

METHOD OF ELECTROLYZING DILUTE CAUSTIC
ALKALI AQUEOUS SOLUTION AND APPARATUS THEREFOR

This invention relates to a method of electrolyzing a dilute caustic alkali aqueous solution and an apparatus therefor.

5 Solutions containing caustic alkali are discharged from various industrial production and treatment processes. Examples of such solutions include reaction waste solutions from various chemical reaction processes, waste solutions from treating metals with alkali, waste
10 solutions from regenerating ion exchange resins, alkali-treatment waste solutions from petroleum refining processes and alkali-treatment waste solutions from nuclear energy facilities. It is industrially important to recover caustic alkali from these waste solutions in
15 view of both the economics of the processes and the need to prevent pollution.

For these reasons, various methods for recovering or detoxicating caustic alkali by treating these waste solutions have hitherto been tried. Most of these
20 alkali-containing waste solutions are aqueous solutions of a relatively low concentration and contain many other co-existing inorganic or organic substances. Therefore, the solutions are often discharged after detoxication by, e.g. neutralization and without a recovery treatment,
25 for technical or economic reasons.

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Electrolytic methods using a cation exchange membrane are known as representative methods for effectively recovering caustic alkali from these waste solutions. For example, a method of treating an alkaline waste water which comprises separating and recovering an alkali from the alkaline waste water by electrodialysis using a cation exchange membrane and discharging the waste water as neutralized water is described in Published Unexamined Japanese Patent Application 16859/1977.

10 However, such electrolytic methods are disadvantageous since material which is highly durable in an oxygen generating reaction is required as an electrode, particularly as an anode, and expensive noble metal or easily exhausted graphite, which has various disadvantages in production and operation, must be used.

Accordingly, it is desirable to develop an economic and industrially-operable electrolytic technology.

Iron, nickel and their base alloys such as stainless steel are inexpensive and easy to process, and have thus been used as electrodes for electrolysis of a caustic alkali aqueous solution in, e.g., water electrolysis. However, these materials can only be used in an aqueous solution having a high caustic alkali concentration and at a relatively high temperature. They cannot be used for electrodes when electrolyzing a low concentration caustic alkali aqueous solution because deactivation

occurs by formation of an oxide on the surface of the electrode due to considerable oxidation of the anode by elevation of the electrolytic voltage, or because, at a low caustic alkali concentration of about 10 wt% or less, particularly 5 wt% or less, dissolution of the surface of the anode occurs.

Furthermore, in the case of electrolysis of a waste solution containing various organic substances and heavy metals, these impurities attach to, and precipitate onto, the ion exchange membrane, electrode or pipework, and make electrolysis difficult.

Accordingly, an object of the present invention is to overcome the above-described problems and to provide a novel electrolysis method which can recover caustic alkali effectively by electrolyzing a dilute caustic alkali aqueous solution in a stable manner for a long period of time using inexpensive electrode materials.

The electrolysis method according to one aspect of this invention comprises supplying a dilute caustic alkali aqueous solution to one electrode compartment of an electrolytic cell partitioned by a cation exchange membrane, electrolyzing said solution therein and recovering concentrated caustic alkali aqueous solution from the other electrode compartment, wherein iron, nickel or a base alloy thereof is used as an electrode-

forming material and electrolysis is conducted with reversals of the polarity of the electrodes such that an electric current is passed periodically therebetween in a direction opposite to the electrolysis direction.

5 In a preferred embodiment, the directions of supplying and discharging the electrolyte are periodically reversed thus permitting concomitant alternations in the direction in which electrolysing current is passed through the cell.

10 The electrolysis apparatus according to this invention comprises an electrolytic cell partitioned by a cation exchange membrane into at least two compartments each containing an electrode formed of iron, nickel or a base alloy thereof, electrolyte supply and discharge
15 means which are symmetrical about a plane defined by the cation exchange membrane or in the case of a bipolar electrode type cell, a central membrane or electrode, means for reversing the polarity of the electrodes, and means for reversing the direction in which electro-
20 lyte is supplied to and discharged from the cell.

 This invention gives excellent results and makes it possible to conduct electrolysis of a dilute caustic alkali aqueous solution in a stable manner for a long period using an inexpensive electrode such as
25 iron or nickel.

 The electrolytic apparatus according to this

invention comprises an electrolytic cell partitioned by a cation exchange membrane and will now be described, together with various methods of operating such cells, with reference to the accompanying drawings in which

5 Figure 1 shows one example of an electrolytic apparatus according to this invention;

 Figure 2 shows another example of an electrolytic apparatus according to this invention;

 Figure 3 is a block diagram showing the general
10 current-applying pattern in the conventional electrolysis method; and

 Figures 4 to 7 are block diagrams showing current-applying patterns in electrolysis methods according to this invention.

15 The following reference numbers are employed in Figs. 1 and 2:-

1	:	Cation exchange membrane
2,3,7	:	Compartments
4,5	:	Electrodes
20 6	:	Bipolar electrode
8,8'	:	Tanks
9,9'	:	Pipes
10,10'	:	Pumps
11,11'	:	Solution supplying pipes
25 12,12'	:	Exhaust pipes

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The electrolysis apparatus shown in Figure 1 is a basic monopolar electrode-type electrolytic cell, in which compartments 2 and 3 are formed by a partitioning cation exchange membrane 1, and electrolysis is conducted by applying an electric current through electrodes 4 and 5.

Figure 2 shows an example of a bipolar electrode-type electrolytic cell, in which the cation exchange membrane 1 and a bipolar electrode 6 are placed between terminal electrodes 4 and 5. The middle compartment is shown as 7 and a plurality of middle compartments can be arranged to form a multi-compartment bipolar electrode-type electrolytic cell. Since the same electrode material can be used as the anode and cathode, this invention is advantageous, particularly in the case of a bipolar electrode-type electrolytic cell, due to the lack of need for combining different materials to form the bipolar electrode. Any conventional cation exchange membrane durable under the electrolytic conditions can be used as the cation exchange membrane 1. Fluorine-containing resins, such as an alkali-resistant perfluoro ion exchange membrane, are particularly preferred.

Iron, nickel or their base alloys are used as the material of the electrode 4 or the electrodes 5 and 6. For instance, carbon steel, Fe-Ni alloy, stainless steel, alloys with Co, Cr or Mo, can be used as the

alloy materials. Each electrode can be composed of the same material or of a combination of different materials.

The electrolytic cell is usually equipped with supply and discharge devices for supplying the electrolyte and discharging the product. In addition, the electrolytic apparatus of this invention is symmetrical about the axis of the cation exchange membrane 1 or the electrode 6, and the direction of application of an electric current and the direction of liquid flow can be inverted at any time. In the multi-compartment bipolar electrode-type electrolytic cell shown in Figure 2, the middle cation exchange membrane becomes the plane of symmetry in the case of using an odd number of cation exchange membranes, and the middle bipolar electrode becomes the plane of symmetry in the case of using an even number of cation exchange membranes.

For instance, the electrolytic apparatus is arranged symmetrically about the plane of the cation exchange membrane 1, wherein the same shaped tanks 8 and 8', pipes 9 and 9' and pumps 10 and 10', which can supply or discharge the electrolyte, are respectively provided for the left-hand and right-hand compartments 2 and 3; optionally, solution-supplying pipes 11 and 11' and exhaust pipes 12 and 12' are provided if desired.

The electrodes 4, 5 and 6 have good electroconductivity, can be of any suitable form such as rod,

plate, mesh or porous plate, and are inexpensive. However, in the conventional electrolysis method, particularly if such an electrode is used in electrolysis of a dilute aqueous solution or waste solution containing caustic alkali, continuation of the electrolysis becomes difficult because the surface of the anode is deactivated by the formation of oxides due to oxidation; and impurities are deposited and adhered onto many portions of the electrolysis apparatus, such as the cation exchange membrane, cathode and pipes, thereby making it difficult to continue electrolysis.

The method of applying an electric current of this invention is now explained in detail.

Figure 3 shows the method of applying electric current conventionally employed for electrolysis. An electric current is applied through the anode in a positive direction at a prescribed current value A for a time T .

On the other hand, according to this invention, as shown in Figs. 4 to 6, an electric current is applied in a reverse direction at prescribed current values a_1 , a_2 and a_3 for prescribed times t_1 , t_2 and t_3 , with the polarity of the electrodes being inverted after each period of electrolysis effected by applying an electric current in a positive direction at the current values A_1 , A_2 and A_3 for prescribed times T_1 , T_2 and T_3 .

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The reason that the above-mentioned effects are achieved by this method of operation is not entirely clear. However, it is believed that the deactivation of the electrodes is prevented and further that their activity is restored by the periodic reverse application of the electric current. Particularly, it has been confirmed that, at the anode, the oxides formed as electrolysis proceeds disappear by the reductive action and an active surface is restored. Furthermore, although impurities such as metal ions, in general, reductively precipitate and adhere onto the surface of the cathode, the surface is cleaned by applying an electric current in a reverse direction. This cleaning action is also effective in removing obstructions which precipitate and adhere onto the cation exchange membrane.

The current-applying time in the positive direction is desirably as long as possible in view of the basic object of achieving electrolysis. However, if the time is too long, the electrode is deactivated and restoration of activity becomes difficult. Therefore, the time is limited to a certain value. Usually, it is safe to set the time at about 15 minutes or less, whereby the activity of the electrode can be easily restored and electrolysis can be conducted in a stable manner for a long period of time.

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The current amount applied in the reverse direction is desirably kept as small as possible, because the application in the reverse direction reduces the efficiency of the intended electrolysis, but must be sufficient to restore the activity of electrode. It has been confirmed that the object of this invention can be achieved effectively by setting the amount of current passed in the reverse direction at about 3 to 30% of the current passed in the positive direction.

Figure 4 shows a typical pattern of applying an electric current in the electrolysis method of this invention. Electrolysis is conducted by applying an electric current in a positive direction at a fixed current A_1 for a prescribed time T_1 and then applying an electric current in a reverse direction at the same current ($a_1 = -A_1$) for a prescribed time t_1 . Electrolysis is continued by repeating the above-mentioned operations. In this case, the current amounts are represented by $A_1 \times T_1$ and $-A_1 \times t_1$ (the area of the hatched portion in the Figure), respectively, and the ratio is determined only by the ratio of each current-applying time. Thus, operation is simple because only control of the time for inverting polarity is required. For example, if T_1 is 10 minutes, the current-applying time in the reverse direction t_1 is about 18 seconds to

about 3 minutes. Then, setting t_1 to an appropriate time within the above range, e.g., 1 minute, it is easy to conduct electrolysis under automatic control of a power source for the electrolytic cell by means of an automatic timer so as to invert the polarity of the electrode according to the chosen cycle.

The current-applying pattern shown in Figure 5 is an example of electrolysis in which both current a_2 and current-applying time t_2 in the reverse direction are changed against current A_2 and current-applying time T_2 in a positive direction.

Figure 6 shows an example of electrolysis in which the current-applying times in the positive direction and the reverse direction are the same ($t_3 = T_3$) and the applied current in the reverse direction a_3 is smaller than in the positive direction A_3 .

Thus there may be employed in this invention any current-applying method in which the current amount in the reverse direction becomes periodically from 3 to 30% of that in the positive direction.

Another current-applying method of this invention is explained in detail by reference to Figure 7.

First, one compartment is employed as an anode compartment and an electric current is applied in a reverse direction at a prescribed current value a_4 for

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a prescribed time t_4 after each electrolysis performed by applying an electric current in a positive direction at a prescribed current value A_4 for a prescribed time T_4 . After conducting the above operation for a certain period L, the compartment is converted to a cathode compartment, an electric current is applied in a reverse direction at a prescribed current value a'_4 for a prescribed time t'_4 by inverting the polarity after each electrolysis performed by applying an electric current in a negative direction for a prescribed time T'_4 , with inversion of the supply and discharge direction of the electrolyte, and this operation is conducted for a certain period L' . Electrolysis is continued by repeating the above-described cycle.

As in previously described embodiments, deactivation of the electrode is prevented and, further, its activity is restored by applying an electric current in the reverse direction periodically. Moreover, the current-application in the reverse direction is also effective for the removal or cleaning of the impurity metals which reductively precipitate on the abode surface and the accretions which precipitate and adhere onto the cation exchange membrane.

On the one hand, the above-mentioned electrochemical action becomes more effective and, on the other, removal or cleaning of the scale deposited on the membranes, pipes, etc. is effectively performed

by the physical action of the backward flow of the solution because the flow direction of all the solution through the electrolytic apparatus as well as the current-applying direction is inverted periodically for a fixed time.

Although long current-applying times T_4 and T'_4 at prescribed current values A_4 and A'_4 in the positive direction or the negative direction are desirable for the purpose of electrolysis, the times should be limited because electrolysis for too long a time causes deactivation of the electrode and also makes the restoration of activity by applying an electric current in the reverse direction difficult. Usually, it is safe to set the time at about 15 minutes or less, whereby the activity of the electrode can be easily restored.

On the other hand, it is preferred that the current amount in the reverse direction should be as small as possible compatible with restoring the activity of the electrode sufficiently, because current application in the reverse direction at current values a_4 and a'_4 and current-applying times t_4 and t'_4 reduces the efficiency of the intended electrolysis. It has been confirmed that the objects of this invention can be achieved effectively by setting the current amount in the reverse direction $a_4 \times t_4$ or $a'_4 \times t'_4$ at about 3 to 30% of the current amounts in the positive

direction or negative direction $A_4 \times T_4$ or $A'_4 \times T'_4$.
For example, when $a_4 = -A_4$ and T_4 is 10 minutes, t_4 is
about from 18 seconds to 3 minutes in this
invention.

5 As previously explained, electrolysis with
periodic current-application in the reverse direction
is conducted for a fixed period L and then electrolysis
is similarly conducted for a fixed period L' after
inverting the supply and discharge direction of electro-
10 lyte. These operations are then repeated to give a
long period of electrolysis. The period L or L' for
which the electrolysis in one direction is continued
can be optionally determined but, usually, it is
preferred to be between 100 and 1000 hours in order to
15 achieve the effects of this invention.

 In the current-applying pattern shown in Figure
7, operation is simplest when the current values in the
positive direction and negative direction are the same
($A_4 = A'_4 = -a_4 = -a'_4$) and each current-applying time
20 is constant ($T_4 = T'_4$, $t_4 = t'_4$, $L = L'$) because then
only control of the period for inverting the polarity
is required. However, it is possible to change each
current value A_4 , A'_4 , a_4 or a'_4 , each current-applying
time T_4 , T'_4 , t_4 or t'_4 and each electrolyzing period
25 L or L' within the scope of the invention.

The following Examples are provided for illustrative purposes and are in no way intended to limit the scope of the present invention.

Example 1

5 An electrolytic cell was partitioned by a cation exchange membrane (trade name Nafion 315, manufactured by Dupont) and a stainless steel plate (SUS 316) of 6 cm x 6 cm size and 1 mm thickness was used as the electrode material for both the anode and cathode.

10 A 0.5% NaOH aqueous solution was supplied into the anode compartment and the electrolysis was conducted at 60°C at a current density of 30 A/dm² by changing the current-applying time in the reverse direction according to the current-applying pattern shown in Figure 4. The cathode
15 compartment was at first filled with a 10% NaOH aqueous solution, then a 0.2% NaOH aqueous solution was discharged from the anode compartment and a 12% NaOH aqueous solution was discharged from the cathode compartment. The results obtained are shown in
20 Table 1.

 Electrode life was judged at the point of 2.0 V elevation of electrolysis voltage from the initial value.

TABLE 1

Current-applying Time						
	T ₁ (Positive direction)		t ₁ (Reverse direction)		Electrode Life (hours)	Efficiency of Electrolysis (%)
	(seconds)		(seconds)			
Example	1	60	15		1000 or more	51
	2	60	10		1000 or more	61
	3	60	6		1000	70
	4	60	4		740	74
	5	60	2		500	80
Comparative Example	1	60	1		100	82
	2	60	20		1000 or more	42
	3	continued	-		(95	85

As clearly shown in Table 1, the electrode life is greatly improved by the periodic current application in the reverse direction. Moreover, the electrode life increases but the efficiency of electrolysis decreases as the current amount in the reverse direction increases. Therefore, the current amount in the reverse direction should be about 3 to 30% of that in the positive direction in order to maintain the efficiency of the entire electrolysis to be 50% or more.

Example 2

An electrolytic cell was constructed in the same manner as in Example 1 except that a Ni plate was used for both the anode and cathode. Electrolysis was similarly conducted by supplying a 4% NaOH aqueous solution into the anode compartment, discharging a 2% NaOH aqueous solution from the anode compartment and discharging a 12% NaOH aqueous solution from the cathode compartment. The results obtained are shown in Table 2.

TABLE 2

Current-applying Time					Efficiency of Electrolysis (%)
	T ₁ (Positive direction)		t ₁ (Reverse direction)		
	(seconds)	(seconds)	(seconds)	(hours)	
Example	1	60	10	2000	65
	2	60	6	1300	75
	3	60	4	950	81
Comparative Example	1	60	20	2000 or more	46
	2	continued	-	220	92

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Example 3

An electrolytic cell partitioned by a cation exchange membrane (tradename Nafion 315, manufactured by Dupont) was constructed in the manner as shown in Figure 1 and a stainless steel plate (SUS 316) of 10 cm $\times$ 10 cm size and 2.5 mm thickness was used as the material for both electrodes 4 and 5. First, the left-hand compartment 2 was used as anode compartment and a NaOH aqueous solution was supplied as the electrolyte. Electrolysis was conducted by applying an electric current in the reverse direction periodically according to the current-applying pattern as shown in Figure 7.

Next, an electrolyte was supplied to the right-hand compartment 3 by valve operation and electrolysis was similarly continued with inversion of the direction of the liquid flow and the direction of the current-application using compartment 3 as the anode compartment. The conditions were as follows:

Electrolyte supplied: 2% NaOH aqueous solution

Solution discharged from the anode compartment:

0.5% NaOH aqueous solution

Solution discharged from the cathode compartment:

12% NaOH aqueous solution

Electrolysis temperature: 55°C

Current density $A_4 = a_4$: 30 A/dm²

Current-applying time $T_4 = T'_4$: 60 seconds

Reverse direction $t_4=t'_4$: 6 seconds

Electrolysis time $L=L'$: 300 hours

As a result, electrolysis treatment could be continued at a total current efficiency of about 71% for 3000 hours without any problems.

On the contrary, in the case of electrolysis without periodic reverse current-application, the current efficiency was about 86% but the electrolytic voltage increased 5 V or more during about 100 hours of electrolysis and it was impossible to continue further electrolysis.

Example 4

A NaOH aqueous solution was recovered from an alkaline waste solution of a Merox process in LPG refining using an electrolytic cell partitioned by a cation exchange membrane (trade name Nafion 324, manufactured by Dupont) and constructed in the manner as shown in Figure 1 wherein a pure nickel plate of 10 cm x 10 cm size and 3 mm thickness was used as the material for both electrodes 4 and 5.

The analytical data of the alkaline waste solution was as follows:

	NaOH	6.0%
	TOC*	20 g/l
25	Ca ⁺⁺	20 mg/l
	Mg ⁺⁺	5 mg/l
	Mn ⁺⁺	5 mg/l
	SO ₄ ⁻⁻	20 mg/l

* Total Organic Carbon

Using this alkaline waste solution as an electrolyte and supplying it into the left-hand compartment 2 which was used as the anode compartment, electrolysis was conducted under periodic current application in the reverse direction according to the current-applying pattern shown in Figure 7. Next, the electrolyte was supplied to the right-hand compartment 3 by valve operation and electrolysis was similarly continued with inversion of the direction of the liquid flow and the direction of current application using compartment 3 as the anode compartment. Only a pure NaOH aqueous solution was recovered by returning the concentrated NaOH aqueous solution to the original waste solution for 15 minutes from the time when electrolysis had been started after inverting the polarity of the compartments.

The electrolytic conditions were as follows:

NaOH concentration of the

electrolyte supplied: 6.0%

NaOH concentration of the

solution discharged from

the anode compartment: 0.6%

Solution from discharged

cathode compartment: 12%

NaOH aqueous solution

Electrolytic temperature: 55°C

Current density $A_4 = a_4$: 30 A/dm²

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Current-applying time $T_4 = T'_4$: 60 seconds

Reverse direction $t_4 = t'_4$: 6 seconds

Electrolytic period $L=L'$: 168 hours (1 week)

As a result, electrolysis treatment could be
5 continued at a total current efficiency of about 73%
for 4500 hours without any problems. Further, the
deposition of precipitates on the cation exchange
membrane was hardly observed.

On the contrary, in the case of electrolysis
10 wherein periodic current in the reverse direction
was not applied, the current efficiency was about 88%
but the electrolytic voltage increased 5 V or more
during about 100 hours of electrolysis and it was
impossible to continue further electrolysis.

15 In the case where periodic current in reverse
direction was applied but the polarity of the
compartments was not inverted, the total current
efficiency was about 73% and electrolysis could be,
at first, conducted for about 1500 hours without
20 any problems but the electrolytic voltage gradually
increased. Upon dismounting the cell, the formation
of a small amount of non-conductive oxidation product
was observed on the anode plate. Moreover, precipi-
tates which were presumably the impurities in the
25 alkaline waste solution supplied, were adhered onto
the surface of the cation exchange membrane, whereupon
the electric resistance of the cation exchange mem-
brane increased about 2 times.

CLAIMS

1. A method of electrolyzing a dilute caustic alkali aqueous solution, which method comprises

5 (a) supplying a dilute caustic alkali aqueous solution into one electrode compartment of an electrolytic cell partitioned by a cation exchange membrane and having electrodes formed of iron, nickel or a base alloy thereof;

10 (b) passing current through the cell to electrolyse the solution contained therein and reversing the polarity of the electrodes to pass current periodically through the cell in the opposite direction to the electrolysis direction; and

15 (c) recovering concentrated caustic alkali aqueous solution from the other electrode compartment.

20 2. A method as claimed in Claim 1, wherein the dilute caustic alkali aqueous solution supplied has an alkali concentration of 10 wt% or less.

25 3. A method as claimed in Claim 1 or 2, wherein the dilute caustic aqueous solution supplied is a waste solution from alkali treatment in a petroleum refining



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process or nuclear energy process facility.

4. A method as claimed in Claim 1, 2 or 3, wherein
the electric current is passed in the electrolysis
5 direction for 15 minutes or less.

5. A method as claimed in any preceding claim,
wherein the amount of the electric current passed in
the reverse direction is from 3 to 30% of that passed
10 in the electrolysis direction.

6. A method as claimed in any preceding claim
and further comprising periodically reversing the
direction of supplying and discharging electrolyte and
15 reversing the direction in which the electrolysis
current is passed correspondingly.

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7. A method as claimed in Claim 6 and which is
performed for a total period of from 100 to 1,000 hours.

8. A method as claimed in Claim 1 and substantially
25 as herein described.



9. A method of electrolysing a dilute caustic alkali aqueous solution substantially as herein described with reference to any one of Figs. 4 to 7 or Examples 1 to 4.

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10. Apparatus for electrolyzing a dilute caustic alkali aqueous solution comprising an electrolytic cell partitioned by a cation exchange membrane into at least two compartments each containing an electrode formed of iron, nickel or a base alloy thereof, electrolyte supply and discharge means which are symmetrical about a plane defined by the cation exchange membrane or in the case of a bipolar electrode type cell, a central membrane or electrode, means for reversing the polarity of the electrodes, and means for reversing the direction in which electrolyte is supplied to and discharged from the cell.

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11. Apparatus as claimed in Claim 10 and substantially as herein described.

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12. Apparatus for electrolyzing a dilute caustic alkali aqueous solution substantially as herein described with reference to Figure 1 or Figure 2 of the accompanying drawings.

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