agents in forming solvent combinations with the N_2O_4 . Cursory examination of such combinations gave no indication of such reactions.

In testing the solubility of cellulose in compositions containing N₂O₄, it is necessary scrupulously to avoid the presence of water, as indicated in the experimental portion. The seven-second cotton linters will dissolve readily in a mixture of 15 parts by volume of pure N₂O₄, to which is added one part of water. It appears that N₂O₈ may be important in determining this solubility for, in comparison, N₂O₄ and pure nitric acid in the ratios comparable to those given do not form a solvent mixture. Aryl sulfonates are seen to be solvents with N₂O₄ for cellulose, but it was impossible to ascertain whether the free aryl sulfonic acids are effective, inasmuch as these bodies are hydrated and strongly hygroscopic.

The several properties which are necessary for producing new solvent combinations for cellulose by the scheme followed in this research may be listed as: (1) a substance having a three-electron bond plus (2) a substance having the following properties: (a) at least one electronegative group stabilized by resonance; (b) either no reactivity with or very slow reactivity with substance (1); (c) miscible with or soluble in the substance (1); (3) the combination of (1) plus (2) in the proper ratios either does not react with cellulose or reacts at a very slow rate which does not interfere with its utility.

Summary

1. A novel type of cellulose solvent or peptizing agent is described which involves the use of a mixture of liquid nitrogen tetroxide and a second (organic) substance miscible with or soluble in this oxide of nitrogen.

2. The second substance must contain an electronegative group in the molecule and exhibit very slow reactivity or none with nitrogen tetroxide as well as a useful range of miscibility or solubility with the latter.

3. Such addends to nitrogen tetroxide include nitroparaffins, certain aromatic nitro compounds, sulfones, nitriles, aryl sulfonates, diaryl ketones, and aromatic, aliphatic and aromatic-aliphatic esters, as well as many others.

4. The effect of such solvent mixtures on the properties of cellulose regenerated therefrom is described; oxidation is extremely slow.

5. Several theories are discussed which might be used to explain these phenomena.

ROCHESTER 4, N. Y. RECEIVED FEBRUARY 20, 1947

[CONTRIBUTION FROM NOVES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND ILLINOIS STATE WATER SURVEY]

Hydrolysis and Chlorinolysis of Cyanogen Chloride¹

By Charles C. Price,² T. E. Larson,³ Karl M. Beck, F. C. Harrington,⁴ L. C. Smith and Ilya Stephanoff

This investigation was undertaken to obtain information concerning the reactivity of dilute aqueous solutions of cyanogen chloride. It was of interest to determine not only the rate of hydrolysis but the reaction, if any, with chlorine or hypochlorite.

Experimental

Hydrolysis.—It has long been known that alkali reacts readily with cyanogen chloride.⁵ Alkaline cleavage is sufficiently rapid and complete to be useful analytically by titrating the chloride ion so liberated.

$$CICN + OH^{-} \longrightarrow CI^{-} + HOCN$$
$$-d[CICN]/dt = k_{1}[CICN] [OH^{-}]$$

By measurement of the rate of this hydrolysis in alkali and bicarbonate-buffered solutions, the value for the rate constant, k_1 , for the second-order

(1) The work reported here was done under a contract, recommended by the National Defense Research Committee, between the Office of Scientific Research and Development and the University of Illinois.

(2) Present address: University of Notre Dame, Notre Dame, Indiana.

(3) Chemist, Illinois State Water Survey, Urbana, Illinois.
(4) The services of F. C. Harrington were available through the

courtesy of Wallace and Tiernan, Inc., Newark, New Jersey.

(5) Sartori, "The War Gases," D. Van Nostrand Co., New York, N. Y., 1989, p. 140. reaction between cyanogen chloride and hydroxyl ion has now been estimated to be 6×10^2 liters mole⁻¹ min.⁻¹ at 25°.

In phosphate buffer, the rate of disappearance of cyanogen chloride was considerably greater than expected for the observed hydroxyl ion concentration. It thus seems that phosphate has a specific accelerating action. The increase in rate could be satisfactorily accounted for by a secondorder reaction of phosphate with cyanogen chloride with a rate constant, k_2 , of 3×10^{-2} liters mole⁻¹ min.⁻¹. The equation is written for monoacid phosphate ion although it is recognized that at the pH used (7.5) there will be an equilibrium distribution between various phosphate ions, any one of which *might* be the reactive species. The value given for k_2 thus includes a factor expressing the fraction of total phosphate ions present in the form of the reactive species.^{5a}

(5a) One might speculate that a hydrated phosphate ion might form an ion-dipole association complex with cyanogen chloride of the

following configuration. Because of the geometry of the phosphate anion, such a complex could decompose to the products outlined above by the simple shift of electrons. The original ion-dipole bonds are indicated by dotted lines, the postulated electron shifts by dashed arrows.



July, 1947

Hydrolysis of Cyanogen Chloride⁶ at pH 10.— An 800-cc. portion of a solution containing about 0.002 *M* cyanogen chloride, was diluted with 400 cc. of 0.002 *N* sodium hydroxide. Solutions were withdrawn at specified intervals, neutralized to phenolphthalein with 0.02 *N* sulfuric acid and titrated for chloride ion by silver nitrate. Samples were also withdrawn for *p*H determinations, using a Beckmann *p*H meter. The experimental data are summarized in Table I.

The pseudo first-order "constants," k', have been estimated from the slope of tangents to the curve obtained by plotting the logarithm of the cyanogen chloride concentration against time. Dividing by the hydroxyl ion concentration gives the second-order constant, k_1 .

$$-d[CICN]/dt = k'[CICN]$$
$$k' = k_1[OH^-]$$

TABLE I

Alkaline Hydrolysis of Cyanogen Chloride at Room Temperature

Time, min.	¢H	[OH-] × 104	[CICN] × 104	$k' \times 10^{2}$ min. ⁻¹	$k_1(=k')/$ [OH ⁻]) ×10 ⁻² min. ⁻¹ mole ⁻¹
0		••	13.0		
5	10.15	1.41		9.1	6.5
10	10.1°	1.26^{a}	5.0	8.0	6.3
20	10.0°	1.00*	2.7	6.0	6.0
30	9.94	0.87	••	4.7	5.4
35			1.3		•••
45	9.91	.81	0.8	4.2	5.1
• Esti	imated.				

Hydrolysis in Tap Water.⁷—Solutions of cyanogen chloride in tap water with initial concentrations varying from about 1.7 to 6.7×10^{-4} M were allowed to hydrolyze at room temperature and the rate of disappearance of cyanogen chloride was determined by Reagent A.8 The results, summarized in Figs. 1 and 2, are in fair agreement with the hydrolysis in alkali. If the rate for the first six hours alone is considered (Fig. 1), the rate constant, $k_1 = 7.5 \times 10^2$, is considerably higher than for the first forty-eight hours (Fig. 2), k_1 = 5 × 10². We have picked $k_1 = 6 \times 10^2$ as a reasonable estimate. The consistently slower rate constant as the hydrolysis proceeded suggests that one of the hydrolysis products exerted a retarding influence on the rate. The agreement of the first order constants for differences in initial concentration of three-fold indicates that the progressive

(6) The cyanogen chloride used was especially purified material obtained from Bdgewood Arsenal in sealed glass ampoules.

(7) The University of Illinois tap water is well-buffered with about 330 p. p. m. of bicarbonate alkalinity (as calcium carbonate) and contains only 3 p. p. m. of chloride ion.

(8) Reagent A is a compound, the identity of which cannot be disclosed, which produces a characteristic yellow color suitable for accurate quantitative colorimetric estimation of cyanogen chloride in squeeus solution. Concentrations of the order of 10^{-4} M can be estimated readily to within 1%.

decrease in rate constant is not due to higher order kinetics.



Fig. 1.—Hydrolysis of cyanogen chloride in Urbana tap water: O, pH 8.05, $k_1 = 7.75 \times 10^2$; \oplus , pH 8.10, $k_1 = 7.52 \times 10^3$; \oplus , pH 8.12, $k_1 = 7.52 \times 10^3$; \oplus , pH 8.15, $k_1 = 7.37 \times 10^2$.



Fig. 2.—Hydrolysis of cyanogen chloride in Urbana tap water: O, pH 8.05; $k_1 = 4.68 \times 10^2$; \bigoplus , pH 7.70; $k_1 = 5.66 \times 10^2$; \bigoplus , pH 8.12; $k_1 = 5.32 \times 10^2$; \bigoplus , pH 8.15; $k_1 = 5.35 \times 10^2$.

Hydrolysis in Phosphate Buffer.—The hydrolyses were run at pH 7.5 in the presence of 0.039 M and 0.153 M phosphate. Analysis for disappearance of cyanogen chloride was by Reagent A. An experiment in which cyanogen chloride was added to Reagent A containing phosphate buffer demonstrated that intensity of color in the presence of either 0.039 or 0.153 M phosphate indicated 45% of the actual concentration of cyanogen chloride added. The results, corrected accordingly and summarized graphically in Fig. 3, indicated a definite effect of phosphate on the disappearance of cyanogen chloride. From the slopes of the two straight lines, the pseudo first order constants, k', are estimated to be 1.43 and 4.35×10^{-3} min.⁻¹ If one assumes that there are



Fig. 3.—Hydrolysis of cyanogen chloride in aqueous phosphate buffer (pH 7.5): •, 0.039 *M* phosphate; O, 0.153 *M* phosphate.

two principal reactions leading to the decomposition of cyanogen chloride, with hydroxyl and phosphate ion, then the pseudo first order constant can be expressed as $k' = k_1[OH^-] + k_2[phos$ phate]. Using the value of k_1 previously determined, 6×10^2 , we may then estimate the values of k_2 as 2.7 and 3.0 $\times 10^{-2}$ liter mole⁻¹ min.⁻¹.

Reaction with Ammonia and Sulfide.—In addition to reaction of cyanogen chloride with water (or hydroxyl ion), experiments were also carried out on the reaction with ammonia and sulfide in very dilute solution.

At pH 8, there was no measurable reaction between 3.3 $\times 10^{-4}$ M cyanogen chloride and 1.8 or 4.1 $\times 10^{-4}$ M ammonia. The rate of disappearance of cyanogen chloride, as measured by Reagent A,⁸ was the same within experimental error as in the absence of ammonia. With 8.8 \times 10^{-4} M ammonia the disappearance was perhaps very slightly accelerated. It therefore appears that the known reaction of cyanogen chloride with ammonia to give cyanamide is very slow in these small concentrations, perhaps because the equilibrium concentration of free ammonia is only a small fraction of the total ammonia present.

Measurements of the reaction of sulfide ion with cyanogen chloride indicate an extremely rapid reaction, even in very dilute solution (Table II).

Conversion to thiocyanate was complete in less than half-an-hour.

 $CICN + S^{-} \longrightarrow CI^{-} + SCN^{-}$ (or CICN + SH⁻ \longrightarrow CI⁻ + HSCN)

The presence of thiocyanate was established by colorimetric determination as ferric thiocyanate. Apparently, about 20% less than the theoretical amount was formed in each experiment.

The Reaction with Sodium Sulfide.—Solutions containing $4.1 \times 10^{-4} M$ cyanogen chloride and varying amounts of sodium sulfide were prepared by appropriate mixing of ammonia-free tap water, stock solutions containing 18.1×10^{-4} M cyanogen chloride by Reagent A and 1.56×10^{-4} M sodium sulfide. Samples were withdrawn at intervals and analyzed by Reagent A. Thiocyanate was also estimated using a colorimetric measurement of ferric thiocyanate. Experiment demonstrated that sulfide did not interfere with the analysis for cyanogen chloride nor did cyanogen chloride interfere with the thiocyanate procedure. The reaction of the sulfide ion with cyanogen chloride was complete within the shortest interval measured, thirty minutes, so the data after this time have been summarized in Table II.

	TABLE II						
REACTION OF 3.7 >	\times 10 ⁻⁴ M Cyano	GEN CHLORIDE WITH					
Sodium Sulfide at Room Temperature							
[S=] added, M × 104	[CICN] reacted, $M imes 10^4$	[SCN ⁻] formed, $M \times 10^4$					

$M \times 10^4$	$M \times 10^4$
1.05	0.73
3.4	2.5
3.7	2.8
	$M \times 10^4$ 1.05 3.4 3.7

Chlorination of Cyanogen Chloride Solutions. —Since cyanogen chloride is prepared by treatment of cyanide with chlorine in water and since it is only very slowly hydrolyzed in water, it was a considerable surprise to find that it reacted readily with hypochlorite at pH 7 to 8. The stoichiometry of this reaction, three moles of chlorine⁹ consumed per two moles of cyanogen chloride has been substantiated under many other conditions and corresponds to the amount necessary to oxidize the nitrogen in the cyanogen chloride to gaseous nitrogen.

Reaction of Hypochlorite with Cyanogen Chloride.—A solution containing $3.3 \times 10^{-4} M$ cyanogen chloride and $7.0 \times 10^{-4} M$ chlorine was prepared by mixing stock solutions of cyanogen chloride and HTH in ammonia-free tap water. To 1.5 liters of this solution was added 20 cc. of a 0.5 M phosphate buffer to bring the pH to 7.09. A control without cyanogen chloride was similarly prepared, pH 7.18. In a third solution, the cyanogen chloride was hydrolyzed completely by addition of alkali and the alkali was neutralized before the HTH and buffer were added. Reagent A indicated no cyanogen chloride.

The reaction mixtures were allowed to stand at room temperature in the dark (black-painted bottles). Samples were withdrawn at specified intervals and the HTH concentration was measured iodimetrically. The reaction was nearly complete within ten minutes and the stable chlorine residual after an hour indicated the consumption of 2.95 (unhydrolyzed sample) and 3.05 (hydrolyzed sample) moles of chlorine for each two moles of cyanogen chloride initially present.

With smaller concentrations of cyanogen chloride and hypochlorite, the rate of loss of chlorine was considerably reduced. Data were obtained for initial concentrations of cyanogen chloride of 7.7×10^{-6} , 3.1, 3.3 and 4.7×10^{-5} M at several different initial chlorine concentrations.

(9) For convenience, the total of the various forms of "active chlorine," hypochlorite ion, hypochlorous acid and chlorine (usually added as HTH, a brand of calcium hypochlorite), is referred to as the "chlorine" concentration. July, 1947

These solutions were prepared from stock solutions of cyanogen chloride and of chlorine, the latter added as HTH in deammoniated tap water. Samples were withdrawn at intervals and the residual chlorine concentration was measured colorimetrically by the *ortho*-tolidine procedure.¹⁰

To obtain some indication of the kinetics of the reaction of chlorine with cyanogen chloride, instantaneous rates were estimated at various reaction times up to 80 or 90% completion by drawing tangents to the curve for the disappearance of chlorine plotted against the time. These rates, $-d[Cl_2]/dt$, when divided by the chlorine and cyanogen chloride concentrations at the particular time, gave numbers (k) which were roughly constant.

$$-d[Cl_2]/dt = k[Cl_2][ClCN]$$

The chlorine concentration at time, t, was a direct experimental measurement. The cyanogen chloride concentration was estimated on the basis of the experimental data indicating that two moles of cyanogen chloride are consumed for three moles of chlorine reacted. In view of the experimental errors in analysis for the low concentrations employed and in temperature control, the difficulty in accurately estimating tangents and the fact that the pH varied from about 7.1 to 7.5 in the chlorination mixtures,¹¹ the agreement for the values of k over the considerable range in concentrations studied (Table II) is sufficient to indicate second-order kinetics for the reaction.

TABLE III

ESTIMATED SECOND ORDER RATE CONSTANTS FOR THE REACTION OF HYPOCHLORITE WITH CYANOGEN CHLORIDE AT ROOM TEMPERATURE

	(pH 7.1 to	7.5)
$[Cl_2]_0, \\ M \times 10^4$	$\begin{bmatrix} C CN]_0, \\ M \times 10^4 \end{bmatrix}$	k, liter mole ⁻¹ min. ⁻¹ \times 10 ⁻²
6.65	0.77	23 ± 1
6.66	3.1	12 ± 2
14.0	3.1	12 ± 2
8.43	3.3	18 ± 2
8.46	3.3	18 ± 2
9.85	3.3	15 ± 1.5
14.06	3.3	11 = 0.5
4.25	4.8	17 ± 4
9.88	4.8	18 ± 2
12.45	4.8	18 ± 3
13.90	4.8	19 ± 3
		Av. 16 ± 3

As was expected, the reaction of chlorine with cyanide paralleled that with cyanogen chloride. One extra equivalent of chlorine was, however, rapidly consumed (less than ten minutes) to con-

(10) Chamberlain and Glass, J. Am. Water Works Assoc., 35, 1065, 1205 (1943).

(11) The pH will, of course, alter the equilibrium concentrations of hypochlorite, hypochlorous acid and chlorine. Without accurate data on the exact change of the rate with pH, it is not possible to decide which molecular species of "active chlorine" is attacking cyanogen chloride. It is our opinion that it is most probably hypochlorite ion.

vert cyanide to cyanogen chloride, followed by disappearance of chlorine at a rate identical to that for the reaction with cyanogen chloride. Two moles of cyanide ion thus consumed a total of five moles of chlorine. The following transformations would account for the observed chlorine demand.¹²

NaCN + HOCl
$$\xrightarrow{pH 8}$$
 · CICN + NaOH
(instantaneous)
2CICN + 3HOCl + H₂O $\xrightarrow{pH 8}$ 5HCl + 2CO₂ + N₂

Since cyanate ion reacted with chlorine at exactly the same rate as did cyanogen chloride, it was concluded that the chlorine consumption of cyanogen chloride must proceed through a very rapid conversion of cyanogen chloride to cyanate to the presence of hypochlorite (or more probably through a rapid conversion of both to the same intermediate product¹³). Measurement of the rate of disappearance of cyanogen chloride (rather than chlorine) in reactions with hypochlorite demonstrated that the cyanogen chloride was almost completely consumed within five minutes under conditions such that the consumption of active chlorine according to the equation above would require at least half-an-hour to reach completion.

require at least half-an-hour to reach completion. Reaction of Hypochlorite with Ammonia, Sodium Cyanide and Potassium Cyanate.— HTH in deammoniated tap water was added to $3.3 \times 10^{-5} M$ solutions of ammonia, sodium cyanide and sodium cyanate. The sodium cyanide solutions were given an extra dose of HTH equivalent to that consumed in the rapid conversion of cyanide ion to cyanogen chloride. The results of these experiments demonstrated that the rate of consumption of chlorine by cyanide and cyanate is almost identical with that of cyanogen chloride, but that the reaction with ammonia is about onehundred fold more rapid.

Chlorinolysis of Cyanogen Chloride by Hypochlorite.-To determine whether the identity in rate of destruction of hypochlorite by cyanogen chloride and by cyanate could be due to a rapid conversion of cyanogen chloride to cyanate, solutions were prepared containing $4.5 \times 10^{-4} M$ cyanogen chloride and 7.1, 14.1, 28.2 and 70.5 \times 10^{-5} M chlorine in deammoniated tap water. Samples were withdrawn, the unreacted chlorine was destroyed by one minute contact with a slight excess of thiodiglycol and the cyanogen chloride was then measured by Reagent A.8 The thiodiglycol treatment was demonstrated by control experiments to effectively destroy the excess chlorine and to have no effect on the analyses. The results demonstrated that there was a very rapid destruction of cyanogen chloride in the presence of hypo-

(13) We have speculated on the possibility that this intermediate might be the N-chloro derivative of carbamic acid (HOCONHCl).

⁽¹²⁾ Since this manuscript was submitted for publication, Friel and Wiest (*Water Works & Sewerage*, **92**, 97 (1946)) have reported the rapid destruction of cyanide by exhaustive chlorination, but have suggested a course for the reaction which does not appear to explain the observations reported herein.

chlorite. Within five to fifteen minutes one mole of cyanogen chloride is destroyed in this rapid reaction for each mole of hypochlorite present.

Summary

The kinetics of hydrolysis of cyanogen chloride in alkaline, bicarbonate-buffered and phosphatebuffered solutions appear to be in satisfactory agreement with the following expression.

 $-d[ClCN]/dt = 6 \times 10^{9}[ClCN][OH^{-}] + 3 \times 10^{-9}$ [ClCN][phosphate] Cyanogen chloride reacts with hypochlorite stoichiometrically corresponding to the oxidation of the nitrogen it contains to gaseous nitrogen. Since the reaction is markedly more rapid than hydrolysis under the same conditions, there must be a rapid direct reaction between cyanogen chloride and hypochlorite. This was shown to be even more rapid than subsequent disappearance of "active chlorine."

Notre Dame, Indiana

RECEIVED JUNE 20, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Thermodynamics of Aqueous Hydrofluoric Acid Solutions

By HERMAN H. BROENE¹ AND THOMAS DE VRIES

Two instances are recorded in scientific literature in which a hydrogen electrode has been used in hydrofluoric acid solutions. Wynne-Jones and Hudleston² measured the e. m. f. at 25° of the cell H₂, HF (N), KCl (sat.), Hg₂Cl₂, Hg, where N varied from 0.03 to 1.55. Jahn-Held and Jellinek⁸ measured the potential of the cell Pb (5% amalgam), PbF₂(s), HF(1 N), H₂ at 15, 25 and 35°.

Ivett and De Vries⁴ have made a study of the cell Na(amalgam), NaF(m), PbF₂(s), Pb(amalgam), and have determined the standard potential of the lead amalgam-lead fluoride electrode. In the present investigation use was made of this standard value to determine thermodynamic properties of hydrofluoric acid solutions. The activity coefficients of hydrofluoric acid were calculated from measurements made on cells of the type: I Pb(5% amalgam), PbF₂(s), HF(m), H₂(g); and the equilibrium constants from cells of the type: II, Pb(5% amalgam), PbF₂(s), HF(m₁), NaF(m₂), H₂(g).

Experimental

Materials.—Lead amalgam, lead fluoride and sodium fluoride were prepared in the manner described by Ivett and De Vries.⁴

Hydrogen from a commercial cylinder was bubbled through a chromous (II) sulfate⁵ or chromous chloride⁶ solution to remove traces of oxygen, and through a solution of copper sulfate to remove any hydrogen sulfide which might have been formed in the first solution.⁷ The hydrogen was bubbled twice through distilled water, and finally through a hydrofluoric acid solution of the same concentration and temperature as that used in the cell.

A few of the hydrofluoric acid solutions were prepared by diluting Baker and Adamson Reagent 48% hydrofluoric acid with conductivity water. Most solutions, however, were made from a stock solution prepared by bubbling Harshaw anhydrous hydrogen fluoride into conductivity water.

(5) Stone and Beeson, Ind. Rng. Chem., Anal. Ed., 8, 188 (1936).

Analysis of Hydrofluoric Acid.—A measured amount of hydrofluoric acid was placed in an Erlenmeyer flask and phenolphthalein added. Sodium hydroxide was run in from a buret until the acid was almost neutralized. The mixture was heated to boiling and the titration finished while hot. The sodium hydroxide solution remaining in the buret was used to titrate a sample of standard hydrochloric acid in the same manner. The results of three or more analyses were averaged. All volumetric ware was carefully calibrated and a correction made to each titration for carbon dioxide dissolved in the acids and wash water. While the titration in bare Pyrex flasks involves the formation of some fluosilicic acid, this will not interfere if the solution is kept above 60°.¹

The molality of each solution was calculated from the normality using the density data of Winteler.⁹

In order to prepare mixed solutions of hydrofluoric acid and sodium fluoride, the acid solution was first prepared and standardized. To a known weight of this solution, a weighed amount of dry sodium fluoride was added and the molality calculated. Apparatus and Procedure.—The apparatus used was of

Apparatus and Procedure.—The apparatus used was of conventional design. The anode and cathode were, however, in two separate compartments connected by a bridge containing the electrolyte. This was necessary to prevent poisoning of the platinized platinum electrode by lead ions. The electrodes were sealed in place with paraffin wax to make the cell air tight. Hydrogen escaped through a trap containing distilled water.

The cell was placed in a water thermostat which held the temperature to $\pm 0.02^{\circ}$. Hydrogen was allowed to ow slowly past the platinized platinum electrode, and after three to five hours the e. m. f. became constant. When changed to another temperature, readings became constant after about an hour and a half. Measurements were made on a Rubicon, type B, potentiometer, using a carefully calibrated standard cell.

A fresh platinized platinum electrode was used for each cell assembled. Platinization was done in two ways: one using chloroplatinic acid only, and one using acid containing a trace of lead acetate. Both methods gave satisfactory electrodes which agreed very closely in e. m. f. readings. Platinization, however, took longer without lead acetate, and it gave a dull gray deposit instead of a black one.

The cell apparatus was constructed of Pyrex glass. The interior was coated with a special lacquer¹⁰ and then with ceresin wax. Before a satisfactory coating of this kind was developed, considerable trouble was experienced.

(10) S-988, Stoner-Mudge, Inc., Pittsburgh, Pa.

⁽¹⁾ Abstract of the Ph. D. dissertation of H. H. Broene whose present address is Bastman Kodak Co., Rochester, N. Y.

Wynne-Jones and Hudleston, J. Chem. Soc., 125, 1031 (1924).
Jahn-Held and Jellinek, Z. Elshirochem., 43, 401 (1936).

⁽⁴⁾ Ivett and De Vries, THIS JOURNAL, 63, 2821 (1941).

⁽⁶⁾ Stone and Skawinski, (bid., 17, 495 (1945).

⁽⁷⁾ Branham, J. Research Natl. Bur. Standards, 21, 45 (1938).

⁽⁸⁾ Swinehart and Flisik, Ind. Eng. Chem., Anal. Ed., 18, 419 (1944).

⁽⁹⁾ Winteler, Z. ongew. Chem., 18, 38 (1902).