite is hazardous.

When introduced into the stomachs of guinea pigs, chlorite was found to be toxic. On the basis of these experiments, 5 to 6 grams of sodium chlorite would produce toxic effects in the average adult man, and twice this amount would be lethal. Hypochlorite apparently is destroyed by reacting with membranes, while chlorite is stable enough to enter the blood stream.

Chlorite reacts with sulfur in a unique manner. A mixture of sulfur and solid chlorite will ignite if rubbed or slightly moistened. There is enough sulfur in a rubber stopper to cause a slight pop when rubbed on moist chlorite. Bottles containing chlorite should be closed with cork or glass stoppers. The use of articles of clothing made of sulfur-bearing rubber is hazardous. The use of neoprene avoids this danger.

As in the case of chlorate, concentrated strong acids should not be allowed to come in contact with chlorite. Since chlorine dioxide can be formed in either case, a knowledge of the behavior of this gas is important. It is more intensely colored than chlorine and has a noticeable odor so that its detection in low concentrations in the atmosphere is relatively easy.

Henderson and Haggard (*10*) list chlorine dioxide as an irritant gas. Chlorine is similarly classified with the further information that 1000 p. p. m. are rapidly fatal for short exposure, which is inferred to mean 30 minutes to 1 hour. Work with guinea pigs has shown that 45 minutes of exposure to an atmosphere containing 150 p. p. m. partial pressure of chlorine dioxide was fatal. Exposure for 40 minutes in 45 p. p. m. partial pressure of chlorine dioxide and for 6 hours in 14 to 17 p. p. m. did not result fatally. It is about as hazardous as nitrogen dioxide. The odor of chlorine dioxide is evident at 14 to 17 p. p. m. partial pressure, and at 45 p. p. m. it is irritating. Adequate ventilation and gas masks should be provided wherever there is a possibility that men may have to be in an atmosphere containing chlorine dioxide.

Since chlorine dioxide is photochemically active, a 200-watt Mazda lamp was used for illumination while investigations were made concerning the effect of temperature and the presence of oxidizable matter. Dust or oil did not result in explosion at partial pressures of chlorine dioxide amounting to 100 mm. The upper limit to which the partial pressure could be raised without explosion was not determined, since it was found that electric sparks would cause explosion of the gas at much lower partial pressures. At 20° C. a spark from an induction coil caused the chlorine dioxide to explode at 36 mm. partial pressure but had no effect at 27 mm. At 60° C. the spark caused explosion at 25 mm. but not at 13 mm.

Thus, comparisons with other chemicals in daily use show that chlorite does not present any unusual degree of hazard. Since it is a new industrial chemical, a high degree of caution is desirable. But its properties are no bar to its use, as shown by the widespread utilization of such materials as chlorine, hypochlorite, and chlorate.

Chemical Reactions of Chlorite

Many of the applications of chlorite involve its use in acid solution. Therefore, experiments were undertaken to determine in what way chlorite reacts with acid. The procedure first used was to add a chlorite solution slowly to the acid while passing nitrogen gas through the reactor. The volatile products formed were thus removed and absorbed in sodium hydroxide. The residue in the reactor and the absorbing solutions were analyzed. The various gases which may be formed would react with caustic as follows:

$$Cl_2 + 2NaOH \longrightarrow NaCl + NaClO + H_2O \quad (3)$$
$$Cl_2O + 2NaOH \longrightarrow 2NaClO + H_2O \quad (4)$$
$$2ClO_2 + 2NaOH \longrightarrow NaClO_2 \longrightarrow NaClO_3 + H_2O \quad (5)$$

It is apparent that determination of Cl^-, OCl^-, ClO_2^-, and ClO_3^- in the absorbers will disclose the composition of the gas formed, provided there is no secondary reaction in the absorbers—for instance, hypochlorite oxidation of chlorite to chlorate. Work with synthetic mixtures under the conditions of concentration and temperature prevailing in the absorbers showed that no appreciable reaction occurred in the time required to carry out an experiment. A representative experiment consisted of adding a 1.3 *M* chlorite solution slowly to a 10 per cent acetic acid solution. Analysis of the generator residue showed that 0.02240 mole of chlorite had been decomposed. The gas absorber analysis showed:

	Total Moles Present	% $NaClO_2$ Decomposed
$NaClO_3$	0.004509	20.2
$NaClO_2$	0.004685	21.0
NaClO	None	..
NaCl	0.00058	2.6
O_2 (detd. as CuO)	0.00084	3.8

Since the main products are chlorite and chlorate in equimolar amounts, it is evident that the gas produced is almost entirely chlorine dioxide. No chlorine or chlorine monoxide is produced. The chloride may be partially accounted for by the small amount of hydrogen chloride carried over with the nitrogen. The small amount of oxygen indicates that the oxygen is strongly held in a combined form under these acid conditions.

All of the gaseous products account for less than half of the chlorine in the chlorite decomposing. A further series of experiments summarized in Table IV were planned to determine the nature and amount of the nonvolatile products. With the exception of experiment 10, the reacting mixture consisted of 200 ml. of solution containing chlorite in the amount shown. In experiment 10, 16 liters of 0.01 *M* sodium chlorite were used. The reaction mixture also contained sufficient buffer to prevent any appreciable change in pH even if hydrogen ions were involved in the reaction. The buffer used for pH 4 was sodium dihydrogen phosphate; for pH 2.5 the buffer was acetic acid. The gaseous products were removed by the passage of one liter of air per minute and absorbed in sodium hydroxide followed by calcium peroxide suspension. The latter material assured complete absorption of the chlorine dioxide by converting it to chlorite without formation of chlorate. The data as given are the total changes in experiments lasting 6 hours. Aeration increased the amount of chlorine dioxide evolved as shown by comparison with similar

TABLE IV. DECOMPOSITION OF CHLORITE IN DILUTE ACID

Expt. No.	Concentration, Moles/Liter	Temp., ° C.	Moles Change/Liter of Generating Soln. In Generator: ClO_2^- Consumed, Mole	ClO_2^- Consumed, %	Formed: ClO_3^-	Formed: Cl^-	In Absorber, ClO_2 formed	Total formed	Found/Consumed, %	Cl^- in Absorber	Cl^-/Consumed, %
					Sodium Dihydrogen Phosphate (pH 4)						
11	0.127	27	0.0015	1.2	0.0015	0.0010	0.0010	0.0035	233	0	...
5	0.254	RT	0.0075	2.9	0.0015	0.0055	0.0045	0.0115	154	0	...
12	0.259	27	0.0085	3.3	0.0005	0.0020	0.0045	0.0070	82	0	...
4	0.508	27	0.0225	4.4	0.0030	0.0050	0.0105	0.0185	82	0.001	4
15	2.394	25	0.2070	8.6	0.0480	0.0405	0.0890	0.1775	86	0.003	1.5
10	0.01	58	0.00261	26	0.00034	0.00063	0.00134	0.00231	88	...	...
9	0.254	62	0.0965	38	0.0225	0.0265	0.0480	0.0970	100	0.003	3
13	0.517	62	0.2070	40	0.0465	0.0420	0.1015	0.1900	92	0.004	2
					Acetic Acid (pH 2.5)						
6	0.254	28	0.1075	42	0.0255	0.0285	0.0530	0.1070	99	0.004	4
16	0.517	24	0.2125	41	0.0475	0.0480	0.1030	0.1985	93	0.003	1.4
14	0.259	62	0.2370	91	0.0490	0.0570	0.1170	0.2230	94	0.005	2
17	0.259	62	0.2390	92	0.0490	0.0565	0.1200	0.2255	94	0.006	2.5

experiments to those given in Table IV wherein aeration was used only in the final 30 minutes. The products found by analysis of the residual solution and the absorbed gases still do not equal the chlorite which disappeared during the course of the reaction. The poor summation of the products is shown by the percentages in the column headed "Found/Consumed". The final columns show the quantity of chloride which appeared in the absorbers without a known source. Perchlorate may have been formed, although qualitative tests have not shown its presence. The evolution of oxygen cannot account for the discrepancy because this reaction would leave chloride in the reacting solution. The analytical methods may account for a considerable portion of the discrepancies, since they involve differences which are small in proportion to the numerical quantities involved; also, the problem of distinguishing between the four oxidation levels of chlorine is not satisfactorily solved.

The first group of experiments at pH 4 and room temperature shows that the extent of decomposition increases out of proportion to the increase in concentration. The data indicate that the reactivity of chlorite is greatly increased by lowering the pH from 4 to 2.5 or by increasing the temperature from room temperature to 62° C. Examination of the individual products in Table IV shows that about twice as much chlorine dioxide is formed as either chlorate or chloride. The chloride is about equal to the chlorate. Eighty-five to ninety-five per cent of the chlorite decomposed has been accounted for, and the proportion of the reaction products is not much affected by the slight variation in conditions used in these experiments. It is possible that a study of other conditions will show that chlorate and chlorine dioxide are produced by separate reactions. The proportions found here could then be due to a balance in the rates of these separate reactions. It appears that under the conditions studied, the reaction involves the consumption of 4 moles of chlorite to produce 2 moles of chlorite and 1 mole each of chlorate and chloride. Under the experimental conditions used involving acid concentrations above pH 2.5 and very little chloride, no chlorine or chlorine monoxide was produced. However, the addition of a sodium chlorite solution to concentrated hydrochloric acid gives a mixture of chlorine and chlorine dioxide. Also, Laséque (*13*) reported that chlorous acid solution reacts as follows:

$$4HClO_2 \longrightarrow 2H_2O + 3ClO_2 + Cl \qquad (6)$$

The reaction of chlorite with hypochlorite or chlorine has become of commercial importance. In solutions whose pH is above about 11 to 12, chlorite reacts with hypochlorite as follows:

$$NaClO_2 + NaClO \longrightarrow NaClO_3 + NaCl \qquad (7)$$

This is a bimolecular reaction. Rate determinations yield closely agreeing second-order reaction constants. If the alkalinity is reduced below 11 to 12, such constants are no longer obtained, and the odor of chlorine dioxide becomes perceptible. As the pH is raised above 11 to 12, the speed of the reaction is decreased. This is probably due to the effect which alkali has of decreasing the concentration of hypochlorous acid formed by hydrolysis of the hypochlorite.

Cunningham and Losch (*4*) discovered that when chlorine is passed into strong chlorite solutions, chlorine dioxide is formed according to the equation:

$$2NaClO_2 + Cl_2 \longrightarrow 2NaCl + 2ClO_2 \qquad (8)$$

Before this patent was issued, Levi and Tabet (*20*) independently arrived at the same equation. If the chlorine dioxide is removed as formed—for instance, by aeration—the efficiency of its production is high. Under these conditions chlorine dioxide equivalent to over 97 per cent of the chlorite decomposing is removed from the solution. The reaction is rapid and the rate of generation can be controlled by adjusting the rate of introduction of the gaseous chlorine. However, if the chlorine dioxide is not removed as formed, it will dissolve in the generating solution to such an extent as to produce a dark red solution. Under these conditions chlorate may be formed equivalent to as much as 30 per cent of the chlorite decomposed in the case of strong solutions.

It would appear that in the reaction of chlorite with chlorine or hypochlorite, acid conditions favor the formation of chlorine dioxide while alkaline conditions tend to produce chlorate. Experiments were carried out in which chlorine was measured into a solution of chlorite and a buffer until one atom of chlorine had been introduced for each molecule of chlorite. The mixture was not aerated, but after the chlorine had been added, the gas space was swept out into an absorber by an air stream, leaving most of the chlorine dioxide in the reactor. The reactor and absorber were immediately analyzed. The results are given in Table V which shows that at pH 4 chlorine dioxide is the main product while at pH 8 to 10, chlorate predominates. It would appear that reaction 8 is occurring simultaneously with the formation of chlorate according to the following reaction:

$$NaClO_2 + Cl_2 + H_2O \longrightarrow NaClO_3 + 2HCl \qquad (9)$$

Dolch (*6*) gives the equation,

$$3NaClO_2 + 2HClO = 2NaCl + NaClO_3 + 2ClO_2 + H_2O \qquad (10)$$

to represent the reaction between hypochlorite and chlorite. His conditions are not clearly described. By introducing the hydrolysis of chlorine so that hypochlorous acid appears on the left-hand sides of Equations 8 and 9, direct addition will give Equation 10. This equation from Dolch represents the

special case in which equal quantities of hypochlorite react in both reactions 8 and 9.

TABLE V. REACTION OF CHLORINE AND CHLORITE

Expt. No.[a]	$NaClO_2$, Mole/L.	pH	Total Moles ClO_2^- consumed	ClO_2^- formed	ClO_3^- formed	Cl^- formed
11	0.5	4	0.0419	0.0339	0.0021	0.0389
18	0.5	4	0.0463	0.0408	0.0003	0.0421
15	0.25	10–8	0.0127	0.0005	0.0113	0.0253

[a] 100 cc. of solution were used in each experiment; gaseous chlorine was added during a few minutes and analysis was made at once.

Parsons and Jackson (*24*) discovered that mixtures of hypochlorite with chlorite give certain advantages in bleaching paper pulp. Chlorine and chlorite used simultaneously are also good bleaching agents for pulp. Bleaching with these combinations proceeds best at pH conditions between 8 and 9. The reactions which occur when chlorite is acidified or when it is mixed with chlorine or hypochlorite in the presence of organic matter—for instance, in bleaching operations—are different from those just described where no organic material is present. In weakly acid solutions, oxidizable material such as paper pulp reduces the formation of chlorine dioxide and chlorate. Bleaching is accompanied by the formation of chloride. Since it has been observed that a slight rise in pH greatly reduces the apparent consumption of chlorite to form chlorine dioxide without affecting the quality of the bleaching, it would appear that the production of chlorine dioxide is not essential to bleaching. The mechanism of the bleaching action when using mixtures of chlorine and hypochlorite is not indicated by the data given above on reactions when no organic material is present. Comparisons of the physical properties of pulps bleached under various conditions do not show that the results obtained with hypochlorite and chlorite are different from those obtained with chlorine and chlorite. The reactions in the absence of pulp or other oxidizable material may be necessary to bleaching or may be competing side reactions.

By employing the reaction of chlorine and chlorite discussed above, chlorite may be made to serve as a convenient source of pure chlorine (*21*). Schmidt and co-workers (*28*) described its use in the study of wood and carbohydrates. Ritter (*27*) applied their method of isolating cellulose by the use of chlorine dioxide to his own study of wood structure.

In alkaline solution Latimer (*14*) gave the oxidation potential of chlorine dioxide as defined by the half-cell equation as follows:

$$ClO_2^- \longrightarrow ClO_2 + e^-; \; E_0 = -1.15 \text{ volts}$$

This value indicates that chlorine dioxide is a relatively powerful oxidizing agent when passed into alkaline solution. This oxidizing power is sufficient to oxidize various forms of carbon to carbon dioxide at room temperature, as Vincent (*33*) showed.

Uses for Chlorite

Sodium chlorite is now being used commercially in bleaching paper pulp. Kraft pulp can be bleached to a high white without loss of strength. A similar degree of whiteness cannot be obtained by known processes using hypochlorite without a loss of strength. In practice, the pulp purification process is usually carried as far as possible without damage, using chlorine and hypochlorite; then the chlorite bleaching process is applied to finish the pulp to a high white while preserving strength (*31*).

Chlorite is finding application in textile mills (*7*) in connection with the bleaching and finishing of cotton, rayon, and Celanese. It is commonly used in acid conditions along with a detergent to obtain scouring and bleaching in one step. It is also employed under extreme alkaline conditions at high temperature in the kiering operation, where it is effective in starch and mote removal and simplifies finishing operations.

Chlorite is of value in the bleaching of linen, wood surfaces, straw, oat hulls, and coarse fibers such as ramie and hemp. It is also useful in purifying cotton linters and rag paper pulp, and in dissolving cellulose.

Chlorite is a convenient source of pure chlorine dioxide which is useful in pulp (*34*) and flour (*2, 25, 29*) bleaching. It also appears to have a potential use in water purification according to Dienert (*5*).

Chlorite quickly poisons chlorophyll-bearing plants (*30*). Its action is more rapid but not so extensive as that of chlorate.

A chemically pure grade of sodium chlorite is available and has been used as an analytical reagent by Jackson and Parsons (*12*) in the determination of sulfur compounds in sulfite pulping liquors and by Yntema and Fleming (*35*) in analysis for iodides.

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