THE EFFECT OF HYDROPHILIC COLLOIDS ON SIZE AND DISTRIBUTION OF PARTICLES IN ELECTROLYTIC PRECIPITATION. I. GELATIN AND BASIC LEAD CARBONATE

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Considerable work appears in the literature on the effect of addition agents in the electro-deposition of metals.[1]   In most cases the observation is made that the presence of such substances as gelatin and tannin in the electrolyte results in a marked improvement in the character of the deposition.   This improvement consists in making the deposit finer grained and more adherent.

From this, one might reasonably expect the character of precipitates formed either chemically or electrolytically, in the presence of small amounts of these addition agents, to be altered in a similar way.   However, but few such investigations of the effect of addition agents on the size and distribution of particles in electrolytic or chemical precipitation have been made.   Free[2] showed that the particles of lead chromate precipitated in the presence of white glue were much smaller than those obtained in its absence.   It is also quite generally known that when silver chloride is precipitated in the presence of small quantities of gelatin, the particles run through the finest grained filter papers.   Miller[3] prepared cuprous oxide by the electrolysis of a hot sodium chloride solution between copper electrodes.   The presence of 0.1 g. of gelatin in 300 cc. of 10% sodium chloride solution resulted in a marked decrease in the size of the cuprous oxide particles.   In this work, it was stated that the precipitate was in an "amorphous form."

It is apparent that a systematic investigation of the effects of colloidal addition agents on the size and distribution of particles of compounds formed by chemical or electrolytic methods is desirable.   Such an investigation should involve a study of all the factors ordinarily affecting any precipitation, temperature, solubility and concentration of electrolytes, together with varying the concentration of different addition agents.

The present work is an investigation of the influence of various concentrations of gelatin in the electrolyte, on the size and the distribution of particles of basic lead carbonate, electrolytically precipitated at 20°.

[1] Kern, *Trans. Am. Electrochem. Soc.*, **15**, 441 (1909). Wen and Kern, *ibid.*, **20**, 121 (1911). Mathers and Overman, *ibid.*, **21**, 313 (1912). Mathers, *ibid.*, **24**, 315 (1913). Watts and Li, *ibid.*, **25**, 529 (1914). Watts and Shape, *ibid.*, **25**, 291 (1914). Müller and Bahntji, *Z. Elektrochem.*, **12**, 317 (1906). Gillett, *J. Phys. Chem.*, **13**, 332 (1909). Bancroft, *ibid.*, **9**, 287 (1905).

[2] Free, *J. Phys. Chem.*, **13**, 135 (1909).

[3] Miller, *ibid.*, **13**, 260 (1909).

The procedure followed for the preparation of the basic lead carbonate was essentially that described by Hopkins.[4]

A solution which contained 3 g. of sodium carbonate and 12 g. of sodium chlorate dissolved in 800 cc. of water was electrolyzed between lead electrodes, using a current density of 0.5 amp. per sq. dm. During the electrolysis a continuous stream of carbon dioxide was bubbled through the electrolyte, near the anode. Runs were made at $20° \pm 1°$, with and without the presence of gelatin. A good grade of commercial gelatin[5] was used, and introduced by adding a definite volume of gelatin solution of known concentration (50 g. per liter) to the electrolyte. The concentrations were varied between 0% and 1%. After each run was made, a small quantity of the precipitate suspended in the electrolyte was removed from the cell. This was placed on a microscope slide, and covered with a thin cover glass, firmly pressed down so that all the liquid was squeezed out at the sides. The cover glass was then cemented to the slide with damar varnish. The precipitates so mounted were photomicrographed, using a 2mm. oil immersion objective and a No. 4 projection eyepiece. A magnification of 1500 diameters was obtained on the photographic plate. Great care was taken in order to assure uniform magnification in all photomicrographs.

The method of determining the size and distribution of particles was that described by Henry Green.[6] As carried out, this consisted in projecting the negatives of the photomicrographs on a calibrated screen, such that a total magnification of 23,000 diameters was obtained. The size of the particles so projected was directly measured on the screen, tabulated as shown in Table I, and the particles of each size were counted.

TABLE I

RECORD SHEET OF PARTICLE MEASUREMENTS

Basic lead carbonate 20° $\times$ 0.5% gelatin

Mm.	Frequency	$F \times$ Mm.	V	$F \times V^2$
1	0	0	0	0
2	5	10	3.3	54.4
3	10	30	2.3	52.9
4	14	56	1.3	23.7
5	37	185	0.3	3.3
6	25	150	0.7	12.2
7	4	28	1.7	11.5
8	3	24	2.7	21.8
9	3	27	3.7	41.0
10	3	30	4.7	66.3
11	2	22	5.7	64.9
Total	106	562		352.0

[4] Hopkins, "Experimental Electrochemistry," D. Van Nostrand Company, 1905, p. 122.

[5] Analysis of gelatin showed that it contained 2% of ash, and was free from chlorides and sulfates.

[6] Green, J. Franklin Inst., 192, 637 (1921). For a very complete review and critical discussion of methods for determining the size, frequency and distribution of particles see the following: Wightman and Sheppard, J. Phys. Chem., 25, 181, 561 (1921); Wightman, Trivelli and Sheppard, ibid., 27, 1 (1923); Wightman and Sheppard, Brit. J. Phot., 68, 169 (1921).

In Table I the column headed Mm. represents the magnified dimensions in millimeters, shown on the calibrated screen; Col. 2 shows the frequency of particles of a given size; Col. 3 is the product of Cols. 1 and 2; Col. 4 is the variation (in mm.) between the average size and the corresponding particle size, shown in Col. 1; Col. 5 is the product of Col. 2 and the square of Col. 4. The values in Cols. 2, 3 and 5 are totaled as shown.

Following the procedure of Green[6] the method of using these values, in calculating the average size, consists in dividing the sum of Col. 3, by the total number of particles (sum of Col. 2), and multiplying by a conversion factor to reduce millimeters measured on the screen to microns. The average size may be represented by the expression $\dfrac{F \times mm.}{n} \times \dfrac{1}{23}$ or $(562/106) \times (1/23) = 0.23$ microns. The distribution is expressed in terms of the uniformity coefficient.[7] It is to be noted that the closer the particles of a given precipitate approach the average particle size, the larger is the numerical value of the uniformity coefficient.

Table II is a summary of the values obtained with the electrolytically prepared basic lead carbonate; to this table have been added the results obtained with two samples of dry commercial white lead. The solid line curve in Fig. 1 shows graphically the relation between the concentration of gelatin, and the average particle size; the dotted line curve in the same figure shows the relation between the concentration of gelatin and the uniformity coefficient. The broken lines A........A on these curves indicate the relative positions of the average particle size and the uniformity coefficient of commercial dry white lead. From Fig. 1 it is seen that the presence of a small quantity of gelatin in the electrolyte exerts a large effect upon the average particle size. As little as 0.013% of gelatin reduces the average size of the particles to approximately one-third that obtained when no gelatin is present. The relative effects of further additions of

TABLE II

SUMMARY OF PARTICLE SIZE AND UNIFORMITY COEFFICIENTS

Source of material	Gelatin %	Average size in microns	Uniformity coefficient
Electrolytic[a]	0.000	1.22	0.052
Electrolytic[a]	.013	0.53	.180
Electrolytic[a]	.070	.36	.230
Electrolytic[a]	.500	.23	.388
Electrolytic[a]	1.000	.16	.710
Commercial White Lead No. 1	0.000	.48	.117
Commercial White Lead No. 2	.000	.48	.134

[a] Temperature $20° \pm 1°$. $CD = 0.5$ amp. per sq. dm.

[7] The uniformity coefficient (U) may be represented by the expression, $U = \sqrt{\dfrac{n}{2FV^2}}$, where n is the total number of particles (sum of Col. 2), and FV^2 is the sum of Col. 5. Calculation: $U = \sqrt{\dfrac{106}{2(352)}} = 0.388$.

gelatin are not so great; however, in all cases the average size continues to be decreased. This decrease, after the first addition is, approximately directly proportional to the concentration of gelatin added. The results expressed in Fig. 1 also show that the presence of small quantities of gelatin in the electrolyte results in a marked increase in the uniformity coefficient.

At present no explanation of the effects of gelatin on the size and distribution of particles has been made; it is hoped that a satisfactory explanation will be offered when the work in progress on the effect of other colloid substances, at various temperatures and concentrations, in electrolytic and chemical precipitation, is completed.
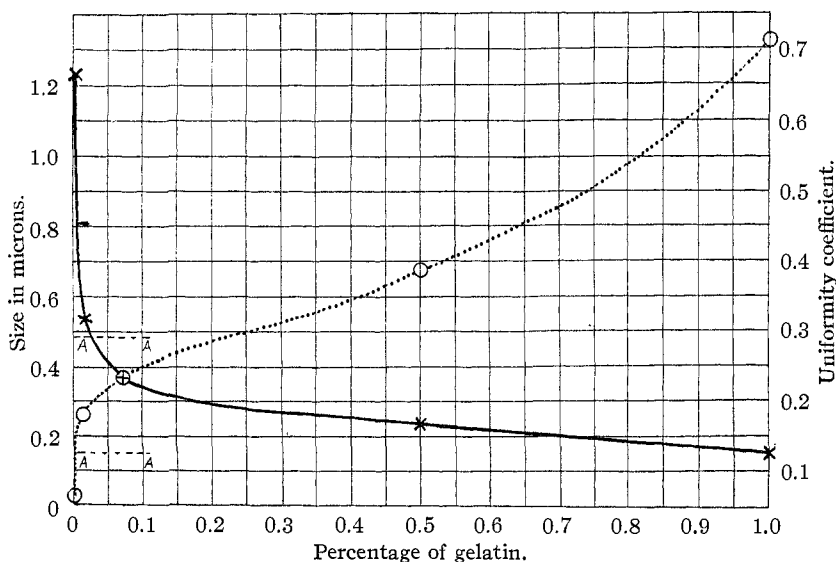

Fig. 1.—Basic lead carbonate —20°. Curve for percentage of gelatin—average particle size x———x. Curve for percentage of gelatin—uniformity ◯••••••◯.

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Summary

1. The possible similarity between the effects of addition agents on electro-deposition of metals, and the electro-precipitation of compounds, has been suggested.

2. The presence of gelatin in the electrolyte used in the electrochemical precipitation of basic lead carbonate has been shown to result in a marked decrease in the average size of particles obtained.

3. It has also been shown that the presence of small quantities of gelatin during the electrolytic precipitation of basic lead carbonate results in a marked increase in the uniformity of the size of particles obtained.

4. A comparison of basic lead carbonate obtained electrolytically, with two samples of dry commercial white lead, indicates that it is possible by the addition of small quantities of gelatin, to obtain a product having particles smaller in average size, and of more uniform distribution, than those of the commercial dry white lead examined.

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HEAT OF VAPORIZATION, A FUNCTION OF THE TEMPERATURE

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The similarity in appearance (but difference in position) of the vapor pressure-temperature curves of quite unrelated substances suggests that in view of the Clapeyron equation the heat of vaporization might be the same function for all substances, differing only in the constants involved. Within recent years, several equations of more or less complexity have been suggested[1] in which the heat of vaporization has been expressed as a function of the temperature, volume, pressure, density, etc., but none of these has been generally accepted. The simplest possible expression is of course desirable, and the calculation presented in this paper has been devised to show that if the heat of vaporization (ΔH) is assumed to be a function of the temperature (T) alone, the same function for all substances but differing in the constants involved (such as in the Kirchhoff-Hertz or Nernst equations), a conclusion is arrived at which indicates the approximate limits of accuracy of such a relation [that is, $\Delta H = F(T)$].

Derivation

Let us take two entirely unrelated, non-associated liquids A and B, with boiling points T_{B_1} and T_{B_2}, and critical temperatures T_{C_1} and T_{C_2}. For these substances, $\Delta H = F(T)$, which can also be written $\Delta H = T f(aT)$, where a is a constant. That is, $\Delta H_1 = T f(kT)$; and $\Delta H_2 = T f(KkT)$, where k and K are constants, and the functions are the same in both cases.

At the critical temperature, Mathias[2] has shown that the heat of vaporization is zero, that is, $\Delta H_1 = T_{C_1} f(kT_{C_1}) = \Delta H_2 = T_{C_2} f(KkT_{C_2}) = 0$, or $f(kT_{C_1}) = 0; f(KkT) = 0_{C_2}$, and since the function is the same in both cases, differing only in the constants, $kT_{C_1} = KkT_{C_2}; K = T_{C_1}/T_{C_2}$.

At the boiling points, $\Delta H_1 = T_{B_1} f(kT_{B_1})$; $\Delta H_2 = T_{B_2} f(KkT_{B_2})$, from which $\dfrac{\Delta H_1}{T_{B_1}} = f(kT_{B_1})$; $\dfrac{\Delta H_2}{T_{B_2}} = f(KkT_{B_2})$, and since for non-associated

[1] See THIS JOURNAL, **36**, 1620 (1914) for a review.

[2] Mathias, *Ann. chim. phys.*, [6] **21**, 69 (1890).