

A Comparison of Alkaline Zinc Plating With Potassium & Sodium Salts

by D.E. Crotty

Alkaline zinc electroplating, both cyanide and non-cyanide, has traditionally been conducted using sodium salts. Several reports have been presented describing the benefits of using potassium salts in non-cyanide zinc electroplating. This presented an opportunity to look closely at the potassium system's properties compared with the traditional sodium system. The report will present throwing power, cathode efficiency and appearance properties of the plating processes. In addition, the conductivity of the solutions and solubility of salts will be discussed. Finally, economic and practical processing considerations will be explored.

Zinc has been electroplated from alkaline solutions, both cyanide and non-cyanide, for some time, and Geduld and Lowenheim^{1,2,3,4} have provided descriptions of these systems. Traditionally these processes have always used sodium salts. Recently, the use of potassium salts has been promoted for the use in alkaline non-cyanide zinc commercially and the properties were described in a recent paper.⁵ These reports indicated that further investigation was required to fully understand the properties of such a system.

In this paper we consider the cost differences, the conductivity of the salts, and the solubility of the salts. Then we consider the plating properties of the two systems, including cathode efficiency, throwing power (distribution) and appearance.

Molecular Weights

The atomic weights of elements and the resulting molecular weights of the compounds that they form strongly affect the amounts of materials that are required to conduct a particular reaction. Table 1 lists the atomic and molecular weights of most of the materials that will be used in this study comparing the properties of sodium and potassium in the non-cyanide zinc electroplating processes.

One of the fundamental principles of chemistry is that the molecular weights of chemicals determine the weights needed to perform a particular function. In the

case of sodium and potassium hydroxides, 39 grams of sodium hydroxide is equivalent to 56 grams of potassium hydroxide, and these amounts are often referred to as a "mole" of the two chemicals. Discussions on this subject are available in any elementary chemistry text.

In alkaline zinc, one of the important considerations is the bath content of hydroxide ions because this ion is responsible for the dissolution of zinc and also provides much of the electrical conductivity of the solution. It can be seen that sodium hydroxide contains 56.4% sodium, potassium hydroxide contains 69.9% potassium and the weight ratio of potassium hydroxide to sodium hydroxide is about 1.44. This means that, for example, if we needed 100 pounds of sodium hydroxide for a particular bath we would need 144 pounds of potassium hydroxide.

Commercial hydroxides are available as solids and liquids. Sodium hydroxide is usually available as a 50% by weight liquid and potassium hydroxide is usually available as a 45% by weight liquid. The liquids are usually a little less expensive than the solids because these products are first synthesized as water solutions and then they are dried, adding expense to the preparation of the solid.

Costs of the Chemicals

The price one pays for a commodity chemical like caustic soda (sodium hydroxide) and caustic potash (potassium hydroxide) can vary rather widely depending on where you are and who you know. The Chemical Marketing Reporter⁶ recently quoted the prices listed in Table 2. These reported prices have been rather stable for the last few years.

We can take the prices of the solid hydroxide products to form a cost comparison. First, we need to remember that we need 1.44 times more potassium salt to obtain an equivalent amount of the sodium salt. Therefore, one pound of caustic soda bead costs \$0.31 and the equivalent amount of caustic potash would be $1.44 \times \$0.47 = \0.68 . This means that the cost of make-up of a bath will be higher because of the more than doubling (2.19X) of the cost of the hydroxide.

Liquid caustic soda or potash will be a little less expensive, however the difference in the weight percent

Table 1
Molecular Weights & Metal Content of Salts

Element or Molecule	Molecule Weights	Weight % of metal
Sodium	22	---
Sodium Hydroxide	39	56.4
Sodium Carbonate	104	42.3
Potassium	39	---
Potassium Hydroxide	56	69.6
Potassium Carbonate	138	56.5

Table 2
Commodity Prices⁶

Chemical	Commodity Price, \$/lb
Caustic Soda Bead	0.31
Caustic Soda 50% Liquid	0.15
Soda Ash	0.079
Caustic Potash Flake	0.47
Caustic Potash 45% Liquid	0.18
Potassium Carbonate	0.40

of the liquids must be considered. First, to obtain one pound of caustic soda we need two pounds of liquid so one pound of solid caustic soda from the liquid will be $2 \times \$0.15 = \0.30 . Next, to obtain one pound of caustic potash we need 2.22 pounds of liquid caustic potash, so the cost of one pound of solid is $2.22 \times \$0.18 = \0.40 . Here we see that the cost increase using potassium is about 1.33 times that of using sodium.

The potassium system proponents suggest that the potassium system needs less of the hydroxide salt than sodium systems need because the potassium ion provided higher conductivity. Therefore, rather than adding 120 gm/L (16 oz/gal) of sodium hydroxide, the potassium system typically on make up will use 120 gm/L (16 oz/gal) of potassium hydroxide rather than the molar equivalent 173 gm/L (23 oz/gal). If this is true then the difference in make up costs between the two systems are not great. However, the most important costs for a zinc bath are maintenance costs. As the hydroxide ion is consumed in the process operation the cost replacing each pound of hydroxide will be 2.19 times more if solid hydroxide is used and about 1.33 times if liquid hydroxide is used.

To summarize, using solid hydroxides, the cost increase from sodium to potassium is 2.19 times and using liquids, the cost increase is 1.33 times. There is a cost savings (at these price quotes) of using the liquids as long as transportation costs are not large.

Conductivity

The conductivity of an electroplating solution is important because the voltage required to drive an electroplating process like zinc plating is partially determined by the conductivity of the salts in solution. Some conductivity data can be obtained from the literature, and in this case Lange's Handbook of Chemistry⁷ is helpful. This reference lists the equivalent conductivity of salts versus concentration measured in normality (N). A typical non-cyanide zinc solution might be 120 gm/L (16 oz/gal) of sodium hydroxide and this can be expressed as 3 N. A discussion of normality can be found in most elementary chemistry texts. The caustic soda concentration might range from as low as 75 gm/L (10 oz/gal; 1.9N) to 188 gm/L (25 oz/gal; 4.7N). Table 3 lists the gram-equivalent conductivity values provide by Lange's Handbook for the range of 1N to 5N.

The table shows that the conductivity of potassium hydroxide solutions can be expected to be higher than sodium hydroxide solutions. This follows the general rule that is used with acid zinc electroplating solutions that the conductivity of chloride salts increase from sodium to potassium to ammonium chlorides. The result of this is that in the concentration range typical of alkaline non-cyanide zinc the voltage requirements will be slightly lower with the use of potassium hydroxide.

An important consideration for conductivity in alkaline solutions is the carbonates. Carbonates build up in a non-cyanide electroplating solution from the decomposition of the brighteners, but mostly from the reaction of carbon dioxide in the air with the hydroxide in the solution. Carbonates can be expected to build slowly in a bath. Our experience is that a seldom-used alkaline plating bath in a pilot lab can build carbonates from an initial concentration of 30 gm/L (4 oz/gal) to about 112 gm/L (15 oz/gal) in about 18 months. This comes to about 5.2 gm/L (0.7 oz/gal) rise each month. The concentration rise can be much lower for barrel operations where drag-out is high, or it can be much higher if air agitation is used or if a filter pump is leaking.

Another important point to note in Table 3 is that Lange's Handbook provides no conductivity figure for the 5N concentration of sodium carbonate. This is because sodium carbonate is not soluble at that concentration, a point that we will explore next.

The use of potassium salts in alkaline zinc increases the conductivity of the bath, resulting in lower voltage being needed to obtain equal current in the plating cell and produces less heating of the bath.

Solubility

The solubility of a salt in water depends on a number of factors, including temperature and the concentration of other salts already present in the solution. The measurement of the maximum solubility of salts in water is a tedious task. Fortunately, much of this data for common salts is available in the literature, and Seidell collected this information⁸ in book form.

The concern for this subject is the concentration of carbonates.⁴ When the concentration of sodium carbonate becomes high it is common practice to set the bath outside in cold climates to allow some of the sodium carbonate to crystallize out. This has been true for both cyanide and non-cyanide zinc processes. There is some concern because it is known that potassium carbonates are very soluble.

The solubility data presented by Seidell is not exactly in the form that we can use immediately. There are considerable data available for the mixture of sodium hydroxide and sodium carbonate but not for the mixture of the potassium

Table 3
Equivalent Conductivity of Sodium & Potassium Salts

Salt	1N	3N	5N
Sodium Hydroxide	160	108	69
Potassium Hydroxide	184	140	106
Sodium Carbonate	45	27	---
Potassium Carbonate	70	55	43

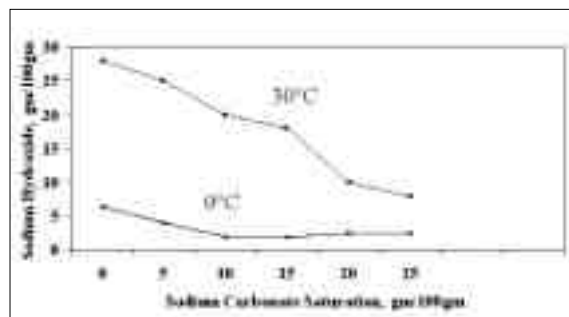


Fig. 1—Sodium carbonate saturation.

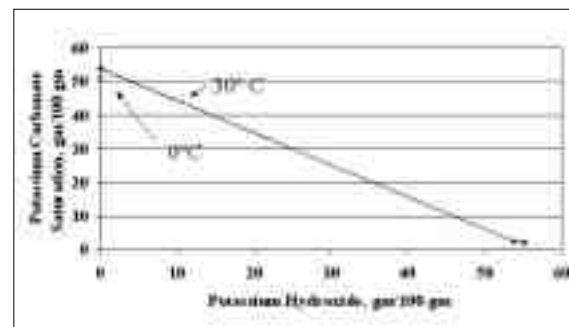


Fig. 2—Potassium carbonate saturation.

salts. To make things more difficult, the data are expressed in the form of gm/100 gm of solution rather than gm/L and the density, which would be needed for the conversion, is absent. Density data for these solutions can be obtained from the Handbook of Chemistry and Physics.⁹ Most of these solutions have a density of about 1.1, except for the more concentrated potassium carbonate solutions, so we can use this figure in our calculations.

Figure 1 shows a plot of data for the solubility of sodium carbonate over a range of sodium hydroxide concentrations at 0°C and 30°C. A typical alkaline zinc plating bath might have about 120 gm/L (16 oz/gal) of sodium hydroxide. At a solution density of 1.1 this translates to about 11 gm/100 gm. From Fig. 1, the saturation concentration of sodium carbonate at this sodium hydroxide concentration is about 18 gm/100 gm, or about 198 gm/L (26 oz/gal) at 30°C. At 0°C sodium carbonate solubility at the same sodium hydroxide concentration drops to about 3 gm/100 gm or 33 gm/L (4.4 oz/gal).

Figure 1 also shows that at zero sodium hydroxide concentration, the solubility of sodium carbonate at 0°C is 6.4 gm/100 gm which translates to 70 gm/L (9.3 oz/gal).

Figure 2 shows a plot of available data for the potassium salts at 0°C and 30°C, and the data are not as complete for the mixture of potassium carbonate and potassium hydroxide. However, we can make some estimates. If the 120 gm/L (16 oz/gal) of sodium hydroxide in the typical alkaline zinc bath is substituted with potassium hydroxide, we can calculate that $1.44 \times 120 \text{ gm/L (16 oz/gal)} = 172 \text{ gm/L (23 oz/gal)}$ is the equivalent amount of potassium hydroxide. Assuming again that the density is about 1.1 then this translates to about 15.6 gm/100 gm. From the curve in Fig. 2 it can be seen that the solubility of potassium carbonate will be about 40 gm/100 gm when that much potassium hydroxide is present. The density of this solution is about 1.4 so this translates to about 520 gm/L (69 oz/gal) and this is the saturation point for potassium carbonate.

Data are not available for mixtures of potassium carbonate and hydroxide at 0°C. However, Seidell does report that without potassium hydroxide present the solubility of potassium carbonate at 0°C is 51.3 gm/100 gm. This translates to about 770 gm/L (102 oz/gal). At 30°C potassium carbonate is soluble to about 53 gm/100 gm. The density here is about 1.5, and this translates to 795 gm/L (105 oz/gal).

Table 4 summarizes the calculations from this data collection. Sodium carbonate solubility, without the presence of sodium hydroxide drops to 70 gm/L (9.3 oz/gal) at 0°C. With sodium hydroxide present the sodium carbonate is soluble only at about 33 gm/L (4.4 oz/gal) at 0°C. Potassium carbonate, by contrast, is soluble to (106 oz/gal (795 gm/L) at 0°C. The obvious result is that potassium carbonate cannot be crystallized from the plating bath.

The effects of rising carbonate salt content in an alkaline zinc-plating bath are well known [Ref. 3, page 178; Ref. 4, page 424]. As the salt content increases, the carrier content

must be higher to eliminate a high current density burn. However, as the salt content increases, the solubility of organic materials decreases. The plating bath seems to need brightener and perhaps carrier as well. However, the addition of more organic materials does not have the desired effect because they are not very soluble in the solution and in some cases will “oil out” to the top of the plating bath. In the case of sodium baths, the carbonates will form crystals that cause roughness when the carbonate concentration is high. At least in the potassium baths this will not happen.

Plating Properties - The Hull Cell Panel

A plater is tempted first to look at the Hull cell panel of any plating process. In this comparison of sodium and potassium plating baths it is helpful to prepare baths and compare the appearance and plated thickness on the Hull cell panels [Ref. 3, page 287].

Baths were prepared at 12 gm/L (1.6 oz/gal) of zinc and 120 gm/L (16 oz/gal) of sodium hydroxide or the equivalent of 172 gm/L (23 oz/gal) of potassium hydroxide. The brightener and carrier used were the normal commercial products that our company sells for alkaline zinc.¹⁰ The panels were plated for 20 minutes at 2 A to build up a measurable thickness of zinc. In addition, a 500 mL Hull cell was used to avoid depleting the plating baths during this test. Both of the Hull cell panels were full bright and free of defects like burns or dull low current density. The only difference observable was that the back of the potassium Hull cell was clearer than the sodium Hull cell. The clarity was equal if a small amount of the normal alkaline zinc purifier was used. This difference could be the result of the higher purity of commercial potassium salts compared with sodium salts.

Figure 3 shows the thickness profile of the two panels. The differences are small and likely to be the result of experimental error.

Similar panels were plated using the commercial brighteners from a competitive system that is provided expressly for the potassium alkaline zinc plating process. Again, the thickness profile was identical. This will be explored further with the study of efficiency and throwing power.

Plating Properties - Cathode Efficiency

The methods used to measure plating efficiency are described in earlier literature.^{3,11} For this study, panels were plated in a rectangular cell and plated at 5, 30 and 50 A/ft². The weight of zinc deposited was compared with the weight of zinc expected if the process were 100% efficient. First, the sodium and potassium baths were prepared using our own commercial process, Process A,¹⁰ and then baths were prepared using the competitive materials sold expressly for the potassium system, Process B with solutions made up according to the data sheet for Process B. Table 5 lists the results of this test

Table 4
Solubility of Sodium & Potassium Carbonate
In Alkaline Solutions

Element	Temp	Hydroxide Conc.	Carbonate Saturation
Sodium	30°C	120 gm/L (16 oz/gal)	198 gm/L (26 oz/gal)
Sodium	0°C	120 gm/L (16 oz/gal)	33 gm/L (4.4 oz/gal)
Sodium	0°C	0	70 gm/L (9.3 oz/gal)
Potassium	30°C	172 gm/L (23 oz/gal)	520 gm/L (69 oz/gal)
Potassium	0°C	0	770 gm/L (103 oz/gal)
Potassium	0°C	0	795 gm/L (106 oz/gal)

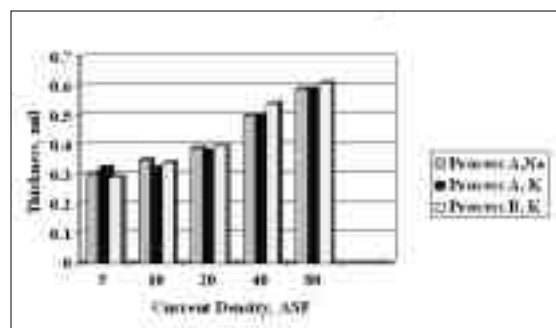


Fig. 3—Hull cell thickness comparison.

	Sodium 7.5 g/L Zn (1.0 oz/gal)	Sodium 12 g/L Zn (1.6 oz/gal)	Potassium 7.5 g/L Zn (1.0 oz/gal)	Potassium 12 g/L Zn (1.6 oz/gal)
Process A				
5 A/ft ²	96	94	99	99
30 A/ft ²	40	44	58	53
50 A/ft ²	27	32	42	35
Process B				
5 A/ft ²	99	100	99	100
30 A/ft ²	39	57	55	69
50 A/ft ²	30	47	40	29

	Sodium 7.5 g/L Zn (1.0 oz/gal)	Sodium 12 g/L Zn (1.6 oz/gal)	Potassium 7.5 g/L Zn (1.0 oz/gal)	Potassium 12 g/L Zn (1.6 oz/gal)
Process A				
5 A/ft ²	73	76	69	71
30 A/ft ²	74	78	75	77
50 A/ft ²	78	80	79	78
Process B				
5 A/ft ²	73	70	77	73
30 A/ft ²	76	78	79	77
50 A/ft ²	76	78	77	77

series. Results are an average of three tests.

The differences that appear in this data collection are small. However, in the sodium systems it appears that the lower metal concentration causes lower efficiency. With the potassium baths there does not appear to be much difference in efficiency with a change in zinc concentration, and overall, the potassium systems seem to be a little more efficient than the sodium systems. There does not seem to be any significant difference between the two brightener systems.

Plating Properties - Throwing Power

The throwing power, or the plating distribution, can be measured in a number of ways.^{3,4,11} The Haring-Blum cell was originally a rectangular cell with two cathodes and an anode in between. The distance ratio between the anode and the two cathodes is the basis for determining the throwing power which is expressed as a percentage. The resulting numbers will vary depending on the distance ratio and the size and shape of the cell.

The throwing power was measured using a 2 x 2 x 10-inch cell with a distance ratio of 5. As with the efficiency study discussed above, two brightener systems were used: Process A, and Process B. The work was repeated for zinc concentrations of 7.5 and 12 g/L (1.0 and 1.6 oz/gal). Table 6 lists the results. Results are an average of three tests.

These results show that the sodium and potassium systems are extremely similar in throwing power. There is no significant difference between sodium and potassium, or between the two brightener systems, nor between the two concentrations of zinc.

It should be noted that the two brightener systems tested for this study were both the "high throwing power" type.¹¹ If either had been the "high efficiency" type then we would most certainly have seen significant differences in the efficiency and throwing power numbers. However, those

Zinc g/L (oz/gal)	NaOH g/L (oz/gal)	Na ₂ CO ₃ g/L (oz/gal)	W/O organics mS	W/ organics mS
12 (1.6)	120 (16)	0.0	225	---
12 (1.6)	120 (16)	30 (4)	246	241
12 (1.6)	120 (16)	75 (10)	226	227
12 (1.6)	120 (16)	150 (20)	198	194

Zinc g/L (oz/gal)	NaOH g/L (oz/gal)	K ₂ CO ₃ g/L (oz/gal)	W/O organics mS	W/ organics mS
12 (1.6)	169 (22.5)	0.0	301	---
12 (1.6)	169 (22.5)	39 (5.2)	306	297
12 (1.6)	169 (22.5)	98 (13)	322	307
12 (1.6)	169 (22.5)	195 (26)	317	300
12 (1.6)	169 (22.5)	225 (30)	302	296

differences would not have been caused by the choice of sodium or potassium salts.

Plating Properties - Appearance

Our study of appearance on panels and parts show that the potassium and sodium systems are very similar. The only significant difference that we can observe between the two systems is that in a fresh plating bath the extreme low current density is considerably clearer without the use of the normal purifiers used in alkaline zinc. Once the purifier is added to the bath the low current densities of the two systems are identical. We feel that the higher purity of commercially available potassium salts is responsible for this appearance difference. This very likely means that during the maintenance of a commercial plating bath there will be less need to pay attention to the purifiers. However, impurities enter the plating tank from other sources than the sodium or potassium hydroxide.

As the carbonate salts increase in concentration in the bath we observe identical responses in the sodium and the potassium systems. As the sodium carbonate concentration rises above 75 gm/L (10 oz/gal) a high current density burn appears that requires a bit more carrier to overcome. The same effect is seen when the equivalent amount of potassium carbonate is added to the bath. The difference between the use of the two salts is that the potassium carbonate will not crystallize. With sodium systems it is known that on cool nights some of the sodium carbonate crystallizes out and settles to the bottom when the carbonates are above 75 gm/L (10 oz/gal). Therefore, in time a thick layer of carbonates forms on the bottom of the tank. This is both helpful and a bother. The crystallization in a certain way keeps the carbonates from climbing in concentration, but this can cause roughness on rack work and when it is time to clean out the tank the carbonates must be shoveled out of the tank. The potassium system will not crystallize. The carbonates will continue to rise until the plating bath no longer functions.

Plating Properties - Conductivity

As mentioned above, the conductivity of the plating bath can have an effect on plating, in terms of the voltages required to obtain a desired current flow. For this reason, plating baths were prepared with and without the organic additives

to determine the effect of carbonate concentration on conductivity. Table 7 lists the concentrations of sodium test baths prepared and the conductivity measure for them. Table 8 lists similar data for potassium test baths. It is very important to note in Tables 7 and 8 that the sodium and potassium salt concentrations are the same in molarity, not weight, because conductivity is a molar property of solutions. The concentrations of KOH and K_2CO_3 chosen for the potassium baths are the amounts needed to obtain the same concentration of hydroxide or carbonate ions as shown for the sodium baths.

Tables 7 and 8 show that as the carbonate concentration increases, the concentration increases until a peak is reached. With sodium baths the peak conductivity is obtained below 75 g/L (10 oz/gal) of sodium carbonate. With the potassium baths the peak conductivity is obtained at about 98 g/L (13 oz/gal) of potassium carbonate, which contains the same concentration of carbonate ion as the 75 g/L (10 oz/gal) sodium carbonate solution. After this point, the conductivity of both types of bath decreases. It is interesting that this effect correlates with the appearance degradation observed on the Hull cell panels.

Summary

Our study comparing the use of sodium and potassium salts in alkaline zinc reveals the following points:

The cost of making up and operating a potassium-based process is higher than the sodium because the potassium salts are more expensive. If powdered caustic is used for maintenance the potassium process will cost about 2.2 times more. If liquid caustic is used the cost increase will be about 1.3 times. Since the commercial potassium system uses less potassium hydroxide than the molar equivalent of the sodium hydroxide need in sodium systems the make up cost differences are not as great as they could be. However, maintenance costs are more important for a zinc bath that is made up once and used for many years. If drag out is high, as with a barrel line, the maintenance cost difference can be significant.

The conductivity of potassium hydroxide solutions is greater than for sodium hydroxide salts. The beneficial result is that a potassium system will require lower voltage to draw equal current across the plating cell and heating effects will be considerably less. This would be especially important in warm climates.

Potassium carbonate is very soluble in water, and, while the presence of potassium hydroxide in the same bath decreases this solubility, it is so soluble that it will not crystallize out of solution at low temperatures. Therefore, as carbonates build in the alkaline plating bath the usual remedy of allowing the carbonates to crystallize in cold climates will not work for the potassium system. While the conductivity of a bath with high potassium carbonate will still be higher than a sodium bath, the solubility of organic components is affected in exactly the same way for both systems. Alkaline baths with high carbonates of either type show the exact same deleterious effects. The major difference being that there is a chance to repair a sodium bath by crystallizing the carbonates at low temperatures. It is impossible to crystallize out potassium carbonate once the concentration has risen.

Cathode efficiencies for sodium and potassium systems are very similar. With both ionic systems the efficiency is lower when the zinc concentration of the bath is lower. The data presented suggests, however, that there is no major

advantage of using the potassium salts to improve cathode efficiency. When we compared the brightener systems sold for the sodium and potassium systems we found very little, if any, difference between them.

Throwing power differences were also investigated. In this case the data show that there is no difference between the sodium and potassium systems, and the two brightener systems studied also provide similar results.

The two brightener systems that were tested in this study were both the "high throwing power" type so it is not surprising that the efficiency and throwing power (distribution) results were similar. If one of them had been the "high efficiency" type then the results would have been considerably different.

The two proprietary brightener systems tested were made up according to their technical data sheets for comparison of plating properties. It happens that on make up both systems specify the same weight of sodium and potassium hydroxide. Therefore, Process A, on make up has more hydroxide than Process B on a molar basis. While there may be some differences in plating properties due to this, the claims for Process B are made for the bath as built by the data sheet. This study shows that there is no basis for these claims of improved efficiency and throwing power.

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