Storage Factors Affecting the Deterioration Rates of Certain Chlorine Preparations of the Sodium Hypochlorite Type*

I. The Effect of Diffused Daylight

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In the course of an investigation conducted on the problem of stabilizers for a chlorine preparation made by one of our western manufacturers, the writers learned that the deterioration rates for such preparations were subject to unexpected vagaries. The exploratory work indicated that not only are extremely rapid deterioration rates an actuality under certain conditions of use, but that the same preparations under other circumstances can be stable to an unsuspected degree. A study of the literature demonstrates, too, how little has been published concerning the effect of factors such as age on the chemicals which are the active agents of such preparations before they are put into solution for use, while in solution as reserve stock, and under other conditions of storage. The investigation clearly showed the possibility that many of the sodium hypochlorite and *p*-toluenesulfonchloramide types of antiseptics now in general use having a variety of purposes might be failing to a hazardous degree in their function because of unrecognized deterioration. Hospitals, manufacturers, the Drug Deterioration Committee of the American Association of Colleges of Pharmacy, and users of the substances other than those directly connected with the public health professions, such as restaurants, taverns, public baths and laundries, are all seriously concerned with the instabilities of such preparations and the things that might be done to alleviate instability.

The research described in this and subsequent papers was designed to study a number of the factors which might logically have some effect on the rate of deterioration of commercial preparations of these chemical types.

The ramifications of the problem made it necessary to divide it into parts and attack each part separately. Since this condition was due in a degree to the large number of both sodium hypochlorite and *p*-toluenesulfonchloramide preparations on the market it was decided to study first only the former. The latter substances would then be left until the completion of the initial phase of the problem. The effect of diffused daylight on the sodium hypochlorite solutions was the first factor considered. Under many conditions of use and storage, chlorine solutions are kept on open shelves without thought of protection from normal diffused daylight as it is found in the average room with two exposures. It is true that at times this light can become quite intense. However, its long-time effect without regard for the periods of high intensity was considered to be the factor of major importance. Since much has been said about the protective effect of colored glass this factor was examined also.

EXPERIMENTAL

Ten commercial preparations of chlorine which covered the field of use from those designed principally as antiseptics to those whose major utility is in the laundry were selected for study. They were purchased in the popular stock bottle sizes. Samples of each were then transferred to clear, blue, green and amber bottles of equivalent size. These were stored on open shelves in a laboratory having window exposure on the east and south. The shades were never drawn. The room temperature was fairly constant throughout the examination because of air conditioning. The number of sunny and cloudy days during the period of examination is shown in Table I.

The determinations of available chlorine were made approximately every 30 days for a series of ten analyses. The initial determination on each specimen was made at the time of transfer from the original or commercial container to the experimental containers. The U. S. P. XI method for the assay of solutions of sodium hypochlorite was used. This procedure was modified to a small degree in

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that 1-cc. samples were taken for the second to fifth determinations inclusive, and 5-cc. samples, accurately measured at 20° C., for the remainder. Also sulfuric acid was used in place of acetic acid, because the former gave more consistent results. This was demonstrated by a series of control assays in which the efficiency of both acids was carefully observed. The results of the determinations showing the rates of deterioration for the ten chlorine solutions studied under the conditions of the investigation are shown in Tables II to XI, inclusive. Because the majority of the manufacturers whose preparations were studied requested that their products be reported by number instead of name, each preparation will be known by the prefix C, with the appropriate serial number following. These designations will be carried throughout the study.

TABLE I.—NUMBER OF CLEAR, PARTLY CLOUDY AND CLOUDY DAYS DURING THE PERIOD OF INVESTIGATION (DATA TAKEN FROM THE OFFICIAL WEATHER REPORTS OF THE UNIVERSITY OF WASHINGTON DEPARTMENT OF GEOLOGY)

	Weather[a]		
Month	No. of Clear Days	No. of Partly Cloudy Days	No. of Cloudy Days
May 24–31	4	1	2
June	18	7	5
July	15	7	9
August	17	3	11
September	13	6	11
October	2	5	24
November	1	3	27
December	8	1	22
January	7	3	21
February	9	2	17
March 1–20	11	3	6

[a] Average light intensity in laboratory: clear days, 50 candle power per sq. ft.; partly cloudy days, 33.5; cloudy days, 22.5.

TABLE II.—RATE OF DETERIORATION OF C-1 UNDER THE CONDITIONS OF THE STUDY

Period of Exposure in Days	Per Cent of Available Chlorine for Various Colors of Storage Bottles			
	Clear	Green	Blue	Amber
0	1.01	0.98	0.99	1.01
28	0.86	0.91	0.90	0.97
62	0.72	0.83	0.74	0.98
94	0.51	0.65	0.58	0.87
127	0.44	0.68	0.59	0.96
160	0.40	0.65	0.52	0.99
188	0.37	0.62	0.47	0.97
234	0.35	0.58	0.39	0.96
256	0.32	0.55	0.33	0.95
275	0.28	0.50	0.32	0.94

TABLE III.—RATE OF DETERIORATION OF C-2 UNDER THE CONDITIONS OF THE STUDY

Period of Exposure in Days	Per Cent of Available Chlorine for Various Colors of Storage Bottles			
	Clear	Green	Blue	Amber
0	4.66	4.65	4.65	4.59
28	4.12	4.48	4.38	4.52
62	3.63	4.09	4.04	4.46
94	2.96	...	...	...
127	2.92	3.78	3.54	4.36
160	2.55	3.52	3.20	4.28
188	2.38	3.45	3.04	4.16
234	2.30	3.31	2.95	4.12
256	2.16	3.18	2.78	3.92
275	1.96	3.09	2.72	3.93

TABLE IV.—RATE OF DETERIORATION OF C-3 UNDER THE CONDITIONS OF THE STUDY

Period of Exposure in Days	Per Cent of Available Chlorine for Various Colors of Storage Bottles			
	Clear	Green	Blue	Amber
0	5.05	4.61	4.68	4.30
28	4.25	4.36	4.33	4.49
62	3.65	4.00	3.95	4.28
94	2.97	...	...	...
127	2.89	3.72	3.49	4.17
160	2.41	3.47	...	4.05
188	2.39	3.40	3.00	4.02
234	2.21	3.21	2.93	3.85
256	2.10	3.08	3.49	3.82
275	1.89	3.08	2.68	3.80

TABLE V.—RATE OF DETERIORATION OF C-4 UNDER THE CONDITIONS OF THE STUDY

Period of Exposure in Days	Per Cent of Available Chlorine for Various Colors of Storage Bottles			
	Clear	Green	Blue	Amber
0	3.40	3.32	3.34	3.43
28	3.01	3.11	3.13	3.32
62	2.58	2.84	2.80	3.19
94	2.03	...	...	...
127	2.01	2.63	2.40	3.19
160	1.71	2.44	2.18	3.17
188	1.61	2.36	2.00	...
234	1.44	2.28	1.83	2.86
256	1.28	2.86	0.23	2.61
275	1.17	2.01	0.04	2.58

TABLE VI.—RATE OF DETERIORATION OF C-5 UNDER THE CONDITIONS OF THE STUDY

Period of Exposure in Days	Per Cent of Available Chlorine for Various Colors of Storage Bottles			
	Clear	Green	Blue	Amber
0	4.73	4.66	4.69	4.80
28	4.17	4.44	3.94	4.52
62	4.15	3.91	3.93	4.41
94	2.85	3.48	3.36	...
127	2.88	...	3.16	4.25
160	2.55	3.45	...	4.26
188	2.45	3.36	3.03	4.15
234	2.12	3.22	2.81	4.03
256	2.06	3.05	2.58	...
275	2.03	3.00	2.56	3.94

TABLE VII.—RATE OF DETERIORATION OF C-6 UNDER THE CONDITIONS OF THE STUDY

Period of Exposure in Days	Per Cent of Available Chlorine for Various Colors of Storage Bottles		
	Clear	Green	Amber
0	6.31	5.92	6.19
28	5.31	5.37	5.56
62	4.40	4.91	5.08
94	3.41	...	...
127	3.08	4.15	4.62
160	2.77	3.85	4.36
188	2.61	3.73	4.01
234	2.45	3.33	4.06
256	2.23	3.15	...
275	2.10	3.10	3.62

TABLE VIII.—RATE OF DETERIORATION OF C-7 UNDER THE CONDITIONS OF THE STUDY

Period of Exposure in Days	Per Cent of Available Chlorine for Various Colors of Storage Bottles			
	Clear	Green	Blue	Amber
0	2.48	2.47	2.25	2.62
28	2.16	2.30	2.39	2.46
62	1.67	2.09	2.19	2.39
94	1.10	1.71	1.73	2.32
127	0.90	1.79	1.04	...
160	0.61	0.67	0.24	2.37
188	0.26	0.12	0.02	2.35
234	0.05	0.04	0.01	1.67
256	0.04	0.03	0.01	0.04
275	0.03	0.03	0.01	0.04

TABLE IX.—RATE OF DETERIORATION OF C-8 UNDER THE CONDITIONS OF THE STUDY

Period of Exposure in Days	Per Cent of Available Chlorine for Various Colors of Storage Bottles			
	Clear	Green	Blue	Amber
0	4.13	4.18	4.15	4.19
28	3.64	3.80	3.70	3.97
62	2.97	3.39	3.09	3.70
94	2.14	2.68	2.24	3.21
127	1.90	2.84	2.05	3.22
160	1.57	2.07	1.62	2.86
188	1.38	1.78	1.40	2.56
234	1.14	1.40	1.13	2.05
256	0.99	1.22	0.97	1.88
275	0.88	1.13	0.90	1.77

TABLE X.—RATE OF DETERIORATION OF C-9 UNDER THE CONDITIONS OF THE STUDY

Period of Exposure in Days	Per Cent of Available Chlorine for Various Colors of Storage Bottles			
	Clear	Green	Blue	Amber
0	4.73	4.76	4.77	4.73
28	4.37	4.46	4.42	4.58
62	3.77	4.22	4.08	4.51
94	3.11	...	...	...
127	3.05	3.88	3.69	4.35
160	2.62	3.71	3.05	4.29
188	2.50	3.58	3.17	4.17
234	2.40	3.42	3.04	3.85
256	2.23	2.87	2.81	4.00
275	2.14	2.87	2.81	3.90

TABLE XI.—RATE OF DETERIORATION OF C-10 UNDER THE CONDITIONS OF THE STUDY

Period of Exposure in Days	Per Cent of Available Chlorine for Various Colors of Storage Bottles			
	Clear	Green	Blue	Amber
0	4.72	4.57	4.59	4.72
28	4.30	4.48	4.34	4.51
62	3.79	4.13	3.98	4.41
94	3.01	...	...	...
127	2.99	3.76	3.50	4.29
160	2.51	3.49	2.84	4.27
188	2.48	3.41	3.09	4.08
234	2.31	3.27	2.93	4.01
256	2.15	3.07	2.75	3.73
275	1.96	3.04	2.70	3.69

DISCUSSION

The data collected are summarized in Tables XII, XIII and XIV. From these tables, it is evident that amber glass containers offer better protection against the destructive effect of diffused daylight than the other bottles used. In order of effective protection value the four containers rate: (1) amber, (2) blue, (3) green and (4) clear glass. It is also apparent that if the majority of the preparations studied are used within a month or so after purchase their approximate maximum utility is available.

TABLE XII.—A COMPARISON OF THE DEGREE OF TOTAL DETERIORATION OF THE SAMPLES STUDIED

Preparation	Per Cent Total Deterioration during Study			
	Clear Bottles	Green Bottles	Blue Bottles	Amber Bottles
C-1	62.38	48.98	67.67	6.93
C-2	58.58	33.54	41.50	14.38
C-3	62.57	33.18	42.73	11.62
C-4	65.58	39.45	98.50	24.78
C-5	57.08	35.62	45.42	17.91
C-6	66.72	47.63	...	41.52
C-7	98.79	98.78	99.55	98.48
C-8	78.69	72.97	78.31	57.75
C-9	54.75	39.70	41.09	18.19
C-10	58.48	33.48	41.18	21.82

TABLE XIII.—ORDER OF DETERIORATION

The products are listed under each container according to their degree of deterioration. The one showing the least deterioration is listed first, and so on.

Clear Bottles	Green Bottles	Blue Bottles	Amber Bottles
C-9	C-3	C-9	C-1
C-5	C-10	C-10	C-3
C-10	C-2	C-2	C-2
C-2	C-5	C-3	C-5
C-1	C-4	C-5	C-9
C-3	C-9	C-1	C-10
C-4	C-6	C-8	C-4
C-6	C-1	C-4	C-6
C-8	C-8	C-7	C-8
C-7	C-7	...	C-7

TABLE XIV.—DETERIORATION RATINGS

The number assigned each product indicates its position according to degree of deterioration in the different containers. Its deterioration rating is obtained by adding all the position numbers and dividing by the number of positions, which is 4.

Preparation	Position in				Total Position Points	Average Position Points
	Clear Glass	Green Glass	Blue Glass	Amber Glass		
C-9	1	6	1	5	13	3.25
C-5	2	4	5	4	15	3.75
C-10	3	2	2	6	13	3.25
C-2	4	3	3	3	13	3.25
C-1	5	8	6	1	20	5.00
C-5	6	1	4	2	13	3.25
C-4	7	5	8	7	27	6.75
C-6	8	7	..	8	23[a]	7.66[a]
C-8	9	9	7	9	34	8.50
C-7	10	10	9	10	39	9.75

[a] Based on three ratings only.