

PRECIPITATION TREATMENT OF SPENT ELECTROLESS NICKEL PLATING BATHS

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Summary

Electroless nickel plating (EN) has become popular because of its many advantages over the conventional electroplating process. A wide variety of technologies is available for treating spent EN baths containing high concentrations of nickel salt, reducing reagents, organic acids and other compounds. Considering capital investment and the operating-maintenance cost, precipitation as nickel hydroxide resulting from pH adjustment alone, using caustic soda or lime, and/or as elemental nickel with further addition of sodium borohydride are often the preferred methods for treating spent EN baths. Chemical principles governing the nickel removal processes are presented. Limitations of the two precipitation methods and the necessary modifications are illustrated with experimental results on nickel removals from eight nickel chloride-organic acid solutions, six typical sodium hypophosphite-reduced EN baths, and three actual spent EN baths. For most spent EN baths, on-site precipitation treatment can be implemented to meet the effluent limits at a cost much less than off-site disposal alternatives.

Electroless nickel plating process

Nickel coating on an object via electroless nickel plating (EN) is produced by controlled chemical reduction of nickel ions on a suitably treated surface. The nickel coating itself is catalytic to the reduction reaction, and the deposition continues as long as the object remains in contact with the EN bath. Many important physical properties such as uniformity, corrosion and wear resistances, hardness, lubricity, and ductility of EN deposit are better than those of electroplated nickel [1]. These advantages have made EN an attractive process for product finishing. EN baths are blends of several chemicals, each performing a specific function — source of nickel ions (nickel chloride or sulfate), reducing agent to supply electrons for the reduction of free nickel ions, complexing agent to control the amount of free nickel ions, buffering agent to resist the pH changes associated with the Ni-reduction, accelerator to

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enhance the speed of the reaction, and inhibitor to moderate the deposition process. The temperature range for EN is 87–93°C [2].

Sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) is by far the most common reducing agent because of the lower cost, greater ease of control, better overall plating quality relative to most other reducing agents — sodium borohydride (NaBH_4), aminoboranes such as dimethylamine borane (DMAB,

TABLE 1

Typical sodium hypophosphite-reduced EN bath compositions^a

Constituents	Basic baths (pH=8–10)		Acidic baths (pH=4–6)			
	Bath 1	Bath 2	Bath 3	Bath 4	Bath 5	Bath 6
nickel chloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	45	30	30			
nickel sulfate $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$				21	34	45
sodium hypophosphite $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	11	10	10	24	35	10
ammonium chloride NH_4Cl	50	50				
sodium citrate $\text{Na}_3\text{OOCCH}(\text{CH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O}$	100					
ammonium citrate $\text{HOOCCH}(\text{CH}_2\text{COONH}_4)_2$		65				
ammonium hydroxide NH_4OH	to pH	to pH				
lactic acid $\text{CH}_3\text{CHOHCOOH}$				28		
malic acid $\text{HOOCCH}_2\text{CHOHCOOH}$					35	
aminoacetic acid $\text{NH}_2\text{CH}_2\text{COOH}$						40
sodium hydroxyacetate $\text{CH}_2\text{OHCOONa}$			10			
propionic acid $\text{CH}_3\text{CH}_2\text{COOH}$				2.2		
acetic acid CH_3COOH						10
succinic acid $\text{HOOCCH}_2\text{CH}_2\text{COOH}$					10	
lead nitrate $\text{Pb}(\text{NO}_3)_2$				0.002		
thiourea NH_2CSNH_2					0.001	

^aAll composition values are given in g/l.

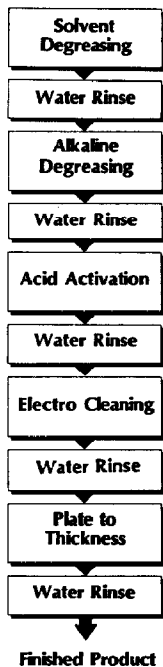


Fig. 1. Typical EN process flow diagram for plating ferrous alloys.

(CH_3)₂NHBH₃) or diethylamine borane (DEAB, (C_2H_5)₂NHBH₃), and hydrazine ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) [3]. Many organic acids — citric, acetic, hydroxyacetic (glycolic), succinic, lactic, malic, propionic, and aminoacetic acids — are employed as the complexing and/or buffering agents [4]. For hypophosphite-reduced EN baths, succinic acid also serves as the accelerator, and thiourea or lead is useful as the inhibitor. Table 1 presents compositions of six typical hypophosphite EN plating baths. Compared to the basic baths which are suited for plating on plastics, the acidic baths are more popular because of higher plating rate, better stability, easier process control, and improved corrosion resistance [5].

A typical EN process flow diagram for plating ferrous alloys is shown in Fig. 1. Nitric acid stripping is often used to remove nickel from improperly plated articles for re-plating and to remove nickel deposits from the surfaces of plating equipment. The major types of wastewater resulting from EN processes are spent EN baths, stripping solutions, and rinse waters. The spent baths are very high in total soluble nickel species (Ni(II)), reducing and complexing agent; the stripping solutions are acidic and usually contain Ni^{2+} but no complexing agents; the rinse waters are diluted plating solutions. On-site treatment of spent EN baths for meeting the effluent discharge limits, often as low as 1.2 mg/l [6], is sometimes difficult due to the presence of complexing agents in high

concentrations, while off-site disposal is very expensive, up to more than \$1.00/gal, if it is feasible at all [7].

Wastewater treatment technologies

Existing treatment methods for removing Ni(II) from industrial wastewaters fall into three general categories: a) reduction to elemental nickel (Ni^0), b) precipitation as insoluble nickel compounds, and c) separation by adsorption, electrostatic force, applied electrical potential and hydraulic or mechanical pressure. Table 2 summarizes methods which have been utilized for treating nickel-containing wastewaters; a brief introduction of these treatment technologies is given below [8,9].

Reduction

Ni(II) is reduced to form Ni^0 and deposit on a cathode or precipitate as sediments. Reduction may be accomplished by application of an electrical potential (electro-reduction), or addition of such reducing agents as sodium borohydride, hydrazine, and sodium hydrosulfite (chemical reduction).

Precipitation

Reactions of Ni(II) with hydroxides, sulfides, carbonates, carbamates, and starch xanthate produce insoluble nickel compounds which are removed after settling. Solubility products of such compounds control the residual concentration of Ni(II) after precipitation treatment at a given pH and concentration of the complexing agent. Settling, compaction, and dewatering of nickel sludge are among factors to be considered in choosing a precipitation method. Precipitation as NiS ($\text{p}K_s = 18.5$) can achieve a lower concentration of Ni(II) over a broader pH range at a chemical dosage less than stoichiometric requirement and produce a better settling sludge than as $\text{Ni}(\text{OH})_2$ [10,11]; however, the final sludge disposal cost would be higher due to the potentials of forming NiSO_4 (upon oxidation) and/or producing H_2S (upon contact with acid) [12]. For many spent EN baths, significant precipitation of $\text{Ni}(\text{OH})_2$ and, to a lesser extent, $\text{NiS}(\text{II})$, only occur after the complexing agents are substantially removed or destroyed in a pretreatment step. Chemical oxidation by ozone, potassium permanganate, sodium hypochlorite, and iron- or UV-catalyzed hydrogen peroxide are reported to be effective pretreatment methods [13,14].

Separation

Using ion exchange, nickel ions are adsorbed onto the cationic resin and replaced by H^+ or Na^+ ions, and the adsorption capacity for nickel ions is refreshed after the spent resin is chemically regenerated. In electro dialysis, electric current induces partial separation of components in an ionic solution. The separation is accomplished by alternately placing cation- and anion-se-

TABLE 2

Summary of nickel removal processes

Treatment technology	Removal mechanism	Energy cost	Capital cost	Treatment cost	Waste volume	Waste disposal	Applications
Electro-deposition	Electrolytic reduction and deposition	medium	medium	medium	very small non-toxic	very low	small hydraulic flow, high concentration of complexed nickel
Catalytic reduction-precipitation	chemical reduction and precipitation	low	medium	low	small non-toxic	low	small hydraulic flow, high concentration of complexed nickel
Hydroxide precipitation	selective precipitation	high	high	medium	large	high	large hydraulic flow, high Ni(II) concentration
Sulfide precipitation	selective precipitation	high	very high	high	large	very high	large hydraulic flow, low Ni(II) concentration
Xanthate precipitation	selective precipitation	medium	medium	very high	large	medium	Ni(II) concentration less than 10 mg/l
Thiocarbamate precipitation	selective precipitation	medium	medium	high	large	medium	Ni(II) concentration less than 50 mg/l
Ion exchange	separation by adsorption	low	medium	high	very large	very high	large hydraulic flow, low Ni(II) concentration
Electro-dialysis	separation due to electropotential	low	medium	medium	low	very low	rinse waters, nickel for recovery and/or reuse
Reverse osmosis	separation due to applied pressure	high	high	medium	low	low	rinse waters, nickel for recovery and/or reuse

lective membranes across the current path. When current is applied, the positive ions pass through the cation-selective membrane in one direction, and the negative ions in the other direction. Semi-permeable membranes are employed in a reverse osmosis process to separate, under an applied pressure, nickel and most other ions from water. Due to the high ionic strength of most spent EN baths, very high pumping pressure, often exceeding 800 psi (~55 bar), would be required. Therefore, reverse osmosis is more suited to treat the rinse waters than the spent baths.

Laboratory evaluation is essential in order to select the best treatment technology and define the optimum operating conditions capable of producing an effluent which meets the discharge limits at a reasonable cost for equipment, labor, power, chemicals, and sludge disposal. Precipitation either as $\text{Ni}(\text{OH})_2$ by caustic addition alone or as Ni° with further addition of sodium borohydride is often the preferred method for treating spent EN plating baths [15–19]. Results of precipitation treatment for eight nickel-organic acid solutions, the six referenced hypophosphite EN baths, and three actual spent EN baths are presented. Effects of type and concentration of complexing agents (organic acids) and reducing agents (hypophosphite and phosphite) on precipitation removal of $\text{Ni}(\text{II})$ are illustrated. Experimental data are discussed in terms of the formation (stability) constants of the stable nickel complexes.

Experimental section

Treatability studies

Extensive investigations of precipitation treatment were performed on three types of nickel-containing wastewater samples, using caustic soda (6 *M* and 50% NaOH) and stabilized water solution of sodium borohydride (SWS, 12% NaBH_4 and 10 *M* NaOH). The effects of types and concentration of complexing agents (organic acids) and reducing agents (hypophosphite and phosphite) on nickel removal by precipitation were first studied in the treatment of eight 0.10 *M* nickel-organic acid solutions. The eight organic acids were those commonly employed in typical sodium hypophosphite-reduced EN baths (Table 1). Table 3 presents dissociation constants for the acids, water, ammonia, and sodium ethylenediamine tetraacetate (EDTA), as well as cumulative formation constants for nickel complexes presented initially or formed during analysis. Table 4 (molar organic acid/total $\text{Ni}=1$), Table 5 (molar organic acid/total $\text{Ni}=3$), and Table 6 ($\text{NaH}_2\text{PO}_2=0.075$ *M*, $\text{NaH}_2\text{PO}_3=0.30$ *M*) summarize the experimental data. Both precipitation methods were then performed on the six referenced EN baths (Table 7) and three spent hypophosphite-reduced EN baths—EN-1 containing lactic acid (Table 8), EN-2 containing ammonium citrate (Table 9), and EN-3 containing acetic acid (Table 10). The oxidation–reduction potential, an indicator of extent of conversion of $\text{Ni}(\text{II})$ to Ni° in redox reactions, was monitored using an Orion platinum redox electrode (Model 977800). The caustic soda requirements for pH adjustment were obtained from titration curves such as those shown in Fig. 2 for spent EN baths. Table 2 presents calculations for estimating the chemical cost for treating the spent EN baths to a residual concentration of $\text{Ni}(\text{II})$ less than 1 mg/l.

Analytical methods

The EDTA titration method [18], based on the principle that Ni-EDTA complexes were much more stable than nickel formed with ammonia and all

TABLE 3

Cumulative formation constants for nickel complexes^a

Complexing agent	Ligand ^b	log K_1	log K_2	log K_3	pK_s^c
water H_2O^d	OH^-	5.0	8.6	11.3	14.0
ammonia NH_3	NH_3	2.8	5.0	6.8 ^e	9.2
sodium-EDTA $(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2$	$(OOCCH_2)_2NCH_2CH_2N(CH_2COO)^{4-}$	18.6			2.0, 2.7, 6.2, 10.3
ammonium citrate, NH_4^+ $HOOCCH_2N(CH_2COOH)_2$	NH_3 $OOCCH_2N(CH_2COO)^{3-}$	2.8 14.3	5.0	6.8 ^e	9.2 3.1, 4.9, 6.4
sodium hydroxyacetate $CH_2OHCOOH$	CH_2OHCOO^-	2.5 ^f			3.8
lactic acid $CH_3CHOHCOOH$	$CH_3CHOHCOO^-$	2.2			3.9
malic acid $HOOCCH_2CHOHCOOH$	$OOCCH_2CHOHCOO^{2-}$	3.4 ^f			3.5, 5.1
aminoacetic acid $+NH_3CH_2COOH$	$NH_2CH_2COO^-$	6.2	11.1	15.0	2.3, 9.8
propionic acid CH_3CH_2COOH	$CH_3CH_2COO^-$	1.2 ^f			4.9
acetic acid CH_3COOH	CH_3COO^-	1.1	1.8		4.8
succinic acid $HOOCCH_2CH_2COOH$	$OOCCH_2CH_2COO^{2-}$	2.4			4.2, 5.6

For a nickel complex, NiL_n ; $Ni^{2+} + nL^{m-} = NiL_n^{2-nm}$. The cumulative formation (stability) constant: $K_n = [NiL_n^{2-nm}]/[Ni^{2+}][L^{m-}]^n$ where: L is the ligand; n may be 1 through 6; m may be 0, and 1 through 4. [species] is molar concentration of the species.

^aAt 25 °C, from Lange's Handbook of Chemistry, 13th ed., McGraw-Hill Co., 1985.

^bThe predominant ligand species at pH > 10 are shown.

^cNegative log of the acid dissociation constant K_a .

^dThe acid form of the complexing agent which has K_a 's as shown.

^elog $K_4 = 8.0$, log $K_5 = 8.7$, log $K_6 = 8.8$.

^fEstimated from log K_1 's for Zn-organic complexes.

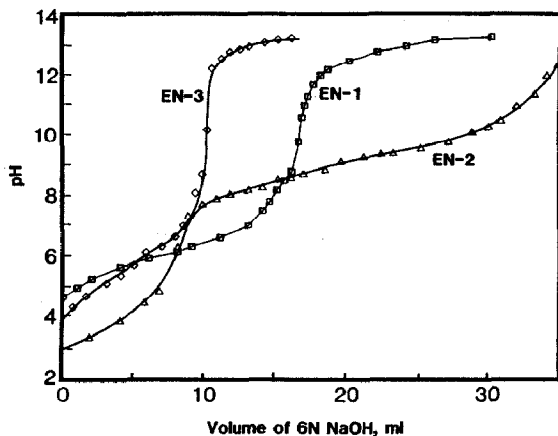


Fig. 2. Titration curves for 100 ml of spent baths.

other organic acids (Table 3), was found very satisfactory for measuring Ni(II) in all filtered (using Schleicher and Schuell No. 605 fine grade filter paper) samples. Ni(II) concentration over a wide range of 20 to 20,000 mg/l was determined directly using 0.05, 0.005, or 0.0005 M EDTA as the titrant. Low concentrations of Ni(II) were measured by the Hach Heptoxime or PAN method [21].

Results and discussion

Because solubility products for most hydroxides of heavy metals are very small, concentrations of soluble heavy metal species are very low in natural waters [22]. Due to the highly electronegative atoms — oxygen (electronegativity=3.44) and, for some, nitrogen (electronegativity=3.04) — most organic acids are capable of forming stable complexes with many metals in aqueous solutions [23]. The high concentration of organic acids in spent EN baths would increase Ni(II) over a wide pH range. Figure 3 depicts the concentration of Ni(II) as a function of pH for nickel chloride solution alone and with one of 0.10 M of acetic acid (HAc), lactic acid (HLac), and malic acid (HMal), while Fig. 4 presents the species distribution diagram for the nickel solution with 0.10 M of aminoacetic acid (HAAc), based on the following equations:



TABLE 4

Effect of organic acid on precipitation removal of nickel^a (Molar organic acid/total nickel=1)

A. pH adjustment by 6 M NaOH

Complexing agent	pH=10			pH=12		
	NaOH (ml)	Ni _{2.5} (mg/l)	Ni ₁₈ ^b (mg/l)	NaOH (ml)	Ni _{2.5} (mg/l)	Ni ₁₈ (mg/l)
ammonium citrate	2.7	5500	5500	3.6	5400	5400
sodium hydroxyacetate	1.6	9.4	0.4	1.9	3.9	<0.2
lactic acid	1.6	21	78	1.9	0.2	<0.2
malic acid	2.8	5400	5400	3.4	5.2	7.2
aminoacetic acid	1.7	2300	2250	2.2	1600	1400
propionic acid	2.3	8.1	610	2.5	1.5	<0.2
acetic acid	2.5	0.7	74	2.7	<0.2	54
succinic acid	3.1	274	<0.2	3.3	0.9	1.7

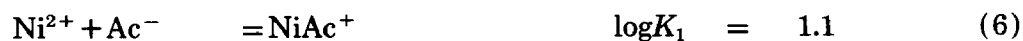
B. pH adjustment to 7.6, then addition of 0.5 ml SWS (12% NaBH₄, 40% NaOH)^c

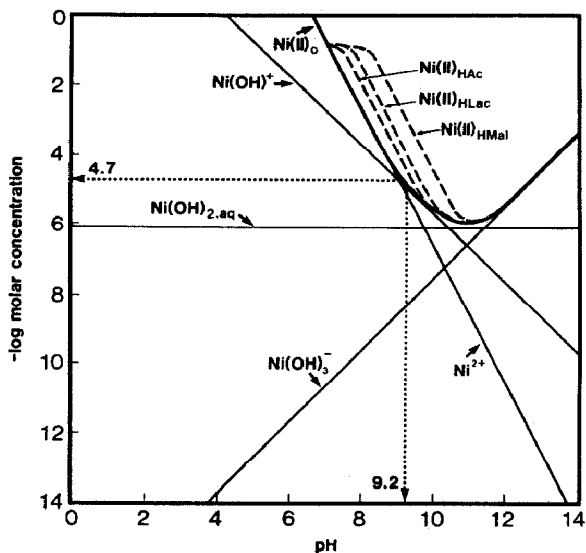
Complexing agent	NaOH (ml)	Final pH 20°C	Ni(II) (mg/l)	
			20°C	65°C
ammonium citrate	1.2	10.2	2470	1900
sodium hydroxyacetate	0.6	10.9	0.2	<0.2
lactic acid	1.6	11.7	<0.2	<0.2
malic acid	2.3	12.3	0.5	<0.2
aminoacetic acid	0.9	11.9	1630	475
propionic acid	2.2	12.1	<0.2	<0.2
acetic acid	2.1	12.2	<0.2	<0.2
succinic acid	3.1	8.8	<0.2	<0.2

^aSample volume: 50 ml, concentration of Ni(II): 6000 mg/l (0.10 M, prepared from NiCl₂·6H₂O), concentration of organic acid: 0.10 M.

^bNi_{2.5} and Ni₁₈ are measured after 2.5 and 18 h of settling.

^cDropwise addition of SWS.





$$[\text{Ni(II)}_o] = [\text{Ni}^{2+}] + [\text{Ni(OH)}^+] + [\text{Ni(OH)}_{2,\text{aq}}] + [\text{Ni(OH)}_3^-]$$

With 0.1 M of organic complexing agent,

$$[\text{Ni(II)}_{\text{HAc}}] = [\text{Ni(II)}_o] + [\text{NiAc}^+] + [\text{NiAc}_{2,\text{aq}}]$$

$$[\text{Ni(II)}_{\text{HLac}}] = [\text{Ni(II)}_o] + [\text{NiLac}^+]$$

$$[\text{Ni(II)}_{\text{HMal}}] = [\text{Ni(II)}_o] + [\text{NiMal}_{2,\text{aq}}]$$

Fig. 3. Concentrations of soluble nickel species vs. pH.

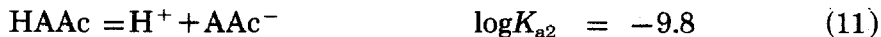


Figure 3 shows that, without complexing agent, precipitation of Ni(OH)_2 from a dilute nickel chloride solution would reduce Ni(II) concentration to 1.2 mg/l at a pH above 9.2. Table 4 results show effective nickel removal at a pH of 10, with more removal at pH = 12, by simple caustic soda addition to 0.10 M NiCl_2 solutions containing equal moles of acetic, hydroxyacetic, lactic, propionic, and succinic acids. For malic acid, a stronger complexing agent, the treatment objective could not be achieved even at pH = 12. Figure 4 shows that precipitation would occur in the presence of 0.10 M aminoacetic acid because there was less than 0.1 M of Ac^- , which was in equilibrium with HAc according to eqn. 11, to complex 0.1 M of Ni(II) . However, Ni-Ac complexes were stable, residual Ni(II) concentration remained very high (1400 mg/l) at pH = 12 after settling overnight. For some samples, residual Ni(II) concentra-

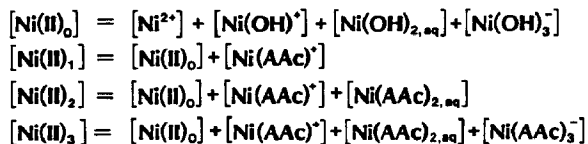
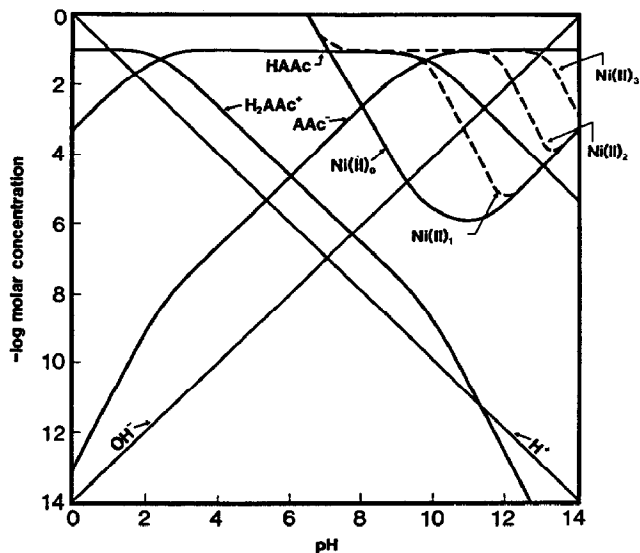
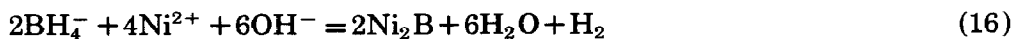
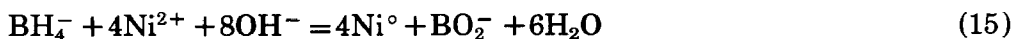


Fig. 4. Solubility diagram for Ni(II) in 0.1 M aminoacetic acid.

tions were found to have increased or decreased when settling of Ni(OH)_2 was extended, corresponding to a small drop or rise in pH. Table 4 also shows that caustic soda treatment of the NiCl_2 -ammonium citrate solution did not produce visible precipitation of Ni(OH)_2 due to formation of highly stable Ni-citrate complex ($\log K_1 = 14.3$).

The strong reducing agent sodium borohydride was effective in removing Ni(II) from all Ni-organic acid solutions; the following two equations describe the removal mechanisms:



Reduction of Ni^{2+} to Ni^0 , which would require a less stoichiometric amount of borohydride, predominated at a pH above 12, while conversion to Ni_2B took place spontaneously at a pH below 12 [2]. Gas production and the black-green precipitates observed in the borohydride treatment indicated that both mechanisms had contributed to the overall nickel removal. Pretreatment by pH adjustment to 9.2, relative to 7.6, reduced borohydride dosage and/or residual Ni(II) concentration. The borohydride treatment was performed both at the room temperature, to avoid the foaming problem due to vigorous gas produc-

TABLE 5

Effect of organic acid on precipitation removal of nickel^a (Molar organic acid/total nickel=3)

A. pH adjustment by 6 M NaOH

Complexing agent	pH=10			pH=12		
	NaOH (ml)	Ni _{2.5} (mg/l)	Ni ₁₈ ^b (mg/l)	NaOH (ml)	Ni _{2.5} (mg/l)	Ni ₁₈ (mg/l)
ammonium citrate	7.4	5380	4943	9.3	5237	4766
sodium hydroxyacetate	1.4	5560	235	1.9	79	24
lactic acid	2.4	76	106	3.2	1.6	<0.2
malic acid	6.2	5119	4943	7.5	1.4	1.7
aminoacetic acid	2.7	6000	5943	3.4	5760	4236
propionic acid	4.3	41	50	5.1	12.5	0.3
acetic acid	4.2	<0.2	1.9	5.6	0.3	1.2
succinic acid	6.9	3.0	1.7	8.3	<0.2	1.4

B. pH adjustment to 7.6, then addition of 0.5 ml SWS (12% NaBH₄, 40% NaOH)

Complexing agent	NaOH (ml)	Final pH 20°C	Ni(II) (mg/l)	
			20°C	65°C
ammonium citrate	2.8	8.9	3060	2970
sodium hydroxyacetate	0.3	11.4	1.4	0.4
lactic acid	0.8	9.5	0.7	<0.2
malic acid	5.5	10.2	4250	0.5
aminoacetic acid	2.1	12.2	3300	2750
propionic acid	3.0	10.3	<0.2	<0.2
acetic acid	3.1	10.4	<0.2	<0.2
succinic acid	5.5	9.6	1.0	<0.2

^aSample volume: 50 ml, concentration of Ni(II): 6000 mg/l (0.10 M, prepared from NiCl₂·6H₂O), concentration of organic acid: 0.30 M.

^bNi_{2.5} and Ni₁₈ are measured after 2.5 and 18 h of settling.

tion, and at an elevated temperature of 65°C, to simulate treating freshly hot spent EN baths. The experimental data demonstrate a higher degree of nickel removal at the higher temperature as a result of faster reaction rate. Table 5 shows that, when 0.30 M organic acids were present (molar acid/Ni=3), more caustic soda was required to accomplish pH adjustment, both for hydroxide precipitation and pretreatment for borohydride treatment which became less effective, except for the ammonium citrate system for which the low final pH had caused precipitation of Ni₂B [2]. Higher concentrations of sodium hydroxyacetate and lactic acid had caused higher residual Ni(II) after pH adjustments to pH 10 or 12. High concentration of aminoacetic acid prevented

TABLE 6

Effect of organic acid, hypophosphite, and phosphite on precipitation removal of nickel^a

A. pH adjustment by 6 M NaOH

Complexing agent	pH=10			pH=12		
	NaOH (ml)	Ni _{2.5} (mg/l)	Ni ₁₈ ^b (mg/l)	NaOH (ml)	Ni _{2.5} (mg/l)	Ni ₁₈ (mg/l)
ammonium citrate	8.5	5890	5850	10.8	5240	4820
sodium hydroxyacetate	3.9	5580	4430	4.6	65	50
lactic acid	5.0	7.2	13	5.1	1.4	15
malic acid	8.7	5520	4940	9.0	150	238
aminoacetic acid	5.1	5990	5920	5.4	5500	5500
propionic acid	6.3	36	85	6.8	19	45
acetic acid	6.3	30	32	7.1	13	<0.2
succinic acid	9.3	2.9	7.7	9.8	0.2	<0.2

B. pH adjustment to 7.6, then addition of 0.5 ml SWS (12% NaBH₄, 40% NaOH)

Complexing agent	NaOH (ml)	Final pH		Ni(II) (mg/l)	
		20 °C	65 °C	20 °C	65 °C
ammonium citrate	5.3	8.5	6.7	3350 ^c	3113 ^c
sodiumhydroxyacetate	2.6	8.6	8.2	2490 ^c	2320 ^c
lactic acid	3.9	8.5	7.9	765 ^c	680 ^c
malic acid	8.0	8.7	7.8	3370 ^c	1500 ^c
aminoacetic acid	4.4	12.5	10.4	4850 ^d	2910 ^c
propionic acid	5.4	11.6	9.2	3.6 ^e	90 ^c
acetic acid	5.4	11.0	8.8	0.6 ^e	28 ^c
succinic acid	8.1	10.3	9.0	2.2 ^e	30 ^c

^aSample volume: 50 ml, concentration of Ni(II): 6000 mg/l (0.10 M, prepared from NiCl₂·6H₂O), concentration of organic acid: 0.30 M; NaH₂PO₂: 0.075 M; NaH₂PO₃: 0.30 M.

^bNi_{2.5} and Ni₁₈ are measured after 2.5 and 18 h of settling.

^cGassing, black precipitate.

^dBlack and green precipitate.

^eSlightly greenish precipitate.

significant precipitation of Ni(II) at a pH as high as 12 (Fig. 4). Table 6 shows that presence of 0.075 M of hypophosphite and 0.30 M phosphite, typical of EN baths spent after five plating cycles, increased caustic soda requirements for pH adjustment and, in some cases, adversely affected treatment performances.

Results of precipitation treatment of the six referenced hypophosphite-reduced EN baths, as shown in Table 7, are consistent with the predictions based on the formation constants of the nickel complexes present in each bath. Baths

TABLE 7

Precipitation treatment of six hypophosphite-EN baths (sample volume: 50 ml)

A. pH adjustment by 6 M NaOH

EN Bath ^a	Ni(II) ₀	pH = 10.0			pH = 12		
		NaOH (ml)	Ni _{2.5} (mg/l)	Ni ₁₈ ^b (mg/l)	NaOH (ml)	Ni _{2.5} (mg/l)	Ni ₁₈
Bath 1	11160	3.1	10500	10700	8.7	9600	9700
Bath 2	7440	6.1	6700	6650	15.8	5700	5700
Bath 3	7440	3.2	6	6	3.8	4.9	4.4
Bath 4	4700	3.4	2200	2150	4.2	400	650
Bath 5	7600	7.0	6850	6850	10.5	0.9	1.7
Bath 6	10100	5.8	8950	8850	6.5	8120	8200

B. pH adjustment to 7.6, then addition of SWS (12% NaBH₄, 40% NaOH)^c

EN Bath	Ni(II) ₀	NaOH	SWS	Final pH	Ni(II) (mg/l)
		(ml)			
Bath 1	11160	0	4.9	12.4	7.2 ^d
			6.4		0.6
Bath 2	7440	0	10.9	10.2	2.1 ^d
			14.3		< 0.2
Bath 4	4700	0.8	2.0	12.2	32 ^e
			2.6		29
Bath 6	10100	4.8	6.3	13.4	129 ^e
			8.6		< 0.2

^aComposition for the EN baths are given in Table 1.^bNi_{2.5} and Ni₁₈ are measured after 2.5 and 18 h of settling.^cDropwise addition of SWS at the room temperature until gassing ceased. Continue with 30% more of SWS solution.^dSlow reaction. Gassing continued for several hours.^eImmediate reaction.

1 and 2, which contained high concentrations of ammonium citrate (molar citrate/total Ni = 1.8 and 2.3, respectively) were indeed very difficult to treat by hydroxide precipitation. Bath 6, with a molar aminoacetate/total Ni of 3.1, and Bath 4, with a molar lactate/total Ni of 3.9, also resisted treatment by caustic soda alone. Borohydride was able to remove Ni(II) from all EN baths; however, the chemical costs would be excessive.

Results shown in Table 8 for treatment of an actual spent EN bath (EN-1)

TABLE 8

Precipitation treatment of spent bath EN-1^a

A. pH adjustment by 6 M NaOH

pH	NaOH (ml)	Ni(II) (mg/l)
8.3	15.0	6200 ^b
9.5	16.8	840
10.5	17.0	28
11.1	18.0	10
12.6	20.0	0.2

B-1. Catalytic reduction by SWS (12% NaBH₄, 40% NaOH)^c

SWS (ml)	ORP (-mV)	pH	Ni(II) (mg/l)
0.00	28	4.7	18500
0.89	580	5.9	
1.78	620	6.8	
2.00	660	7.5	275
2.44	850	9.7	
2.89	1020	10.9	
3.11	1040	10.9	7.5

B-2. pH adjustment to 7.6 followed by catalytic reduction

SWS (ml)	ORP (-mV)	pH	Ni(II) (mg/l)
0.00	117	7.6	18500
0.44	584	6.8	-
0.89	598	7.0	1700
1.00	599	7.1	300
1.33	611	7.5	15
1.56	660	9.0	0.8
1.78	702	9.5	0.3
2.00	800	10.6	0.2
2.11	915	10.9	<0.2

^aSample volume: 100 ml, concentration of Ni(II) = 18500 mg/l, concentration of complexing agent (lactic acid) = 0.22 M.

^bResidual Ni(II) after 2 h.

^cDropwise addition of SWS at the room temperature.

TABLE 9

Precipitation treatment of spent bath EN-2^a

Test run number and conditions	NaOH (ml)	SWS (ml)	Final pH	Ni (II) (mg/l)
1. NaOH alone to pH=9.2	3.5		9.2	7300
2. 15.6 ml NaOCl (14%) + NaOH	6.0		12.0	4760
3. NaOH (to pH=9.2) + 15.6 ml NaOCl + NaOH	6.0		12.0	1170
4. NaOH + 1.6 g CaCl ₂	6.0		12.0	1700
5. NaOH (to pH=10) + 3.3 g KMnO ₄ + 5.7 g Ca(OH) ₂	4.0		12.4	1500
6. 3.3 g Ca(OH) ₂ + 1.5 g KMnO ₄ + 2.8 g Ca(OH) ₂			12.4	4.6
7. 3.3 g Ca(OH) ₂ + 1.9 g KMnO ₄ + 2.8 g Ca(OH) ₂			12.4	0.2
8. NaOH + 1.6 g CaCl ₂ + SWS (85°C)	6.0	0.3	12.0	80
9. NaOH + 6.4 g CaCl ₂ + SWS (65°C)	6.0	0.5	12.0	0.8
10. 4.2 g Ca(OH) ₂ + SWS (65°C)		0.3	10.8	138
11. 1.6 g NaOH + 4.2 g Ca(OH) ₂ + SWS (65°C)		0.3	12.0	11.5
12. 1.1 g Ca(OH) ₂ + SWS + 2.0 g Ca(OH) ₂ (65°C)		0.3	10.9	4.3
13. NaOH (to pH=9.2) + SWS	3.5	4.0	12.8	7
14. NaOH (to pH=9.2) + SWS (65°C)	3.5	2.3	9.6	11
15. NaOH (to pH=9.2) + 6.1 ml NaOCl + SWS	3.5	3.4	12.6	3430
16. NaOH (to pH=9.2) + 12.2 ml NaOCl + SWS	3.5	3.4	11.3	190
17. NaOH (to pH=9.2) + 1.5 g KMnO ₄ + SWS	3.5	4.3	12.5	50

^aSample volume: 50 ml, Ni(II) = 7300 mg/l, ammonium citrate = 0.29 M, initial pH = 3.5, reagent: 50% NaOH solution, SWS (12% NaBH₄, 40% NaOH), dropwise addition of SWS until gassing ceased. Unless noted otherwise reactions were at room temperature and pH adjusted to 10.0.

containing high concentrations of Ni(II) (18500 mg/l or 0.32 M) and lactic acid (0.22 M) are also consistent with theoretical predictions. Simple hydroxide precipitation, using caustic soda alone, was effective in reducing the Ni(II)

TABLE 10

Precipitation treatment of spent bath EN-3^a

A. pH adjustment by 6 M NaOH

pH	NaOH (ml)	Ni(II) (mg/l)
7.6	4.8	1840 ^b
8.3	4.9	1560
9.0	5.0	368
10.0	5.2	7.2
11.0	5.3	0.9

B. Catalytic reduction by SWS (12% NaBH₄, 40% NaOH), pH pre-adjusted to 7.6

SWS (ml)	pH		Ni(II) (mg/l)	
	20°C	65°C	20°C	65°C
0.2	7.3	8.1	1300	396
0.3	7.9	9.4	1190	17.5
0.4	11.1	11.3	<0.2	<0.2
0.5	12.2	12.0	<0.2	<0.2

^aSample volume: 50 ml, concentration of Ni(II) = 2830 mg/l, concentration of complexing agent (acetic acid) = 0.6 M, initial pH = 3.9.

^bResidual Ni(II) after 2 h.

concentration to 0.2 mg/l. Sodium borohydride treatment, using SWS, was also effective, and the dosage requirement was reduced by first adjusting the pH to 7.6 or higher. Since the amount of sodium borohydride required for treatment, with pH adjustment, was less than stoichiometric requirement (0.25 vs. 0.30 g per 100 ml, based on eqn. (15) the nickel removal was accomplished, at least partially, by catalytic reduction as described in the following equation:

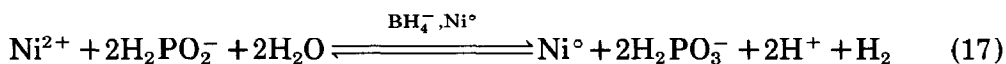


Table 9 shows that the spent EN bath containing a high concentration of ammonium citrate (0.29 M, molar citrate/total Ni = 2.3) could not be treated by caustic soda alone. Borohydride treatment was too costly. Caustic precipitation results were much improved by addition of NaOCl, which served to oxidize the citrate to species with less complexing power, or CaCl₂, which reacted with a portion of citrate in forming stable Ca-citrate complexes [20]. The improved hydroxide precipitation was also observed using lime, Ca(OH)₂ or CaO. Sodium borohydride treatment did not produce acceptable results at a reasonable dosage of less than 1.0 ml per 50 ml (equivalent to \$500 per 1000 gal). Pretreatment by oxidation using NaOCl or KMnO₄ did not improve the borohydride treatment results. The improved caustic precipitation, i.e., with

TABLE 11

Chemical costs for precipitation treatment of spent EN baths

Spent bath	Organic acid/ concentration (<i>M</i>)	Chemical cost ^a (\$/1000 gal)	
		Ni(OH) ₂	Ni(OH) ₂ and Ni ^o
EN-1 Ni(II) = 18500 mg/l pH = 4.7	lactic acid/ 0.22	99 ^b	467 ^c
EN-2 Ni(II) = 7300 mg/l pH = 3.5	ammonium citrate/ 0.29	398 ^d	565 ^e
EN-3 Ni(II) = 2830 mg/l pH = 3.9	acetic acid/ 0.60	58 ^f	226 ^g

^aCosts are calculated based on chemical dosages per 100 ml of spent EN bath samples (Tables 8, 9, and 10). Prices: NaOH - \$0.275/lb; CaCl₂ - \$0.10/lb; NaBH₄ (from SWS) - \$17.5/lb and KMnO₄ - \$1.17/lb.

^b18 ml of 6 *M* NaOH.

^c14 ml of 6 *M* NaOH (adjust pH to 7.6) and then 1.56 ml of SWS.

^d6.1 g Ca(OH)₂ and 1.9 g KMnO₄. Concentration of total phosphorus was also reduced to less than 0.2 mg/l.

^e12 ml of 50% NaOH, 12.8 g of CaCl₂, and then 1.0 ml of SWS.

^f10.6 ml of 6 *M* NaOH.

^g9.6 ml of 6 *M* NaOH (adjust pH to 7.6), and then 0.7 ml of SWS.

addition of CaCl₂, followed by polishing treatment using sodium borohydride was able to produce a residual Ni(II) concentration less than 1 mg/l.

Table 10 shows that simple pH adjustment, to pH=11, was sufficient for treating a spent bath containing a very high concentration (0.60 *M*) of acetic acid which as shown earlier was a weak complexing agent. Combined caustic and borohydride treatment was also effective.

Table 11 summarizes costs of chemicals required for treating the three spent EN baths to a Ni(II) concentration less than 1.2 mg/l. It is clear that simple pH adjustment, for Ni(OH)₂ precipitation, was much less costly than treatment by caustic and borohydride. The chemical cost would be substantially lower to meet an effluent Ni(II) concentration limit of 2.38 mg/l under the EPA regulation for treatment or pretreatment of metal finishing wastewaters from new and existing sources [24].

Conclusions

1. The Ni-EDTA complex ($\log K_1 = 18.6$) was much more stable than all other Ni-organic acid complexes tested. The standard EDTA titration method was modified into a fast and accurate procedure for measuring concentrations of all soluble nickel species, i.e., Ni(II), in EN baths.
2. Nickel removal by precipitation as $\text{Ni}(\text{OH})_2$, Ni° , and NiB_2 were interfered by the presence of organic acids which form stable nickel complexes.
3. The degree of interference due to organic complexing agent was dependent on both the concentration of the organic ligand and the formation constants of the nickel-organic complexes.
4. Ammonium citrate was the most powerful complexing agent employed in the six hypophosphite-reduced EN baths. pH adjustment alone using caustic soda was ineffective in removing Ni(II) from spent EN baths containing citrates.
5. At pH = 10, hydroxide precipitation was unable to substantially lower the Ni(II) concentration from EN baths containing either malic acid or aminoacetic acid. Nickel-aminoacetic acid complexes remained stable at pH = 12.
6. Depending on pH, the type and concentration of complexing agent present in the nickel solution, extended settling of $\text{Ni}(\text{OH})_2$ may increase or decrease the residual Ni(II) concentration.
7. Ni(II) was removed from all test solutions, as Ni° or NiB_2 , by reaction with sodium borohydride. In the precipitation treatment of EN baths, NH_4^- served both as a primary reducing agent and as a catalyst which initiated reduction by hypophosphite, as evidenced by the fact that the required dosage was less than the stoichiometric requirement.
8. Pretreatment, such as adding CaCl_2 or $\text{Ca}(\text{OH})_2$, to tie up a major portion of the complexing agent or to precipitate most of the phosphite improved removal of nickel by either pH adjustment and/or chemical reduction.
9. As expected, the spent EN bath containing lactic acid (EN-1) was easy to treat, even with an initial Ni(II) concentration as high as 18500 mg/l. Both precipitation methods were successful in reducing Ni(II) to less than 1 mg/l. Less sodium borohydride would be required with pretreatment by pH adjustment to 7.6 or above. Borohydride treatment was more expensive in chemical cost; however, sludge disposal cost would be lower. Substantial credit may even be realized if nickel precipitate is dissolved in H_2SO_4 or HCl and then reused in the EN baths.
10. Also as expected, either caustic soda or lime was able to remove Ni(II) from the spent EN bath containing ammonium citrate (EN-2). Pre-oxidation improved hydroxide precipitation but had an adverse effect on borohydride treatment. The three-stage treatment — lime pretreatment, KMnO_4 oxidation, and final lime precipitation — removed essentially all Ni(II) and total phosphorus.

11. With proper modifications, precipitation methods can be applied to treat most spent EN baths, at a cost less than off-site disposal alternative.

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References

- 1 K. Parker, Recent advances in electroless nickel deposits, paper presented at the 8th Interfinish Conference, Basel, 1972.
- 2 G.O. Mallory, The electroless nickel plating bath, paper presented at the 1st Electroless Nickel Conference, Cincinnati, Ohio, November 1979.
- 3 G.G. Gawrilov, Chemical (Electroless) Nickel Plating, Portcullis Press, Redhill, 1979.
- 4 G.O. Mallory, Influence of the electroless plating bath on the corrosion Resistance of the deposits, *Plating*, 61 (11) (1974) 1005.
- 5 W.D. Fields, R.N. Duncan and J.R. Zickgraf, Electroless Nickel Plating, in: *Metal Handbook*, 9th ed., Vol. 5, American Society for Metals, Metals Park, Ohio, 1982, p. 219.
- 6 G.C. Cushnie, Jr., *Electroplating Wastewater Pollution Control Technology*, Noyes Publications, Park Ridge, NJ, 1985, p. 4.
- 7 K. Parker, The waste treatment of spent electroless nickel baths, paper presented at the 1st AES Electroless Plating Symposium, St. Louis, Mo., March 1982.
- 8 E.A. Ramirez, Design and Engineering of a wastewater pretreatment facility, *Metal Finishing*, 82 (11) (1984) 15.
- 9 K. Parker, Waste treatment of spent electroless nickel baths, *Plating and Surface Finishing*, 70 (2) (1983) 52.
- 10 D. Bhattacharyya, A.B. Jumawan, G.Sun, C. Sund-Hagelberg and K. Schwitzgebel, Precipitation of heavy metals with sodium sulfide: Bench-scale and full-scale experimental results, *Water-1980*, AIChE Symposium Series, 1981, p. 31
- 11 R.W. Peters and Y. Ku, Removal of heavy metals from industrial plating wastewaters by sulfide precipitation, paper presented at the 57th Annual Water Pollution Control Federation Conference, New Orleans, La., October 1984.
- 12 G.C. Cushnie, Jr., *Electroplating Wastewater Pollution Control Technology*, Noyes Publications, Park Ridge, New Jersey, 1985, p. 90.
- 13 G.A. Kretas, *Solution Waste Treatment*, U.S. Patent 4,260,493, April 1981.
- 14 D. Kunces and W. Toller, Waste treatment of electroless nickel to remove heavy metal, phosphites, and chelators, paper presented at the 4th Electroless Nickel Conference, Chicago, Ill, April 1985.

- 15 Environmental Pollution Control Alternatives, EPA 625/5-79-016, June 1979.
- 16 K. Dickie, H. Gardner, and J. Moss, Waste treatment of electroless nickel, paper presented at the 2nd Electroless Nickel Conference, Cincinnati, Ohio, March 1981.
- 17 M. Fleming and J. Ulman, Sodium Borohydride environmental control application: reduction of nickel(II) complexes in spent electroless plating baths, paper presented at the 4th Electroless Nickel Conference, Chicago, Ill, April 1985.
- 18 R. Wing, W. Rayford, and W. Doane, Treatment of electroless nickel plating rinse waters, *Metal Finishing*, 76 (1) (1978) 54.
- 19 R.E. Duncan and J.R. Zickgraf, One way to treat spent EN baths, *Products Finishing*, 35 (1) (1982) 54.
- 20 1985 Product Finishing Directory, Gardner Publications, Inc., Cincinnati, Ohio, 1985, p. 172.
- 21 Water Analyses Handbook, Hach Company, Loveland, Colorado, 1982, pp. 2-147.
- 22 W. Stumm and J.J. Morgan, *Aquatic Chemistry*, 2nd ed., John Wiley and Sons, New York, NY, 1981, Ch. 5.
- 23 V.L. Snoeyink and D. Jenkins, *Water Chemistry*, John Wiley and Son, New York, NY, 1980, Ch. 5.
- 24 *Federal Register*, Vol 48, No. 137, July 15, 1983, 32462.