The Current Distribution in an Electrolytic Cell

- Application of the Elliptic Integral to the Chemical Engineering -

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Synopsis

The state of the electrical field in an electrolytic cell cannot be explained completely by the electrostatic or electromagnetic theory, because in this field the chemical polarization always appears near the electrode surface. But we will neglect the effects of this polarization, and present the two-dimensional discussions on the forms of the electrolytic cell or field. The effects of the polarization can be introduced very easily by our previous research, so the following discussions will be directly useful from the point of view of the chemical or electrochemical engineering.

In this paper,

a) A Krebs Amalgam Type Chlorine Cell,

- b) The Graphite Anode with Many Grooves of a Horizontal Amalgam Type Chlorine Cell, and
- c) A Rectangular Electrolytic Cell are included.

(I) Introduction

When the electrochemical reaction takes place, the chemical polarization always appears. There are different kinds of chemical polarization, and they produce very difficult problems in electrochemistry. Therefore, many people have studied on the subject. But their researches have been conducted on one-dimensional problems.

According to our previous works¹), the chemical polarizations—the activated overpotential and the concentration polarization—near the perfect conductive electrode surface are constant or uniform, or in other words, independent of the coordinate of the point on the electrode surface under consideration, at constant external applied voltage. So, the ohmic voltage drop, V_0^* , which is represented as

Okada, Yoshizawa and Hine: "On the Distributions of the Electrolytic Potential in Solution.", J. Electrochem. Soc., Japan, 18-, (1950-).

$$V_0^* = V_0 + \pi_i$$
, $(\pi_i < 0)$

where V_0 and π_i are the terminol voltage and the polarization factor, respectively, becomes constant, when the electrodes are the perfect conductive metals. Therefore, this field can be analyzed by the conformal mapping method as the electrostatic field.

The electric field in the electrochemical process is only in the cell, so when Schwarz-Christoffels' transformation is done, there are to be taken into account some square root factors, which are corresponding to the apexes of the right angle at the z-plane, in this relative equation. Therefore, that equation must be calculated by the elliptic integral. Several examples of this problem are shown in the following pages.

(II) A Krebs Amalgam Type Chlorine Cell.

The development of the artificial fibre and plastic industries in these days requires the best quality and a great quantity of caustic soda and chlorine gas. For this reason, the amalgam process in the caustic soda industry has become very important, and the electrical current of each cell has been increased. Therefore, the various problems must be reconsidered. The potential distribution is one of these problems. Moreover, the form of the graphite anode has to be discussed. The grooves on the surface of the graphite anode, which will be explained in the next section, are one of the examples.

The details of the mathematical treatment of the potential distribution of a Krebs amalgam type chlorine cell will be explained at the first meeting of the National Union of Theoretical and Applied Mechanics in Japan, dated November, 3rd, 1951. So in this paper, we will explain very simply.

The widths of the cell and of the graphite anode are much larger than the thickness of the anode, the distances between the electrodes, between the graphite anode and the free surface of brine, and the gap between the anode and the insulating wall of this cell. Therefore, for convenience's sake, we assume that the cell

and the graphite anode are semi-infinite, and moreover we take the symmetrical porfile. The profile of this cell is shown in Fig. 1. And parameter plane ζ and potential plane w are represented in Figs. 2 and 3, respectively. And the ζ -plane is transformed again as follows:

$$\zeta = snu, \qquad (1)$$

and the other parameter, or Jacobi's elliptic function, is shown in Fig. 4.



Fig. 1

The Current Distribution in an Electrolytic Cell



In the ζ -plane, the coordinate of point A must be noticed, i.e., constant b must take a complex number such as

$$b = c + iK'$$

where c represents an arbitrary real number, and by Jacobi's transformation, we obtain

 $1/k \cdot snb = snc < 1$.

The relations of the above-shown variables are as follows:

$$z - (u + j\beta)\frac{u}{K} = \frac{\delta}{\pi} \log \frac{\Theta(u-a)}{\Theta(u+a)} - \frac{\beta}{\pi} \log \frac{\Theta(u-b)}{\Theta(u+b)}$$
(2)

and

$$W = -\frac{V_0^*}{\pi} \log \frac{\sin(\varphi - \theta)}{\sin(\varphi + \theta)} + jV_0^*$$
(3.)

where $a, \beta, \gamma, \delta, a$ and b are the constants, and

$$\varphi = \cos^{-1}\left(\frac{sna}{snb}\right)$$
, $\theta = \cos^{-1}(ksna \cdot snu)$.

At present, the scales of each part of the cell are being taken as follows:

$$\beta = 0.5 \text{ Cm.},$$

$$\gamma = 4.0 \text{ Cm.},$$

$$\delta = 2.0 \text{ Cm.}$$

And we take two cases for a:

- i) when $\alpha = 1.0$ Cm., and
- ii) when $\alpha = 0.2$ Cm.

Also, the length of the graphite anode is about 40 Cm. Hence, the percentage of the current along each surface of the anode, AB, BC and CD in Fig. 1, is shown as

Case i) AB 96.88% BC 2.63% CD 0.487% Case ii) AB 97.78% BC 2.19% CD 0.033%

From these results, we can neglect the currents along the side surface and the upper surface of the graphite anode.

(III) The Graphite Anode with Many Grooves of a Horizontal Amalgam Type Chlorine Cell.

Recently, the graphite anode with many grooves came to be used in caustic soda industry. As a result, we must consider or discuss the following two problems :

- i) The sectional area of the graphite anode is increased, so that the total current will be increased.
- ii) The relaxation time of the generated chlorine gas under the anode is decreased, and so electric resistance by the gas film will decay.

The second problem may be all right, but the first problem must be closely examined, the problem of the amount of the total electrical current being not so simple. We will consider this subject as this field is

the electostatic field.

The distance between the graphite anode and the mercury cathode is much smaller than the distance between the two neighbouring grooves, so that we can assume that the potential distribution near one groove is not effected by the other. The profile of this field, the z-plane,

and parameter plane ζ are shown in Fig. 5 and Fig. 6, respectively. And the upper half of the ζ -plane is mapped into the z-plane by Schwarz-Christoffels' transformation :



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$$\varepsilon = A' \int \frac{\sqrt{\zeta^2 - \frac{1}{k^2}}}{\sqrt{\zeta^2 - 1} \left(\zeta^2 - \frac{1}{k^2 s n^2 c}\right)} d\zeta . \qquad (4)$$

By substituting the relation

 $\zeta = snu$

in Eq. (4), we obtain

$$z = A \int \frac{1 - k^2 s n^2 u}{1 - k^2 s n^2 c s n^2 u} du$$
 (5)

where

$$A = -A' \cdot ksn^2c . \tag{6}$$

Eq. (5) is integrated:

$$z = A \left[u - \frac{cnc}{snc \cdot dnc} \cdot \Pi(u, c) \right].$$
(7)

Here the integral constant is zero, because the origin of the z-plane is transformed into the origin of the ζ -plane.

Next, we must define constant A. Let us take a very small circular arc at point C in the ζ -plane. When its radius tends to zero, we obtain

$$\int_{j\beta}^{j(\beta+\gamma)} dz = -\lim_{\rho \to 0} A' \int_0^{\pi} \frac{\sqrt{\left(\frac{1}{ksnc} + \rho e^{j\theta}\right)^2 - \frac{1}{k^2}}}{\sqrt{\left(\frac{1}{ksnc} + \rho e^{j\theta}\right)^2 - 1}} \cdot \frac{j\rho e^{j\theta}}{\left(\frac{1}{ksnc} + \rho e^{j\theta}\right)^2 - \frac{1}{k^2sn^2c}} d\theta$$

$$\therefore \quad A = \frac{2}{\pi} \gamma \frac{snc \cdot dnc}{cnc} .$$

By substituting this in Eq. (7),

$$z = \frac{2}{\pi} \gamma \left[\frac{snc \cdot dnc}{cnc} \cdot u - II(u, c) \right].$$
(8)

Moreover, by considering the correspondence of the coordinate at point A, we obtain

$$a = \frac{2}{\pi} \gamma K \left[\frac{\operatorname{snc} \cdot \operatorname{dnc}}{\operatorname{cnc}} - Z(c) \right],$$

so

$$\frac{\operatorname{snc} \cdot \operatorname{dnc}}{\operatorname{cnc}} = \frac{\pi}{2K} \cdot \frac{\alpha}{\gamma} + Z(c) . \qquad (9)$$

By substituting Eq. (9) in Eq. (8),

$$\mathbf{z} = \frac{u}{K}u + \frac{2}{\pi}\gamma \Big[uZ(c) - \Pi(u,c) \Big] \,.$$

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But we have a well-known relation

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$$II(u,c)-uZ(c) = \frac{1}{2}\log\frac{\Theta(u-c)}{\Theta(u+c)}$$

And so by substituting this in the above equation, we obtain

$$z = \frac{\alpha}{K}u - \frac{\gamma}{\pi}\log\frac{\Theta(u-c)}{\Theta(u+c)}.$$
 (10)

Further, if we take the correspondence at point B, then from Eq. (10),

$$a+j\beta=a+j\frac{1}{K}(aK'-\gamma c) \ .$$

Here, a well-known relation

$$\Pi(K+jK',c) = K \cdot Z(c) + j \left\{ K' \cdot Z(c) + \frac{c\pi}{2K} \right\}$$

is used, and from the imaginary part of this equation we obtain

$$\beta K = a K' - \gamma c . \tag{11}$$

Constants k and c are known from Eqs. (9) and (11).

Next, we consider the potential plane. The relation between the ζ -plane and the *w*-plane, both of which are shown in Fig. 7, is obtained by Schwarz-Christoffels' transformation as follows:





$$dw = A \frac{d\zeta}{\zeta^2 - \frac{1}{k^2 s n^2 c}}$$

or this integral is

$$w = \frac{A}{2}k \cdot snc \cdot \log \frac{\zeta - \frac{1}{ksnc}}{\zeta + \frac{1}{ksnc}} + B$$

When a circular arc is considered at point C in the ζ -plane, the relation

$$\frac{A}{2}k \cdot snc = \frac{V_0^*}{\pi}$$

is introduced; hence, by substituting this in the above equation we have

$$w = \frac{V_0^*}{\pi} \log \frac{\zeta - \frac{1}{k \cdot snc}}{\zeta + \frac{1}{k \cdot snc}} + B$$

But at point 0

$$jV_0^* = rac{V_0^*}{\pi} \log{(-1)} + B$$

is obtained, and then we obtain B=0; therefore,

$$w = \frac{V_0^*}{\pi} \log \frac{k snc \cdot snu - 1}{k snc \cdot snu + 1}$$
(12)

is obtained. The w-plane and the the u-plane are shown in Fig. 7.

For example, the size of each part of the field is given as follows:

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Case i)
$$\alpha = 0.25$$
 Cm., $\beta = 2.5$ Cm., $\gamma = 0.5$ Cm.
Case ii) $\alpha = 0.5$ Cm., $\beta = 2.5$ Cm., $\gamma = 0.5$ Cm.

In the first place, the constants are defined as follows:

Case i)
$$k = 3.79 \times 10^{-7}$$
, $K = 1.5707963$, $K' = 16.1719637$,
 $c = 0.4640007$,
Case ii) $k = 7.019232 \times 10^{-4}$, $K = 3.1415927$, $K' = 5.5054761$,
 $c = 0.794000$.

We will calculate the rate of the current at each part of the graphite anode. For this purpose, we must find the corresponding point on the ζ -plane which is defined by the length of the lower surface of the graphite anode. To expedite this calculation, Eq. (10) is transformed, i.e., the term of Θ -function is

$$\log \frac{\Theta(u'-c+jK')}{\Theta(u'+c+jK')}.$$

But we have a well-known equation

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$$\Theta(a+jK') = \vartheta_4\left(\frac{a}{2K}+j\frac{K'}{2K}\right) = jq^{-\frac{1}{4}}e^{-j\frac{\pi x}{2K}}\vartheta_1\left(\frac{a}{2K}\right),$$

so we obtain

$$\log \frac{e^{-j\frac{\pi(u'-c)}{2K}}\vartheta_1\left(\frac{u'-c}{2K}\right)}{e^{-j\frac{\pi(u'+c)}{2K}}\vartheta_1\left(\frac{u'+c}{2K}\right)} = j\frac{\pi c}{K} + \log \frac{\vartheta_1\left(\frac{u'-c}{2K}\right)}{\vartheta_1\left(\frac{u'+c}{2K}\right)}$$

By substituting this in Eq. (10), the real part of this equation is obtained as follows:

$$x = \frac{u}{K}u' - \frac{\gamma}{\pi} \log \frac{\vartheta_1\left(\frac{u'-c}{2K}\right)}{\vartheta_1\left(\frac{u'+c}{2K}\right)} .$$
(13)

But q is much smaller than the others, and therefore, we obtain

$$\vartheta_1(a) = 2q^{\frac{1}{4}}(\sin \pi a - q^{\frac{1}{2}}\sin 3\pi a + \cdots) \doteq 2q^{\frac{1}{4}}\sin \pi a \; .$$

By substituting this equation in Eq. (13),

$$x = \frac{\alpha}{K}u' - \frac{\gamma}{\pi} \log \frac{\sin \frac{u' - c}{2K}}{\sin \frac{u' + c}{2K}}$$

is obtained.

Now, when the length of the lower surface of the graphite anode is given as 3 Cm., the corresponding coordinate value of each case is as follows:

Case i)	$u' = c + 2.439 \times 10^{-5}$,
Case ii)	$u' = c + 5.64648 \times 10^{-5}$

And the rate of the anode is calculated and the results follow:

Case i)	On the lower surface	98.50%
	On the side surface	1.495%
Case ii)	On the lower surface	93.95 <i>%</i>
	On the side surface	6.053%.

Further, the rate of the total current of these cases to the case of the anode without grooves is as follows:

Case i) 87.80% Case ii) 71.04%.

Hence, from the point of electrical power it is not strongly recommended that the anode with many grooves be used, but since the loss of the anode is very uniform, from such a point of view this anode will be better than the other.

(IV) A Rectangular Electrolytic Cell.

In experiments of electrochemistry, a cell which is formed as the z-plane in Fig. 8 is frequently used. In such cases, the potential and the current distribution do not agree with these in the case of the field which is shown in Fig. 9, with the exception of the neighbourhood of the electrode. In other words, the effect of the insulating wall must be examined. We will consider this problem. The upper half of the ζ -plane can be transformed into the z-plane by Schwarz-Christoffels' transformation as follows:



$$\frac{dz}{d\zeta} = c \frac{\zeta - \frac{1}{k^2 s n^2 b}}{\zeta \sqrt{\zeta - 1} \sqrt{\zeta - \frac{1}{k^2}}}$$
(14)

Let us take

$$\zeta = sn^2 u , \qquad (15)$$

and by substituting this relation in Eq. (14), we obtain

$$dz = \frac{2C}{ksn^2b} \cdot \frac{1 - k^2 \cdot sn^2b \cdot sn^2u}{snu} du , \qquad (16)$$

or this integral is

$$z = \frac{2C}{k s n^2 b} \log \left[\frac{s n u}{c n u + d n u} \right] - 2C \cosh^{-1} \left(\frac{d n u}{k'} \right) + B ,$$

where B is the integral constant. Now, we consider the correspondence of point in the z- and u-planes; then

$$0 = 2C\left\{\frac{1}{k \cdot sn^2b}\log\frac{j}{k'} - \cosh^{-1}(0)\right\} + B$$

is obtained, but

$$\log \frac{j}{k'} = \frac{1}{2} \log (-1) - \log k' = \frac{1}{2} j\pi - \log k' ,$$

and $\cosh^{-1}(0)$ is not recognized as existing in the real domain, and we must remark that

$$\cosh j\omega = \cos \omega = 0$$
,

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$$\cosh^{-1}(0) = j\pi/2$$
.

Therefore, we obtain

$$B = -2C\left\{j\frac{\pi}{2}\left(\frac{1}{k \cdot sn^2b} - 1\right) - \frac{1}{k \cdot sn^2b} \cdot \log k'\right\} .$$

Next, a small circular arc at point C on the ζ -plane is considered, and from Eq. (14)

$$C = -\frac{\gamma k' s n^2 b}{\pi}$$

$$\therefore \quad B = -\frac{2\gamma}{\pi} \log k' + j\gamma (k s n^2 b - 1)$$

is introduced. And by substituting this relation in z, we obtain

$$z = \frac{2\gamma}{\pi} \left\{ \log \frac{cnu + dnu}{k' \cdot snu} + k \cdot sn^2 b \cdot \cosh^{-1}\left(\frac{dnu}{k'}\right) \right\} + j\gamma(k \cdot sn^2 b - 1) .$$

Moreover, the correspondence at point D is considered as

$$j(\beta+\gamma) = \frac{2\gamma}{\pi} \left\{ \log 1 + k \cdot sn^2 b \cdot \cosh^{-1}(1) \right\} + j\gamma(k \cdot sn^2 b - 1) ,$$

and from the imaginary part of this equation,

$$sn^2b = \frac{1}{k\gamma}(\beta + 2\gamma) \tag{17}$$

is obtained.

By substituting Eq. (17) in z, we obtain

$$z = \frac{2\gamma}{\pi} \log \frac{cnu + dnu}{k' \cdot snu} + \frac{2}{\pi} (\beta + 2\gamma) \cdot \cosh^{-1} \left(\frac{dnu}{k'} \right) + j(\beta + \gamma) .$$
(18)

Next, when we consider the correspondence at point B,

$$z = a + j\beta$$
, $\zeta = 1/k^2 \cdot sn^2 b$ at point B.

So,

$$u = b + iK'$$

is reduced, but clearly we know

 $1/k^2 \cdot sn^2b > 0$;

hence, if we take

$$b = jc$$
,

by Jacobi's transformation, we obtain the following relations:

Firstly, by substituting jc in Eq. (18) the first term is shown as

$$\log\left\{\frac{-\frac{dnc}{k \cdot snc} - \frac{1}{snc}}{-jk'\frac{cnc}{k \cdot snc}}\right\} = \log\left(\frac{\overline{dnc} + k}{jk' \cdot cnc}\right) = \log\left(\frac{\overline{dnc} + k}{k' \cdot cnc}\right) - j\frac{\pi}{2} ,$$

and the second term is represented as

$$\cosh^{-1}(-1/k' \cdot snc)$$
.

But as the hyperbolic sine cannot take the negative value in the real domain, let us take

 $\cosh^{-1}(-x) = p + jq$ (x is a real and positive number),

and again we take the inverse function as

$$\cosh(p+jq) = -x$$

$$\therefore \quad \cosh p \cdot \cos q + j \cdot \sinh p \cdot \sin q = -x ;$$

hence,

$$\cosh p \cdot \cos q = -x , \qquad (19a)$$

$$\sinh p \cdot \sin q = 0 . \qquad (19b)$$

From Eq. (19a), we obtain

 $\sinh p = 0$ or $\sin q = 0$.

First, we consider the case of sinh p=0. From Eq. (19b)

$$\cos q = -x$$

$$\therefore q = \pi + \cos^{-1}x;$$

hence,

$$\cosh^{-1}(-x) = j(\pi + \cos^{-1}x)$$
 (20a)

is introduced.

Next, from $\sin q = 0$,

$$\cosh p = x$$
, $q = \pi$,

because we have the relation

$$\cosh p \cdot \cos q = -x$$
.

Hence,

$$\cosh^{-1}(-x) = \cosh^{-1}x + j\pi \tag{20b}$$

is reduced. Eqs. (20a) and (20b) are the same, essentially. Because if we take that

$$j \cdot \cos^{-1} x = \eta ,$$

the relation:

$$\cos\left(-\cos^{-1}x\right) = \cos\left(j\eta\right)$$

is introduced. But the cosine is a even function, so we have

$$x = \cos(j\eta) = \cosh \eta$$
 or $\eta = \cosh^{-1}x$.

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Thus we have proved that Eqs. (20a) and (20b) are the same essentially. Now, if we use Eq. (20a), we obtain

 $\cosh^{-1}(dnu/k') = j\left\{\pi + \cos^{-1}(1/k' \cdot \overline{snc})\right\}$, at B

and by substituting this in Eq. (18),

$$a+j\beta = \frac{2\gamma}{\pi} \log\left(\frac{\overline{dnc}+k}{k'\cdot \overline{cnc}}\right) - j\gamma + j\frac{2}{\pi}(\beta+2\gamma) \left\{\pi + \cos^{-1}\left(\frac{1}{k'\cdot \overline{snc}}\right)\right\} + j(\beta+\gamma) ,$$

so we obtain

$$a = \frac{2\gamma}{\pi} \log\left(\frac{\overline{dnc} + k'}{k' \cdot \overline{cnc}}\right)$$
(21a)

and

$$\pi + \cos^{-1}\left(\frac{1}{k' \cdot \overline{snc}}\right) = 0 \quad . \tag{21b}$$

And from Eq. (21b),

$$k' \cdot \overline{snc} = -1 \tag{21c}$$

is reduced.

Next, on the potential plane, we obtain

$$dw = A \frac{1}{\sqrt{\zeta \left(\zeta - \frac{1}{k^2}\right)}} \tag{22}$$

by Schwarz-Christoffels' transformation. Now, if we take $\theta = \zeta - \frac{1}{2k^2}$,

$$w = A \log \left\{ \theta + \sqrt{\theta^2 - \left(\frac{1}{2k^2}\right)^2} \right\} + B$$

is introduced.

From the correspondence at point 0 and C

$$A = \frac{V_0^*}{\pi}$$
, and $B = -\frac{V_0^*}{\pi} \log\left(\frac{1}{2k^2}\right)$

are obtained, so

$$w = \frac{V_0^*}{\pi} \log \left(\frac{\theta + \sqrt{\theta^2 - \left(\frac{1}{2k^2}\right)^2}}{\frac{1}{2k^2}} \right) = \frac{V_0^*}{\pi} \cosh^{-1}(2k^2\theta) .$$

By substituting ζ in this equation, we obtain

$$w = \frac{V_0^*}{\pi} \cosh^{-1}(2k^2\zeta - 1) .$$
 (23)

The above-shown analysis is very difficult. If we have the symmetrical profile, we can analyze more easily. Of this problem, we will explain simply as follows:

The profile of this field, the z-plane, parameter plane ζ and potential plane w are shown in Fig. 10. And the potential of electrode A'B'C' is equal to that of



Fig. 10

electrode ABC. So that the relation between the parameter plane is essentially simillar to the above-shown case of a Krebs amalgam type chlorine cell. So we do not explain the relation. The relation between the z-plane and the ζ -plane is shown as follows by Schwarz-Christoffels' transformation:

$$\frac{dz}{d\zeta} = A \frac{\zeta^2 - b^2}{(\zeta^2 - a^2)(\zeta^2 - c^2)} .$$
(24)

And the integral of this equation is

$$z = \frac{A}{a^2 - c^2} \left[2\zeta - \frac{a^2 - b^2}{2a} \log \frac{\zeta - a}{\zeta + a} + \frac{b^2 - c^2}{2c} \log \frac{\zeta - c}{\zeta + c} \right] + B$$

From the correspondences at points A and C, we obtain

$$A = -\frac{2\beta}{\pi} \cdot \frac{a(a^2 - c^2)}{a^2 - b^2}$$
(25a)

and

$$A = -\frac{2\gamma}{\pi} \cdot \frac{c(a^2 - c^2)}{b^2 - c^2} , \qquad (25b)$$

respectively. Further, if we consider the correspondence at the origin,

$$B=-j\frac{\pi}{2}A$$

is obtained, so

$$z = \frac{\beta}{\pi} \log \frac{\zeta + a}{\zeta - a} + \frac{\gamma}{\pi} \log \frac{\zeta + c}{\zeta - c} + \frac{4}{\pi} \frac{a\beta}{b^2 - a^2} \zeta + ja\beta \frac{c^2 - a^2}{b^2 - a^2} .$$
(26)

From Eqs. (25a) and (25b),

$$\frac{a\beta}{a^2 - b^2} = \frac{c\gamma}{b^2 - c^2} \tag{27}$$

is reduced, and from Eq. (27), we can define the constant. Fig. 11 represents the state of this field.





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