

February 27, 1958

To: George Case  
From: P. P. Coppola  
Subject: Sylvania Electrophoretic Heater Coating

Attached is a copy of a memo to me from John Festa of G.E. Palo Alto concerning Sylvania's present heater coating recipe. Attached also is a copy of a general information paper on electrophoresis co-authored by Festa. You may be already familiar with the latter item. Festa has been intimately associated with Sylvania's coating techniques and I believe would cooperate in supplying to us more detailed information if we find it necessary to obtain same. The most important information, namely the recipe, is disclosed, however. Other problems concerning exact voltages, time, etc. can be determined empirically if no more information is supplied.



P. P. Coppola  
Mono. Picture Tube Prod. Engg.  
CATHODE RAY TUBE DEPARTMENT

PFC:jfe  
attach.

Copies to: WL Jones  
P Librizzi  
RT McKenzie  
AC Nonnekens ←  
J Shepp  
FE Sullivan  
LE Swedlund

**GENERAL ELECTRIC**  
ELECTRONICS DIVISION

SUBJECT

COPIES:

17 February 1958

Pat Coppola  
Cathode Ray Tube Dept.  
SYRACUSE

As per your request, I am sending you a copy of my paper on electrophoresis. As you will note, it is quite vague on suspension compositions. The following is the basic heater coating suspension that works very nicely:

200 g.  $Al_2O_3$  (Norton 38-900, Acid washed)  
100 cc Isopropanol  
60 cc Raffi and Swanson L-18 lacquer  
475 cc Amyl Acetate  
2-3 cc Polyethylene glycol No. 300

Mill 16 hours in porcelain mill using alundum balls.  
Voltage required is in 1000-2500 volt range.  
Coated heaters are fired at 1650°C.

A suspension that works for cathode coatings is:

240 g carbonates  
40 cc Raffi and Swanson lacquer No. 2695  
15 cc Polyethylene glycol No. 300  
400 cc amyl acetate

Mill 72 hours - dilute to 800 cc with amyl acetate.

I do not have any literature on a Land Polaroid Camera Attachment for your metallo-graph. However, I did find a Land Polaroid Attachment, AD No. 2475 to fit in place of a standard 5" x 7" double plate holder. I believe this is an American Optical number and you may find it in a Fisher or similar catalog.

From what I've read in the papers, it looks as if I just managed to get out of Syracuse on time.

J. Festa

JF/gsd

*John*  
*Convey to George Case  
that we have the above information*

*PP Coppola*

# Some Aspects of Electrophoretic Deposition

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## ABSTRACT

An electrophoretic deposit of aluminum oxide, typical of those employed in the electron tube industry, is described with regard to suspension composition, equipment required, and nature of the deposits obtained. Quantitative results for a variety of conditions are presented. These are also discussed in electroplating terms, for the superficial resemblance between electrophoretic deposition and electroplating permits the two different processes to be treated by equations and relations of the same form.

The suspension investigated, as typical of practical suspensions, contained two liquids of differing polarity. It is proposed that a sheath of the more polar liquid forms on the ionic surface of these particles. Qualitative observations on the stability, mobility and deposition process are in accord with this concept. Experimental evidence on the effects of added moisture, and at partial settling, also supports this view.

It is pointed out that the three electrode processes, neutralization of charged particles, their deposition, and the electrode reaction, although occurring concurrently, can well occur independently, and it is suggested that the deposition process may occur as the migration of particles causes a build-up in dielectric constant of the medium at the electrode, so reducing the electrokinetic potential below the limiting value for stability.

## INTRODUCTION

ELECTROPHORESIS IS THE MIGRATION of charged colloidal particles in an electric field. Under suitable conditions these particles will deposit on an electrode and form a coating over it. In the electron tube industry this coating process is employed as an alternative to spray or dipping methods. Typical applications are insulating, non-emissive heater coatings of aluminum oxide, and electron-emitting surfaces for hot cathodes. It is the purpose here to describe the electrophoretic process and to offer a theoretical explanation of some of the effects observed with one particular, but typical, suspension.

Electrophoretic deposition may be from either aqueous or non-aqueous suspensions, but the non-aqueous types have usually been preferred. Deposit adherence from these is generally better, and interfering ionic conductance and gas evolution at the electrodes are reduced. With non-aqueous suspensions, however, relatively high voltages are required, and potential differences of the order of several hundred to more than a thousand volts may be needed. It is apparent that such voltages could be hazardous; this hazard should be taken into account.

## THEORETICAL

Electrophoretic suspensions useful for deposits are lyophobic in nature. They necessarily are composed of charged particles; electrical neutrality is preserved by a diffuse double layer of counter charges of opposite polarity in the suspending medium. The suspensions show

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many of the properties of ordinary colloids; for example, they are flocculated by electrolytes. Electrophoretic deposition of the particles is closely analogous to sedimentation.<sup>1</sup> Only the lyophobic suspensions can form a compact sediment under gravity; these also are the suspensions that can form an adherent electrophoretic deposit. Analysis of the electrophoretic process leads to the Hamaker relation<sup>2</sup> for electrophoretic yield  $Y$ , obtained in time  $t$ , as

$$Y = \sigma C \iint \frac{dV}{dn} ds dt \quad (1)$$

where  $C$  is the particle concentration,  $dV/dn$  the potential gradient normal to surface  $s$ , and  $\sigma$  the electrophoretic mobility. Equation (1) is quite applicable to situations where all particles arriving at an electrode are deposited there, for essentially it is a description of this process in mathematical terms.

The electrophoretic mobility  $\sigma$  of Eq. (1) is analogous to ionic mobility; typical values<sup>3</sup> are, however, only about one per cent of the values for most ions. The actual electrophoretic velocity of a particle is given as the product of mobility and the potential gradient,  $dV/dn$ . (The terms mobility and velocity have at times been used interchangeably.) A relation for the electrophoretic mobility, and hence, also for the velocity in a given field, can be obtained by applying the Stokes law describing the movement of particles in a viscous fluid.<sup>4,5</sup> This gives the Smoluchowsky-Henry relation\* for mobility  $\sigma$  as

$$\sigma = D\zeta/4\pi\eta \quad (2)$$

where  $D$  is the dielectric constant and  $\eta$  the viscosity of the medium, and  $\zeta$  the electrokinetic (or zeta) potential of charges associated with the particle. This relation assumes no interaction of particles, uniform dielectric constant, etc., and hence is best regarded as a sort of limiting law applicable only to dilute suspensions. Its utility in this connection is well established.

The electrokinetic potential  $\zeta$  is the potential of the charges associated with a particle with respect to some

1. HAMAKER, H. C., and VERWEY, E. J., *Trans. Faraday Soc.* 36, 180 (1940)
2. HAMAKER, H. C., *Trans. Faraday Soc.* 36, 279 (1940)
3. KOELMANS, H., and OVERBECK, J. Th. G., *Disc. Faraday Soc.* 18, 52 (1954)
4. OVERBECK, J. Th. G., "Electrokinetic Phenomena," part V of "Colloid Science," edited by Kruyt, H. R., Elsevier, Rotterdam (1952)
5. TROELSTRA, S. A., *Philips Technical Review* 12, 293 (1951)

\*The numerical coefficient 4 in the denominator of Eq. (2) is applicable in the situation of spherical non-conducting particles with quite diffuse ionic atmospheres. For other situations, see reference 4, pages 207-209.

remote point in the medium. Measurements indicate that stable lyophobic suspensions are obtained only if the electrokinetic potential is perhaps 25 millivolts or more. This potential is necessarily related to surface charge density, but the many possible interactions make the relation a complex one. With the aid of simplifying assumptions such as spherical symmetry and uniform dielectric constant, an expression for the electrokinetic potential given by charge  $Q$  on a particle of radius  $r$  can be obtained as

$$\zeta = Q Dr(1 + kr) \quad (3)$$

Here  $k$  is the Debye-Huckel reciprocal length (as in the theory of strong electrolytes), and the term  $(1 + kr)$  may be regarded as a correction to a conventional relation to account for the effects of the electrical double layer. A corresponding equation for electrophoretic velocity in terms of surface charge becomes

$$V = \frac{Q}{4\pi\eta r(1 + kr)} \frac{dV}{dn} \quad (4)$$

Measurements indicate that lengths  $1/k$  for stable lyophobic suspensions in a non-polar medium are ordinarily several times the particle radius; that is, the double layer here is quite diffuse. Because of the assumptions necessary for their development, Eqs. (3) and (4) must be regarded as having a limited reliability.

#### WORKING RELATIONS

The theoretical relations above, whatever their difficulties and limitations, are important and do present the basic principles of electrophoresis. For practical or routine purposes, however, it would be more convenient if, instead, relations which parallel the less elegant ones customarily used in electroplating practice were available. Here the role of the potential gradient would be conceived as one that merely controls the electrode current density. A yield equation would so be written

$$\left( \frac{\text{amount deposited}}{\text{per unit area per unit time}} \right) = \left( \text{Current density} \right) \times \left( \frac{\text{Electrochemical equivalent}}{\text{equivalent}} \right) \times \left( \frac{\text{current efficiency}}{\text{efficiency}} \right) \quad (5)$$

The electrochemical equivalent of equation (5) is the ratio of the mass of a deposited particle to the charge required for its deposition. There is no prior reason, however, for identifying this charge with that represented by  $Q$  in Eqs. (3) or (4). Observed values for the electrochemical equivalent are necessarily based on deposition charge requirement, and depend not only on the initial chemical composition of a suspension, but also on its age and the conditions under which deposition occurs. Experience indicates that the deposition electrochemical equivalent is a reproducible attribute even if its theoretical significance can be questioned. Hence, its use in Eq. (5) can be justified on the practical grounds of convenience.

The current efficiency item of Eq. (5) represents a ratio of charges actually required for deposition to the total discharge at the electrode. The lack of fundamental significance to the electrochemical equivalent for these colloidal situations means that current efficiencies are also arbitrary values. In practice, conditions are selected to minimize side reactions such as gas evolution, and to insure that all particles reaching the electrode are deposited there; conditions which may be said to conform to a 100% current efficiency. But lesser amounts of deposit, even approaching zero, may well be observed. Thus a suspension may simply precipitate out near the electrode, rather than deposit on it, a process known as electrodecantation. Part of the art of electrophoretic coating is to find conditions which minimize such effects.

A quantitative analogy between electrophoresis and electroplating is expressed in Eq. (5). There is also a qualitative similarity in the two processes. Thus in each the adherence, the porosity, and the general appearance of deposits depends to a considerable extent on rather intangible items such as the composition of the medium and the type and amount of additive agents ("brighteners" for electroplating, "activators" for electrophoresis). Differences in the two processes are their voltage requirements, and the fact that electrophoretic deposits even if relatively thick are obtained in quite short times and with very low currents. The electrophoretic deposits are usually of non-conducting materials, mixtures of which may be deposited directly from a suspension without fractionation effects. As a rule the deposits are rather porous, and show densities of only 40%-60% of the theoretical. A treatment such as sintering must be used to convert such deposits to hard coatings.

#### SUSPENSION COMPOSITION

The compositions of many of the electrophoretic suspensions useful in the electron tube industry have been given in various publications and patents. They may contain up to 50% solids in a suspending medium that is usually a mixture of organic liquids such as the lower alcohols, ketones, or esters, although water has sometimes been used as one component. Typical suspensions are described in references 6, 7 and 8. Thus barium-calcium carbonate suspensions in methanol-amy acetate are prepared by ball milling the mixture for several hours. Particle size in these suspensions is somewhat larger than that ordinarily regarded as characteristic of colloids, and ranges from perhaps one to twenty microns. For suspensions of this type to be stable, the particles must be above a certain minimum size<sup>3</sup> which, for suspensions in xylene, for example, is something of the order of one micron. These suspensions are stable<sup>1</sup> in the sense that they do not flocculate and do not settle out as long as stirring is continued.

The charges which give these suspensions stability, and which also cause them to exhibit electrophoresis, accrue on the particles by an absorption of ions or of ionized material. Ions of the type which are combined to form the particles are taken on readily, and these seem actually to fit onto the surface lattice, being adsorbed there in specific locations. But other ions may also be adsorbed, so that the net effect depends on

conditions and may vary not only in amount but also in algebraic sign. Recipes for the preparation of electrophoretic suspensions frequently call for the addition of electrolytes specifically for the purpose of providing charges for the particles. These electrolytes are called "activators"; an example is the chromium and/or nickel ions added to suspensions of oxides of these metals.<sup>9</sup> The amount of such activators to be added may be quite critical, for too little may not suffice, and too much may cause electrolytic flocculation. Small amounts of materials such as polyvinyl acetate or cellulose nitrate are also called for in most recipes. One function of these may be to act as a source of charges, but they also assist in adherence of the deposit and are added to a formulation primarily for this purpose.

The properties of the liquid suspending medium that are important include the dielectric constant and the viscosity, as shown in Eqs. (2) and (3). In general the polar liquids (those with high dielectric constant) provide suspensions with greater electrical conductivity and which, therefore, operate with smaller potential gradients. From a practical standpoint other liquid properties such as volatility and toxicity are also important. Many of the suspending media employed are mixtures of two liquids with differing polarity. The behavior of these is not necessarily a simple composite of that of its components. For example, the electrical conductivity of a suspension in xylene is increased by as much as 10,000 times by the addition of methanol.<sup>3</sup> This may be due to the conductivity of methanol—it is more conductive than pure water. But there is also a marked increase in stability of the suspension as measured by settling times, and a general lessening of the electrokinetic potentials, two possibly conflicting observations. Although evidence is very meager, these effects seem to be characteristic.<sup>3,4,8</sup>

An explanation offered here for the effects observed in suspensions in liquid mixtures is that the ionic surfaces of the suspended particles preferentially select and hold the more polar molecules. Thus a sheath of high dielectric constant material is formed. Circumferential repulsions by like adsorbed ions for each other

while on the surface are thereby reduced by this sheath, but radial effects normal to the surface and response to gross potential gradient are much less modified. The result is an increase in amount of adsorbed charge without an increase in electrokinetic potential as per Eq. (3), and an increase in electrophoretic velocity, as per Eq. (4). That is, it is postulated that around particles suspended in a solution of two liquids of differing polarity there is a high dielectric sheath as well as an ionic atmosphere. It is possible that in some cases a small amount of moisture, perhaps included accidentally, may function as the more polar liquid and provide the high dielectric sheath.

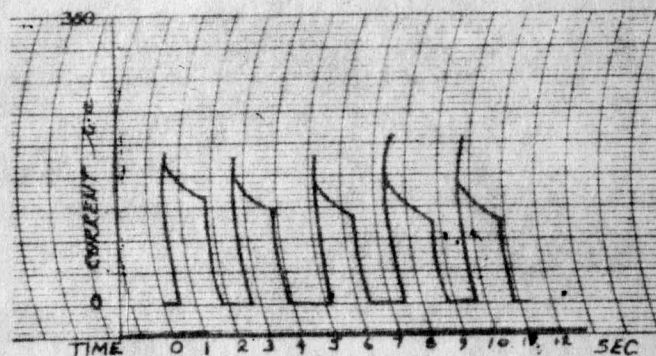


FIG. 2 Current vs. time during deposition with chart speed of one division per second. Area corresponds to  $7.36 \times 10^{-4}$  coulomb and 16.4 mg. at 925 volts.

#### APPARATUS

An electrophoresis apparatus adapted for test runs was constructed of a glass vessel with circular outer electrode 6.25 cm diameter by 2.10 cm high. This was filled with suspension prepared as described above, and mounted beneath an insulating board with small access hole. A central electrode 0.075 cm diameter, with conducting length limited to 1.25 cm, was kept at ground potential and high voltage of required polarity applied to the outer electrode. Direct voltages up to 2000 volts were obtained from the power line with an adjustable autotransformer, half-wave rectifier, and a simple resistance-capacity filter. Provision was made for magnetic stirring, which was turned off during the runs. An automatic timer provided direct current for a predetermined interval, 1.20 seconds, in the experiments described here. Longer times were obtained by a succession of such intervals. The deposit was applied to the central electrode, after which it was dipped into petroleum ether, dried in warm air, and weighed to the nearest tenth milligram on an analytical balance.

The current flow in the external circuit during the process was measured on a recording microammeter. Typical traces as obtained are shown in Figs. 1 and 2. Figure 1, at higher chart speed, shows an initial throw of the pointer associated with inertia and with a dielectric charge throughout the 1.20-second period. Figure 2, at the lower chart speed, shows the trace obtained for total time 6.0 seconds—five 1.2 sec pulses.

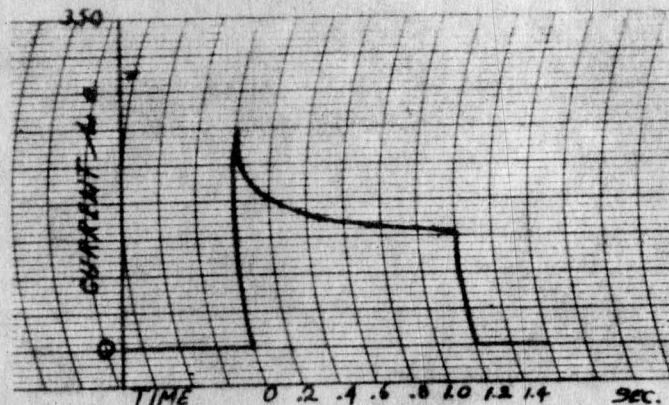


FIG. 1 Current vs. time during deposition with chart speed of five divisions per second. The area under the curve corresponds to  $1.68 \times 10^{-4}$  coulomb and a deposit of 3.7 mg of  $Al_2O_3$  at 925 volts.

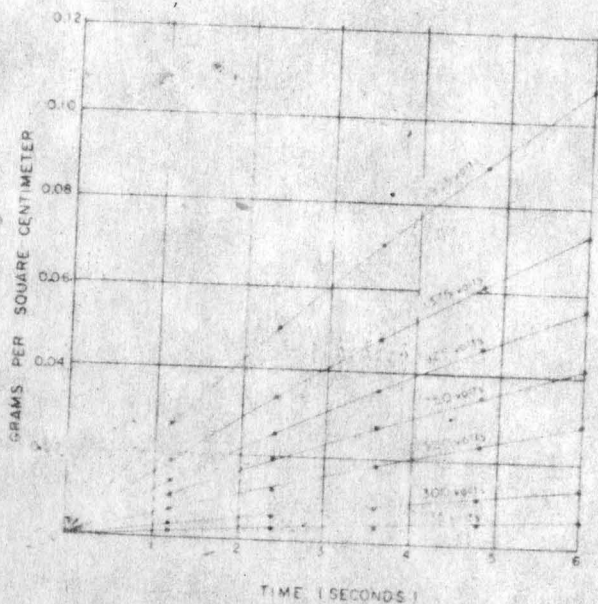


FIG. 3 Amount of  $\text{Al}_2\text{O}_3$  deposited as a function of time and applied voltage.

#### EXPERIMENTAL DEPOSITS

Preliminary runs established that, within experimental error, the amount of deposit was proportional to the number of coulombs (area under the current-time curve) for a given operating voltage, but that the proportionality constant is different for different voltages, an observation also made by other investigators.<sup>2</sup> The results obtained from a 900-mesh aluminum oxide suspension in amyl acetate-methanol with added cellulose nitrate are shown in Fig. 3, where amount of deposit is plotted as a function of time and applied voltage. Figure 4 shows photographs of typical deposits of this type.

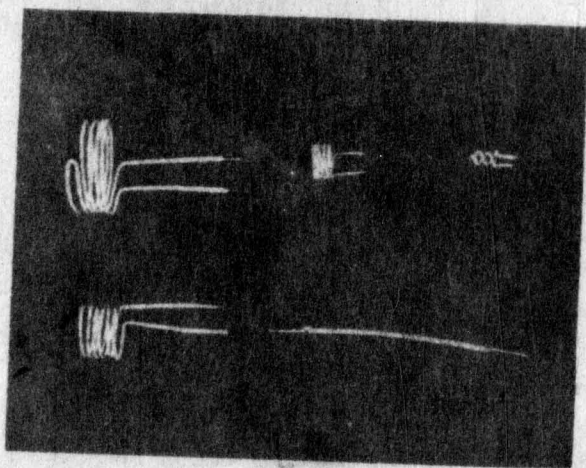


FIG. 4 Typical deposits of  $\text{Al}_2\text{O}_3$  on tungsten heaters.

The results shown in Fig. 3 can be compared with those which might be obtained from an electroplating set-up with electrodes of the same geometry. Thus the current density for the electrophoretic deposits varied from about 70 to about 800 microamperes per square centimeter; these are perhaps only one hundredth those required for electroplating. The potential gradient at the central electrode can be computed to cover the range from about 800 to over 10,000 volts per centimeter; these values are about a thousand times the corresponding ones for electroplating. The specific resistivity of the suspension is given as the quotient of the potential gradient by the current density; this becomes about  $1.2 \times 10^7$  ohm-cm for the aluminum suspensions used for Fig. 3, a value which is many times that of electroplating solutions. The energy requirements for the deposit of a gram of material can be computed as about 70 joules for cataphoresis in this instance, versus perhaps 4000 joules-per gram for a typical copper bath.

#### ELECTROCHEMICAL EQUIVALENT

The deposition electrochemical equivalent for deposits can be computed as the number of grams of deposit obtained per coulomb. Alternatively, it may be computed as the number of grams per Faraday of 96,500 coulombs. This has an advantage in that it gives results on the same basis as the chemical equivalent of 1.008 for hydrogen, or 63.57/2 for cupric ion, etc. On this basis the aluminum deposits described above show values of the equivalent in the order of two or three million, but this varies with the current density. This is shown in Fig. 5, where observed values, in grams per Faraday, are plotted versus (initial) current density at each applied voltage.

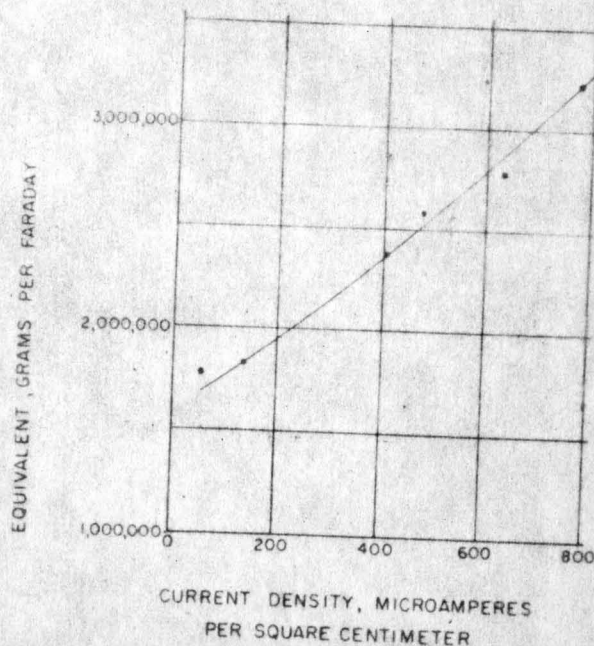


FIG. 5 Indicated deposition electrochemical equivalent for  $\text{Al}_2\text{O}_3$  suspension.

This increase in equivalent with current density is apparently characteristic of this type of suspension, and is in accord with the observations of Hamaker<sup>2</sup>, but who also quotes a reference otherwise. It is apparent that all such variations could also be ascribed to variations in current efficiency, perhaps as related to electro-decantation or to gas evolution. However, the lack of detection of these effects makes it logical to regard Fig. 5 as evidence that the current required for deposition is rather distinct from that associated with the charges carried by the particles.

#### EFFECT OF MOISTURE

The curves of Fig. 3 indicate that the rate of electrophoretic deposition decreases with time. This effect has been attributed to the electrical resistance of the deposit,<sup>9</sup> but this seems inadequate when the porous nature of these deposits is considered. The effect has also been attributed to an electrode polarization,<sup>2</sup> particularly that associated with moisture in the suspension.<sup>6</sup> To test this hypothesis, runs were made on suspensions to which small amounts of water were added. The traces obtained on the recording microammeter remained substantially unchanged, except that at higher water content the average current was somewhat increased. However, the amount deposited decreased, with a resulting decrease in yield per coulomb. The results are summarized in Table I. These indicate that the presence of moisture is not the determining factor in the polarization effects, at least for these suspensions, but that the deposition is markedly influenced by moisture content. These results also imply that the deposition and the neutralization reactions are not identical.

TABLE I

Added Moisture	Coulombs	Deposit (grams)	Yield (gm./coulomb)	Relative Current Efficiency
% of Total				
None	$7.28 \times 10^4$	.0176	24.2	(100%)
.05%	7.3	.0166	22.8	94%
.15%	7.4	.0144	19.5	81%
.30%	8.7	.0156	17.3	72%
.50%	10.6	.0140	13.2	55%

Voltage—925 volts Time—6 seconds

#### DEPOSITION KINETICS

The observation that deposition charge and adsorbed charge are not necessarily identical implies also that the electrode reaction is not a simple neutralization process. With regard to the electrical effects, it can be shown that the low mobility, and hence low transference num-

ber of the suspended particles, makes their contribution to the electric current quite small. Hence the electrical characteristics of the liquid should be relatively insensitive to the presence of the suspended particles. This was observed, and current-time pulses obtained on the recording microammeter for the supernatant liquid from a settled suspension are substantially identical with those from a stirred suspension, although there is no deposit. Table II indicates some results from experiments on partially-settled suspensions.

TABLE II

Suspension	Resistivity (ohm-cm)	Yield (gm./coulomb)	Indicated Equivalent (gm./Faraday)	Relative Current Efficiency
Stirred	$1.19 \times 10^7$	22.3	2,150,000	(100%)
Settled one hour	$1.07 \times 10^7$	4.8	(467,000)	22%
Settled two hours	$1.10 \times 10^7$	3.1	(300,000)	14%
Settled 24 hours	—	0	(0)	0

Recently it has been suggested<sup>3</sup> that the deposition is actually an electrolytic flocculation caused by ions generated by an electrode reaction. Another, and perhaps competing mechanism whereby deposits might be obtained, follows from the concept of a high-dielectric sheath around each particle. As the potential gradient causes these particles to concentrate they produce a medium richer in the more polar component. On reaching the situation where the effective dielectric constant of this enriched medium is sufficiently high, the suspension flocculates because its electrokinetic potential is reduced, according to Eq. (3), below the minimum value for a stable suspension. Actual neutralization of the adsorbed charge by an electrode reaction is incidental, and may not be necessary, as is the case with deposits formed in a gravitation field.

#### ACKNOWLEDGMENT

The invaluable assistance of Mrs. B. Boggs in performing these experiments is gratefully acknowledged.

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