

# Heavy Metal Removal Using Dithiocarbamates

By R. E. Wing and W. E. Rayford

**Dithiocarbamates effectively precipitate heavy metals from plating rinsewater over a wide pH range. Concentrations of residual metal are well below established EPA discharge limits.**

**M**ajor emphasis is placed today on treating plating solutions and rinsewater to reduce the concentration of toxic metals to below established limits prior to discharge or water reuse. Available technology is adequate for partial treatment of most wastewater; however, new technology is needed to scavenge heavy metals from complexed or chelated compounds in rinsewater. Several reports<sup>1-15</sup> from this laboratory have addressed treatment methods effective for most types of rinsewater but that have some limitations. The use of sodium dimethyl- or diethyldithiocarbamate (DTC) as a metal scavenger in wastewater treatment is known,<sup>16-19</sup> although a full-scale report on its use is lacking. This paper will show the effectiveness of metal removal with DTC in hard-to-treat rinsewater.

**Copper Etchant**—Ammonium persulfate solutions containing ammonium hydroxide and ammonium chloride or carbonate are useful in the printed circuit industry to etch copper from circuit boards. Processes for copper removal from completely exhausted alkaline etch baths involve<sup>12</sup>: (a) treatment with aluminum, (b) water dilution for copper carbonate precipitation, (c) caustic heat treatment or (d) acid sulfide treatment. The "Caper" process is effective in keeping the etching rate high by continuously removing the dissolved copper from ammonium persulfate baths by crystallization. Rinsewater from etching operations contains the  $\text{Cu}(\text{NH}_3)_4^{2+}$  complex (Fig. 1), which cannot be treated effectively by conventional techniques.

Alkaline etchant rinsewater (pH 9-10) is stable at high pH unless the ammonia is driven off by aeration or heat. Rinses from ammonium persulfate etching operations are acidic; raising the pH above 6 with caustic removes some of the copper as  $\text{Cu}(\text{OH})_2$ , but all of the ammonia must be driven off to remove the remaining copper.

**Copper Pyrophosphate**—Rinsewater from this type of plating solution contains copper pyrophosphate [ $\text{Cu}(\text{P}_2\text{O}_7)^{2-}$ ], pyrophosphate ( $\text{P}_2\text{O}_7^{4-}$ ), and orthophosphate ( $\text{HPO}_4^{2-}$ ). Good removal of copper hydroxide is obtained by adjusting the rinsewater to pH 12 with caustic; however, no

**Table 1**  
Decreasing Order of the Binding  
Of Metals with Diethyldithiocarbamates

Metal <sup>20</sup>	Solubility product constant, $K_{sp}$ <sup>21</sup>
Hg <sup>+2</sup>	—
Ag <sup>+1</sup>	$2.51 \times 10^{-21}$
Cu <sup>+2</sup>	$1.58 \times 10^{-28}$
Ni <sup>+2</sup>	—
Co <sup>+2</sup>	—
Pb <sup>+2</sup>	$3.98 \times 10^{-24}$
Cd <sup>+2</sup>	$6.31 \times 10^{-21}$
Zn <sup>+2</sup>	$5.01 \times 10^{-18}$
Mn <sup>+2</sup>	$7.94 \times 10^{-12}$
Fe <sup>+3</sup>	—

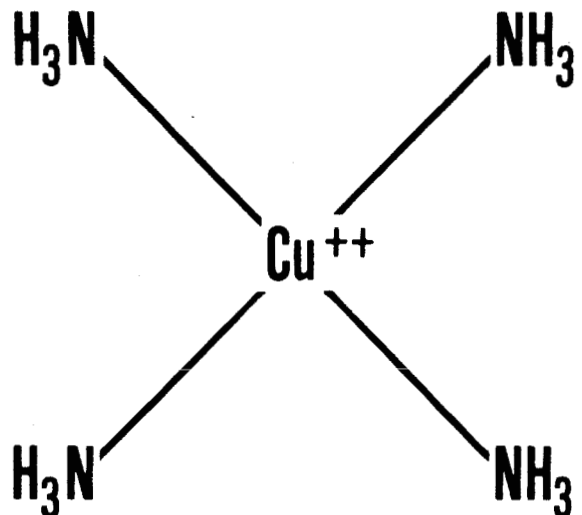


Fig. 1—Copper ammonia complex.

**Table 2**  
**Amounts of DTC Used Experimentally for Rinsewater Treatment**

Initial metal conc., mg/L	DTC theoretically required, mg		Treatment*							
	Cu	Ni	A		B		C		D	
			mL	mg	mL	mg	mL	mg	mL	mg
1.0	4.5	4.87	0.08	4	0.08	4	0.08	4	0.08	4
10	45	48.7	0.8	40	0.4	20	0.4	20	0.4	20
50	225	243.5	2.4	120	2.4	120	0.8	40	1.6	80
250	1125	1217.5	20.0	1000	4.0	200	2.4	120	3.2	160

\*Treatments with a 5 percent solution of sodium dimethyldithiocarbamate prepared by diluting a 40 percent solution (DX-2000, Pollution Technology Systems, Garland, TX). The complexed metal solutions initially were treated with the amount of DTC given in Treatment A. Aliquots (5 mL) were removed, filtered and analyzed for residual metal. The supplemental amounts of DTC listed in Treatments B, C and D were successively added to the 100-mL samples with residual-metal analysis after each addition.

pyrophosphate or orthophosphate is removed.

An excess of cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{Fe}^{3+}$  form insoluble precipitates with  $\text{HPO}_4^{2-}$  and  $\text{P}_2\text{O}_7^{4-}$ . Calcium hydroxide, lime, and calcium chloride are economical sources of  $\text{Ca}^{2+}$ , and when added to the rinse,  $\text{Ca}^{2+}$  complexes with the  $\text{HPO}_4^{2-}$  and the excess  $\text{P}_2\text{O}_7^{4-}$ , precipitating them as insoluble calcium salts. After excess  $\text{P}_2\text{O}_7^{4-}$  is removed, the copper precipitates as  $\text{Cu}_2\text{P}_2\text{O}_7$ .

**Electroless Copper**—The electroless plating of Cu on PC boards and plastics usually is an autocatalytic formaldehyde reduction of a complexed alkaline copper. Commercial formulations contain strong chelating agents such as EDTA, tartrate and Quadrol. For concentrated plating baths, treatments<sup>11</sup> such as (a) raising the temperature to 49 to 66° C, (b) adding excess formaldehyde (1.5 percent by volume), (c) adding palladium activator (1 to 50 mg/L), and (d) lowering the pH all have been used successfully in decomposing the copper complexes. However, these treatments for the most part are ineffective on rinsewater from these baths. Some recent reports<sup>3,7,12</sup> show that this type of rinsewater is treatable with insoluble starch xanthate, lime or ferrous sulfate.

**Electroless Nickel**—The electroless deposition of nickel is a controlled autocatalytic reduction. Both acidic (pH 4-6) and alkaline (pH 8-10) formulations are used, containing a nickel salt ( $\text{NiSO}_4$  or  $\text{NiCl}_2$ ), a reducing agent [ $\text{NaH}_2\text{PO}_2$ ,  $\text{NaBH}_4$  or  $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_3$ ], a chelating agent (citrate or glycolate) and a pH-control agent ( $\text{H}_2\text{SO}_4\text{-NH}_4\text{Cl}$  or  $\text{NH}_4\text{OH}\text{-NH}_4\text{Cl}$ ). The chelating agents and the ammonium ion or ammonia serve a twofold purpose: (a) they keep the nickel phosphite from precipitating by forming soluble nickel complexes, and (b) they buffer the pH of the bath, since the acid that is formed during the nickel reduction would lower the power of the reducing agent.

Electroless nickel rinsewater contains complexed Ni, which must be removed to prevent potential undesirable ecological effects that can result from its introduction into receiving waters or biological sewage-treatment systems. Treatment with caustic or lime at high pH has had limited success in nickel removal.<sup>8</sup>

**Experimental Procedure**

Synthetic<sup>3</sup> and commercial rinsewater (1 to 250 mg/L of copper) was prepared by dilution of concentrated baths or etchants. Solutions (1L) were treated with a 5 percent solution of sodium dimethyldithiocarbamate (Table 1) by stirring for 30 min. The solids were flocculated with cationic polymer (1 to 7.5 mg/L) and filtered. The supernatant liquid was analyzed for residual metal concentrations via atomic

absorption with a Varian Techtron AA120 spectrophotometer.

Reagents for the determination of residual sodium dimethyldithiocarbamate in wastewater were: toluene; concentrated ammonium hydroxide; copper sulfate solution (2 percent  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ ); and standard copper dimethyldithiocarbamate solution.

The standard solution was prepared by dissolving 0.1000 g of copper dimethyldithiocarbamate\* in toluene and diluting to 1,000 mL in a volumetric flask. The solution was warmed if necessary and allowed to stand overnight to ensure

\*Methylcumate, R. T. Vanderbilt Co., Norwalk, CT.

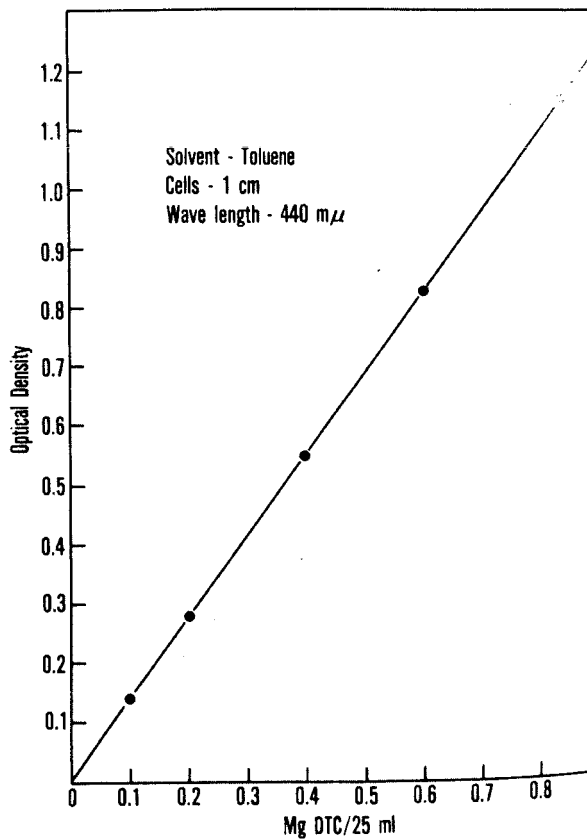


Fig. 2—DTC estimation in wastewater.

Treatment	Initial conc., mg/L
Quadrol	1
	10
	50
	50
	50
	250
EDTA	1
	10
	50
	50
	50
	250
Tartrate	1
	10
	50
	50
	50
	50
	250
Ethylenedi...	1
	10
	50
	50
	50
	250
Pyrophosph...	1
	10
	50
	50
	50
	250

\*See Table 2  
\*Contact time  
\*Concentration  
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1. Take a...
2. DTC, ...
3. Total w...
4. Transff...
5. Add 5...
6. After s...
7. Filter t...

**Table 3**  
**Treatment of Synthetic Copper Solutions with DTC**

D	Initial Cu conc., mg/L	pH	Residual copper conc., mg/L DTC treatments <sup>a</sup>			
			A	B	C	D
L	<b>Quadrol</b>					
	1	7	1.33	1.30	1.14	1.13
	10	7	2.34	1.28	0.72	0.81
	4	3	22.13	0.39	0.47	0.42
	5	7	21.40	0.22	0.26	0.47
	2	10	22.34	0.08	0.42	0.46
	250	7	37.80	0.55	0.60	0.70
	<b>EDTA</b>					
	1	7	0.80	0.40	0.37	0.53 <sup>b</sup>
	10	7	2.04	0.53	0.31	0.71
	50	3	26.38	26.10	16.95	0.57
	50	7	26.72	26.72	17.15	0.40
	50	10	27.48	2.85	0.54	1.13
	250	7	38.93	0.28	0.28	0.13
	<b>Tartrate</b>					
	1	7	0.95	0.50	0.37	0.34
	10	7	4.17	0.43	0.61	0.40
	50	3	34.68	6.44	0.17	0.09
	50	7	33.40	5.27	0.86	0.30
	50	10	32.02	5.30	0.28	0.31
	250	7	93.20	74.0	43.93	9.21
	<b>Ethylenediamine<sup>c</sup></b>					
	1	7	0.86	0.55	0.68	0.71
	10	7	3.11	1.80	0.98	1.95
	50	3	24.25	0.73	0.18	0.16
	50	7	22.98	2.40	0.40	0.38
	50	10	22.77	0.78	1.60	0.96
	250	7	48.70	10.68	5.50	1.53
	<b>Pyrophosphate</b>					
	1	7	1.00	1.19	1.18	1.24
	10	7	2.02	2.34	3.24	3.65
	50	3	17.40	0.12	0.24	0.23
	50	7	20.25	2.57	6.49	6.62
	50	9	20.00	0.74	7.02	3.20
	250	7	1.14	0.67	0.51	0.51

<sup>a</sup>See Table 2.

<sup>b</sup>Contact time of 16 hr. Residual copper content was 0.28 mg/L.

<sup>c</sup>Concentrated solution consisted of 5.0 g CuSO<sub>4</sub>·5H<sub>2</sub>O and 12 mL ethylenediamine.

complete solubility. Several test tubes or 25-mL volumetric flasks containing varying amounts of this standard solution (e.g., 0.5, 1, 5, 10, 12, 14, 16, 18, 20 and 25 mL) were made up to exactly 25 mL with toluene.

These standards were used to prepare a reference curve at 440 μm (Beckman DB) using toluene as the blank. Concentration was plotted vs. percent transmission on semilogarithm paper or as optical density on regular graph paper. The usual procedure for determining the residual DTC concentration in treated rinsewater is given below:

1. Take a known volume of wastewater (5 mL of 500 mg DTC, or 100 mL for 1-2 mg DTC).
2. Total water volume should be at least 50 mL. Add 50 mL of toluene.
3. Transfer quantitatively the water-toluene mixture to a 250-mL separatory funnel.
4. Add 5 mL of concentrated ammonium hydroxide and 10 mL of 2 percent copper sulfate. Shake thoroughly.
5. After separation is complete, draw off the aqueous layer into a beaker.
6. Filter the toluene layer by gravity into a 250-mL graduate.

**Table 4**  
**Treatment of Electroless Copper Solutions with DTC**

Initial Cu conc., mg/L	pH	Residual Cu conc., mg/L DTC treatments <sup>a</sup>			
		A	B	C	D
<b>Quadrol</b>					
2	7	1.76	1.87	2.00	2.03
10	7	4.30	1.55	2.13	1.68
50	3	22.30	0.35	0.13	0.28
50	7	20.80	0.47	0.47	0.49
50	10	38.50	3.40	4.19	2.16
250	7	34.00	0.50	0.49	0.71
<b>EDTA</b>					
1	7	1.10	1.10	1.10	0.78
10	"	1.30	1.30	0.71	0.58
50	"	17.70	0.59	0.53	0.39
250	"	5.10	0.51	0.49	0.30
<b>Tartrate</b>					
2	7	1.10	1.30	1.40	1.40
10	"	5.20	1.60	1.50	1.40
50	"	42.70	10.20	0.77	0.30
250	"	83.20	47.10	19.90	0.40
<b>EDTA-Tartrate</b>					
1	7	0.87	0.72	0.70	0.40
10	"	9.20	5.77	1.04	0.33
50	"	49.20	26.80	17.48	0.30
125	"	83.10	65.90	60.20	31.20

<sup>a</sup>See Table 2.

7. Add 50 mL of toluene to the aqueous layer, shake, separate, and collect the toluene in the same graduate.
8. Repeat until the toluene extract is colorless.
9. Transfer colored toluene solution from the graduate to a volumetric flask. Use toluene to rinse any remaining colored solution and to dilute to volume.
10. Place aliquot in spectrophotometer using toluene as reference standard and note transmission. Convert percent transmission to optical density.
11. Use optical density to determine the mg/25-mL (M) value from Fig. 2.
12. Calculations:

$$\frac{V \times M \times 1,000 \times 0.942}{25 \times S}$$

= mg/L sodium dimethyldithiocarbamate

V = size volumetric flask (mL)

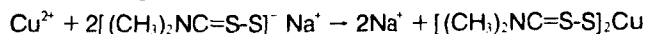
M = mg/25-mL value

S = sample size (mL)

$$0.942 = \frac{2(\text{CH}_3)_2\text{NCSS Na}}{[(\text{CH}_3)_2\text{NCSS}]_2\text{Cu}}$$

### Results and Discussion

DTC is a useful precipitant to achieve low concentrations of heavy metal. The precipitation of copper is represented by the following equation:



When metals are precipitated by reaction with DTC, very insoluble sludges result (Table 1).

Table 2 shows the volumes and weights of sodium dimethyldithiocarbamate used on metal solutions containing 1 to 250 mg/L of copper or nickel. Results of analysis on synthetic copper solutions<sup>3</sup> (prepared as discussed previously) after treatment with DTC are shown in Table 3. For the most part, only a slight excess (10-30 percent) of DTC was required to lower the copper concentration to a level below accepted discharge

D  
L mg

18 4  
4 20  
5 80  
2 160

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esidual sodium  
were: toluene,  
sulfate solution  
copper dimethyl-

solving 0.1000 g  
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**Table 5**  
Treatment of Copper Ammonia Etchant Rinsewater With DTC

Initial Cu conc., mg/L	pH	Residual Cu conc., mg/L DTC treatments*			
		A	B	C	D
1	7	0.43	0.36	0.46	0.58
10	7	2.23	0.54	1.28	1.08
50	3	20.94	0.21	0.24	0.37
50	7	20.94	0.50	0.56	1.04
50	10	16.50	1.08	1.10	1.40
250	7	29.00	0.52	0.32	0.32

\*See Table 2.

concentrations. Similar results were obtained when concentrated commercial electroless copper baths were diluted and analyzed (Table 4). Table 5 shows good removal of copper with DTC from copper ammonia rinsewater. The results of treatment of electroless nickel rinsewater with DTC, at various pH values and without pH adjustment, are shown in Table 6.

The most effective removal of metal by DTC occurred when the copper or nickel concentration was above 10 mg/L. At lower concentrations, solutions usually were turbid and very poor floc formation occurred. Stoichiometric amounts of DTC usually will lower the metal concentrations to 1 mg/L. A 10 to 30 percent excess of DTC generally will reduce metal concentrations to less than 0.2 mg/L. Effective metal removal was obtained over the pH range of 3-10. Longer contact times (Table 4) resulted in even greater metal removal. Cationic polymers (1 to 7.5 mg/L) aided flocculation and sludge settling. The sludge volume after settling (50 mg/L initial copper concentration) was about 1 percent of the total volume. Sludge filtration and handling compared favorably with that of copper or nickel hydroxide sludges. The metal/DTC sludge-cake (40 percent solids) was more stable [the solubility product constant,  $K_{sp}$ , of  $\text{Cu}(\text{OH})_2$  is  $1.6 \times 10^{-19}$ ] than metal hydroxide sludges (Table 1) and is expected to pass the EPA leaching test (Federal Register, May 19, 1980) in view of the effectiveness of DTC for precipitating copper in low-pH solutions in the presence of complexing or chelating agents. The recovery of metal via incineration should be possible.

DTC usually is supplied as a 25- or 40-percent solution of the dimethyl or diethyl derivative.\*\* One liter of the 40 percent solution contains 0.4 kg of DTC (~\$1.80/L, equivalent to 3.33 lb/gal or ~\$7/gal), which can remove the quantities of metal shown in Table 7. In batch treatment, the initial concentration of metal is determined and the required amount of 40 percent DTC is added. In continuous-flow operations, 40 percent DTC should be diluted to 1-5 percent before metering-in. Plant personnel should handle the caustic DTC with care.

Some dithiocarbamates are fungicides, so a large excess of DTC should not be used. Residual DTC can be determined by the system described under the "experimental procedure" section of this paper. Even though DTC has a fairly low toxicity (acute oral  $\text{LD}_{50} = 1000$  mg/kg for rats) and is reported to degrade rapidly in water, some companies may be required to remove residual DTC from effluent after treatment. Table 8 shows that activated carbon effectively removes DTC from water and treated electroless copper solutions.

\*\*Enthone, Inc., New Haven, CT, MacDermid, Inc., Waterbury, CT, and Pollution Technology Systems, Garland, TX.

**Table 6**  
Treatment of Electroless Nickel Solutions with DTC

Initial Ni conc., mg/L	pH	Residual Ni conc., mg/L DTC treatments*			
		A	B	C	D
With pH adjustment					
<b>Basic</b>					
1	7	0.89	0.59	0.69	0.58
10	7	5.99	1.12	0.06	0.08
50	3	44.90	22.90	14.01	0.14
50	7	44.40	19.90	10.14	0.14
50	10	41.55	18.10	9.52	0.23
250	7	110.00	82.70	66.96	35.26
<b>Acidic</b>					
1	7	0.62	0.52	0.54	0.13
10	7	4.38	0.06	0.03	0.06
50	3	37.34	13.38	4.13	0.13
50	7	25.23	9.05	1.67	0.11
50	10	14.28	4.48	2.19	1.23
250	7	90.00	64.80	41.40	12.14
Without pH adjustment					
	$\text{pH}_{\text{initial}}$	$\text{pH}_{\text{final}}$			
<b>Basic</b>					
1	7.8	8.4	0.47	0.39	0.49
10	8.2	8.7	2.70	0.04	0.11
50	8.5	9.1	24.60	5.30	0.04
250	8.8	9.6	53.40	39.60	28.60
<b>Acidic</b>					
1	4.8	9.3	0.99	0.96	1.04
10	4.9	9.4	4.20	0.59	0.85
50	4.7	9.5	20.60	10.00	4.21
250	4.6	9.7	55.90	36.50	29.90

\*See Table 2.

**Table 7**  
Weight of Metal Removed with DTC

Metals	Metal recovered	
	Diethyl, kg/L (lb/gal)	Dimethyl, kg/L (lb/gal)
Ag <sup>+</sup>	0.25 (2.10)	0.32 (2.52)
Au <sup>+</sup>	0.46 (3.84)	0.55 (4.59)
Cd <sup>2+</sup>	0.13 (1.10)	0.16 (1.31)
Co <sup>2+</sup>	0.07 (0.58)	0.08 (0.69)
Cu <sup>2+</sup>	0.07 (0.62)	0.09 (0.74)
Fe <sup>2+</sup>	0.07 (0.55)	0.08 (0.65)
Hg <sup>2+</sup>	0.24 (1.96)	0.28 (2.34)
Mn <sup>2+</sup>	0.06 (0.54)	0.08 (0.64)
Ni <sup>2+</sup>	0.07 (0.57)	0.08 (0.68)
Zn <sup>2+</sup>	0.08 (0.64)	0.09 (0.76)

\*Concentration of DTC was 0.40 kg/L (3.33 lb/gal).

Rinsewater after treatment still would contain the complexing or chelating agents, which are biodegradable. Care should be taken when discharging the effluent because these agents will combine with other heavy-metals when segregated streams are further treated (as in a clarifier with other process waters) or discharged into streams or sewers. Oxidants (e.g., ozone - UV light) could be used to decompose the organic complexing agents, or activated carbon could be used to adsorb them and thus prevent recomplexation with other heavy metals.

Sample  
Water  
1  
2  
3  
4  
5

Electroless  
1  
2  
3  
4  
Electroless  
1  
2  
3  
4

\*A solution (1 amount of) Wilmington, residual DTC  
\*A solution (1 amount of) treated with mL, 1 mg/m was treated DTC. Aliquot  
\*A solution (1 amount of) treated with quantities of after each acc

**Case Hist**  
A large MI plating ba ammonia ff treatment 18,000 gal Laboratory (initially 16) concentrat

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**Conclusion**  
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**Acknowled**  
The authors concentrate Carson City New Haven, Nutley, NJ; of firm name endorsed or over other fil

**Table 8**  
**DTC Removal with Activated Carbon**

Sample	Activated carbon, g	Residual DTC, mg/L
<b>Water<sup>a</sup></b>		
1	0	594.7
2	1	463.5
3	2	297.3
4	4	96.2
5	6	2.1
<b>Electroless Copper Rinsewater<sup>b</sup></b>		
1	0	508.9
2	1	247.8
3	2	48.8
4	4	1.4
<b>Electroless Copper Rinsewater Containing Sludge<sup>c</sup></b>		
1	0	529.9
2	1	223.0
3	2	44.5
4	4	2.1

<sup>a</sup>A solution (1,000 mL) containing DTC (594.7 mg/L) was treated with various amounts of activated carbon (Darco G-60, powdered, Atlas Chemical Ind., Wilmington, DE 19899). Aliquots were removed, filtered, and analyzed for residual DTC.

<sup>b</sup>A solution (1,000 mL) of a Quadrol-based electroless copper (250 mg/L) was treated with DTC (8 mL, 25 percent solution). After 30 min, cationic polymer (5 mL, 1 mg/mL) was added and the solution was filtered. The filtered solution was treated with various amounts of activated carbon to remove residual DTC. Aliquots were removed, filtered, and analyzed.

<sup>c</sup>A solution (1,000 mL) of a Quadrol-based electroless copper (250 mg/L) was treated with DTC (8 mL, 25 percent solution). After 30 min, the indicated quantities of activated carbon were added. Aliquots were removed and filtered after each addition. Residual DTC concentrations were then determined.

### Case History

A large Midwestern company, using an electroless nickel plating bath containing  $\text{Ni}^{2+}$ , hypophosphite, citrate, and ammonia for plating on plastics, adopted the described DTC treatment for rinsewater. Previously, the firm hauled away 18,000 gal/week for a yearly (1979) cost of \$163,000. Laboratory evaluations of their counterflowed rinsewater (initially 160 to 190 mg/L of nickel) with DTC gave residual Ni concentrations of less than 0.2 mg/L.

The company batch-treats 8,500 gal every two days with DTC (34 gal, 40 percent solution). After 1 hr of contact time, a cationic polymer (17 gal, 1 mg/L) is added and the floc is allowed to settle. The sludge is filtered and the sludge-cake is hauled away. The effluent is tested for nickel (usually about 1 mg/L) and DTC (usually negligible) and is discharged with other process water to meet the nickel discharge limit of less than 0.5 mg/L. Cost of the DTC treatment per year for this company is \$13,500, a saving of \$150,000 in comparison with the former disposal cost.

### Conclusions

DTC effectively precipitates copper and nickel from rinsewater containing complexing or chelating agents. Solutions with metal concentrations greater than 10 mg/L are easily treated over the pH range of 3 to 10. Low concentrations of residual metal allow direct discharge of the effluent.

### Acknowledgments

The authors thank the following companies for supplying concentrated baths used in this study: Chemline Industries, Carson City, NV; Elnic, Inc., Nashville, TN; Enthone, Inc.; New Haven, CT; MacDermid, Inc., Waterbury, CT; Sel-Rex, Nutley, NJ; and Shipley Co., Inc., Marlboro, MA. The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Dept. of Agriculture over other firms or similar products not mentioned.

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