Electroless Nickel Plating from a Methanesulfonate Solution

By N.M. Martyak

The effects of sulfate and methanesulfonate anions during electroless nickel plating from a medium phosphorus solution containing either are presented. At the early stages of aging the solutions, the effects of the sulfate and methanesulfonate anions on the deposition rate, internal stress, microstructure, crystallization behavior and appearance are similar. The deposits plated from the methanesulfonate solution are harder than the sulfate deposits. After eight metal turnovers, the surfaces of both EN deposits were nodular, the coatings exhibited tensile stresses and the plating rates dropped to about 70 percent of their original rates. Treatment of the EN solutions with calcium to remove orthophosphite results in smooth and compressively stressed coatings and high deposition rates from the methanesulfonate solution, but poor quality coatings and continued slower plating rates from the sulfate-based solution.

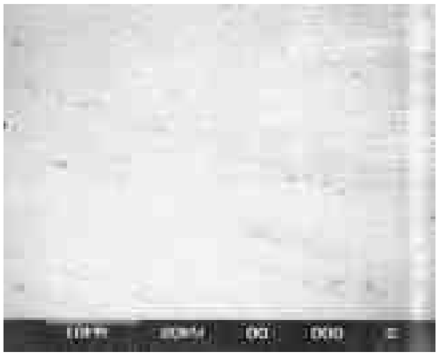

Fig. 1—SEM of EN deposit at the onset of aging.

Fig. 2—Development of nodules after three MTO.

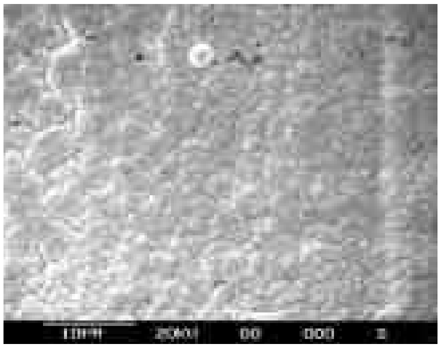

Fig. 3— Growth of nodular structures after six MTO.

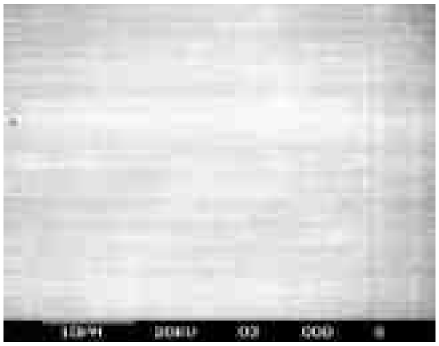

Fig. 4—Surface of EN deposit after calcium treatment.

There have been numerous studies given toward understanding the chemistry of electroless nickel (EN) solutions. Most agree the stability and solution longevity of EN solutions are controlled by a balance of the EN solution components and the concentration of by-products from the deposition reactions. The two main by-products produced during EN deposition from a sulfate-type solution are the sulfate ion, SO_4^{-2}, and the phosphite ion (sometimes referred to as orthophosphite), $H_2PO_3^-$. Lloyd and Mallory[1] showed the concentration of phosphite does not affect the kinetics of deposition. The useful operating lifetime of an EN solution, however, governed by the deposit properties (*e.g.*, internal stress, corrosion resistance, microhardness etc.), is dictated mainly by the concentration of phosphite. The main reaction in the sulfate process is:

$$NiSO_4 + 3NaH_2PO_2 + 3H_2O \rightarrow Ni^0(P) + 3NaH_2PO_3 + H_2 + H_2SO_4$$

leading to phosphite, $H_2PO_3^-$ and sulfate, SO_4^{-2}. For each metal turnover, MTO (*i.e.*, complete replenishment of the concentration of Ni^{+2} in solution), about 35 g/L of phosphite is produced. Gantner *et al.*,[2] understanding the role of phosphite on the deposition process and deposit properties, used Raman spectroscopy to monitor hypophosphite

Nuts & Bolts: What This Paper Means to You

Electroless nickel solutions eventually run out of steam as phosphites build-up in solution after a few metal turnovers. Here, Dr. Martyak has studied the replacement of the venerable electroless nickel sulfate bath with a nickel methanesulfonate solution. Bath life, in terms of deposit quality, can be extended through regeneration with calcium to remove phosphites. Afterwards, you still produce smooth and compressively stressed coatings and high deposition rates from the methanesulfonate solution. This can't be done with the sulfate bath.

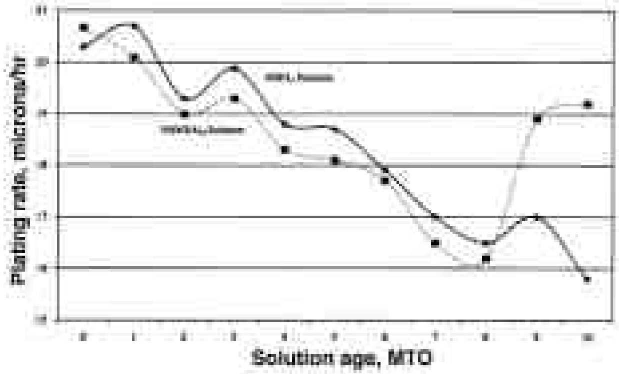

Fig. 5—Effects of bath age on plating rate.

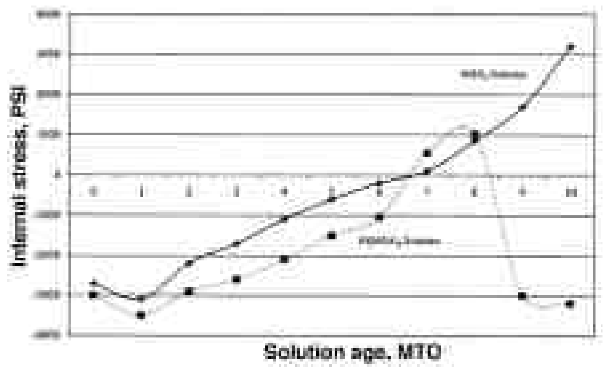

Fig. 6—Effects of aging the EN solution on the internal stress of the deposits.

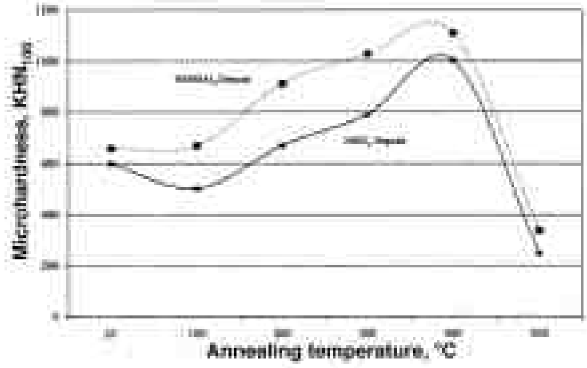

Fig. 7—Changes in microhardness with annealing temperature.

and phosphite ion concentrations. The longevity of the EN solution is about three to five MTOs when plating aluminum, and about five to eight MTOs for ferrous-based plating. If the concentration of phosphite is too high, the stress in the EN coatings usually changes from compressive to tensile and the corrosion resistance drops dramatically. The brightness of the deposits also decreases because of an increase in the surface roughness.

Numerous investigators are trying to determine the best means of separating phosphite from the EN solution, thereby increasing bath life. Iacovangelo[3] showed additions of lactic acid (to complex the nickel ions) increased bath lifetime to about 18 MTOs. However, changes in tensile stress and deposit toughness varied and concomitant changes in pH were necessary to produce acceptable EN deposits.

Electrodialysis is another alternative to remove or decrease the concentration of by-product anions.[4,5] This technique uses selective membranes that pass sulfate and phosphite from used EN solutions toward one of the electrodes. The orthophosphite is concentrated in one compartment of the electrochemical cell, and the remaining portion of the "cleaned" EN solution is returned to the plating tank. These membranes are not totally selective for orthophosphite, however. A significant amount of the necessary hypophosphite anion is also removed from the EN solution during electrolysis, making electrodialysis costly.

Precipitation of $H_2PO_3^-$ is another possible way to increase the operating lifetime of these solutions. Mallory[6] was issued a patent that claimed the use of Li^+ as a precipitating aid in removing $H_2PO_3^-$. Alkaline earth metal salts also remove $H_2PO_3^-$, but in the case of the nickel sulfate solution, a considerable amount of calcium sulfate ($CaSO_4$) sludge is also produced.

A new approach to increasing EN lifetimes is to change the counter-ion of the nickel salt. Various monovalent counter-ions, such as acetate, nitrate and methanesulfonate, were used in conjunction with a solvent extraction process to remove phosphate.[7] Of these monovalent anions, only methanesulfonate ($CH_3SO_3^-$) shows promise in extending bath lifetime without adversely affecting the deposit qualities. The methanesulfonate EN process is similar to the EN sulfate deposition reaction:

$$\begin{gathered} Ni(CH_3S0_3)_2 + 3NaH_2PO_2 + 3H_2O \rightarrow Ni^0(P) \\ + 3NaH_2PO_3 + H_2 + 2NaCH_3S0_3 \end{gathered}$$

also producing $H_2PO_3^-$ and methanesulfonate, $CH_3SO_3^-$. Although the sulfate and MSA reactions produce the expected Ni_3P alloy, the principle by-products are the phosphite and either the sulfate or methanesulfonate anion.

This study was done to determine the role of the nickel counter-ion on the deposit properties and its role in regenerating an aged EN solution. Precipitation of phosphite with calcium allows for continued use of the EN solution using the methanesulfonate anion.

Experimental

A nickel sulfate EN solution was prepared using two stock solutions. The nickel sulfate solution was prepared by dissolving nickel carbonate into sulfuric acid, so the final concentration was 75 g/L as Ni^{+2}. Cadmium acetate, $Cd(CH_3COO)_2$, was used as the brightener and thiourea was used as an exhalant. The stock hypophosphite make-up solution contained 200 g/L NaH_2PO_2, lactic acid as the chelating agent and acetic and propionic acids as buffers. Sodium hydroxide was added to this stock solution to neutralize the three acids. Lead nitrate, $Pb(NO_3)_2$, was used as a stabilizer. The initial EN solution was prepared by using 8% v/v of the nickel sulfate solution and 15% v/v of the stock sodium hypophosphite solution. Prior to plating, the solution was filtered.

During plating, the EN solution was prepared by using the stock nickel sulfate solution as described above. A replenishment sodium hypophosphite solution was prepared by dissolving 375 g/L NaH_2PO_2 and small amounts of lactic, acetic and propionic acids into one liter of water. The amount of the three carboxylic acids was dependent on drag-out because they were not consumed during plating. $Pb(NO_3)_2$ and $Cd(CH_3COO)_2$ were added to maintain bath stability and brightness, respectively. The nickel and sodium hypophosphite replenishment solutions were used at 8% v/v each per metal turnover.

The stock nickel solution for the $Ni(CH_3SO_3)_2$ process was reformulated using nickel methanesulfonate. Nickel carbonate, 150 g/L, was dissolved into 70-percent MSA until all the carbonate was removed. This 75 g/L Ni^{+2} solution was diluted to one liter and filtered. Thiourea and cadmium ethanesulfonate, $Cd(CH_3CH_2SO_3)_2$ were added at the same concentrations used in the nickel sulfate

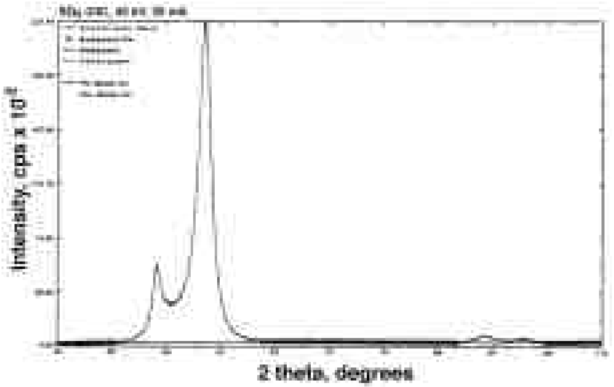

Fig. 8a—X-ray diffraction pattern for the as-deposited $NiSO_4$-based coating.

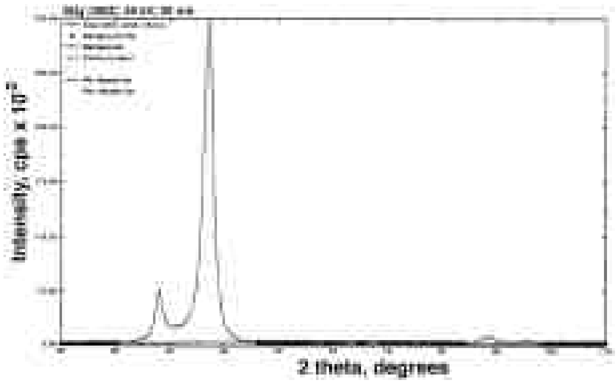

Fig. 8b—X-ray diffraction pattern of the $NiSO_4$-based coating anneal at 300°C (572°F).

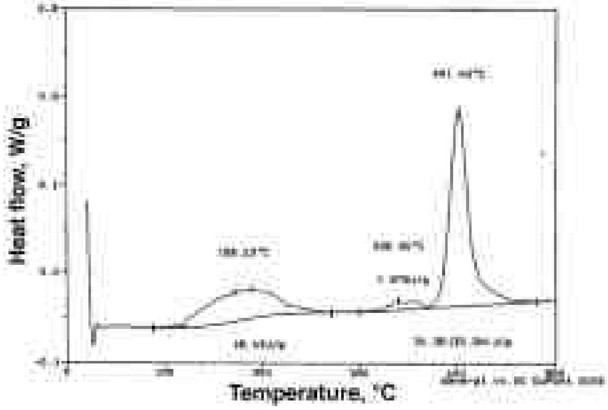

Fig. 9a—Differential scanning calorimetry (DSC) trace for the $Ni(CH_3SO_3)_2$-based coating showing Ni_3P precipitation about 400°C (752°F).

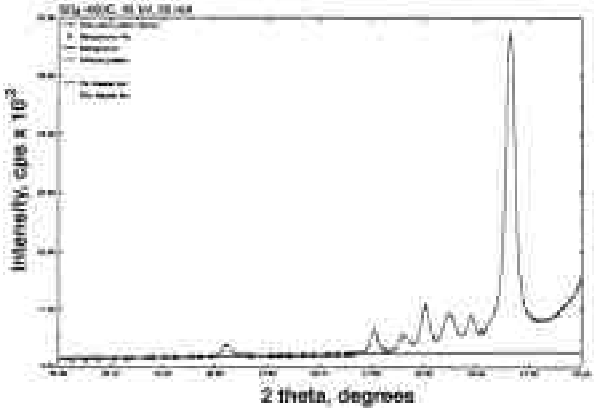

Fig. 9b—X-ray diffraction pattern of the $NiSO_4$-based deposit annealed at 400°C (752°F) showing Ni_3P precipitation (smaller reflections).

solution. Slightly more $Cd(CH_3CH_2SO_3)_2$ was used to account for the difference in molecular weights between $Cd(CH_3CH_2SO_3)_2$ and $Cd(CH_3COO)_2$. The Cd^{+2} concentration was the same in both stock nickel solutions. The same stock and replenishment sodium hypophosphite solutions used in the nickel sulfate study were also used in this investigation.

The operating EN solution contained: 6 g/L Ni^{+2}, 30 g/L NaH_2PO_2, lactic, acetic and propionic acids, NaOH, $Pb(NO_3)_2$, $Cd(CH_3COO)_2$ and thiourea. The pH of the solutions was 4.8 ± 0.05 and maintained with ammonia. It was operated at 90°C ± 2°C and filtered every two MTOs. The bath loading was held at 125 cm^2/L (~0.5 ft^2/gal).

The nickel, hypophosphite and orthophosphite concentrations were measured after each MTO. After eight MTOs, calcium carbonate was added to the room-temperature EN solutions to remove orthophosphite. During phosphite precipitation, the pH was adjusted to 7.0 to 8.0 and constantly stirred to facilitate precipitation. After 24 hr of mixing, the $CaHPO_3$ was removed by filtration. The solutions were again analyzed for Ni^{+2}, $H_2PO_2^-$ and $H_2PO_3^-$.

Electron micrographs of the as-deposited surfaces were made after each MTO using a Cambridge 250k Stereoscan microscope. Elemental analysis for occluded phosphorus and nickel was done using a Tracor EDS detector. X-ray photoelectron spectroscopy (XPS) studies were done on the as-deposited surfaces using a Kratos Axis instrument. An aluminum target with a monochromator was used, and the scans were made from 0 to 1400 eV.

The EN samples were annealed from 100 to 500°C for 60 min. X-ray diffraction patterns were acquired on the as-deposited and annealed samples using a Philips APD 3720 instrument with variable slit optics. Scans were done from 30 to 100° using a 0.01° step scan. The K_β was removed using a nickel filter. The diffraction patterns were analyzed using computer programs.[8] A convoluted algorithm combining an instrumental broadening and Lorentzian function was used in the curve-fitting analysis.

Thermal analysis of the deposits was done using a Dupont 910 differential scanning calorimeter (DSC). Measurements were made under nitrogen from 25 to 550°C at scan rates varying from 5 to 50°C/min. Microhardness measurements were made on cross sections of the deposits. The deposit was at least 25 microns thick for microhardness testing. An average of 10 readings is reported. The stress was measured *in situ* using a modified bent strip method.[9]

Results & Discussion

The two EN solutions were aged plating low-carbon steel. Approximately 35 g/L $H_2PO_3^-$ was produced per metal turnover (MTO). The addition of Ca^{+2} after eight MTOs removed all the phosphite (about 250 g/L) from the methanesulfonate solution, but only about 35 percent from the nickel sulfate solution. However, a large amount of sludge, as $CaSO_4$, was produced during the precipitation reaction in the nickel sulfate solution. No $Ca(CH_3S0_3)_2$ sludge was produced because it was found that $Ca(CH_3S0_3)_2$ is water soluble.[10] The solubility of Ca^{+2} in CH_3SO_3H is ~90 g/L.

The effects of solution age (*e.g.*, MTOs) on the appearance and surface morphologies are shown in Table 1 and Figs. 1–4. Both coatings are smooth and bright at the onset of aging. Small surface features are seen in Fig. 2 after about three MTOs. The size of these surface irregularities increases with EN solution age. After about five to six MTOs, large rounded-mound structures or nodules are seen throughout the surface (Fig. 3). The size of these nodules further increases with bath age, resulting in a semi-bright appearance. Calcium treatment restored the smooth, bright deposits seen in the early aging of the methanesulfonate solution (Fig. 4). Although the

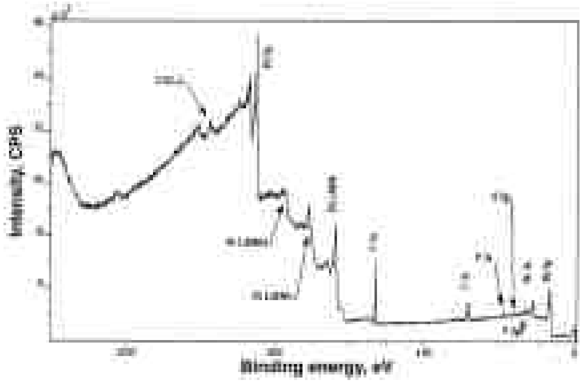

Fig. 10—XPS survey scan for the Ni(CH_3SO_3)$_2$-based coating.

Table 1
Effects of EN Solution Age on Surface Quality

↓MTO / Coating→	$NiSO_4$ Bath Deposit	Ni(MSA)$_2$ Bath Deposit
1	Smooth	Smooth
2	Smooth	Smooth
3	Slightly Smooth	Slightly Smooth
4	Slightly Nodular	Slightly Nodular
5	Slightly Nodular	Slightly Nodular
6	Nodular	Nodular
7	Very Nodular	Very Nodular
8*	Very Nodular	Very Nodular
9	Slightly Nodular	Smooth
10	Slightly Nodular	Smooth

**Calcium treatment given after eight MTOs*

Table 2
Microhardness of EN Coatings vs. Annealing Temperature

↓Deposit / Hardness→	$NiSO_4$ Bath Deposit	Ni(MSA)$_2$ Bath Deposit
As-Deposited	598	658
100°C	593	669
200°C	669	911
300°C	792	1029
400°C	103	1111
500°C	247	337

nickel sulfate deposit still exhibited surface nodules, they were not as large as those seen after seven to eight MTOs. The inability of Ca^{+2} to remove all the orthophosphite from the sulfate process is because of extraneous $CaSO_4$ precipitation, leading to continued poor deposit quality seen in Fig. 3.

The plating decreased with bath age, as shown in Fig. 5. In both solutions, the drop in plating rate is about 0.6 µm per MTO. The plating rate is only slightly higher in the nickel sulfate early in the bath life, but about equal in plating rate after five MTOs. After Ca^{+2} treatment, the plating rate continues to slow in the nickel sulfate solution because not all of the orthophosphite was removed during the precipitation process. Complete removal or $H_2PO_3^-$ in the Ni(CH_3SO_3)$_2$ solution resulted in an increase in plating rate after Ca^{+2} treatment, similar to that seen in the virgin solution. The Ni(CH_3SO_3)$_2$ solution continued to operate as though it were a fresh solution until about 15 to 16 MTOs. Calcium treatment after 17 MTOs again resulted in an increase in plating rate.

The internal stress was also affected by bath age or orthophosphite concentration (Fig. 6). The internal stress was compressive in both solutions at the start of plating and increased slightly during plating. After about six to seven MTOs (about 225 g/L $H_2PO_3^-$), the stress changed from compressive to tensile. Usually, tensile-stressed EN coatings have poorer corrosion resistance than compressively stressed deposits. The tensile stress increased in magnitude with bath age until the solutions were treated with Ca^{+2}.

The microhardness of the methanesulfonate deposits was greater than the sulfate coatings, as seen in Table 2 and Fig. 7. In the as-deposited state, the deposits are semi-crystalline, identified by the XRD scans in Figs. 8 and 9. Both Ni_3P coatings follow the typical precipitation hardening process with heat treatment. The XRD reflections sharpen between 100 and 300°C (212 and 572°F) (Figs. 8 and 9). This sharpening of the (111) and (200) reflections may be related to either an increase in nickel crystallite size or removal of lattice strains. Peak profile analysis of as-deposited and annealed EN coatings showed that this sharpening of the principal XRD reflections is primarily because of removal of lattice strains.[11] During this low-temperature anneal, the methanesulfonate deposit hardness is shifted about 150 hardness numbers (KHN_{100}) higher between 100 and 300°C (212 and 572°F). Both coatings exhibit maximum hardness at about 400°C (752°F). The DSC trace shown in Fig. 9(a) reveals an exothermic reaction occurring in both deposits at about 400°C (752°F). These exotherms are from the precipitation of Ni_3P, as evident from the XRD pattern in Fig. 9(b). Concomitant with the precipitation of nickel phosphide is a sharp decrease in the microhardness (Fig. 5).

Because of the relatively high temperature of the EN solutions and the role sulfur(II) compounds (*e.g.,* thiourea) exert on bath stability, studies were done to determine if the methanesulfonate anion decomposed, resulting in occluded sulfur in the deposits. XPS measurements made on the sulfate and methanesulfonate solutions showed the S(2p) peak at 160 eV in both deposits plated with thiourea (Fig. 10). Removal of thiourea from the EN solutions and replaced with dimethyl amine as the stabilizer did not result in the S(2p) signal, even from the methanesulfonate solution. Therefore, the methanesulfonate anion showed no signs of instability under EN deposition conditions.

The ability to extend the operating lifetime of EN solutions is dependent upon the choice of the counter-ion of the nickel salt. In the case of nickel sulfate, the plating rate decreases with bath age and the internal stress of the coating changes from compressive to tensile after about seven or eight MTOs. Similar results were found for the methanesulfonate solution. However, treatment of the solutions to remove the phosphite anion with calcium is incomplete in the sulfate solution because of the co-precipitation of $CaSO_4$. It was difficult to remove all the phosphite because of this co-precipitation, and the EN-sulfate solution was never regenerated to its original condition. Calcium additions to the methanesulfonate solution removed all the phosphite without any co-precipitation reaction. It was therefore possible to increase the plating rate to its original rate—the EN deposits were again bright and the stress changed from tensile back to compressive after phosphite removal. This is only possible when the nickel counter-ion forms a soluble complex with Ca^{+2}, such as is the case for methanesulfonate.[10]

Conclusions

The effects of anions in electroless nickel solutions were studied. The anions do not significantly affect the deposition rate, internal stress or appearance of the deposits at low phosphite concentrations. Coatings plated from the methanesulfonate solution are slightly harder than those deposited from the sulfate solution.

As the two solutions are aged, the phosphite ion concentration increases with a decrease in the plating rates and an increase in the internal stress and surface roughness. The hardness of both deposits increases with heat treatment and follows a precipitation hardening mechanism. Removal of orthophosphite was complete in the methanesulfonate solution because $Ca(CH_3SO_3)_2$ was soluble. The EN-methanesulfonate solution can be regenerated, prolonging the bath life. Regeneration of the sulfate solution is difficult because of co-precipitation of $CaSO_4$.

References

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