THE SILVER VOLTAMETER—PART II

THE CHEMISTRY OF THE FILTER PAPER VOLTAMETER AND THE EXPLANATION OF STRIATIONS

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CONTENTS

I. THE QUALITATIVE EXPERIMENTS WITH THE SILVER VOLTAMETER

A. INTRODUCTION

The qualitative work with the voltameter began early in July of 1909, following the quantitative experiments recorded in Part I,[1] and continued until the middle of the following December. During this time only five quantitative experiments were made and these have been included with the earlier measurements. The qualitative experiments consisted in making silver deposits under varying conditions in small voltameters, which could be easily examined under the microscope or photographed. In addition to these we made some deposits in the field of a microscope and investigated the potential relations between anode and cathode. After resuming the quantitative work we still made a few qualitative tests from time to time and have included them here. In Section II of this paper some further qualitative work will be described in connection with the chemistry of the filter paper voltameter.

1. JUSTIFICATION OF THE QUALITATIVE METHOD

From the first experiment in which we used the porous pot we have been impressed with the difference in appearance between deposits made when filter paper is present and when it is not. As the work progressed we found the appearance under a binocular microscope so reliable a criterion for the presence of such impurities as considerably affect the weight of deposit that we felt justified in hastening the work by making qualitative instead of quantitative experiments in order to test the effect of a large number of impurities. These were added to pure silver nitrate solution in the hope of throwing light on the chemical or mechanical processes by which filter paper and kindred substances not only modify the crystalline structure of the deposited silver, but also appreciably increase its weight.

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[1] This Bulletin, 9, p. 151.

Although the appearance to the eye of the deposit may change with the depth of deposit, the appearance of the deposit under the microscope indicates whether it has come down from an electrolyte containing filter paper, or the products of filter paper, or certain other organic impurities, or whether it has come down from a pure electrolyte of $AgNO_3$ and water uncontaminated by such foreign substances. In the first case the deposit is noncrystalline or imperfectly crystalline, according to the quantity of the impurity. It may resemble molten metal that has been dropped on a cold plate and spattered, or lava having a rough, irregular surface, and the deposit more or less massed together; or it may be in needle-shaped crystals, or imperfectly crystalline when the impurity is slight. The color may be grayish when relatively large quantities of impurities are present, or merely tarnished when very small quantities are present. The pure electrolyte in a Richards or Poggendorff voltameter [2] gives a beautiful crystalline deposit, the crystals having well-defined faces and angles, and looking much like glass or diamonds under the microscope, as they are generally without a metallic luster. In the larger cups (with one-half ampere for two hours) the crystals are well separated, the clean platinum surface showing between the crystals. In the smallest cups, where the quantity of silver is twice as much per unit of area, the crystals are elongated, but otherwise similar.

2. APPARATUS EMPLOYED

The results of most of the qualitative experiments are most easily presented by showing the photographs of the deposits obtained. These photographs were made by means of a vertical camera and microscope for the more highly magnified (5 to 16 times). For the smaller magnifications an ordinary camera, with bellows extended, and a symmetrical lens was generally used.

Many of the qualitative runs were made in two small platinum dishes 4 cm in diameter by 1.5 cm deep, having approximately 25 sq cm surface. As the large cups ordinarily used had seven times this area, the current through the small voltameters was made correspondingly small, the current density and time remaining the same.

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[2] These and other forms of voltameter are described in Part I of this series of papers.

3. STANDARD TYPES OF DEPOSIT

As we have before stated, the difference between the deposits made in the Rayleigh and Richards voltameters is very striking and is shown in the following photographs:

Fig. 1 shows some of the deposit removed from a normal Rayleigh voltameter of large size, having one sheet of filter paper to separate the anode and cathode, while Fig. 2 shows five striations stripped from the sides of a dish in which the electrolyte had been contaminated with an excess of filter paper. These are to be contrasted with Fig. 3, which is from a normal Richards voltameter, large size, and Fig. 4 from a normal Richards, small size, and Fig. 5 from a Poggendorff voltameter. Considering these as standard types of deposit we now turn to the tests made in a qualitative way only.

B. FILTER PAPER EFFECT

1. ACTION OF WATER UPON FILTER PAPER

In the investigation of the action of filter paper on silver nitrate we were led to inquire whether it was essential that the filter paper should come in contact with the silver nitrate itself or whether it was sufficient to immerse the paper in water subsequently used for making the $AgNO_3$ solution. This was tried in several ways. A 15 per cent solution of $AgNO_3$ was prepared from 300 cc of double-distilled water in which about 6 grams of No. 595 S & S filter paper had soaked over night. The deposit was strongly striated, indicating an action between filter paper and water. The bottom of the platinum cup with this deposit is shown in Fig. 6. The water used in this experiment after being drawn off from the filter paper was filtered through one sheet of the same kind of filter paper to free it from suspended matter. On adding the silver-nitrate crystals to it a slight bluish tinge was noted. This gradually turned to a reddish brown, suggestive of a colloidal solution. After standing some hours this finely divided substance coagulated and settled to the bottom, leaving the liquid again clear. This experiment was repeated several times with like results.

Fig. 1.—*Deposit removed from a normal Rayleigh voltameter.* × 16

Fig. 2.—*Striations stripped from the sides of a voltameter having electrolyte contaminated with an excess of filter paper.* × 16

Fig. 3.—*Crystalline deposit from Richards voltameter, large size.* × 16

Fig. 4.—*Crystalline deposit from Richards voltameter, small size.* × 16

Fig. 5.—*Crystalline deposit from Poggendorff voltameter.* × 16

Fig. 6.—*Star in bottom of bowl due to contaminated electrolyte.* × 8

Fig. 7.—*Striated deposit from contaminated electrolyte. 10 g of No. 590 filter paper stood in 300 cc of water used for making the electrolyte. For comparison with Fig. 8.* × 1.5

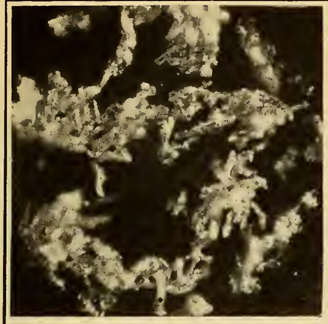
Fig. 8.—*Striated deposit made under same circumstances as in Fig. 7, except that No. 595 filter paper was used, showing that striations are not due to the quality of the paper.* × 1.5

Fig. 9.—*Deposit from a solution contaminated with thoroughly washed filter paper.* × 16

Fig. 10.—*Deposit from an electrolyte contaminated with writing paper.* × 16

Fig. 11.—*Deposit from an electrolyte contaminated with blotting paper.* × 16

Fig. 12.—*Deposit from an electrolyte contaminated with rag paper.* × 16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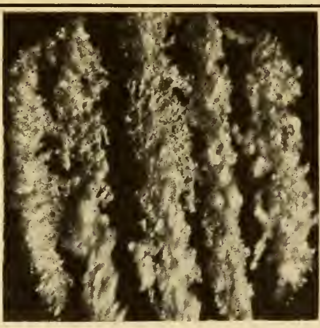
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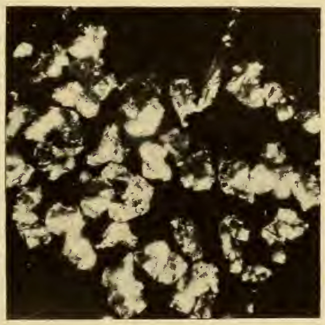
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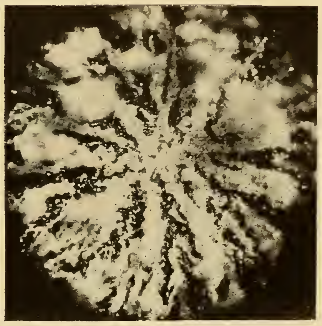
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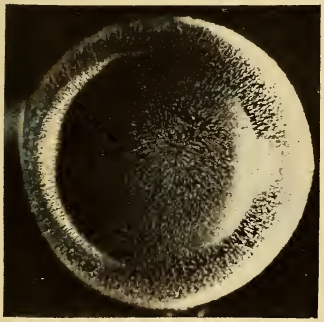
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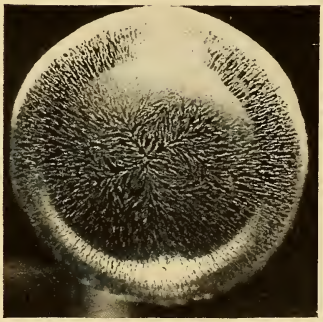
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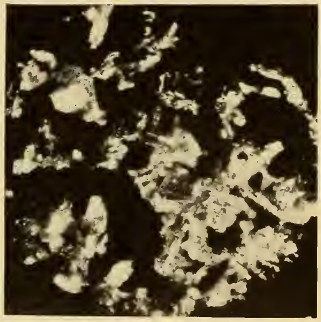
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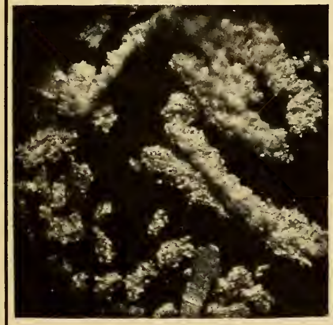
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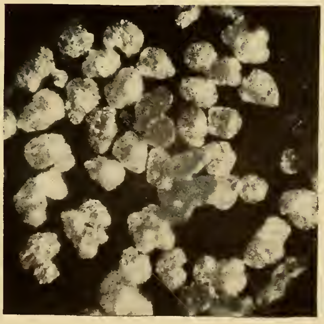
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2. COMPARISON OF DIFFERENT GRADES OF FILTER PAPER

It seemed of interest to determine whether different grades of filter paper produced sensibly equal effects upon the deposit. To test this point, two 10-g samples of No. 595 S & S and No. 590 S & S were weighed out and each put to soak in 300 cc of double-distilled water. On the following day these were used to make up two 15 per cent solutions of $AgNO_3$ for use in the small platinum dishes. These two voltameters were run simultaneously, and except for the chance configuration on the bottom of the cups the two deposits are identical. They are shown photographically in Figs. 7 and 8. As No. 590 filter paper is a higher grade than No. 595 it seems that the effect is the same regardless of the kind of paper, provided the relative amounts of paper to solution are the same, a fact which had been found already in our previous quantitative work.

3. EFFECT OF WASHING THE FILTER PAPER

Prolonged soaking of filter paper in cold distilled water did not apparently lessen its power to react with water or silver nitrate, and thus to alter the deposit. A sample of filter paper which had been repeatedly washed during the preceding 12 days was placed in distilled water for some hours and then poured off. This water was then used to make up a 15 per cent solution of $AgNO_3$. The deposit from this was not strongly striated, but was very loose and not distinctly crystalline as from an uncontaminated solution. It is shown in Fig. 9.

4. TESTS WITH OTHER KINDS OF PAPER

On trying other kinds of paper than filter paper we again found the deposit greatly altered although not always in the same way. Fig. 10 shows the result of soaking common writing paper in silver nitrate solution and Fig. 11 the result of white blotting paper. A sample of all-rag paper with sizing produced a very remarkable deposit shown in Fig. 12. The electrolyte for this last was brownish even after filtering, and the deposit was laid down in rounded heads, with here and there a blossom of crystallized silver.

An examination of various samples of filter paper showed that they were made from linen and cotton rags.

Hence, in order to learn which of these substances was producing the effect on the silver nitrate, Mr. W. S. Lewis, of this bureau, kindly prepared for us three sheets of unsized paper, one made exclusively from cotton rag, one from linen rag, and one from wood pulp. These were used in place of filter paper in a quantitative experiment on August 26, 1909. The weights of these papers compared with the weight of a sheet of the same size of No. 595 S & S are as follows:

TABLE I

	Grams
No. 595 S & S	1. 90
Cotton paper	1. 63
Linen paper	1. 04
Wood paper	2. 11

The cotton and linen papers were thin and tough, but the wood paper was thick and so easily torn that in dismantling the voltameter after the run the bag broke and precipitated the anode slime down on the deposit, so that the weight could not be ascertained. All the deposits were striated, particularly that from the wood paper, and we believe this deposit would have been found to be much the heaviest if it could have been weighed. The heaviest of the other deposits was from the linen paper. This showed about 30 parts in 100 000 excess over the two standard Richards voltameters that were included in the same run. The deposit from the cotton paper showed only 17 parts in 100 000 excess.

5. EFFECT OF PINE-WOOD SHAVINGS

Several experiments with pine-wood shavings were made and these showed very great changes in the deposit from electrolyte contaminated with it. When the wood was soaked in the electrolyte itself we obtained the deposits shown in Figs. 13 and 14. Even thoroughly washed wood soaked for a short time in water subsequently used for making up the electrolyte showed a marked effect on the deposit, as appears in Fig. 15.

C. ADDITION OF CERTAIN OTHER SUBSTANCES TO SILVER NITRATE

1. ACID

The addition of acid to $AgNO_3$ solutions even in small amounts reduces the size of the crystals with consequent increase in the number. So far as we have observed the crystalline structure of the deposit is not altered if the electrolyte does not contain organic impurities.

The crystals resulting from the addition of 0.15 per cent of nitric acid are shown (Fig. 16). At a later date we investigated the increase in the number of crystals as the acid was added in successive portions. For this purpose a small piece of platinum ruled in squares 0.2 mm on a side was used as cathode in a pure 15 per cent solution of $AgNO_3$ to which we added tenth normal acid a few drops at a time. The number of crystals in any square were counted under a microscope. For each observation four squares chosen at random were counted and averaged. After being counted the deposit was removed from the cathode, which was then washed and made ready for the next deposit. The experimental difficulties are very great because the surface conditions of the platinum exercised so pronounced an effect upon the deposit. We maintained these conditions as nearly constant as possible and found increasing numbers of crystals as the acid was added. Twenty-three one-thousandths per cent of acid about doubled the number observed from the same solution when neutral.

2. COPPER SALTS, SILVER ACETATE, ALKALI, COLLOIDAL SILVER, ETC.

In the same manner as above we added small quantities of copper nitrate, which increased the number of silver crystals deposited. But the greatest effect was produced by silver acetate, which increased the number of crystals about 100 times when the silver nitrate was saturated with the acetate. On the other hand, the addition of sodium hydroxide, colloidal solutions prepared by Bredig's method and the extract of filter paper produced no appreciable change in the number of crystals, although modifying their crystalline structure. There is no apparent connection between these effects on the number of crystals and the resulting electrochemical equivalent from solutions containing these substances as impurities. Thus we know from our quantitative

Fig. 13.—*Deposit from an electrolyte contaminated with wood fiber.* × 16

Fig. 14.—*Star in bottom of bowl due to contamination of electrolyte with wood fiber.* × 5

Fig. 15.—*Deposit from an electrolyte contaminated with thoroughly washed wood fiber.* × 16

Fig. 16.—*Deposit showing the small crystals resulting from the addition of acid to the electrolyte.* × 16

Fig. 17.—*Deposit from an electrolyte contaminated with gelatine.* × 5

Fig. 18.—*Same more highly magnified.* × 16

Fig. 19.—*Striated deposit from contaminated solution for comparison with Fig. 20*

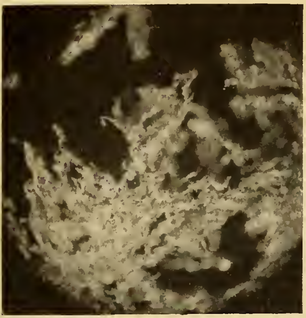
Fig. 20.—*Same electrolyte as for Fig. 19 filtered through a porous cup. Striations eliminated*

Fig. 21.—*Crystalline deposit showing absence of effect of the added silver nitrite.* × 16

Fig. 22.—*Striated deposit due to dextrose*

Fig. 23.—*Same as Fig. 22, but more highly magnified.* × 16

Fig. 24.—*Noncrystalline, deposit due to phloroglucinol.* × 16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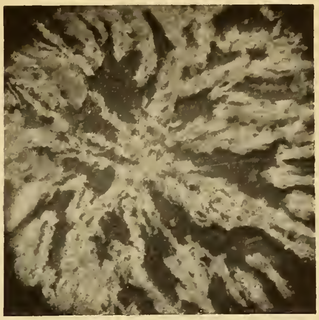
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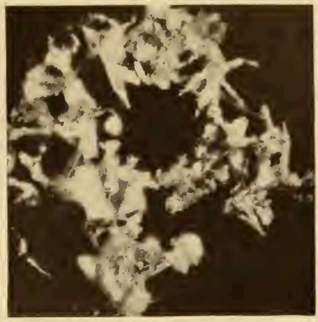
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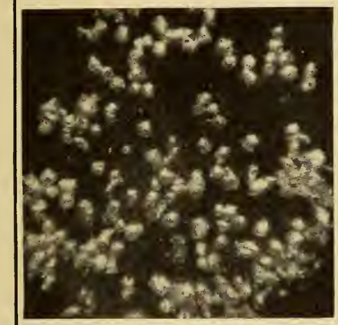
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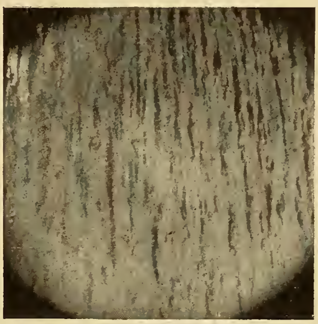
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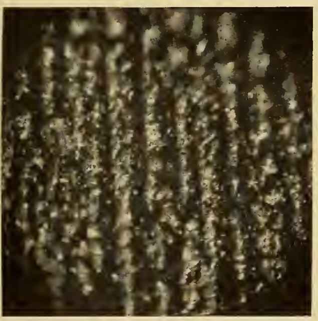
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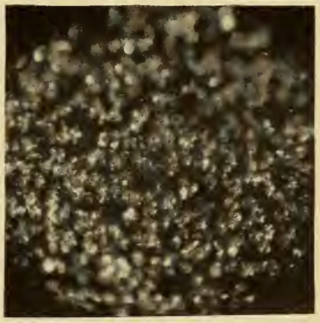
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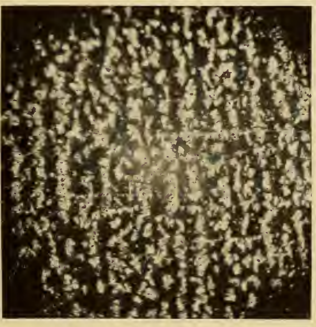
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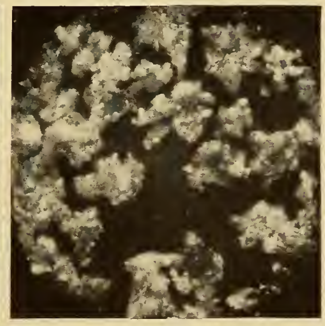
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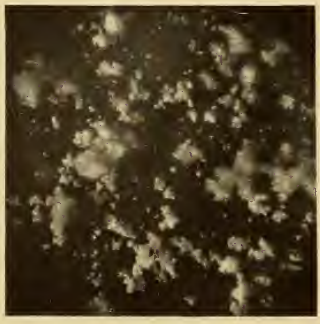
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experiments that the presence of nitric acid causes a reduction in deposit made from very pure solutions as well as increasing the number of crystals, but silver acetate gives an increased weight of deposit. Sodium hydroxide and filter paper extracts cause large increases in the weight of deposit, but appear to be without effect on the number of crystals.

3. GELATINE

Gelatine is one of the "addition agents" occasionally employed in electroplating and is recommended by Betts & Kern[3] for *preventing* crystallization of the deposit in the lead voltameter which they propose as a means of measuring current. We added 1 part in 2000 of pure soluble gelatine to a 15 per cent solution of silver nitrate and electrolyzed it in a small voltameter. The resulting deposit looked more like lead than silver. The striations were very prominent and from the bottom feather-like projections over a centimeter long grew up toward the anode. The deposit to the naked eye appeared amorphous, but under the microscope is was seen to be made up of very small crystals without any regular arrangement. The electrolyte in the mean time turned a bright straw yellow changing to a deep red. This we believe due to colloidal silver thrown out of the solution as a result of the gelatine, but this will be more fully discussed further on in this paper. Samples of the deposit are shown in Figs. 17 and 18.

D. COLLOIDAL SOLUTIONS

1. MIGRATION OF THE COLLOID

By Bredig's method we prepared a considerable quantity of colloidal silver. At first this was a neutral color which slowly turned greenish until at the end of almost a year it is about the color of olive oil. A similar solution of colloidal gold prepared at the same time, which was almost black at first, is now purple.

A U tube 1 square centimeter in cross section and 20 centimeters axial length was filled with the colloidal silver solution and electrodes of platinum foil were fixed in the two ends of the tube. With 120 volts a current of 0.00006 ampere could be passed through it. Clouds appeared in the colloidal solution soon after starting the current and a little gas on the anode. After 20 minutes the color of the solution around the anode was paler than around the cathode,

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[3] The Lead Voltameter, Electrician; 54, p. 16, 1904.

but to make certain that the colloid was actually traveling with the current we reversed the polarity and allowed the current to flow during the night. In the morning the liquid was clear and all the colloid was hanging loosely on the cathode while bubbles of gas were on the anode. When the deposit was heated it turned white like silver, and this was dissolved in HNO_3 and then precipitated as silver chloride to establish the identity of the deposit. The important fact for our present work is that the colloid was carried with the current. On this point there has been some difference of testimony among investigators.[4]

We added a small amount of the same colloidal solution to some of the best 15 per cent silver nitrate solution and electrolyzed it. Although there were no striations resulting, the crystalline structure was modified. What are usually single crystals in a deposit made under normal conditions were now aggregates of many small crystals. This we think may be explained by supposing that the colloidal particles as they are laid down become nuclei on which the silver precipitated from the electrolyte itself, grows. This fact also is important and will be taken up again in Section III describing the formation of striations.

2. FILTERED SOLUTIONS

We filtered some of the colloidal solution through a filter made from one of the porous cups as used in the voltameter, employing a vacuum to hasten the filtering. The liquid after passing through the filter was colorless and could only be distinguished from distilled water by a very slightly higher conductivity. This complete elimination of the colloidal silver suggested the possibility of purifying a contaminated solution of $AgNO_3$ by the same process, particularly since in deposit No. 66 we had placed a quantity of filter paper inside the porous cup without producing any apparent effect on the silver deposited outside.

To make a rigid test we prepared a solution of $AgNO_3$ in which filter paper had been soaked over night to insure very marked striations. The electrolyte was then divided into two equal portions, one of which was filtered through the porous cup. The two portions were electrolyzed in two small voltameters in series

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[4] Allgemeine chemie der Kolloide, Müller, p. 43, 1907.

and identical in every respect except the electrolyte. As one would expect, the unfiltered portions gave *very heavy striations and a decided yellowish deposit.* The filtered portion, on the other hand, gave a deposit that was crystalline, *entirely free from striations, and white.* These are shown in Figs. 19 and 20.

Because of the importance of this point we made a further test as follows: A strip of platinum serving as a cathode was placed inside a porous cup partly filled with pure silver nitrate. Outside the porous cup was a badly contaminated solution and anode contained in a beaker. In order that the diffusion through the pot should be with the current—that is, from the impure solution into the pure electrolyte—the liquid was made to stand about 1 centimeter higher outside than inside the porous pot. At the end of one hour the deposit was examined under a microscope and found to be good, without any suggestion of filter paper contamination. To make the experiment complete we then put the pure solution outside the porous cup and the impure electrolyte inside under the same conditions as before and obtained a deposit characteristic of filter paper. Because of these experiments we believe the porous cup a very efficient separator between anode and cathode without introducing considerable resistance or other difficulties. As we have used the Richards voltameter we find its resistance about 2 ohms. We have found the resistance of the small Richards voltameter to be from 1.7 to 2.0 ohms, while a voltameter of the same size but without the porous cup showed 1.2 ohms. The resistance of the large size Richards voltameter as used in our early work with a large anode is 0.8 ohm as compared with 0.34 ohm for the same without the porous cup. In our later work we have used small anodes in the large dishes and find the resistance about 1.7 ohms with the porous pot. All the values given are for 15 per cent silver nitrate solution.

E. EFFECT OF OXYGEN AND HYDROGEN IN THE PLATINUM CATHODE

One further qualitative experiment remains to be discussed, and that is an investigation on the effect of gases in the platinum cathode. A part of a strip of platinum was oxygenized by electrolysis in dilute sulphuric acid, and then another part of it was hydrogenized by the same method. When the whole was immersed in silver nitrate and a deposit of silver made on it we found *a large number of small crystals* where the hydrogen had been applied and *a small number of large crystals* where the *oxygen* had been applied to the cathode. We also arrived at the same result during the course of some single potential measurements.

The significance of this result will appear more fully in connection with the discussion of the cause of striations.

II. CHEMISTRY OF THE FILTER PAPER VOLTAMETER

A. ASSUMED INACTIVITY OF FILTER PAPER IN THE VOLTAMETER

1. HISTORICAL

It is evident from the long-continued use of filter paper in the silver voltameter that investigators generally have assumed that filter paper is without appreciable chemical action upon silver nitrate solutions, or at least that the effect of any such action is negligible in the silver voltameter. This assumption seems quite natural when one reflects that filter paper is composed of very pure cellulose, a substance which possesses an extraordinary degree of resistance to the action of most chemical reagents.

Filter paper is first specifically mentioned as a septum in the silver voltameter in the classical work of Lord Rayleigh and Mrs. Sidgwick in 1884.[5] Since that time it has been quite generally used by numerous investigators.[6]

T. W. Richards and his co-workers in 1899 discarded filter paper as a septum and substituted a porous pot in its place. So far as they state, this substitution was not made because of any supposed chemical action of the filter paper upon the electrolyte, but because they desired a septum which would more effectually prevent certain anomalous products, which they supposed were formed at the anode, from reaching the cathode. Indeed, in one experiment, to show the "gain in weight of silver in contact with anode solution" they wrapped the anode of the voltameter from

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[5] F. Kohlrausch (1873) merely states that he wrapped the anode in thin material ("zeug"), which probably refers to a textile material.

[6] Kahle; Leduc; Roger and Watson; Smith, Mather, and Lowry; Laporte; and others.

which the anode solution was obtained with filter paper "to retain the fine crystal powder which always separates from it." It is evident from this that they did not suspect any chemical action of the filter paper upon the electrolyte which might affect the result of these tests.

Mylius,[7] at the Physikalisch-Technische Reichsanstalt, stated in 1902 that filter paper reacts on silver nitrate and that this might be a source of error. Guthe[8] (1904) states that for this reason he avoided the use of filter paper in the preparation of his solutions of silver nitrate. Carhart, Willard, and Henderson (1906)[9] observed that some kinds of filter paper, at any rate, gave the deposited silver a faint yellowish tinge and attributed this to impurities in the paper. "We raise the question," they add, "whether the effect of the filter paper itself on the amount of the deposit has been sufficiently investigated."

Smith, Mather, and Lowry (1907)[10] in their elaborate investigation observed an increase of weight of the deposit when the silver nitrate was filtered hot through filter paper, and also when a large quantity of filter paper was used in the voltameter. They noted further that the deposit in such cases was striated, whereas under normal conditions it was not. However, they believed that as ordinarily used the effect of filter paper in the voltameter was negligible and used it throughout their own work.

Since the higher grades of "ash free" filter paper consist of the purest known form of cellulose, the question of chemical reaction between filter paper and the electrolyte resolves itself into one which has to do mainly with the chemical action of water or of an aqueous solution of silver nitrate upon cellulose.

A very brief summary of the current views regarding the constitution and chemical properties of cellulose is perhaps not inappropriate at this point. These views furnished a working hypothesis in our efforts to discover what possible reactions might take

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[7] Zs. f. Instrk, 22, p. 155.

[8] This Bulletin, 1, p. 21, 1904; Phys. Rev., 19, p. 138.

[9] Trans. Amer. Elec. Ch. Soc., 9, p. 375.

[10] Phil. Trans., 207, p. 545; 1908.

place between filter paper and silver nitrate solutions, and furthermore they probably account for the assumption that filter paper must be inert in the voltameter. No attempt will be made to give a thorough or critical discussion of these views, but merely an outline of the more salient points of the generally current theory of the chemical constitution of cellulose will be presented.

2. OUTLINE OF THE CHEMICAL CONSTITUTION AND PROPERTIES OF CELLULOSE

Cellulose is generally regarded as a polyose of very high molecular weight,[11] i. e., its molecule is composed of a very large number of molecules of a monose or simple sugar (dextrose in the case of cellulose from cotton, etc.) combined with each other (with the elimination of water), so that its formula may be represented thus:

$$n(C_6H_{12}O_6) - (n - 1)(H_2O)$$

or, with close approximation by the simpler formula $(C_6H_{10}O_5)n$, since n is a very large number of unknown magnitude and n − 1 differs from n therefore by an inappreciable amount.[12] In this sense cellulose may be regarded as an anhydride of dextrose. This view is based mainly on the percentage composition of cellulose and the fact that dextrose is formed by the hydrolysis of cellulose, thus:

$$\underset{\text{cellulose}}{(C_6H_{10}O_5)n} + nH_2O = \underset{\text{dextrose}}{n(C_6H_{12}O_6)}$$

The reaction expressed in the above equation takes place in successive steps by the gradual interaction of water (hydration and hydrolysis) and cellulose under the influence of certain hydrolyzing or hydrating agents.

The complete hydrolysis to dextrose is difficult to attain, requiring a quite drastic chemical treatment of the cellulose. The successive steps by which this reaction takes place (due to the increasing amounts of water which combine with the cellulose) give rise to intermediate cellulose-water compounds with elementary percentage compositions varying between that of cellulose on the one hand and of dextrose on the other. When the amount

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[11] Holleman: Text Book of Organic Chemistry, 1902, p. 287.

[12] Since the atoms of the first molecule of water are split off from two molecules of the monose (or condensation products), the total number of molecules of water thus split off must be one less than the total number of dextrose molecules.

of water which enters into the reaction is relatively small, so that the percentage composition differs only slightly from that of cellulose itself, the cellulose-water compounds are generally referred to as cellulose hydrates, and the process is generally termed hydration. On the other hand, when the amount of water entering into the reaction is relatively large, so that the percentage composition is quite appreciably different from that of cellulose, the process is generally referred to as hydrolysis, a decomposition of the cellulose into products of lower molecular weight in this case being assumed. However, in the literature on cellulose the terms hydrolysis and hydration have often been used interchangeably, notwithstanding the well-known distinction between these terms as ordinarily used with reference to the reaction of substances with water.

The following general facts are of fundamental importance in this connection:

The extent of the hydration or hydrolysis of cellulose depends upon the intensity of the hydrating or hydrolytic treatment used.[13] The drastic hydrolyzing agents, such as strong acids at high temperatures, give rise to products which approach more or less closely to dextrose in percentage composition and molecular weight, while weaker hydrating agents produce cellulose hydrates differing only slightly in percentage composition from cellulose itself.

The chemical reactivity in general of the products of hydration or hydrolysis is directly dependent upon the extent of their hydration or hydrolysis.[13]

The members nearest cellulose in percentage composition differ only very slightly in their properties from cellulose itself—chiefly in their greater capacity for holding hygroscopic moisture. As the degree of hydration or hydrolysis increases, however, the products become gradually more reactive, as exhibited by their behavior toward special solvents, the greater ease with which they form esters, etc., and in the lower members of the series (i. e., those nearest dextrose in percentage composition and molecular weight) by the gradual increase in their reducing properties.

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[13] Cellulose, Cross and Bevan, Longmans & Co., 1903, p. 5 et seq.; ibid. pp. 20–21.

This gradual development of reducing properties in the lower members of the series finds its explanation in the manner in which dextrose molecules are supposed to be linked together in cellulose or hydrated cellulose. According to this view the linking together of the dextrose molecules is accomplished through the medium of the CO group, to which the strongly reducing character of dextrose is ascribed. The exact mechanism of this linking need not be discussed here. It should be said, however, that in the combination (or condensation) of the dextrose molecules the CO groups are destroyed as such through their interaction with hydroxyl groups, water being eliminated in the process. Consequently, the molecules formed by this condensation are devoid of reducing properties, provided, of course, all the CO groups of the dextrose molecules have thus entered into reaction.

In the hydrolysis of the lower members of the cellulose-water compounds, these CO groups are successively liberated, giving rise to the gradual increase in the reducing properties of the products.

It should be borne in mind, however, that it is only in the comparatively recent work upon cellulose that it has been recognized that even these more completely hydrolyzed cellulose-water compounds possess reducing properties characteristic of the CO group.[14]

In the formation of cellulose-water compounds containing relatively less amounts of combined water than those just discussed, the addition of water does not bring about decomposition in the sense that CO groups are liberated. In such cases, if actual hydrolysis has occurred the inference is that the linking together of the proximate constituents of the molecule has taken place between hydroxyl groups only, so that no CO groups are involved, and consequently these are not liberated by the hydrolysis.

The less completely hydrolyzed products and of course the merely hydrated celluloses are quite generally regarded as nonreducing carbohydrates, i. e., they show no reduction of Fehling's solution nor any other reactions indicating the presence of free CO groups. Indeed, as we have already stated, the hydrated celluloses at least are said to differ from cellulose itself only in

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[14] See, for example, Vignon, C. R., **126**, p. 1355 (1898).

respect to what are considered to be their less essential chemical properties, such, for example, as their varying resistance to hydrolysis, esterification, or solution in certain special solvents. In general their very close resemblance to cellulose is shown by their negative or nonreactive characteristics.

Quite separate from all questions of constitution, the one generalization most emphasized regarding the chemical nature of cellulose is its great resistance toward the action of the most various chemical reagents. It is quite frequently pointed out that this nonreactive character is in fact a necessary consequence of its method of isolation from the woody tissue of plants, inasmuch as cellulose is simply the insoluble residue left after various drastic treatments of the raw material have removed the more reactive impurities with which it is associated.

3. SOME CHEMICAL PROPERTIES OF SILVER NITRATE SOLUTIONS

Remembering what has just been said regarding the chemical nature of cellulose, it becomes apparent why one would not expect a solution of silver nitrate, when pure, to react upon cellulose to an appreciable extent. A solution of pure silver nitrate, even if slightly acid from its own hydrolysis, should possess only exceedingly weak hydrolyzing power upon cellulose, and one would not expect it to have any action at all upon cellulose in the sense of the production of substances having free CO groups, and therefore possessing strong reducing properties. So far as hydrolytic action is concerned, therefore, one would expect at most merely the formation of slightly hydrated modifications of cellulose, which, while being somewhat more soluble than cellulose itself, would otherwise differ only inappreciably from the latter in all their more essential chemical properties.

Furthermore, neutral or acid solutions of silver nitrate are only very slightly reduced even by carbohydrates containing free CO groups. It is for this reason that in the well-known silver-mirror test for aldehydes (or for the free CO group in general) only strongly alkaline ammoniacal silver solutions are employed. On the other hand, polyoses, such as cane sugar, which do not contain this group, do not show the characteristic reduction of even the strongly alkaline ammoniacal silver solutions if the conditions are regulated so as to avoid hydrolysis of the carbohydrate. Since both cellulose and its hydrated modifications are regarded as belonging to this latter class of polyoses, which contain no free CO groups, one would not expect them, when pure, to reduce to any appreciable extent even these strongly alkaline solutions of silver nitrate, much less that they could reduce neutral or slightly acid solutions of silver nitrate, which are much more stable toward reducing agents than are alkaline solutions.

B. EFFECT OF ORGANIC MATERIAL IN THE VOLTAMETER

1. DARKENING OF SILVER NITRATE BY ACTION OF ORGANIC MATERIAL

The statement is frequently made that silver nitrate becomes darkened by the action of "organic substances" under ordinary conditions in the light, the inference of course being that silver nitrate is reduced to finely divided metallic silver, to which the dark color is due. This should not be taken to mean that all organic material of whatever nature can reduce silver nitrate to metallic silver under ordinary conditions.

So far as we are aware no instance has been described where a reduction of pure silver nitrate to metallic silver is brought about by the action of organic substances which are not themselves reducing agents and which are incapable of hydrolytic decomposition into strong reducing agents of some kind.[15] It seemed safe to infer therefore that in most cases where "organic substances" are mentioned in this connection some kind of paper or other textile material is probably meant. In fact, we were unable to detect any darkening either of solutions of pure silver nitrate or of the dry crystals when allowed to remain in contact with paraffin for several days, whereas with paper or silk the darkening always occurred. In accord with this fact it was found that neither paraffin nor the lighter hydrocarbon oils such as hexane and heptane had any effect upon the appearance of the silver deposit when these substances were added to the electrolyte.

We therefore believed almost from the first that notwithstanding the resistant nature of cellulose hydrolytic decomposition probably took place to a very slight extent when silver nitrate was

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[15] This statement refers to the influence of the organic material itself and not to the action of light alone. Later it will be shown that a solution of pure silver nitrate free from all organic impurities is not appreciably reduced even by the prolonged action of light.

brought in contact with filter paper or similar organic material and that the products thus formed gave rise to the formation of striæ. The excess weight of the silver deposit might be due to silver thrown down by purely chemical action. We therefore added a number of organic substances to the electrolyte to see whether our supposition were true that any hydrolyzable organic material of the nature of cellulose could produce the abnormal, striated deposits of the same character as those which are obtained with filter paper. The results previously obtained with various kinds of paper, wood fiber, linen, etc., had seemed to support this view. (See p. 216.)

2. EFFECT OF CANE SUGAR AND STARCH IN THE VOLTAMETER

Among the first examples of hydrolyzable organic material whose effects in the voltameter were tried were cane sugar and starch. They were selected because of their very close chemical relationship to cellulose. We were surprised, however, to find that neither of these substances when added to the electrolyte produced any indications of the formation of striated deposits when the solutions were electrolyzed in the voltameter in the usual manner. The solutions electrolyzed contained approximately 1 per cent of each of these substances. The starch used was Kahlbaum's cornstarch. The cane sugar was prepared by Mr. R. F. Jackson, of this bureau, for use as a standard in saccharimetry, and was very pure. There was no darkening of the electrolyte after standing 24 hours, such as is observed if filter-paper extract is present in the electrolyte.

These results showed that the disturbances which give rise to the abnormally heavy, striated deposits are not due to the action of organic material as such, nor even to such organic material as is easily hydrolyzed, but depend in some way upon the specific nature of the organic material used. It was clear that filter paper is more reactive under the conditions present in the voltameter than either cane sugar or starch. This fact is quite out of harmony with the current views regarding the relative reactivities of these substances and suggested the possibility that the activity of the filter paper might possibly be due to the presence in it of impurities of a more reactive nature than cellulose.

C. IMPURITIES IN FILTER PAPER

1. ORGANIC IMPURITIES

The very pronounced effects produced by raw woody fibers (described on p. 216) led us to suspect that if, as suggested above, impurities in the filter paper were producing the disturbing effects they might be resins, pectocelluloses, glucocides, or similar organic impurities which are closely associated with cellulose in plant tissue and which are very difficult to separate completely from the pure cellulose. These impurities are much more reactive than cellulose itself and some of them are very easily decomposed by hydrolysis or decay into strong reducing agents, such as dextrose, phenols, or similar substances.[16] That they are, however, not the cause of these disturbances is shown by experiments described below (p. 231).

2. INORGANIC IMPURITIES

It is well known that even the purest forms of ash-free filter paper contain small amounts of inorganic salts. It appeared possible that these could precipitate insoluble silver salts which in some manner might produce the disturbing effects in the voltameter. Smith and Lowry, indeed, came to the conclusion that insoluble silver salts were responsible for the high values for the electrochemical equivalent obtained with used solutions of silver nitrate. They, however, considered that these impurities resulted chiefly from the action of contaminations in the atmosphere, such as hydrochloric acid and hydrogen sulphide, rather than from the filter paper. They pointed out that many of the so-called insoluble silver salts are soluble to an appreciable extent in relatively concentrated silver nitrate solutions, from which they are precipitated upon dilution, and emphasized the fact that the conditions at the cathode favor such a precipitation, owing to the thin film of dilute solution of silver nitrate which is formed there by the deposition of silver. For example, they obtained high values for the electrochemical equivalent by adding silver chloride or silver sulphide to the electrolyte. In one case,

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[16] Tannin yields the trioxybenzoic acid, gallic acid, and glucose. Coniferin yields dextrose and coniferyl alcohol, which latter is a phenol derivative. The mere decay of protoplasm yields paracresol, which is a very strong reducing agent.

namely, with silver hyponitrite, they actually obtained a deposit which was strongly striated, a result which they attributed to the hyponitrite, although filter paper was used in preparing this salt. They proposed a theory of the formation of striæ based upon these observations.

That the effects of filter paper in question can not be due to these inorganic impurities is shown by the experiments described in the following section.

3. SOLUBLE IMPURITIES

In harmony with the idea that striæ are caused by impurities of some kind it had been found early in our work that aqueous extracts of filter paper were quite as effective in producing striated deposits as the sheets of filter paper themselves.

To test the whole matter as to the effect of impurities, whether organic or inorganic, therefore, it was only necessary to extract these impurities as completely as possible and then test the influence of both the extracted filter paper and the extract itself in the voltameter.

The extraction was carried out in a Soxhlet apparatus made entirely of resistent glass to avoid possible contamination from cork or rubber stoppers. The experiment continued for six hours and the heating was regulated so that a complete extraction took place about every half hour. Thus the filter paper was extracted about 12 times with freshly distilled water. This thoroughly extracted filter paper was allowed to remain in the extraction apparatus until comparatively dry, being protected from possible contact with acid or ammonia fumes of the laboratory by means of guard tubes of soda lime and concentrated sulphuric acid connected to the upper outlet of the condenser tube. The boiling flask containing the extract had previously been removed and the lower opening of the condenser and the siphon closed by means of rubber stoppers.

The dry, extracted filter paper was then removed and tested as to its "activity" in the voltameter in the usual manner by noting whether it produced a striated deposit. Contrary to expectations, it was found that if there were any differences at all, the extracted filter paper was even more active than that which had not been treated. Moreover, the active soluble substance evidently accumulated in the water as the extraction continued. The extract was distinctly straw colored and was very much more active in producing striæ when added to the electrolyte than the extract obtained by a single treatment or merely a few such treatments with water.[17]

It was later found that immediately after such an extraction filter paper is comparatively inactive, indicating that on standing a spontaneous change of some kind takes place which results in the paper becoming active again. The nature of this change will be discussed later.[18]

D. PRODUCTION OF ABNORMAL DEPOSITS BY ADDITION OF CERTAIN IMPURITIES

1. GENERAL STATEMENT—HISTORICAL

Having determined that the effects of filter paper in question were not due to the fact that it is of an organic nature merely, nor to the influence of impurities (organic or inorganic) contained in the filter paper, it became of importance next to investigate certain other explanations of the influence of filter paper which the experiments of previous investigators had led us to postulate.

In investigating the nature of the changes occurring in the electrolyte at the anode, Richards and Heimrod [19] state that they obtained reactions showing the presence, among other products, of silver nitrite. They therefore tried the effect of adding silver nitrite to the voltameter and concluded from these results that when perpared from potassium nitrite and silver nitrate this salt had the effect of increasing the mass of the electro-deposited silver by between 30 and 80 parts in 100 000. They do not state whether the deposit was striated, but from our own experience it seemed probable that it must have been. Obviously, filter paper

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[17] Our experience with glass vessels precludes the possibility that the pronounced effects in this case could have been due to the solution of a portion of the glass.

[18] When raw unwashed silk is extracted in like manner the extract, when added to the voltameter, brings about the formation of heavy striated deposits, but the extracted silk, even when allowed to stand, does not become active again in the sense that it produces heavy deposits. If used again it affects the results in the opposite sense, i. e., the deposits are made lighter. With repeated use of the same silk this effect persists, and is accompanied by an increase in the acidity of the electrolyte. This effect also will be discussed more fully.

[19] Proc. Amer. Acad., **37**, p. 422.

might reduce silver nitrate to nitrite, and thus explain the fact (which we had found) that the abnormalities are due to the filter paper itself, and not to the anode electrolyte. Smith and Lowry (loc. cit.), however, had repeated these tests, using their form of the filter paper voltameter, and had come to the conclusion that the nitrite could have no appreciable influence. We obtained the same result with silver nitrite prepared from potassium nitrite (see Fig. 21). Continuing further in this direction they also tried the effect of adding silver hyponitrite to the electrolyte. They found that when a 20 per cent silver nitrate solution was saturated with silver hyponitrite (prepared from freshly formed potassium hyponitrite made by reducing the nitrite with sodium amalgam) the deposit of silver was abnormally heavy and very strongly striated. This observation led them to suggest that the disturbing effects of filter paper (which they had observed only when large amounts were used) might be due to the formation of silver hyponitrite by the reducing action of the filter paper. They made no tests for the presence of hyponitrite in any of these cases, and in this connection make the following statement: "We do not wish to commit ourselves to the view that hyponitrite is the only or even the main source of the disturbances which have been noticed by ourselves and others." They proposed it merely as a suggestion. Nevertheless this explanation appeared worthy of further investigation, especially since it was the only instance of which we were aware where it had been claimed that the addition of a single definite chemical compound to the electrolyte produced the peculiar striated appearance of the deposit, although there was some uncertainty even in this case as to whether the use of filter paper in preparing the hyponitrite had not vitiated their results.

It was of course difficult to see, on the basis of this explanation, just why other kinds of organic material, especially cane sugar and starch, which are so closely related to cellulose, do not produce the effects in question. It seemed possible, of course, that hyponitrite might be formed by the reducing action of pure cellulose and not by starch or cane sugar; the effects could then be attributed to some peculiar property of hyponitrite not possessed by the reduction products formed in the case of cane sugar or starch. But just why the products should differ so sharply in the two cases, where the chemical relationships of the reducing substances are known to be so close, was of course very difficult even to surmise. It was decided, however, to repeat these experiments of Smith and Lowry in the hope that some additional information might be obtained which would lead to a more definite and satisfactory explanation of the peculiar effects of filter paper.

2. EFFECT OF SILVER HYPONITRITE

In testing the influence of hyponitrite the conditions as described by Smith and Lowry were modified somewhat by using a more dilute solution of silver nitrate (15 per cent) in order to duplicate more nearly the conditions which obtain in the filter-paper voltameter. Such a solution does not dissolve as much silver hyponitrite as one more concentrated, but since strongly striated deposits had been obtained with the more dilute electrolyte, it seemed best to use the same conditions in the test. If the production of striæ were due primarily to silver hyponitrite, a solution of the electrolyte of the same strength as that used in the voltameter completely saturated with respect to hyponitrite should show the effect in a very marked manner. The silver hyponitrite was prepared from Kahlbaum's potassium nitrite. The procedure followed was essentially the same as that described by Hantzsch and Kaufmann.[20] This method yields a pure product especially free from traces of hydrazine and hydroxylamine, which are usually present in silver hyponitrite prepared by reduction of nitrite, unless special care is taken to remove them. The whole process was carried out in a dark room and the material was very carefully protected from contamination of filter paper or other organic material. The salt was spread upon an unglazed porcelain plate and preserved in the dark in a desiccator over sulphuric acid.

The electrolyte was prepared by adding a weighed amount of silver nitrate to a saturated solution of the hyponitrite (free from the solid salt) contained in a brown glass-stoppered bottle. That the electrolyte was saturated with respect to hyponitrite was indicated by the formation of a cloud when the silver nitrate

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[20] Ann. d. Chem. u. Physik, **292**, p. 320 (1896).

crystals were added. Without waiting for this cloud to settle the solution was immediately electrolyzed in a small voltameter under normal conditions. We were surprised to find that the silver deposit was in all respects similar in appearance to those obtained from pure silver nitrate. There was not the faintest indication of the presence of striæ.

3. PRODUCTION OF STRIÆ BY THE ADDITION OF HYDRAZINE AND HYDROXYLAMINE TO THE ELECTROLYTE

The effect of hydrazine and hydroxylamine upon the appearance of the silver deposited in the voltameter was tested because of their relationship to nitrous and hyponitrous acid as members of the series of compounds produced by the electrolytic reduction of nitric acid. Also, hydrazine and hydroxylamine are usually present as impurities in silver hyponitrite, unless special care is taken to remove them, and it was thought possible that the formation of striæ in the experiments of Smith and Lowry might have been due to the effect of these impurities rather than to the hyponitrite, since we had found the latter to be inactive.

A series of electrolyses was carried out, therefore, with electrolytes containing about 0.5 per cent by weight of the nitrates of hydrazine and hydroxylamine respectively. The hydrazine and hydroxylamine were added in the form of their hydrochloride salts, the silver chloride thus formed being filtered off through asbestos, leaving these compounds in solution in the form of their nitrate salts. When these solutions were electrolyzed it was found that the silver deposit obtained in each case was distinctly striated.

Until the results just described were obtained the formation of striated deposits had been observed only when some form of natural woody fiber (or silk) had been in contact with the electrolyte. Even substances which are considered to be very closely related chemically to cellulose, such as starch and cane sugar, had failed to produce this very peculiar effect. It was evident, therefore, that a promising clue had been uncovered. [21]

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[21] The fact that these two reduction products of nitric acid were the only definite chemical compounds tried so far which possessed the peculiar property of producing striated silver deposits seemed in itself

4. PRODUCTION OF STRIÆ BY THE ADDITION OF STRONG REDUCING AGENTS TO THE ELECTROLYTE

Many experiments were carried out in the attempt to discover in what manner hydrazine and hydroxylamine produce striæ. It was finally concluded that the strongly reducing character of these substances was the essential condition. To test this hypothesis a large number of strong reducing agents, mostly aldehydes and phenols, were separately added to the electrolyte and their effect upon the appearance, and in some cases upon the mass, of the deposit was carefully noted. Among those tried were the following: Dextrose, invert sugar, formaldehyde, acetaldehyde, furfuraldehyde, benzaldehyde, phenol, resorcinol, hydroquinone, and phloroglucinol. Approximately 1 per cent of the reducing agent was added in each case.

The electro-deposited silver obtained from electrolytes containing in each case one of these reducing agents was carefully examined, both as to its general appearance (whether striated and to what extent) and also as to the appearance of the silver crystals under the microscope. A few photographs of these silver deposits were made and are shown in Figs. 22 to 25. The deposits were striated in all cases, the more marked effects in general being produced by the stronger reducing agents of the group.

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sufficient to warrant a careful search being made for their presence in silver nitrate solutions contaminated with filter paper.

In the present instance the more commonly used tests with permanganate or other strong oxidizing agents could not be used on account of the presence of oxidizable organic material, and on the other hand the less vigorous oxidizing agents, such as Fehling's solution and mercuric chloride, were not considered sufficiently characteristic for the case in hand. In other words, none of the tests which depend upon the reducing properties of these substances could be used. Tests of a more characteristic nature were desirable. For hydroxylamine, the test of Bamberger (Ber., **32**, p. 1803, (1899)) was found to be the most satisfactory for our purpose; Angeli's (Gazz. Chim. Ital., **23**,p. 101, (1893)) test with nitroprussiate is not so easily controlled and is less sensitive than the former. (See also L. J. Simon, C. R., **137**, p. 986, (1903)).

It was found possible by means of this test to detect with certainty as little as one part of hydroxylamine hydrochloride added to 100 000 parts of water or aqueous filter paper extract. We were unable, however, to detect the presence of even the slightest trace of hydroxylamine either in concentrated filter paper extracts which had been acidified with varying amounts of nitric acid or in silver nitrate solutions contaminated with filter paper. In the latter case before making the test the silver was completely precipitated as chloride with potassium chloride solution and the precipitate removed by filtering the solution through asbestos.

In testing for hydrazine we employed its property of forming the very insoluble benzalazine when treated with benzaldehyde in acid or alkaline solution. This test was first used by Curtius and Jay (Ber., **22**, p. 134 (1889)), but they make no statement as to its sensitiveness in detecting minute traces of hydrazine. We found that it is possible to detect by this means a few parts of hydrazine hydrochloride in 100 000 of solution. Examination of numerous concentrated extracts of filter paper to which either nitric acid or silver nitrate had been added and which were allowed to stand for varying lengths of time gave no evidence of the presence of hydrazine, although 0.005 per cent of hydrazine hydrochloride when added to such aqueous filter paper extracts could be detected easily.

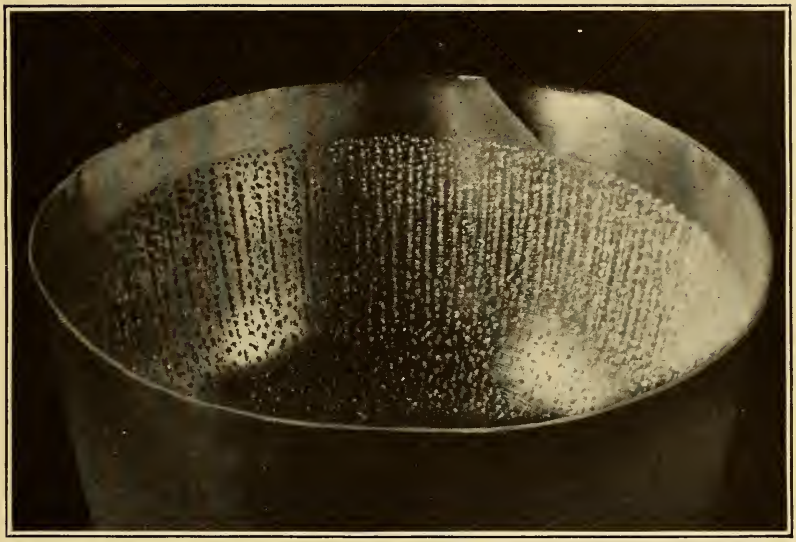

Fig. 25.—*Striated deposit caused by the addition of polymerized furfuraldehyde to the electrolyte*

It has been pointed out already that such mild reducing agents as starch and cane sugar are without appreciable influence upon the appearance of the electro-deposited silver. It would appear, therefore, from the similarity in the effects upon the silver deposit of filter paper, on the one hand, and of these very strong reducing agents, on the other, that the filter paper actually functions as a very strong reducing agent, much stronger than either cane sugar or starch. Also, the extraction experiments already described show that this action in the voltameter can not be due to impurities, but must be attributed to the cellulose itself. It became of importance, therefore, to carefully examine the products formed by the interaction of these cellulose extracts with silver nitrate in order to determine whether the action is one of actual reduction, as the above results so strongly indicate, and especially to determine whether metallic silver is actually formed by the reaction and to compare the results in this case with the action of cane sugar or starch under the same conditions. As a problem of secondary importance in its relation to the voltameter, but of even greater import in other respects, it was of interest to determine in what way cellulose could thus function as a much stronger reducing agent than either starch or cane sugar. These questions we shall discuss in the subsequent sections.

E. REDUCTION OF SILVER NITRATE TO METALLIC SILVER BY FILTER PAPER EXTRACTS—COLLOIDAL SILVER

1. PREPARATION OF CONCENTRATED SILVER HYDROSOLS BY MEANS OF FILTER PAPER EXTRACT

In studying the reaction between silver nitrate and cellulose, those constituents of the cellulose which have the greatest effect in the voltameter were concentrated. This was done for two reasons. First, it was desired to study only that reaction, of several possible concomitant ones, which was responsible for the particular effects in question of filter paper in the voltameter. In the second place, it was desired to obtain as much of the products of the reaction as possible, so that their properties could be more readily examined and their nature determined. This concentration of the active material was effected by extracting a given mass of filter paper with the smallest volume of water practicable, repeating the extraction several times with the same portion of water until no more material seemed to be extracted, as judged by the activity of the extract in the voltameter. This usually required about three or four extractions. Later it was found that the active material could be further concentrated by evaporation; but since a portion of the active material volatilized with the steam, it was decided to make the tests upon the extract as obtained, so as not to depart in the least from the conditions which actually obtain in the voltameter. If the extracts are evaporated to dryness on the steam bath, an amorphous, slightly brown residue is left which volatilizes completely upon ignition in the bunsen flame. (A single extraction of 50 grams of filter paper with 300 cc of distilled water at 35° C for 15 minutes yielded approximately 75 milligrams of residue when evaporated to dryness on the steam bath; by repeating the extraction, extracts of greater concentration have been obtained.) When one-half per cent of silver nitrate is added to such extracts the slightly straw-colored liquid gradually assumes a deep red wine color which begins to develop in from 10 to 15 minutes. The resulting solution appears perfectly homogeneous to the eye and can be filtered through ordinary filter paper without any visible change in its appearance. This solution is practically permanent without further treatment. In one case no change was noticed after standing two months in a glass-stoppered bottle; after five months a dark red-brown sediment had collected at the bottom and a faint metallic mirrorlike film had formed underneath the sediment, although no film was visible on the sides of the bottle. The red color of the solution itself had become somewhat fainter, but was still a deep clear red.

The appearance and properties of these solutions prepared from filter paper extracts are entirely similar to the colloidal silver solutions of Muthmann,[22] Carey Lea,[23] and others,[24] except that the solutions prepared from the concentrated filter paper extracts are if anything still more permanent than those of Muthmann and Lea and even more difficult to coagulate from the mother liquor,

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[22] Ber., **20**, 983 (1887).

[23] Amer. Jour. Sci. (Sill), [3] **37**, 476; **38**, 47; **41**, 482; Chem. N., **59**, 34; **43**, 53; Phil. Mag., [5] **31**, 497.

[24] Schneider, Ber., **25**, 1164 (1892); Prange, Rec. Trav. chim. Pays-Bas, **9**, 121. Lottermoser and Meyer, J. prakt. Chem., **56**, 241.

as will appear later. When the less concentrated filter paper extracts were used the solution was much less deeply colored, usually having a faint purple to bluish tinge; the sediments formed more quickly and also had a much darker color. This sediment, as well as that from the dark red solutions, consists almost entirely of finely divided metallic silver, as will be shown later on. Solutions of cane sugar of many times the concentration of these cellulose extracts gave no such evidence of the formation of colloidal metallic silver, thus confirming our first inference from their relative activity in the voltameter.[25]

2. "PROTECTED" AND "UNPROTECTED" COLLOIDAL SILVER; INFLUENCE OF ORGANIC COLLOIDS

The greater permanency of the colloidal solutions prepared from concentrated filter paper extracts and the fact that they are only very slowly coagulated in the presence of the unreduced silver nitrate, which is a strong electrolyte, suggests that the colloidal silver is "held up" by the "protective" action of the organic material in the extract, which is itself a well-defined colloid. (Preliminary examinations of concentrated filter paper extracts made in this laboratory by means of the ultramicroscope show that they exhibit the characteristic appearance of colloidal solutions.) Furthermore, the organic colloids in the extract belong to the class of so-called reversible colloids, if we adopt the restricted and more rational classification of Zsigmondy,[26] for after evaporation even at the temperature of the water bath the residue may again be "redissolved" in water. On the basis of the same classification, colloidal silver solutions prepared by Bredig's method in the absence of other colloids are irreversible.[26] Since, as a general rule, the protective colloids belong to the class of "reversible" colloids,[26] it is seen that we have ideal conditions for the formation of a protected colloidal solution of silver in this case.

As already stated, the colloidal silver coagulates and settles more readily from silver nitrate solutions only slightly contaminated with filter paper extract than from those prepared with

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[25] Further on in this chapter the relative rates of these reactions are given, and this conclusion is thus established in a very definite manner.

[26] Colloids and the Ultramicroscope, Zsigmondy-Alexander; 1902, p. 25 et seq.

concentrated extracts. This indicates that the protective action is dependent upon the amount of cellulose extract present relative to the amount of silver nitrate, and that under actual conditions in the filter paper voltameter the colloidal silver is protected to some extent from the coagulative action of silver nitrate and other electrolytes. This condition may account for the greater effectiveness of filter paper in the voltameter as compared with that of the other strong reducing agents, such as dextrose, formaldehyde, etc., which, although strongly reducing in character, are not protective colloids.

Whether the greater effectiveness of "protected" colloidal silver is due to a greater permanency, to a greater concentration, or to some other difference in the properties of the colloidal silver solutions, or whether due in part to the independent action of the protective colloid itself, is a matter about which there may be some question. While the migration experiments described on page 219 show that colloidal silver migrates to the cathode, it is of course possible that the protective colloid itself may migrate to the cathode in exactly the same manner and there bring about entirely similar results as to the production of striations, etc. However, all of the data which we have been able to find indicate that not only cellulose, but practically all other kinds of organic colloids as well, migrate toward the anode.[27] Moreover, since non-reducing organic colloids are "inactive" in the voltameter, and further, since "unprotected" colloidal silver produces similar effects (as shown by the results obtained with the strong reducing agents, such as dextrose, formaldehyde, phloroglucinol, etc., and also with Bredig's colloidal silver), it would seem more probable that the effects are due primarily to the colloidal silver itself and that the greater effectiveness of the "protected" colloid should be attributed to its greater concentration and greater permanency. Undoubtedly some of the organic colloid is dragged along, so to speak, with the colloidal silver and is deposited upon the cathode, but this can hardly constitute more

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[27] See Spring, Bull. de l'Acad. roy de Belg. (3), **35**, 780–784, 1898. Larquier des Bancels, C. R., **149**, 316–319; 1909. Also Graf von Schwerin und Farbwerke vorm. Meister, Lucius und Bruning, D. R. P. 124509, 124510, 128085.

than a small percentage by weight of the total colloid so deposited. In instances where the electrolyte contained unusually large amounts of filter paper extract (colloidal cellulose hydrates, etc.), we have been able actually to separate this included organic colloid from the silver deposit by amalgamating the silver with mercury.

In one case a deposit (not weighed) made from an electrolyte containing an unusually large amount of filter paper extract, after thorough washing, was amalgamated with 50 times its mass of mercury and extracted with water. The amorphous cellulose was plainly visible suspended in the water. Its total mass obtained by loss on ignition (after evaporating) was 4.5 milligrams. The total weight of the silver deposit was about 4 grams. Judging from the character of the striæ and general appearance of the deposit it probably was heavier than a normal deposit by not less than one-half of 1 per cent. But, under the usual conditions at least, in the filter paper voltameter, the weight of this included organic material is only a small fraction of the total excess weight of the deposit. This excess appears, therefore, to be due mainly to the colloidal silver alone, since the remainder of the deposit amalgamates completely. In another instance a weighed deposit from an electrolyte contaminated with filter paper, made in a voltameter in series with a standard voltameter, showed an excess weight of about 4 mg. After carefully amalgamating with 50 times its weight of mercury, then extracting the amalgam with very pure water, and evaporating the extract, a residue judged to be organic material was obtained which weighed 0.43 mg, and which showed a loss upon ignition of 0.38 mg. In other words, only about one-tenth of the total excess weight could be attributed to the included organic material liberated in this way.

Other instances of the pronounced effects produced by reducing agents which can function as protective colloids are seen in the effects produced by the addition of gelatin and unwashed raw silk (due to the silk glue), both of which give well-defined colloidal solutions in water and very easily reduce silver nitrate to colloidal silver solutions in a manner similar to that shown by cellulose.

F. PROPERTIES OF COLLOIDAL SILVER PREPARED BY MEANS OF FILTER PAPER EXTRACT

1. COAGULATION OF THE "PROTECTED" COLLOIDAL SILVER BY MEANS OF ALCOHOL

By magnifying the conditions actually present in the filter paper voltameter, i. e., by increasing the proportion of "soluble" cellulose relative to the silver nitrate, it has been possible, as already stated, to prepare permanent colloidal solutions of silver which are not only not coagulated by the silver nitrate present, but which are extremely stable toward all other electrolytes that have been tried. In fact, considerable time was expended in searching for a means of coagulating these concentrated hydrosols so that sufficient hydrogel (coagulated silver) could be collected to enable its properties to be examined. The addition of potassium nitrate in practically all proportions up to saturation had very little effect upon the rate of coagulation. The same was found true of sodium nitrate and ammonium nitrate as well as of the acetates of the alkali metals. Of course, only such salts could be added as do not form an insoluble precipitate with the silver nitrate. Dilute acetic acid brought about partial coagulation on standing two days. Potassium fluoride had no effect when the solutions were kept in platinum.[28]

A highly satisfactory coagulating agent was found in alcohol. When approximately two volumes of alcohol (95 per cent or 98 per cent) are added to one volume of the concentrated silver hydrosol, a dark red sediment begins to form in about an hour, and the solution becomes clear on standing over night. This sediment may be collected on an asbestos filter and washed free from silver nitrate by means of absolute alcohol.

2. PROPERTIES OF THE COAGULATED COLLOIDAL SILVER OR HYDROGEL

(*a*) **Transformation to Ordinary White Silver.**—If a thin film of the silver hydrogel is spread upon a microscope slide, it assumes upon drying a faint greenish tinge by reflected light, but is still a dark reddish brown by transmitted light. When kept at 100° to 110° it gradually assumes a more yellowish tinge by reflected

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[28] It would be of interest from the standpoint of the general properties of colloids to remove the silver nitrate completely by dialysis so that electrolytes other than nitrates, acetates, or fluorides could be used in order to determine whether this silver hydrosol is stable toward all electrolytes when so protected by the reversible cellulose colloid. This has not yet been done. The effect of the electrolytes mentioned above refers to silver hydrosols containing approximately one-half per cent silver nitrate. Their effect in the absence of silver nitrate could hardly be different.

light, finally becoming opaque and having the gray metallic appearance of ordinary finely divided silver. Upon standing several weeks under a bell jar it gradually undergoes the same changes at ordinary room temperatures. This spontaneous change to ordinary gray silver takes place more readily with the darker sediment which settles from the weaker silver hydrosols containing much less filter paper extract than with those just described.

However, it has not been possible always to obtain this spontaneous transition of the colloidal to ordinary silver. Very slight variations in the conditions under which the material is prepared or preserved apparently make a great deal of difference in the ease with which it is transformed. This behavior was noticed and investigated by Lea,[29] who states that moisture and light together are favorable to the transition, but that if some specimens are dried and subsequently exposed to light they become very insoluble (i. e., irreversible) and do not undergo transformation to ordinary silver. A very similar behavior has been observed with the red variety precipitated by alcohol. In one instance a specimen of the dark brown variety (from alcohol precipitation) withstood a temperature of 150° C for five hours without losing its characteristic dark brown color by transmitted light, although by reflected light it showed a greenish yellow appearance similar to that of gold. Another sample of the same silver hydrogel treated in the same manner, except that it was not heated, changed to ordinary gray silver on standing under an inverted crystallizing dish in diffuse daylight, the change being observed at the end of eight days. This may have been favored by the presence of moisture as suggested by Lea, but at the time we were not aware of this phase of Lea's investigations and could find no explanation of the difference in the behavior of the two specimens. However, with the very dark brown or black silver sediment which settles spontaneously from silver nitrate solutions that are only slightly contaminated with filter paper, it has been observed that this change from dark brown or blue to yellow and then gradually to ordinary gray or white silver always occurs upon heating for a few minutes at 130° or upon long standing at ordinary temperature.

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[29] Amer. J. Sci., [3] 38, pp. 129 and 237.

In addition to the spontaneous change of the coagulated colloid into ordinary silver, its percentage composition and behavior toward various reagents show conclusively that it is practically pure metallic silver.

(*b*) **Percentage Content of Silver.**—The percentage content of silver was estimated in the following manner: Fifty grams of No. 595 Schleicher and Schüll filter paper was first freed from soluble chlorides and other soluble impurities as far as possible by several extractions with water. These first extracts were discarded to avoid contaminating the silver hydrogel (subsequently to be formed) with silver chloride or other insoluble silver salts. This thoroughly extracted filter paper was then allowed to stand in a covered beaker until practically dry and then again extracted in the usual manner, the extract being filtered first through a sheet of the same filter paper and then through a thick asbestos mat. The hydrosol produced in the usual way was coagulated by the addition of two volumes of alcohol and was collected on asbestos in a weighed Gooch crucible. The gel was washed first with absolute alcohol until the filtrate was free from silver salts and then with a little water; dried at 100° for a few minutes, then over sulphuric acid in a vacuum desiccator and weighed again to determine the mass of residue. The material, after moistening with hot water, was then washed with 30 per cent nitric acid and this treatment repeated until there was no further decrease in weight. In some cases where the precipitate had been subjected to prolonged drying and long exposure to light the dark brown material dissolved very slowly in the strong acid and several treatments with acid were required to produce a constant weight. In one instance concentrated nitric acid was used to hasten the solution, with the surprising result that the residue was transformed from almost black to a brilliant purple color and then dissolved with very great difficulty. Some of this purple material passed through the filter, evidently in colloidal condition, and did not become colorless until after standing several hours in the strongly acid filtrate. This is evidently still another allotropic form of silver which has the very remarkable property of almost complete insolubility in concentrated nitric acid. In no other case was difficulty of this sort encountered, the precipitate being soluble in 30 per cent nitric acid. The silver in the filtrate was estimated with standard ammonium thiocyanate in the usual manner. The results of three analyses of samples varying in weight from 10 to 20 milligrams prepared at different times were:

	Per cent silver
No. 1	97.0
No. 2	96.8
No. 3	96.6
Average	96.8

The remaining 3.2 per cent was probably organic material, since on ignition samples lost approximately this per cent of volatile and oxidizable material.

(*c*) **Behavior toward Various Reagents.**—The following experiments on the behavior of the coagulated colloid, obtained from silver nitrate solutions treated with filter paper extract, were carried out to further strengthen the evidence that this colloid is nearly pure metallic silver.

As already indicated, the behavior of the precipitated silver toward chemical reagents varies somewhat according to the method of preparation. An illustration of this is the purple form, obtained by prolonged drying of the dark red hydrogel precipitated by alcohol, which is practically insoluble in concentrated nitric acid. There are certain properties, however, more or less common to all the forms so far obtained, and these will now be briefly described.

Nitric Acid.—Toward nitric acid all the forms obtained from filter paper extract seem to behave quite differently from those described by Carey Lea. For while they resemble some of his forms in being practically insoluble in very dilute nitric acid, they are not readily converted into ordinary white silver by contact with dilute acids as are his forms. In other words, the presence of dilute acid does not seem to hasten this spontaneous change to ordinary silver which sometimes takes place. The only similar effect is the one mentioned where concentrated nitric acid transformed a dark brown variety to a brilliant purple one.

Ammonia.—The coagulated silver sediments are not dissolved to colorless solutions even by concentrated NH_4OH. This behavior in itself eliminates all the ordinary compounds of silver except silver sulphide, which is excluded by the percentage content of silver and other chemical properties of the material, such as its catalytic action upon hydrogen peroxide. When concentrated ammonia is added to the deep red wine-colored hydrosols, the solution remains practically unchanged except that after the addition of ammonia the hydrosol seems to be more stable, since it is not so readily coagulated by the addition of alcohol. Similar stable colloidal solutions are formed when the coagulated, practically insoluble, sediments are treated on the filter with ammonia water. The precipitate then passes through the filter in colloidal condition. This behavior is similar to that observed by Muthmann with colloidal silver prepared by the reduction of silver citrate by means of hydrogen, except that the ammoniacal hydrosols in the present case are much more stable and are not differently colored from the original hydrosol.

Potassium Cyanide.—All the forms of silver sediment are readily soluble to a clear solution in this reagent.

Hydrogen Peroxide.—A thin film of the red-brown hydrogel (which had been thoroughly washed with absolute alcohol) was spread upon glass and dried in a desiccator over sulphuric acid. When this film, which was slightly yellowish green by reflected light and red brown by transmitted light, was covered with a few drops of a 3 per cent solution of hydrogen peroxide, a copious evolution of gas began immediately. After the action had ceased the film was washed and again dried. The slight green appearance (by reflected light) had entirely disappeared, leaving a homogeneous dark red-brown film.

Here again this striking behavior is entirely similar to that observed by Carey Lea [30] and also by McIntosh [31] with colloidal silver, except that there was very little evidence of a partial solution of the silver, as was observed by the latter, unless the disappearance of the green color may be attributed to the solution of a very thin film of some kind. While it is true that silver oxide acts catalytically upon hydrogen peroxide in a similar manner, the possibility of any appreciable proportion of the sediment consisting of oxide is excluded by its behavior with ammonia, its behavior toward dilute and concentrated nitric acid, and its ready amalgamation with mercury.

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[30] Amer. J. Sci. [3], 38, pp. 129 and 237.

[31] J. Phys. Chem., 6, p. 15 (1902).

Amalgamation with Mercury.—If a little of the dry dark-brown powder obtained from the red hydrosol by precipitating with alcohol be placed in a small porcelain crucible and treated with a globule of mercury, the whole of the powder amalgamates with the mercury at ordinary temperature. The two materials must be brought into intimate contact by stirring with a glass rod. If the silver is in the form of an adherent film upon the glass or porcelain, the amalgamation does not take place, but if the film is scraped loose the action immediately takes place.

(*d*) **Summary.**—It is difficult to explain these properties of the hydrogel obtained from silver nitrate and pure filter paper extract upon any other assumption than that the material is nearly pure metallic silver.

When considered in connection with the other properties described, the evidence is certainly conclusive that filter paper acts chemically upon silver nitrate solution at ordinary temperatures with the production of colloidal metallic silver. The mechanism of the chemical reactions which bring about this result have been examined somewhat in detail and will be discussed later. The manner in which this colloid produces the peculiar striated deposits of silver in the voltameter will be explained on page 279.

G. CHANGE IN THE CONDITION OF NEUTRALITY OF SILVER NITRATE SOLUTIONS PRODUCED BY FILTER PAPER EXTRACT

When silver nitrate is reduced to metallic silver, one equivalent of nitric acid must necessarily be liberated for each equivalent of silver thrown out; consequently, if filter paper extract reduces silver nitrate to colloidal metallic silver, the solution should become acid. The demonstration of this change was considered a very important link in the evidence that the above reaction does actually take place; but when this seemingly simple task was undertaken serious difficulties were encountered. It was soon discovered that the tests could not be made in the presence of the silver nitrate by means of the usual indicators. Litmus solution forms a precipitate with silver nitrate, masking the color reaction and showing that a disturbing chemical change takes place. With litmus paper the results depend upon the manner in which the test is made. If only the end of the paper is dipped into the solution the reaction usually appears to be acid, but this was found to be due to the capillary action of the paper, which results in the acid being drawn up more rapidly than the base (AgOH). A pink band travels up the paper, immediately followed by a blue band. If, on the other hand, the whole strip of paper is immersed at once in the solution, the reaction is invariably basic even after 1 part in 100 000 of free acid is added to solutions prepared from repeatedly recrystallized salt.

With methyl orange, silver nitrate solutions invariably show an acid reaction even after the addition of indefinite amounts of pure sodium or barium hydroxide. So long as any silver nitrate remains the reaction is acid.[32] Since there is no evidence of any reaction between the silver salt and this indicator, and, further, since the intensity of color is uniform for all solutions of the same concentration, this result strongly indicates that silver nitrate is slightly hydrolyzed. When the silver was removed as silver chloride by precipitating with neutral sodium or potassium chloride and filtering, it was found that the filtrate from recrystallized and supposedly neutral silver nitrate usually showed a basic reaction toward methyl orange, litmus, phenolphthalein, and iodeosine. The same results were obtained with solutions strongly contaminated with filter paper, i. e., they usually reacted basic toward all indicators after precipitating the silver as chloride and removing it by filtration. Occasionally a solution which had been standing for many weeks would show an acid reaction, but the freshly contaminated solutions were invariably basic even after considerable of the dark brown sediment had settled from the solutions.

These difficulties were finally explained by the observation that the filter paper extracts themselves show a pronounced basic reaction toward the indicators mentioned.[33] This behavior

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[32] Richards, Collins, and Heimrod (Proc. Amer. Acad., 35, p. 123) state that the electrolyte near the anode gave an acid reaction with methyl orange, whereas the cathode electrolyte remained neutral toward the same indicator. Later, however (Jour. Amer. Chem. Soc., 29, p. 808), Richards and Forbes state that silver nitrate solution is acid toward methyl orange even after the addition of base. We were not aware of this last observation when the above tests were made.

[33] So far as we are aware this observation is new and should prove of some importance in relation to the chemistry of cellulose. It is no doubt closely related to the electrochemical and absorptive properties of cellulose in general. See Cross and Bevan, Researches on Cellulose, 1900–1905, pp. 7, 103, 128, 131, 157. Also experiment mentioned in this paper on pp. 262–263.

explained the results just mentioned which were obtained with the recrystallized and supposedly neutral silver nitrate, for the silver chloride was filtered off by means of filter paper, the filtrate extracting more or less basic cellulose from the filter according to how thoroughly it had been washed. Later work showed that recrystallization from neutral solution itself produces a trace of basic silver hydroxide, but this is slight in comparison with the effect of the oxycelluloses. When asbestos filters were employed the recrystallized salt showed a practically neutral reaction after precipitating the silver as chloride. The basic reaction of the freshly contaminated silver nitrate solutions was therefore real, and was due to the filter paper extract itself.[34]

The reduction of silver nitrate (by filter paper extract) results in the production of free acid, which is immediately neutralized by the basic oxycellulose present, the basicity of the solution gradually diminishing until it is entirely neutralized by the acid. As the reduction continues the solution becomes acid,[35] the acidity increasing until a condition of equilibrium is finally reached. This final acidity is often sufficiently high to be detected with litmus paper without previous precipitation and removal of the silver as chloride and may account for the observations of Kahle and others upon the acid reaction of very old repeatedly used solutions, a change which they attributed to the process of electrolysis itself instead of to the reducing action of oxycelluloses from filter paper upon the silver nitrate.

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[34] Ten grams of No. 595 S & S filter paper yield a basic extract (when treated in the manner described) which is equivalent to approximately .47 milligram of sodium hydroxide. The residue left upon evaporation of such an extract at a temperature of 100° C is approximately 17 milligrams. If it be assumed that this is a single definite oxycellulose and not a mixture, we have the result that the equivalent weight of oxycellulose is approximately 1447 (in terms of hydrogen). These figures are to be considered only very rough approximations, but they illustrate what we believe to be a new means of estimating the equivalent magnitude of one of the modified forms of cellulose (oxycellulose). The fact, however, that this material is colloidal may vitiate this method of determining the molecular weight of the substance, since its basic reaction may be an absorption phenomenon rather than a true reaction of hydroxyl ions. The colloidal phase of the chemistry of cellulose has recently been emphasized by Cross and Bevan. (Researches on Cellulose, 1900–1905, Longmans & Co., 1906, pp. 6, 126, and 177.)

[35] The neutral nitrate salts or esters of these basic compounds are evidently as strongly reducing in character as the free bases themselves.

TABLE II

Formation of Acid by Action of Filter Paper Extract on 10 per cent Silver Nitrate Solution

Solution tested	Time	Reaction toward iodeosine.	Amount of free acid in parts per million of HNO_3	Amount of free base (in parts per million of equivalent amount of HNO_3
Original aqueous filter paper extract.	Immediately after preparation...	Basic....	....	24
Contaminated solution.............	After 2 hours.................	...do.....	....	12
Blank solution.......................	.....do..........................	...do.....	....	3.6
Contaminated solution.............	After 2 days....................	...do.....	....	0.6
Blank solution.......................	.....do..........................	...do.....	....	2.4
Contaminated solution.............	After 11 days..................	Acid....	1.8	....
Blank solution.......................	.....do..........................	Basic....	....	2.4
Contaminated solution.............	After 60 days..................	Acid....	10.8	....
Blank solution.......................	.....do..........................	Basic....	....	2.2
Contaminated solution.............	After 177 days................	Acid....	10.2	....
Blank solution.......................	.....do..........................	Basic....	....	3.0

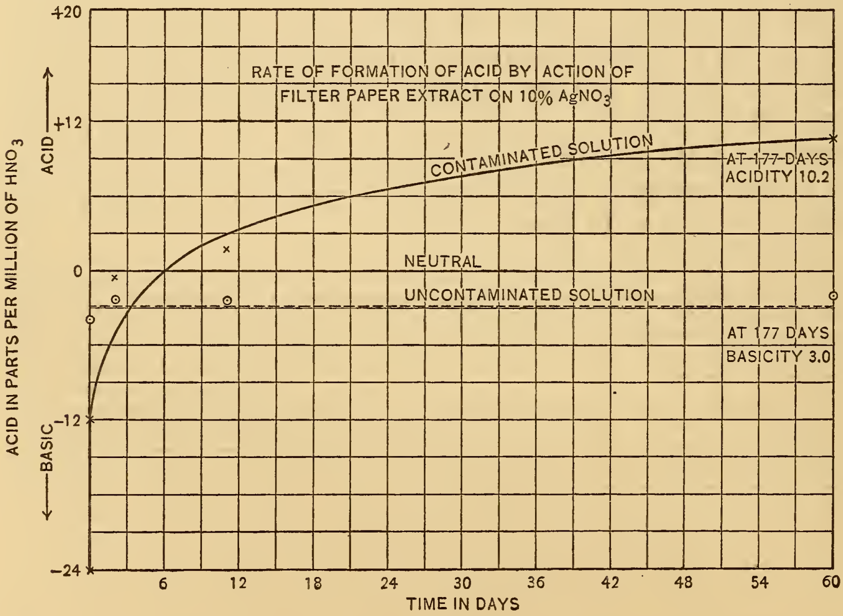

Fig. 26.—*Curve showing the rate of formation of acid by the action of filter paper extract on 10 per cent* $AgNO_3$

Many observations have been made upon electrolytes strongly contaminated with filter paper, and it has been uniformly observed that they are always basic immediately after preparation, the basicity gradually decreasing with time until neutral and then gradually increasing in acidity. The accompanying table (II) and curve (Fig. 26), prepared from the data given, is a single illustration of the course of this reaction. It will be seen that an uncontaminated solution was subjected to the same treatment and tested in the same manner as a control experiment. The contaminated solution was prepared by adding 10 per cent of pure neutral silver nitrate crystals to 50 cc of a filter paper extract made by several extractions of 12.5 grams of No. 595 S & S filter paper. This extract was approximately 24 parts per million basic. Two hours after adding the silver nitrate the basicity had decreased to only 12 parts per million, thus showing that a corresponding amount of reduction had taken place (equivalent to approximately 20 parts per million of colloidal metallic silver) during the time required to make a voltameter determination. No test was then made until after two days, when the solution was found to be practically neutral, but this condition was probably reached much sooner, so that the curve is probably not sufficiently steep in this portion to represent the true change. After becoming neutral or slightly acid the change progresses more slowly.

It should be stated also that the red color of the silver hydrosol begins to develop in such strongly contaminated solutions after a very few minutes at the usual temperature of the electrolyte in the voltameter, i. e., 25° to 30°. This is further evidence that colloidal silver is actually formed in the filter paper voltameter during the time required for a determination. Of course with slightly contaminated electrolytes this color change is not visible.

H. CELLULOSE AS A STRONG REDUCING AGENT

1. GENERAL STATEMENT

The remarkable similarity in the effects of filter paper on the one hand and of very strong reducing agents on the other upon the appearance of the electro-deposited silver had furnished striking evidence that the activity of the cellulose must be due to its action as a very strong reducing agent. This action of cellulose was in strong contrast to that of such mild reducing agents as cane sugar and starch, which were found to be inactive in the voltameter. This indirect evidence of the strongly reducing character of filter paper extracts had been fully confirmed by the experiments just described, in which permanent colloidal solutions of metallic silver were prepared from filter paper and silver nitrate and the metallic silver coagulated and identified by its properties. Moreover, these colloidal silver solutions were prepared under exactly the same conditions which obtain in the voltameter itself. The relative inactivity of cane sugar under the same conditions is further discussed in the next paragraph.

2. RELATIVE RATES OF REDUCTION OF SILVER NITRATE BY CELLULOSE AND BY CANE SUGAR

A better appreciation of the strength of the reducing action of cellulose is obtained when one considers the rate at which acid is produced by the reducing action of filter paper extract as compared with that of cane sugar. Even when relatively very large quantities of cane sugar are added to silver nitrate solution the neutrality remains practically unchanged for several days, as shown by the iodeosine test described in a later section. Less than one part of nitric acid in a million is formed after two days, whereas in the case of filter paper extract more than 12 parts per million of nitric acid is formed in 2 hours, as is shown in table II. In other words, the rate of reduction by filter paper extract is at least three hundred times greater under the same conditions than the rate of reduction by cane sugar.

3. CELLULOSE NOT READILY DECOMPOSED INTO REDUCING CARBOHYDRATES

The question at once arises: How does cellulose function as a stronger reducing agent (under the conditions named) than other carbohydrates of lower molecular weight, such as cane sugar? It seemed probable, notwithstanding the generally greater reactivity of the simpler carbohydrates, that in the present instance the cellulose might be thus easily hydrolyzed, to a very slight extent at least, into reducing carbohydrates of some kind. The concentrated filter paper extracts were therefore carefully examined for such "reducing sugars" by the usual methods, viz, by means of Fehling's solution and also with the polariscope, but with negative results. Owing to the well-known difficulty of standardizing the Fehling test, the method used in the present case is described somewhat in detail.

It had been observed that the aqueous extract of a given weight of filter paper prepared by repeated extraction with the same portion of water is even more efficient in producing striæ than the filter paper itself; consequently it seemed probable that the reducing carbohydrates could be concentrated in this manner. It was therefore thought best to test such aqueous extracts for "reducing sugars" rather than to apply the test directly to the cellulose fiber, especially since the separation of the cuprous oxide would in the latter case not be complicated by the presence of the cellulose fibers. Moreover, solubility in water is a characteristic property of the "active" material (or of the material from which it is formed), so that the test upon aqueous extracts would have a correspondingly greater significance.

In preparing these extracts 50 grams of the filter paper was cut into small pieces about a centimeter square, placed in a beaker, covered with 300 cc of distilled water, and kept at 35° for from 10 minutes to several hours. The water was either drained off in the centrifuge or squeezed out with thoroughly cleansed hands and the extract filtered through a sheet of the same kind of filter paper. Usually this treatment was repeated several times with the same portion of water in order to concentrate the "active" substance, and in some instances large volumes of the extract so prepared were evaporated nearly to dryness for the same reason. These extracts were rendered very faintly acid by the addition of from 1 to 10 parts of nitric acid to each 100 000 parts of extract and allowed to stand for varying lengths of time before being tested for reducing carbohydrates. The amount of nitric acid added was intended to be slightly in excess of the quantity likely to be present (due to hydrolysis) in 10 per cent solutions of silver nitrate.

With the filter paper extracts prepared as described above and acidified by the addition of a few parts in a hundred thousand of nitric acid, we were unable to obtain any test for reducing sugars either by means of the polariscope or with Ost's modification of the Fehling test.[36] In several instances the acidified extracts were allowed to stand several days at ordinary temperature before being tested in order to allow ample time for any hydrolytic action which might take place (under conditions of temperature and concentration of acid comparable to those which obtain in the filter paper voltameter) to complete itself; but the results of these tests were the same as for the recently acidified extracts. Extracts prepared by digesting the filter paper with 10 per cent solution of silver nitrate likewise gave no test for reducing sugars. Several trials showed that a few parts in one hundred thousand of dextrose, if added either to the plain aqueous extracts or to extracts containing silver nitrate, could readily be detected by means of Ost's test. The polariscope method was less sensitive, but filter paper extracts to which a part in ten thousand of dextrose had been added showed a very small but appreciable rotation in the polariscope. (The column of solution examined was 20 cm in length and the rotation corresponded to approximately 0.03 per cent of cane sugar on a scale calibrated directly in percentages of cane sugar.)

It is certain, therefore, that if dextrose or any similar sugar is formed in the filter paper voltameter it can not be present in amounts greater than 1 part in 100 000. The limit is probably very much lower than this, since the tests were made on much more concentrated extracts than are normally present in the filter paper voltameter.

4. MECHANISM OF THE REDUCING ACTION OF CELLULOSE EXTRACTS—DECOMPOSITION INTO FURFURALDEHYDE

The fact that these filter paper extracts do not exert an appreciable reducing action upon Fehling's solution and are not optically active, is in strong contrast with their very vigorous reducing

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[36] Of the numerous modifications of the Fehling test, best results were obtained with Ost's modification (Chemiker-Zeitung, **19**, pp. 1784, 1829 and 1830), using a solution containing only 1 gram of $CuSO_4+5H_2O$ per liter. The great advantage of this test lies in the greater certainty with which the blank determinations may be controlled, since no weighable precipitate is formed upon boiling the solution for ten minutes, even after diluting it with half its volume of water.

In carrying out the test for reducing sugars with this reagent 50 cc of the extract and 100 cc of the copper solution in an Erlenmeyer flask of 500 cc capacity was quickly heated and maintained at the boiling temperature for 10 minutes. The solution was then quickly cooled under the tap, filtered through an asbestos Gooch, in the usual manner, the precipitate washed successively with measured volumes of 10 per cent potassium bicarbonate solution, hot water, alcohol, and ether, dried at 110°C, allowed to cool, and then weighed. The weight of cuprous oxide was checked by washing the filter with dilute nitric acid, then with water, drying and weighing again. In some instances, as a further check upon the blank tests, the nitric acid filtrate was tested for copper with ammonia. It was found possible by means of this test to detect 0.001 per cent of dextrose in solution in distilled water.

action upon neutral or slightly acid silver nitrate solution and further emphasizes the radical difference in the behavior of these "soluble" celluloses on the one hand and of the simpler carbohydrates such as cane sugar and starch upon the other, especially toward silver nitrate solution. Furthermore, this behavior strongly indicates that the decomposition of these "soluble" celluloses takes place in an entirely different manner from that of a resolution by hydrolysis into hydrocelluloses or reducing carbohydrates having free CO groups, as is the case with cane sugar and starch.

The conclusion was finally reached that the reducing action upon silver nitrate solution takes place through the intermediate formation of furfuraldehyde (or some of its homologues). This could result either from the decomposition of pure cellulose hydrates or possibly from the closely related pentosans which might be so intimately associated or combined with the cellulose that they could not be further separated from pure cellulose by any of the means which we had employed for extracting the soluble impurities from filter paper.

Furfuraldehyde, when present in solution to the extent of 0.1 per cent or less, does not reduce Ost's modification of Fehling's solution (with 10 minutes' boiling) to any appreciable extent, and hence might not have been detected in the tests made with this reagent. With ordinary Fehling's solution it can be more readily detected, but even with this reagent it is necessary to boil the solution for a much longer time (a half hour) to insure complete oxidation of the aldehyde.[37] Being optically inactive it could not be detected by means of the polariscope test. It seemed perfectly possible therefore that furfural might have been present in the extracts which were tested for "reducing sugars" and yet have escaped detection by the tests used.

We were aware that this aldehyde is generally regarded as a product of the condensing action of strong acids upon pentoses only. Since pure cotton cellulose ($C_6H_{10}O_5$) is a hexopolyose, one would not expect it to yield furfuraldehyde. Indeed, as is well known, the yield of furfuraldehyde is taken as the indirect meas-

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[37] This difficulty with ordinary Fehling's solution may be due to the resinifying action of the strong alkali upon furfural, which is much more sensitive to this effect of alkalis than dextrose.

ure of the amounts of certain "modified" or "noncellulose" constituents present as "impurities" more or less intimately mixed or combined with the pure cotton cellulose.

Examination of the more recent literature pertaining to this phase of the chemistry of cellulose disclosed the fact, however, that all classes of celluloses, hexopolyoses as well as pentopolyoses (or pentosans), yield furfural, but in greatly varying amounts, on treatment with strong condensing agents. For example, Suringar and Tollens (Zs. angew. Chem., 1897) found that raw cotton, while containing no pentosans, yet yielded very slight traces of furfural as one of the products of acid hydrolysis. Therefore it seemed well worth while to test various filter paper extracts to determine whether this strongly reducing aldehyde is formed under conditions comparable to those which obtain in the voltameter.

5. TESTS FOR FURFURALDEHYDE

The test employed for furfural was that described by Förster (Ber., 15, 320), in which two-thirds of the liquid to be tested is distilled off, the distillate extracted three times with chloroform, the combined extracts evaporated nearly to dryness, taken up with a little alcohol, and tested with an equal volume of a mixture of equal parts of glacial acetic acid and redistilled, colorless xylidine. If furfural is present, a red color develops. The first tests for furfural in acidified filter paper extracts were made in November, 1909. About 20 grams of Schleicher and Schüll filter paper (No. 595) was extracted with 300 cc distilled water in the manner described on page 253. This was acidified by the addition of approximately 0.01 per cent of nitric acid and allowed to stand overnight before distilling. The amount of nitric acid added was intended to be no greater than that probably present in pure silver nitrate solutions due to slight hydrolysis. When tested in the way described above, these distillates showed very distinctly the presence of furfural. In later experiments an attempt was made to form an estimate of the amounts of furfural which could be obtained under these exceedingly mild conditions from definite weights of filter paper and also the effect of various treatments of filter paper upon the yield. These tests were carried out according to the method adopted by the Association of Official Agricultural Chemists for the estimation of furfural in distilled liquors (Bull. No. 107, U. S. Department of Agriculture, p. 96).

In each of these tests 50 grams of the filter paper to be tested was digested with 350 cc of water for 30 minutes at a temperature of 35°. The extract was acidified by the addition of approximately 0.01 per cent of nitric acid, and after being allowed to stand for varying lengths of time 200 cc was distilled off. Of this distillate, 50 cc was tested directly with 2 cc of colorless xylidine and 0.5 cc of hydrochloric acid (sp. gr. 1.12) and kept for 15 minutes in a water bath at about 15° C. The estimation was made by comparing the intensity of the color developed with that obtained from standard solutions of furfural of known strength tested in the same manner. The solutions and reagents were always cooled to the same temperature before mixing, and blank tests with distilled water were carried out as checks upon the purity of the reagents used. The color develops in from 5 to 15 minutes, after which it may fade or the blank may show a brownish red color. It was found to be advantageous to make the test (as described) without the use of alcohol, which had a tendency to give a yellow color which partially masked the red. In fact, in several instances tests which showed bright red color without the alcohol turned yellow upon the addition of alcohol. This was probably due to the more complete solution by the alcohol of coloring matter (oxycelluloses?) present.

The results obtained with different samples of filter paper after having been subjected to various treatments intended to remove impurities are tabulated in Table III, following.

TABLE III

Showing Yield of Furfuraldehyde from Filter Paper

Previous treatment of filter paper	Solvent	Treatment of acidified extract		Yield of furfuraldehyde
		Time	Temperature	
		Hours	° C	(Mg)
None	Water	2	70	2
Do	do	12	35	Trace
Extracted with water and immediately tested	do	12	70	None
None	1% KOH	2	35	20
Extracted with 1% KOH, then with water, and immediately tested	do	2	35	Trace
Do	Water	2	70	None
Extracted with water and allowed to dry one week	do	2	70	5
Do	do	24	35	Trace

The yield of furfural is expressed in milligrams obtained from 50 grams of dry filter paper when treated in the manner described.

These experiments show conclusively that furfuraldehyde is formed by the action of nitric acid of a concentration comparable to that probably present in 15 per cent silver nitrate solution due to hydrolysis. Treatment with concentrated hydrochloric acid as in the standard methods used in estimating the furfural constituents of cellulose would undoubtedly yield much larger amounts. But this of course was not the object of the present tests.

The amounts of furfural obtained by the methods in the foregoing tests are of course not to be considered as an accurate measure of the total quantities which can be formed by the action of silver nitrate in the voltameter, for the conditions, while as nearly alike as it was possible to make them, are yet dissimilar in some important respects. Under actual conditions the furfural may be removed from the field of action as rapidly as it is formed by interaction with silver nitrate. Thus the condition of equilibrium existing between the soluble cellulose product and furfural would continually be disturbed so that more furfural would be formed. The amounts obtained from acidified aqueous extracts would therefore probably be far less than the amounts formed by the action of silver nitrate under the same conditions.

When furfural reduces silver nitrate, it is itself of course oxidized to pyromucic acid.[38] The presence of pyromucic acid (or its derivatives) in silver nitrate solutions which have been partially reduced to metallic silver by filter paper extracts would constitute, therefore, the most direct evidence possible to obtain that the reduction had been brought about primarily by the decomposition of the filter paper into furfuraldehyde. We have made a few preliminary qualitative tests for this acid, but those so far employed do not appear to be sensitive enough for the present case, so that a complete isolation of the acid seems to be necessary.[39]

In this connection the decomposition products of furfural itself when treated with silver nitrate should be examined.

I. EFFECTS OF FURFURALDEHYDE IN THE VOLTAMETER

When testing the effects produced by the addition of strong reducing agents to the electrolyte we had observed that, of all the aldehydes tried, furfural seemed to be the most efficient in imparting a striated appearance to the electro-deposited silver. (Fig. 25). These results were obtained with Kahlbaum's c p furfural from freshly opened, hermetically sealed, glass bulbs. With redistilled furfural the effects were not so pronounced. Repeated tests showed that the dark colored polymerized furfural was most effective in reproducing the effects caused by filter paper. In one experiment a sample contained in a sealed glass bulb was heated in water contained in a glass beaker for several days while exposed to strong sunlight until it had become quite dark and viscous. An electrolyte containing one one-thousandth of 1 per cent of this polymerized furfural when electrolyzed gave a strongly striated deposit similar in all respects to that obtained in the filter paper voltameter. In fact the deposit could not be distinguished from that obtained from a Rayleigh voltameter. Under the microscope the deposit had the noncrystalline "lava like" appearance so characteristic of deposits obtained from

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[38] One of the standard methods for preparing pyromucic acid is to oxidize furfural with moist silver oxide.

[39] We hope to be able to return to this phase of the question in the near future, not only because of its bearing upon the voltameter problem, but more especially because of its relation to the chemistry of cellulose.

electrolytes strongly contaminated with filter paper. Just why this polymerized furfural should give more pronounced effects than the redistilled liquid was not quite clear. However, it did not seem improbable that the furfural formed from filter paper (assuming this actually occurred) would be in a similar physical state (i. e., polymerized or condensed) when first formed. In this connection it may be well to mention the fact that a very dilute solution of polymerized or "metafurfural" has a light yellow color exactly similar to that of concentrated filter paper extracts. However, we do not wish to place emphasis upon this circumstance, but it undoubtedly indicates a close relationship of both furfural and the filter paper extract to the oxycelluloses. This subject will be referred to again in the next section.

J. SPONTANEOUS DECOMPOSITION OF CELLULOSE INTO OXYCELLULOSE AND THE RELATION OF OXYCELLULOSE TO FURFURALDEHYDE

The effects of the various treatments of the filter paper upon the yield of furfural obtained from the aqueous extracts indicate that the soluble substances which yield furfural can be removed from the filter paper by extracting with water or more effectively with caustic alkali. These soluble furfural-yielding substances are formed again, however, if the filter paper is allowed to stand for some time before a second extraction. In the experiment described on page 231, the filter paper was subjected to repeated treatments with water to completely extract the "active substance" (which we then thought must be present as an impurity), but it was found that this treatment apparently had no effect upon the activity of the filter paper in the voltameter. This result was no doubt due to the fact that the extracted filter paper had been allowed to stand several days to dry before again testing its effect in the voltameter.

This behavior of thoroughly extracted filter paper on standing exposed to ordinary conditions has been observed a great many times. If the extracted paper has stood four or five months the extract then is even more strongly colored (yellow) than the original extract and possesses all the other properties of the first extract to the same or even greater degree; it reduces silver nitrate to colloidal silver quite as readily, yields furfural when distilled with very dilute nitric acid, and shows the basic reaction with iodeosine and methyl orange. If after the first thorough extraction the moist pulp is again extracted within two or three days, the washings are then not so strongly colored as in the first case, but are even more basic and quite as strongly reducing toward silver nitrate. In one case the second extract (made two months after the first treatment) was 7 parts per million basic, whereas the first extract made in the same manner was only 1.8 parts per million basic. The relation between these properties and the amounts of soluble solids extracted under varying treatments is an interesting field which we hope to investigate further at some future time.

The foregoing observations indicate that the soluble furfural-yielding substances are formed by a spontaneous decomposition of the cellulose, due perhaps to slow oxidation in the air or to fermentation or to both causes combined, the final result being the formation of oxycelluloses, as is shown both by the readiness with which the extracted material yields furfural when distilled with dilute acid and also by the yellow color of the aqueous extracts and especially of the alkaline extracts.

The spontaneous decomposition takes place only to a limited extent and seems to be confined mostly to the surface of the fibers.

Undoubtedly the physical structure of cotton cellulose, offering as it does an enormous surface for the action of atmospheric oxygen, explains in part at least this tendency of filter paper to become superficially oxidized. In this connection, it should be mentioned that Förster has observed the similar decomposition of cane sugar into furfural by the action of very dilute acids, and it seems entirely probable that in this case also the decomposition into furfural is rendered possible by a previous slight oxidation of the sugar—a process which probably takes place much more slowly and to a less extent than in the case of cotton cellulose, owing to the difference in surface conditions; hence the greater activity of cellulose in the voltameter. This spontaneous decomposition of cellulose probably accounts also for the results of Suringer and Tollens in obtaining furfural from pure hexopolyoses.[40]

Before leaving this phase of the problem it is desired to again emphasize the striking similarities between solutions of polymerized or condensed furfural and concentrated filter paper extracts (oxycellulose), especially as regards their action in the voltameter. These effects were so similar that this fact alone was at the time considered sufficient evidence that the effects of filter paper were due entirely to furfural. In addition it should be stated that when silver nitrate is added to such furfural solutions colloidal silver hydrosols are obtained which are exactly similar in color and other properties to those prepared with filter paper extract. When these facts are considered in connection with the fact that furfural is so readily formed from these filter paper extracts, the similarities between these two substances certainly appear to be more than a coincidence and indicate a very close relationship in their chemical constitution. The one important dissimilarity is their reaction toward indicators—oxycellulose showing a well-marked basic reaction toward both methylorange and iodeosine, whereas polymerized furfural is neutral or faintly acid toward the same indicators. However, it should be stated in this connection that upon electrolysis we have recently found that oxycellulose is decomposed into equivalent amounts of an acid

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[40] Many well-known facts are in accord with the foregoing views, that the decomposition of pure cotton cellulose into furfuraldehyde takes place through the intermediate formation of oxycellulose. A few of these facts may be mentioned at this point: (1) The yield of furfural is used as an approximate measure of the oxygen in oxycelluloses in excess of that indicated by the formula $C_6H_{10}O_5$ as determined by elementary analysis. (2) All carbohydrates, including hexoses and polyoses derived from them, yield large amounts of furfural when treated with concentrated sulphuric acid, which is a strong oxidizing as well as a strong hydrolytic agent. This decomposition is not brought about by nonoxidizing acids, e. g., HCl. (3) Hexoses can be oxidized first to the corresponding acid, then by means of H_2O_2 to a pentose which decomposes directly into furfural by the condensing action of HCl, the reactions involved being expressed by the following equations:

$$\underbrace{CH_2OH(CHOH)_4CHO}_{\text{hexose}}+O=\underbrace{CH_2OH(CHOH)_4COOH}_{\text{corresponding acid}}$$

$$CH_2OH(CHOH)_4COOH+O=\underbrace{CH_2OH(CHOH)_3CHO}_{\text{pentose}}+CO_2+H_2O$$

(4) Levulose (a keto-hexose) is converted directly into a derivative of furfural by treatment with anhydrous hydrobromic acid, which is both a very strong condensing acid and a strong oxidizing agent.

In general, the conversion of either a simple hexose or a hexopolyose, such as cotton cellulose or cane sugar, into furfural or its derivatives by the condensing action of acids seems to be conditioned by a previous oxidation of the carbohydrate. The mechanism of this decomposition may be as indicated in (3) above. However, it is not necessary to assume that a pentose is actually formed, for the three processes—hydrolysis to hexose, oxidation to pentose (accompanied by elimination of water), and finally the condensation of the pentose to furfural—may be in the end equivalent to oxidation and condensation, so that complete hydrolysis need not take place.

variety and a basic variety, both of which retain their colloidal character and reducing power toward silver nitrate.

III. STRIATIONS AND THEIR EXPLANATION

A. INTRODUCTION

During the interval between September 22 and December 17, 1909, a large number of qualitative experiments were conducted, and the chemistry of the silver voltameter further studied. Among other things, we studied the question as to what causes the striæ in a filter paper voltameter, or in a deposit which is made from a solution that has been contaminated by filter paper extract, or by linen, cotton, wood fiber, or certain other substances. Striæ have been observed in silver voltameter deposits by a great many observers, ever since the experiments of Kirmis published in 1876. Few observers have ever hazarded an opinion as to their cause, and no one has given a satisfactory explanation of their production. We have confirmed the observations of Smith that the presence of striæ is evidence of an impure electrolyte, which is quite contrary to the opinions of earlier observers, who believed striæ were always present.

Before describing our own experiments, however, we shall describe briefly some of the previous work on the subject.

B. EARLY WORK

1. KIRMIS

In 1876 Kirmis undertook some experiments on the migration of the ions at the University of Berlin upon the suggestion of Helmholtz, in which he employed a silver voltameter to measure the quantity of electricity passing through his apparatus. His attention was drawn to the various forms in which silver is deposited out of a silver nitrate solution, and he described some of these forms in a separate paper.[41] Well-marked striæ appeared on the bottom of the cylindrical vessel radiating from a center immediately under the pointed anode, and these lines extended up the sides of the vessel as parallel lines at a constant distance from one another. He made a large number of experiments, varying the

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[41] Pogg. Ann., 158, p. 121, 1876.

strength of current, duration of the deposit, concentration of the electrolyte, and total electromotive force in the circuit. He found the best results with 5 to 10 per cent solutions of $AgNO_3$, current not greater than sufficient to deposit 0.28 mg of silver per minute per sq. cm, and a sharp-pointed anode. He also thought a high voltage an advantage, even if the current were unchanged. He does not offer any explanation of the cause of striations, but says that the assumption that they are caused by currents in the electrolyte is not very probable, the regularity of spacing seeming to offer a serious difficulty to this view.

2. BEHN

In 1894 Behn published an elaborate paper [42] on the subject of striated deposits in the silver voltameter. This work was done under the direction of Kundt and, like that of Kirmis, was carried out at the University of Berlin. He studied very carefully the conditions under which striations occur, and sought for an explanation of the cause of striations. He first used a platinum crucible as a cathode and a vertical rod (pointed at the bottom) as an anode. No filter paper or other substance surrounded the anode, and no glass or other dish was placed under it. A 25 per cent solution of silver nitrate was used as electrolyte. With a single accumulator as a source of current he passed 0.1 ampere for one hour through the voltameter, and obtained a well-marked striation of the deposit, as Kirmis had obtained. He therefore concluded that a high electromotive force was unnecessary if the resistance of the circuit was not large.

In order to photograph the deposits easily he replaced the platinum crucible by a cylindrical glass cup lined with sheet platinum, a disk of platinum covering the bottom and a long strip of platinum bent into a circle forming a lining to the walls of the cup. After a deposit was made using the sheet platinum as a cathode the latter was removed from the cup and laid out flat and photographed. Numerous pictures of deposits are given by Behn, which agree in appearance with some of the deposits made by ourselves. Behn found (confirming Kirmis) that the striæ radiate

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[42] Wied. Ann., **51**, p. 105, 1894.

from the point at the bottom of the cup under the anode, and are vertical on the sides of the cup. That the direction of these striæ was determined by the convection currents circulating in the electrolyte, he showed by numerous ingenious experiments. First of all, he made a special voltameter cell with parallel walls of glass, a section of which is shown in Fig. 27, which permitted seeing the convection currents while the electric current was flowing and the striated deposit was forming. The cathode was a strip of sheet platinum bent into a semicircle. As soon as the current begins the electrolyte around the anode begins to increase in density, whereas the electrolyte on the surface of the cathode decreases in density. Hence convection currents are set up, as shown in the figure, which are the more rapid as the current is stronger. The direction of these currents is precisely the same as the direction of the resulting striæ. This was found to be true when the cell was closed at the top and turned on its side; the striæ changed in position to correspond with the new course of the convection currents. When, however, the cathode was horizontal and at the top of the cell and the anode at the bottom, so that the heavy anode liquid remained at the bottom and the impoverished cathode liquid collected at the top, there were no appreciable convection currents and *no striæ appeared* in the deposited silver. It was therefore clear that the direction of the striæ was determined by the direction of the convection currents, and that striæ could not occur in the absence of convection currents. Why this was so and what was the primary cause of striations was a question Behn studied carefully, but could not answer satisfactorily to himself. He did, however, venture a suggestion. He says: "But how the striæ arise is by far harder to answer. Apparently the flow in the liquid hinders the deposit of silver crystals. At first, the latter deposit themselves on the smooth surface in a completely irregular manner. Through these hindrances the current of liquid upon the cathode is split up into separate filaments and now the deposit takes place almost exclusively between each pair of such filaments. However, this is only an attempt at an explanation."

Behn "attempted to learn by the aid of a microscope the manner in which the silver crystals which deposit out at first irregularly arrange themselves in striæ. This did not, however, succeed.

It is probable that the crystals thrown down later deposit themselves in the shelter of those deposited earlier, that is, behind the first with respect to the direction of flow." This is of course no explanation of the phenomenon.

Behn also investigated the effect of varying the concentration of the electrolyte and the density of the electric current. He found the striæ more distinct and farther apart in the more concentrated solutions, and more distinct with smaller current density at the cathode than with larger. With increasing temperature the striations become more distinct, and with purer solutions less distinct. He was surprised at the change in the striæ due to very small impurities in the electrolyte, but apparently did not obtain deposits entirely free from striations.

3. SMITH, MATHER, AND LOWRY

Smith, Mather, and Lowry [43] in their work published in 1908 gave considerable attention to the subject of striations. They observed, as others have done before them, that with pure electrolyte striæ do not appear in the Richards form of voltameter. Also with pure $AgNO_3$ in the Rayleigh voltameter as they employed it the striæ were faint or absent. They regarded striæ as evidence of an impure electrolyte, and attempted to explain the greater tendency for striæ to appear in the Rayleigh voltameter than in the Richards type, by a difference in the convection currents. They varied the concentration and the density of the electric current at the cathode and confirmed Behn's observations as to the marked differences in the striation produced thereby. After giving a careful description of the convection currents arising from the differences of pressure due to the heavy anode liquid in the center of the voltameter and the lighter cathode liquid adjacent to the outer walls of the platinum dish, they give the following statement of their interpretation of the observed effects:

> We interpret these results in the following manner: The film of liquid in contact with the cathode has a greater mean thickness in the 1½ per cent solution than in the 15 per cent solution. This follows because the rate of deposition of silver is the same in each voltameter. If the film is very thin, it is unstable and breaks up into cylindrical columns of liquid. Hence, in contact with the cathode surface there are columns of liquid of low concentration, and in between these the electrolyte is of approximately normal concentration. The latter has the higher conductivity, and since in addition

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[43] Phil. Trans. 207, p. 545.

there is an E. M. F. acting from the columns of low concentration toward the main body of the electrolyte, the current will pass into the cathode through the liquid in between the columns. Immediately the concentration falls and possibly the resultant liquid of small density is pulled into the columns of low concentration. If our assumptions are correct, an increase in the current should result in the cathode film becoming thicker and more stable, and when it is sufficiently stable to remain as a film a striated deposit should not be formed. This was tested by experiment and found to be so.

The following table indicates the results. All the solutions were pure, and the same volume of electrolyte (350 cc) was taken in each case.

Experiment	Electrolyte	Current	Character of deposit
	Per cent	Amperes	
1	1.5	0.1	No striæ
2	3.0	0.7	Do.
3	2.0	1.0	Do.
4	15.0	0.1	Marked striæ
5	15.0	0.3	Do.
6	15.0	0.7	Striæ, but not so marked as in (4)
7	15.0	1.0	Very faint striæ at bend of bowl
8	15.0	2.0	No striæ
9	15.0	4.0	Do.
10	15.0	8.0	No striæ; fine matte surface
11	50	1.0	Striæ

It appears that for solutions of all concentrations striated deposits are obtained for small current densities at the cathode, and matte deposits for very large current densities.

We may now compare the changes in the Rayleigh and Richards forms of voltameter. In the latter case there is no descending anode liquid, and there will be, therefore, less tendency for a star-like deposit to be formed on the base of the bowl. In our own form of Richards voltameter the volume of cathode liquid was in general about 250 cc, and during electrolysis the mean concentration of the solution must have diminished from 15 to 10.6 per cent. The mean concentration of the electrolyte in the Rayleigh form remains constant and, in consequence, for the same current density striæ were produced in the Rayleigh form when they were absent in the Richards form. This effect has also been observed by Guthe[44] and by van Dijk.[45] In the Richards form, as employed by the latter observer, the cathode liquid consisted of about 30 cc of a 20 per cent solution, and at times nearly 3 grams of silver were deposited, the concentration being thus reduced to about 4.3 per cent. Professor van Dijk observed little or no striæ in the Richards form, but marked striæ in the Rayleigh form.

It will be observed that the explanation of Smith, Mather, and Lowry is similar to that of Behn in supposing that the electrolyte next to the cathode surface is split up into columns or filaments.

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[44] Phys. Rev., **19**, p. 147; 1904.

[45] Ann. der Phys., **19**, p. 271; 1906.

Behn supposes this to be due to the crystals themselves, and that the silver deposits out after this condition is established chiefly between the filaments, thus causing the more or less distinct ridges of silver which constitute striæ.

Smith, Mather, and Lowry, however, suppose that if the film of low concentration in contact with the cathode is very thin, as when the body of the electrolyte is of relatively high concentration, "it is unstable, and breaks up into cylindrical columns of liquid," and that these columns of low concentration are interspersed regularly with columns of high concentration and that the current enters the cathode through the latter.[46] This gives rise to the ridges of silver constituting the striæ, the spacing between which give a measure of the width of the columns.

This explanation is unsatisfactory for several reasons:

1. The existence of separate columns of liquid of different concentrations, or of the same concentration (Behn), is an assumption for which there is no satisfactory evidence.

2. The striæ disappear completely when the electrolyte is pure, and the existence of the columns of electrolyte assumed by Behn and Smith, Mather, and Lowry is in no way dependent upon the slight impurities which are essential to striations.

3. It is impossible to conceive columns of liquids of so small lateral dimensions as the distance between striæ maintaining themselves intact, with other columns between them of greatly different concentration; especially since the silver is supposed to deposit out of the columns of high concentration, which "immediately" reduces the concentration. How these depleted columns could have their concentration suddenly restored in order to keep up the process is impossible to imagine.

4. The lack of striæ in the Richards voltameter is not due to the hindrance which the porous cup offers to the convection currents, as Smith, Mather, and Lowry suppose. For if the porous cup be removed and no filter paper or any septum employed in its place the striæ are still absent, supposing pure electrolyte to be employed. We have demonstrated this repeatedly, and give in Fig. 28 a picture of such a deposit.

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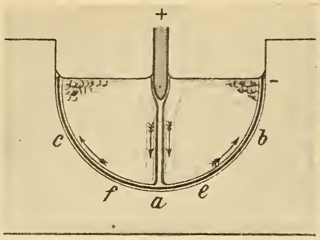
[46] See paragraph quoted above, p. 267.



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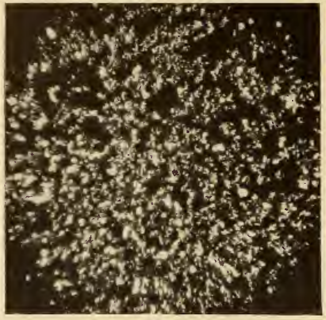

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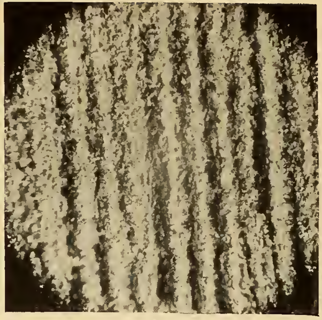

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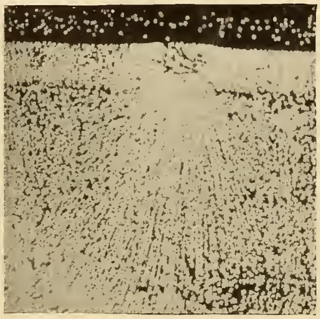

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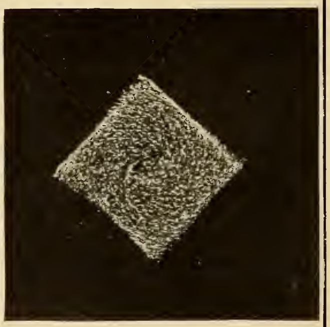

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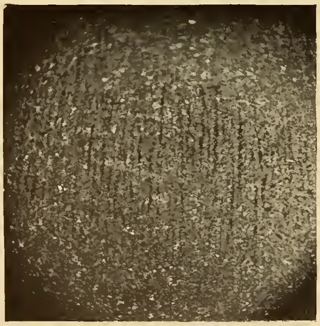

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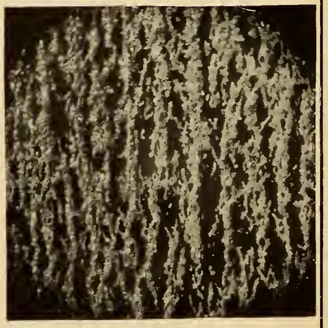

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Fig. 27.—*Behn's special cell with semicircular cathode and parallel glass walls*

Fig. 28.—*Unstriated deposit made in voltameter without septum*

Fig. 29.—*Parallel vertical striae on side of dish.* × *8*

Fig. 30.—*Striations radiating from point of discharge of a contaminated electrolyte*

Fig. 31.—*Spiral striae due to rotating the cathode in a contaminated electrolyte, natural size*

Fig. 32.—*Striae growing horizontally from edge of stationary cathode, due to rotation of the electrolyte around it.* × *8*

Fig. 33.—*Noncrystalline, slightly striated deposit on under side of cathode inclined 25° to the horizontal.* × *16*

Fig. 34.—*Noncrystalline, nonstriated deposit on under side of horizontal cathode.* × *16*

Fig. 35.—*Spiral striae forced from a pure electrolyte by rotation of the cathode, natural size*

Figs. 36, 37, 38.—*Showing that the spacing of the striae is dependent on the cathode curren density; currents 0.044, 0.0075, 0.0010 ampere per sq. cm, respectively* × *5*

We were therefore driven to the conclusion that the cause of striæ is something entirely different from what has been suggested, and we made a large number of experiments before we arrived at what we believe to be the true explanation. Before stating our theory of striæ, however, we shall prepare the way by describing some of these experiments, which were for the most part completed before we were aware of the work by Kirmis and Behn. We have confirmed most of Behn's results, but have made many additional experiments of a different character.

C. EXPERIMENTAL FACTS REGARDING STRIATIONS

1. STRIÆ ARE NOT PRODUCED IN PURE SOLUTIONS

We have made hundreds of deposits of silver without filter paper, both in the Richards voltameter and in voltameters without a porous cup, and in no case have we seen striations when the electrolyte was known to be pure. The crystals are distinct, with beautifully developed faces and angles, and no suggestion of striations. But with filter paper as a septum between anode and cathode, or with electrolyte that has been filtered through filter paper, or with the addition of "filter paper extract" or of certain chemicals, striæ are produced more or less distinctly according to circumstances. (Photographs of these shown earlier in this paper.)

2. ONLY CERTAIN KINDS OF IMPURITIES PRODUCE STRIATIONS

Not only filter paper, but linen, cotton, and wood-pulp paper, wood fiber, linen, cotton, and silk textiles, furfuraldehyde, and other strong reducing substances produce striations. The purest of filter paper, which is practically pure cellulose, is effective in producing striations. On the other hand, cane sugar, starch, acids, and a large number of other chemical substances do not produce striations. It is not enough that the electrolyte be impure, but it must contain substances which reduce silver nitrate, as we have explained elsewhere (p. 247), thus producing colloidal silver. This we believe to be the first essential condition for striations.

3. MOTION OF THE ELECTROLYTE OVER THE SURFACE OF THE CATHODE IS NECESSARY

We have confirmed the conclusion of Behn and others that the direction of the striæ is determined by the convection currents of the electrolyte flowing over the surface on which silver is being deposited. The radial striæ on the bottom of the platinum dish (Fig. 6), the parallel vertical striæ on the sides (Fig. 29), the diverging striæ produced where the electrolyte is discharged as a jet upon a cathode surface (Fig. 30), the circular striæ produced on a horizontal cathode in rotation (Fig. 31), the inclined striæ produced on a vertical plate when the electrolyte is given a horizontal motion by rotating the dish containing the electrolyte (Fig. 32), all indicate that the striæ lie along the lines of flow of the electrolyte. On the other hand, if the cathode plate be inclined to the vertical, the striæ are less marked and decrease the more as the inclination to the vertical is greater. (Fig. 33.) When the cathode is horizontal they disappear altogether. (Fig. 34.) Similarly, striæ due to rotation of the vessel, or of a horizontal plate in a stationary electrolyte, are the more pronounced as the speed of rotation is greater. There is thus ample evidence that a motion of the electrolyte over the surface of the cathode is the second essential condition for striations.

4. FORCED STRIÆ IN A PURE ELECTROLYTE

We have stated above that for striæ to appear certain impurities are needed in order to produce colloidal silver in the electrolyte. There is, however, an exception to this statement, namely, where the velocity of the electrolyte is very great. Natural convection currents are sufficient to produce the heaviest of striations when the solution contains considerable of the filter paper impurity. But in a very pure solution, as already stated, not the faintest suggestion of striations is ordinarily seen. However, if a horizontal cathode be rotated in its own plane at a very high speed in a pure electrolyte slight circular striations are produced. (Fig. 35.) The explanation of these forced striæ is in harmony with the explanation of ordinary striæ. (See below.)

5. SPACING OF THE STRIÆ

Striæ are sometimes coarse and far apart and sometimes fine and very close together. It was long ago noticed that variations in the strength of the electric current and of the concentration varied the distinctness of the striæ. Careful observation shows that many deposits which appear unstriated are really very finely striated, but that the striæ have grown together and disappeared. As striæ do not appear at the very beginning of a deposit, and may have appeared and disappeared before the end, it is necessary to look for the striæ during the deposit in cases where they are found very close together. Sometimes they appear at the bend of the bowl near the bottom and not on the sides. This is because the deposit of silver is thinner in the former place, whereas on the sides where the deposit is heavier they have been covered up by the depth of the deposit.

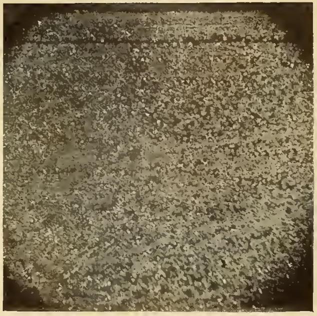
In order to ascertain what determined the spacing of the striæ we made a large number of deposits, varying such conditions as current density, concentration, and temperature, one at a time. In some cases the deposits were photographed and the photographs measured. In other cases the deposits were measured. The spacing does not depend on the degree of impurity, although the distinctness of striation, its microscopic appearance, and its appearance to the unaided eye do depend on the degree and character of the impurity.

6. EFFECT OF VARIATIONS OF CURRENT DENSITY, CONCENTRATION, AND TEMPERATURE

Increasing the current density decreases the distance between striæ. Hence small currents give coarse striæ, heavy currents fine striæ. (See Figs. 36, 37, 38.) The latter are quickly covered up, hence it is sometimes stated that certain current densities give no striæ. Increasing the concentration increases the distance between striæ. Hence weak electrolytes give fine striæ, and stronger electrolytes coarser and more distinct striæ. Increasing the temperature of the electrolyte makes the striæ farther apart. The effect of changes in concentration and temperature may be expressed by saying that increasing the conductivity of the electrolyte increases the distance between striæ.

7. SIZE AND SPACING OF CRYSTALS IN PURE SOLUTIONS

We very early noticed that the size and mean distance apart of the crystals deposited out of pure solutions vary in much the same way as the spacing of the striæ. Sometimes the crystals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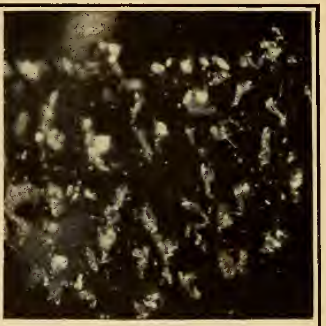
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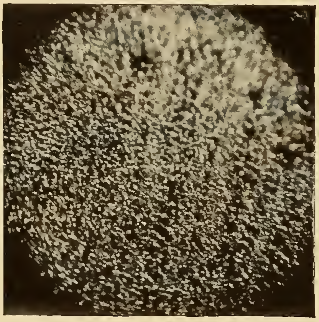
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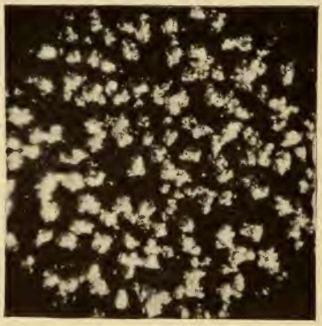
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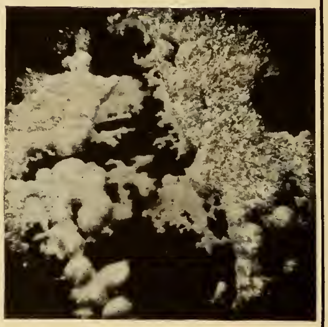
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(a) (b) (c)

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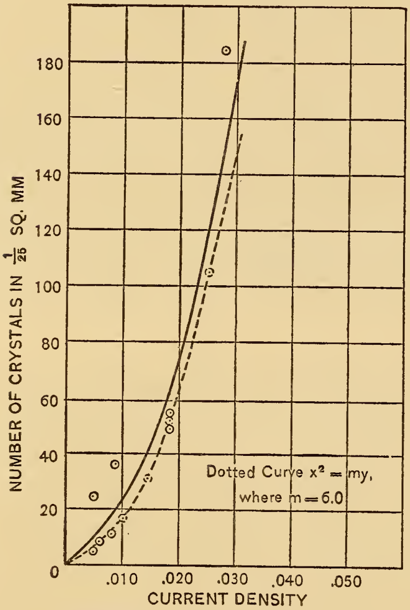
Figs. 39, 40, 41.—*Current density series for pure electrolytes, showing that the size and spacing of the crystals is dependent on the cathode current density, the concentration being the same; currents 0.028, 0.0028, 0.00028 ampere per sq. cm, respectively.* × 5

Figs. 42, 43.—*Showing that the size and spacing of the crystals is dependent on the concentration of the electrolyte, the current being the same; concentrations 5 per cent, 15 per cent, respectively*

Fig. 45.—*Deposit from a silver nitrate solution to which silver acetate has been added. Showing two kinds of deposit.* × 16

Fig. 47.—(*a*), (*b*), (*c*), *have been prepared to illustrate the statements made above respecting the relation between the distance apart of the crystals, the conductivity of the electrolyte, and the density of the electric current. Two equipotential surfaces that lie within the platinum are shown as emerging into the electrolyte around the silver crystal*

are fine and very close together and sometimes they are coarse and relatively far apart, and between these extremes any size or spacing may be obtained by varying the conditions. These conditions are the same as those which determine the spacing of striæ, namely, the current density (see Figs. 39, 40, 41), concentration (see Figs. 42, 43), and temperature. In order to obtain quantitative results a large number of deposits were made in the field of a microscope on a platinum cathode that had been ruled into squares by a fine diamond. The rulings were 0.2 mm apart, so that each square millimeter was divided into 25 equal squares. Thus the crystals could be counted, using a certain current density and time and a definite concentration of the electrolyte. Then the conditions could be varied, and so the relation between these conditions and the number of crystals per unit of area could be determined.



RELATION OF NUMBER OF CRYSTALS TO CURRENT DENSITY.
PURE ELECTROLYTE.

Fig. 44

At the start crystals were deposited and a map of a portion of the field made, locating every crystal. Then the cathode was cleaned and the operation was repeated a number of times. This was to see whether crystals always appeared at the same places. There were of course in the surface of the platinum plate minute scratches and irregularities which under the microscope were plainly visible, and although sometimes the crystals would be seen lying along a scratch like beads on a string, generally their distribution was quite independent of any such markings and quite independent of the straight lines ruled by the diamond on the platinum cathode. No two distributions of crystals over a given area were alike, and we noted no points or spots where crystals tended to appear repeatedly by preference.

With a variation of current density the number of crystals is approximately proportional to the square of the current density. Fig. 44 gives the results of some measurements. Thus with small current density the crystals would be large and relatively few; with large current density the crystals are small and more numerous, the total quantity of silver deposited being the same in each case. With increasing concentration the crystals are larger and fewer, and so also with increasing temperature. That is, increasing the conductivity of the solution increases the distance between crystals (as it does between striæ) and increases the size of the crystals. As the size of the crystals is inversely proportional to their number, and their mean distance apart is inversely proportional to the square root of their number, we see that the mean distance apart of the crystals is approximately inversely proportional to the current density. Photographs of deposits under different conditions illustrating these facts are shown in Figs. 39, 40, and 41.

8. EFFECT OF ACID AND ACETATE

A trace of acid in the electrolyte makes the crystals finer, and hence gives the deposit a different appearance, but does not produce striations. For a given total weight of silver deposited the average size of crystal is of course inversely proportional to the number. The number of crystals is determined the first moment of the deposit. Thereafter they increase in size quite uniformly, except that if the deposit continues a considerable time they grow together in many cases, so that the number decreases and the variation in size is accentuated. Very few new crystals start after the first instant, unless the current is considerably increased.

A trace of silver acetate dissolved in the silver nitrate makes the crystals *very* fine—that is to say, starts the crystals very close together and in great numbers. Thus the platinum surface becomes covered by a more or less continuous deposit, which under the microscope looks like a surface of frozen snow. The crystalline deposit from the pure nitrate, on the other hand, consists of a great many relatively large and separate crystals, with large areas of bare platinum between. The contrast is very striking.

In addition to the white deposit of fine crystalline silver, in the case of the solution containing silver acetate, there is present when filter paper has been used (or filter paper extract) a black deposit of silver which we believe has been laid down from the colloidal condition, but which on heating turns first yellow and then white. (Fig. 45.) It is readily distinguished under the microscope from the normal silver deposit, and its presence makes the weight of silver too heavy. The silver acetate is more easily broken down by the reducing agents (chiefly furfuraldehyde) formed from the cellulose of the filter paper, and so increases the weight of the deposit much more than when the silver acetate is not present.

9. VELOCITY OF THE CONVECTION CURRENTS

We have stated that we believe the motion of the electrolyte over the cathode is one of the essential conditions for the production of striæ. These convection currents can be seen in a voltameter with glass sides, since the variation of the density of the electrolyte between the anode and the cathode is considerable. By the aid of the microscope and ruled cathode plate employed in counting the crystals we succeeded in measuring approximately the relative velocity of these convection currents under different conditions. Using a small voltameter with parallel glass sides, the cathode plate was vertical, and the microscope was focused on the plate. Small particles of the anode slime which became detached from the anode circulated around with the convection currents, and served as an index of its velocity. Of course, the velocity of the liquid was different at different distances from the cathode, but by focusing on the plate tiny particles even a short distance away could not be seen distinctly. Thus we observed the sharply defined particles falling in the field (they were rising in reality) at a uniform rate, and by timing them with a stop watch as they crossed the horizontal lines ruled on the cathode their speed was measured with fair accuracy. The speed varied with the density of the electric current, as would be expected, increasing with greater current. The speeds observed (Fig. 46) varied from 0.1 mm per second to 0.7 mm per second,[47]

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[47] This is much less than the estimate given by Smith, Mather, and Lowry, namely, 1 cm per second. However, their estimate was based on the inclination of striæ and was not a direct measurement.

using concentrations and current densities such as are used in practice. Probably in larger voltameters the speed would be greater.

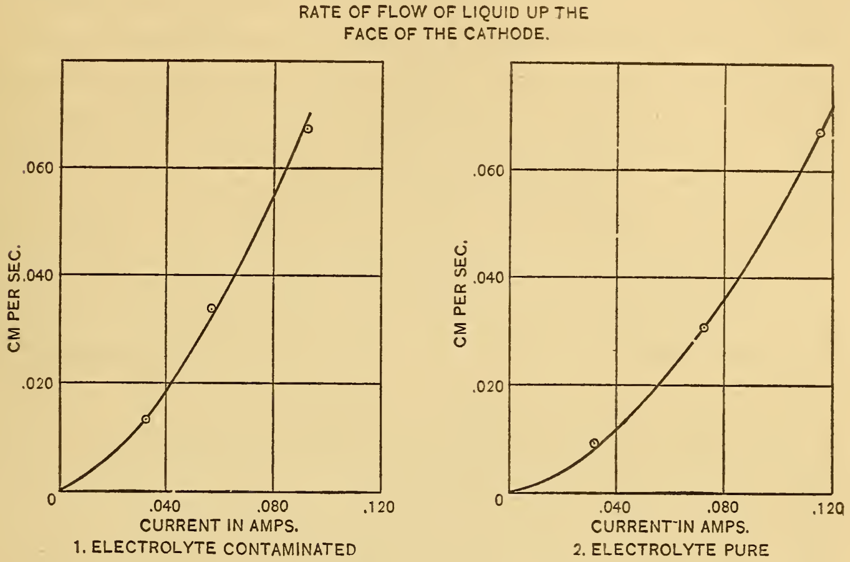

Fig. 46.—*Curves showing the rate of flow of liquid up the face of the cathode as dependent on the current*

D. THEORY OF DISCONTINUOUS DEPOSITS

We have described the deposits of silver from pure solutions of silver nitrate as invariably crystalline, the bare platinum cathode being plainly visible between the crystals; from impure solutions it appears noncrystalline, but a microscope shows the irregular masses of silver to be aggregates of fine crystals. In neither case is the cathode completely covered. On the other hand, the deposits from a solution of cyanide of silver appear perfectly continuous even under a very high magnifying power, and are therefore radically different from the deposits from the nitrate.

It is an interesting and important question to determine *why* the crystals are deposited in the manner described above, and why the current is concentrated into the silver crystals initially started, instead of spreading out over the surface of the platinum as it does when a solution of cyanide of silver is used. It is a striking phenomenon to see the area of bare platinum on the cathode surface of a silver voltameter, a thousand times greater than the area of the silver crystals, in the early stages of the deposit, and yet no current flowing to the platinum surface, but only to the tiny silver crystals. As Ohm's law holds in the electrolyte, it is evident that there is at the surface of the platinum *a potential difference opposing the current, which brings the electrolyte in contact with the platinum to a higher potential than that of the electrolyte in contact with the silver*, and so the current is turned away from the platinum surface, finding numerous outlets to the platinum cathode through the silver crystals. It is as though the potential difference at the start breaks through the surface film (which offers a counter electromotive force) at numerous points, and these initial outlets, which increase in area as the crystals grow, are sufficient, unless the current density is suddenly increased.

The surface potential differences taken in connection with the specific resistance of the electrolyte and the current density determine the distance apart of the crystals. In a very concentrated solution the specific resistance is less, and hence the fall of potential corresponding to the surface differences of potential occurs in a greater distance. Hence the crystals will be farther apart than in a normal solution. On the other hand, in a very weak solution of higher specific resistance the fall of potential is steeper and hence the given potential difference will occur in a shorter distance. Hence the crystals will be nearer together and more numerous, and hence also the crystals very small. Heating the solution increases its conductivity, and therefore has the same effect as increasing the concentration; that is, the crystals are further apart and of larger size. (See Fig. 47.)

We have attempted to develop this theory of surface potentials to explain the form of electrolytic deposits from other silver salts and salts of other metals, and have had some success in doing so, but we found ourselves getting so far away from the problems of the silver voltameter that we abandoned that work for the present and returned to the question which directly concerned the silver voltameter.

E. EXPLANATION OF STRIATIONS

After having given this question careful study, we offer the following explanation, which we believe is in accord with the known facts regarding striæ.

In the first place it should be remembered that silver crystallizes according to the cubical system, and when deposited out of a pure solution of silver nitrate various modifications of cubical crystals are formed, as octagonal, dodecehedral, etc., in addition to cubes and rectangular parallelopipeds. These crystals are formed more perfectly in very pure solutions, and deposits examined under a binocular microscope show beautifully the perfect faces and angles of these various geometrical forms. Slightly impure solutions have their crystalline forms greatly modified, aggregates of needle-shaped crystals predominating in deposits made from solutions slightly contaminated by filter paper. As the impurity increases, the crystalline character disappears, the deposits being masses that often look like molten metal, cinders, or slag. High magnification shows that such deposits are made up of aggregates of very small crystals. The regular crystalline growth that takes place normally in electrolytic deposits from a pure solution of silver nitrate, whereby large crystals are built up, can not occur when the solution is strongly contaminated by filter paper or other forms of cellulose, or by furfuraldehyde.

The reason why a regular crystalline growth does not occur when filter paper extract is present is, we believe, that colloidal silver is produced by the reaction of furfuraldehyde (produced from oxycelluloses) on silver nitrate and that this colloidal silver is deposited on the silver and breaks up the regular growth of the crystals, each particle probably serving as a nucleus for a new crystal. Thus the deposit in such cases is an aggregate of very small crystals instead of relatively large crystals.

When the current starts the deposit begins at many isolated points, the distance between crystals being hundreds of times the linear dimensions of the crystals themselves at the end of the first few seconds. The stream lines along which the current flows are thus concentrated at the cathode end, upon these incipient crystals, no current flowing to the bare platinum after the first instant. The upward current of liquid along the crystal surface (due to the smaller density of the impoverished electrolyte at the cathode) carries the chain of ions which lie along a given stream line upward out of its normal course, so that the current tends to reach the upper surface of a crystal. We must suppose that in a pure electrolyte the force of crystallization constrains the silver atoms to be deposited in regular order, thus building up, as we know, crystals of relatively large size, in spite of the tendency of the convection currents in the liquid to distort the crystals by building them upward. For we find the same regularity of crystalline growth on the vertical sides of a cathode vessel as on or near the bottom. But in an impure solution the regular crystalline growth is interfered with by the deposit upon the initial crystals of particles of colloidal silver. Thus, as new crystals are started at every point where a particle of colloidal silver has been deposited, the silver grows by preference upward in the direction favored by the upward movement of the liquid. Watching this process under the microscope one sees the small crystals which appear at the start grow upward so that after a time instead of a large number of silver crystals of approximately equal dimensions in different directions one sees a great number of elongated deposits, the longest dimension being vertical. These tend to grow into one another, so that after a time striations have developed, that is, there are ridges of silver of more or less equal distance apart, separated by intervals of bare platinum.

The striation can not even be suspected at the start, but after a time it becomes well marked, and then if the deposit is continued long enough the ridges of silver growing in width join together, the platinum surface is gradually covered, and the striation finally disappears.

If the current density is relatively small at the start, the initial points of deposit are comparatively far apart, and when they have become elongated vertically and joined together more or less they form striæ, which will be comparatively wide apart. On the other hand, if the current density be larger, the points of deposit initially will be more numerous, and the striæ will be closer together. Observation shows that the number of striae per centimeter is approximately proportional to the current density, or the distance between striæ is inversely proportional to the current density. In the same way, the initial distance between crystals (in a nonstriated deposit) is inversely proportional to the current density, or the number of crystals per square centimeter is proportional to the square of the current density. This explains why a small current gives coarser crystals than a larger current for a given weight of deposit, for doubling the current multiplies the number of crystals by four, and hence reduces the average weight of each crystal to one-half. The original incipient crystals appear in the field of the microscope almost at once, perhaps within a second or two after closing the circuit. They are so tiny when first seen that millions would be required to weigh a milligram, and as they grow larger they amalgamate more or less, so that the number of separate crystals decreases.

Adding a trace of acid changes the potential difference at the surface of the platinum in such a way as to make the crystals nearer together and hence more numerous and smaller in size for the same weight of deposit.

We have spoken above of an exception to the general rule regarding striæ in what we call forced striæ. If a cathode be rotated at a moderate speed in a pure electrolyte, no evidence of striation appears, but if the speed of rotation be increased there is a slight circular striation, although the deposit is crystalline. The high speed constrains the crystals to grow in the direction of motion, for the same reason as in an impure deposit, except that it requires a much higher speed in the pure solution. The result is, however, radically different in the two cases, the deposit in the case of the pure solution where the speed of the electrolyte over the cathode is high being crystalline and only slightly striated. This case of forced striæ in a pure solution is thus quite in harmony with the explanation here offered for normal striæ.

This paper is to be followed by two more, of which the first will deal with the quantitative experiments preliminary to the meeting of the International Technical Committee and will also contain a discussion of the purification and testing of silver nitrate. The final paper will deal chiefly with the determination of the voltage of the Weston normal cell and the question of specifications for the voltameter.

WASHINGTON, October 1, 1912.