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Recovery of Chromium From Surface-Finishing Wastes

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UNITED STATES DEPARTMENT OF THE INTERIOR

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CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	2
Experimental procedure.....	2
Spent etchants.....	2
Reagents.....	3
General procedure.....	3
Specific procedure.....	3
Sodium benzoate regeneration.....	4
Results.....	4
Recovery procedure.....	6
Conclusions.....	8
References.....	8

ILLUSTRATION

1. Flow diagram for chromium recovery from waste..... 7

TABLES

1. Composition of waste etchants after hexavalent chromium reduction..... 3
2. Analysis of chromium and zinc contained in waste etching solutions and separated products..... 5
3. Distribution of chromium and zinc in the filter cake and filtrate..... 5
4. Copper distribution resulting from the benzoate treatment procedure..... 6
5. Distribution of copper in the filter cake and filtrate..... 6
6. Recovery of chromium oxide from chromium benzoate..... 6

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

° C	degree Celsius	pct	percent
g	gram	pH	negative logarithm of hydrogen ion activity
L	liter	ppm	part per million
<u>M</u>	molar concentration	wt	weight
min	minute		
ml	milliliter		

RECOVERY OF CHROMIUM FROM SURFACE-FINISHING WASTES

By H. O. McDonald¹ and L. C. George²

ABSTRACT

The Bureau of Mines has demonstrated a hydrometallurgical method to separate chromium from other metals in a variety of surface-finishing wastes by precipitation with benzoate ion. The resulting chromium salt may then be converted to the hydroxide, and the benzoate may be recycled. Chromium recoveries of 92 to 100 pct are obtained.

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INTRODUCTION

The objective of this investigation was to reclaim chromium from various surface-finishing liquid wastes. The wastes of primary concern are those produced by electroplating, brass finishing, printed-circuit-board etching, and other surface-treating industries that use chromic acid or sodium dichromate in their surface preparation or other process operations.

Many plating and etching wastes contain considerable amounts of chromium as well as other metal values such as copper and zinc. The usual disposal technology involves the reduction of any remaining Cr^{6+} to Cr^{3+} , followed by the addition of alkali to precipitate chromium and other metallic hydroxides. The resulting sludge is usually landfilled. This method not only creates disposal problems but also wastes potentially valuable resources. Current Environmental Protection Agency (EPA) regulations prohibit sewerage a waste water containing >0.25 ppm Cr^{6+} or >4.6 ppm Cu^{2+} by plants discharging more than 38,000 L/day (9).³ In addition, landfill areas suitable for heavy-metal hydroxide sludge disposal are scarce, and the use of waste contractors is becoming expensive (3).

Prior removal of copper from those wastes would be one step in the

conservation of valuable metals. Cochran and George (1) have shown that copper can be electrowon from spent brass etchants after Cr^{6+} has been reduced to Cr^{3+} . Copper can be cemented out from a variety of waste solutions by the use of zinc (6) or other metals such as iron (2). Copper can be won electrochemically on copper-coated steel spheres in a tumbled-bed system (8). McDonald, Soboroff, and Cochran (5) have shown that copper can be electrowon from spent brass etchants while simultaneously reducing Cr^{6+} to Cr^{3+} . This patented process employs petroleum coke as the anode and as the cathode (7).

The procedure described in this report concerns the selective separation of chromium from solutions in which the copper concentration has been considerably lowered and in which the chromium is in the trivalent state. In the procedure, sodium and/or ammonium benzoate salts are employed to selectively precipitate chromium as an insoluble benzoate salt that can be readily filtered from the other metal values in the waste solution. This report and patent (4) further describes the procedure for regeneration of sodium benzoate for recycle, while producing a high-grade chromium hydroxide product.

EXPERIMENTAL PROCEDURE

SPENT ETCHANTS

Three types of spent etchants were used in this research. Solution A was a typical spent brass etchant that contained Cr^{6+} and Cr^{3+} as well as Cu and Zn. Solutions B and C were spent etchants that had been treated to lower or to

remove the copper content, and the hexavalent chromium had been reduced to the trivalent state. These etchants were originally prepared from a mixture of sodium dichromate and sulfuric acid. The Cr^{6+} that remained in solution A was reduced just prior to the separation trial with solid Na_2SO_3 . The composition of the spent etchants after the hexavalent chromium was reduced is presented in table 1.

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

TABLE 1. - Composition of waste etchants after hexavalent chromium reduction, grams per liter

Solution ¹	Cr ³⁺	Zn ²⁺	Cu ²⁺	SO ₄ ²⁻
A.....	36.9	22.0	44.4	290
B.....	30.5	6.29	4.43	238
C ²	31.6	12.3	Trace	240

¹The pH was about 1.1 to 1.3. Solution A also contained spectrographic traces of Ca, Co, Fe, Mg, Mn, Ni, Pb, Si, and Sn.

²Copper was removed by zinc cementation.

REAGENTS

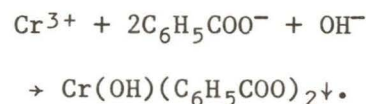
All of the chemicals used in this work were reagent grade except sodium benzoate (laboratory grade) and ammonium benzoate (purified grade), which were used as obtained. All benzoate solutions were prepared using distilled water and were as concentrated as practical to facilitate their use; thus ammonium benzoate was about 1.0M and sodium benzoate was 2.0M.

GENERAL PROCEDURE

The solution containing chromium and other metallic impurities was treated with a reducing agent to insure that all the hexavalent chromium was converted to the trivalent state. The solution was adjusted to a pH of 3 to 4 with ammonium hydroxide, heated to approximately 80° C, and ammonium benzoate was added. The solution was digested for 30 to 60 min and sodium benzoate added. The solution was filtered while still warm, and the other metallic values were washed out of the insoluble chromium benzoate precipitate using hot distilled water.

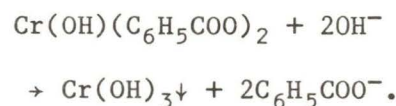
The total benzoate concentration for proper reaction stoichiometry should be at least 2.5 times (but not more than 5 times) the initial Cr³⁺ concentration.

It is also necessary that the ratio of sodium benzoate to ammonium benzoate be close to 2:1, since this ratio of solutions may provide a buffering effect on the system. The most probable reaction for the separation is



The benzoate ion may also combine with other metallic values, but only Cr³⁺, Fe³⁺, and Al³⁺ yield insoluble benzoates (10).⁴

The chromium benzoate product was slurried with a solution of either sodium hydroxide, sodium carbonate, or a mixture of the two, which converts it into chromium hydroxide and sodium benzoate. The apparent reaction is



The sodium benzoate can be filtered from the Cr(OH)₃ for recycle.

SPECIFIC PROCEDURE

A sample of type A spent etchant, 50.0 ml (containing 0.035 mole of Cr), was pipetted into a 2-L beaker containing 100 ml of distilled water. Approximately 3.6 g of Na₂SO₃ was slowly added with stirring to reduce the hexavalent chromium to the trivalent state. Ammonium hydroxide was then added until the pH was between 3 and 4; monitoring of this step was done using pH test papers.

⁴Due to the pH adjustment of 3 to 4, there is the possibility that Sn, Sb, and Bi, if present, will precipitate as hydroxides, oxides, or oxyhalides.

The solution was diluted with distilled water until the volume was doubled. The mixture was stirred, heated to a temperature of approximately 80° C, and 40 ml of 1M (0.040 mole) ammonium benzoate solution was then added with stirring. The mixture was digested for approximately 20 min, and 75 ml of 2M (0.15 mole) sodium benzoate was added. The resulting bluish-green precipitate was stirred and allowed to cool nearly to room temperature before being vacuum filtered. The filter cake was washed at least three times with hot (80° C) distilled water (50- to 100-ml washes). Because of its crystallinity, the bluish-green filter cake was easy to filter and wash. The filtrate was clear when copper was absent and pale blue when copper was present.

SODIUM BENZOATE REGENERATION

The chromium benzoate filter cake can be treated with sodium hydroxide or

sodium carbonate (or a mixture of the two) to form chromium hydroxide and sodium benzoate. This was demonstrated by reacting 10.5 g of chromium benzoate filter cake (containing 11.8 pct Cr) with 30 ml of 1.5M (0.045 mole) sodium carbonate and 50 ml of 1M (0.050 mole) sodium hydroxide (approximately 1.5 to 2 times the stoichiometric quantity needed) in a 400-ml beaker. The mixture was heated until a reaction occurred, which was indicated by the color change from bluish green to grayish green. After complete reaction, the product hydroxide was filtered from the soluble sodium benzoate and washed several times with distilled water. The sodium benzoate solutions were partially evaporated to reclaim the solid, which crystallizes upon cooling.

RESULTS

Table 2 shows some typical results for the separation of chromium from the spent etchants. The letters A, B, and C refer to sample types as given in table 1. Table 3 gives the distribution for the chromium and zinc values in the filter cake and filtrate. Samples 3C and 4C in tables 2 and 3 are typical of the results obtained when recycled sodium benzoate was employed (compared to samples 1C and 2C in which fresh sodium benzoate was employed). Results using recycled sodium benzoate are comparable to those using regular sodium benzoate.

Theoretically, the procedure should remove chromium from a spent etchant, leaving zinc and copper in the filtrate.

However, the copper was only partially separated by the benzoate procedure. It was thus necessary to remove copper from the spent etchants by zinc cementation. Tables 4 and 5 show some typical data for copper contained in the spent etchants.

Sodium benzoate solutions prepared from laboratory-grade sodium benzoate were used in tests 1A, 2A, 3A, 4A, 1C, and 2C; reclaimed sodium benzoate obtained from carbonate treatment of previously used solutions was used in tests 1B, 2B, 3C, and 4C (tables 2 and 3). In the tests using reclaimed sodium benzoate, it was necessary to add sulfuric acid to re-adjust the solution to within the range of pH 3 to 4.

TABLE 2. - Analysis of chromium and zinc contained in waste etching solutions and separated products

Sample ¹	Head		Filter cake		Filtrate	
	g/L	g	pct	Mass balance, g	g/L	Mass balance, g
1A:						
Chromium.....	36.9	1.84	7.24	1.62	0.20	0.14
Zinc.....	22.0	1.10	1.01	.23	1.0	.71
2A:						
Chromium.....	36.9	1.84	8.25	1.65	.10	.07
Zinc.....	22.0	1.10	1.01	.20	1.0	.71
3A:						
Chromium.....	36.9	1.84	8.42	1.77	<.01	<.02
Zinc.....	22.0	1.10	.74	.15	.50	.90
4A:						
Chromium.....	36.9	1.84	8.58	1.73	<.01	<.02
Zinc.....	22.0	1.10	.67	.14	.50	.90
1B:						
Chromium.....	30.5	1.52	12.1	1.37	.046	.046
Zinc.....	6.29	.315	.117	.013	.194	.310
2B:						
Chromium.....	30.5	1.52	12.5	1.48	.048	.077
Zinc.....	6.29	.315	.098	.012	.199	.318
1C:						
Chromium.....	31.6	1.58	15.0	1.58	2.83	<.01
Zinc.....	12.3	.62	1.23	.13	.40	.48
2C:						
Chromium.....	31.6	1.58	15.0	1.53	2.42	<.01
Zinc.....	12.3	.62	1.56	.16	.38	.46
3C:						
Chromium.....	31.6	1.58	16.9	1.58	2.62	<.01
Zinc.....	12.3	.62	1.54	.14	.39	.47
4C:						
Chromium.....	31.6	1.58	16.5	1.54	2.23	<.01
Zinc.....	12.3	.62	1.94	.18	.36	.43

¹The letters A, B, and C refer to sample types as given in table 1.

²Parts per million.

TABLE 3. - Distribution¹ of chromium and zinc in the filter cake and filtrate, weight-percent

Sample ²	Chromium		Zinc	
	Filter cake	Filtrate	Filter cake	Filtrate
1A.....	92.0	8.0	24.5	75.5
2A.....	95.9	4.1	22.0	78.0
3A.....	98.9	1.1	14.3	85.7
4A.....	98.9	1.1	13.5	86.5
1B.....	96.8	3.2	4.1	95.9
2B.....	95.1	4.9	3.6	96.4
1C.....	~100	~0	21.3	78.7
2C.....	~100	~0	25.8	74.2
3C.....	~100	~0	23.0	77.0
4C.....	~100	~0	29.5	70.5

¹Obtained by assuming that the total weight is the sum of the parts contained in the filtrate and filter cake values given in table 2.

²The letters A, B, and C refer to sample types as given in table 1.

TABLE 4. - Copper distribution resulting from the benzoate treatment procedure

Sample ¹	Head		Filter cake		Filtrate	
	g/L	g	pct	Mass balance, g	g/L	Mass balance, g
1.....	44.4	2.22	10.5	2.19	<0.01	<0.09
2.....	44.4	2.22	10.7	2.16	<.01	<.09
3.....	44.4	2.22	15.9	1.50	.37	.68
4.....	4.43	.221	1.21	.134	.053	.085
5.....	4.43	.221	.86	.105	.066	.106

¹Samples 1, 2, and 3 are type A spent etchant; samples 4 and 5 are type B etchant.

TABLE 5. - Distribution¹ of copper in the filter cake and filtrate, weight-percent

Sample	Filter cake	Filtrate	Sample	Filter cake	Filtrate
1 ²	96.1	3.9	4.....	61.2	38.8
2.....	96.0	4.0	5.....	49.8	50.2
3.....	68.8	31.2			

¹Obtained by assuming that the total weight is the sum of the parts contained in the filtrate and filter cake values given in table 4.

²Samples 1, 2, and 3 are type A spent etchant; samples 4 and 5 are type B spent etchant.

RECOVERY PROCEDURE

The chromium recovery procedure outlined under Experimental Procedure is shown schematically in figure 1. The scheme illustrates the recovery of chromium hydroxide from liquid chromium-bearing waste after copper has been removed. Table 6 gives some typical results obtained from the conversion of the

chromium benzoate product to chromium hydroxide (or hydrated chromium oxide). The chromium hydroxide may be a source of chromium for stainless steelmaking operations. Other possible end uses are in leather tanning, chrome green production, and paint pigment production.

TABLE 6. - Recovery of chromium oxide from chromium benzoate

Sample	Benzoate fraction before treatment			Oxide fraction after treatment		
	Product, g	Cr content		Product, g	Cr content	
		pct	g		pct	g
1D....	23.0	6.88	1.58	11.7	14.0	1.63
2D....	23.0	6.76	1.55	13.3	12.1	1.61
3D....	10.5	11.8	1.24	5.09	25.6	1.30
4D....	10.5	11.7	1.23	4.82	26.9	1.30

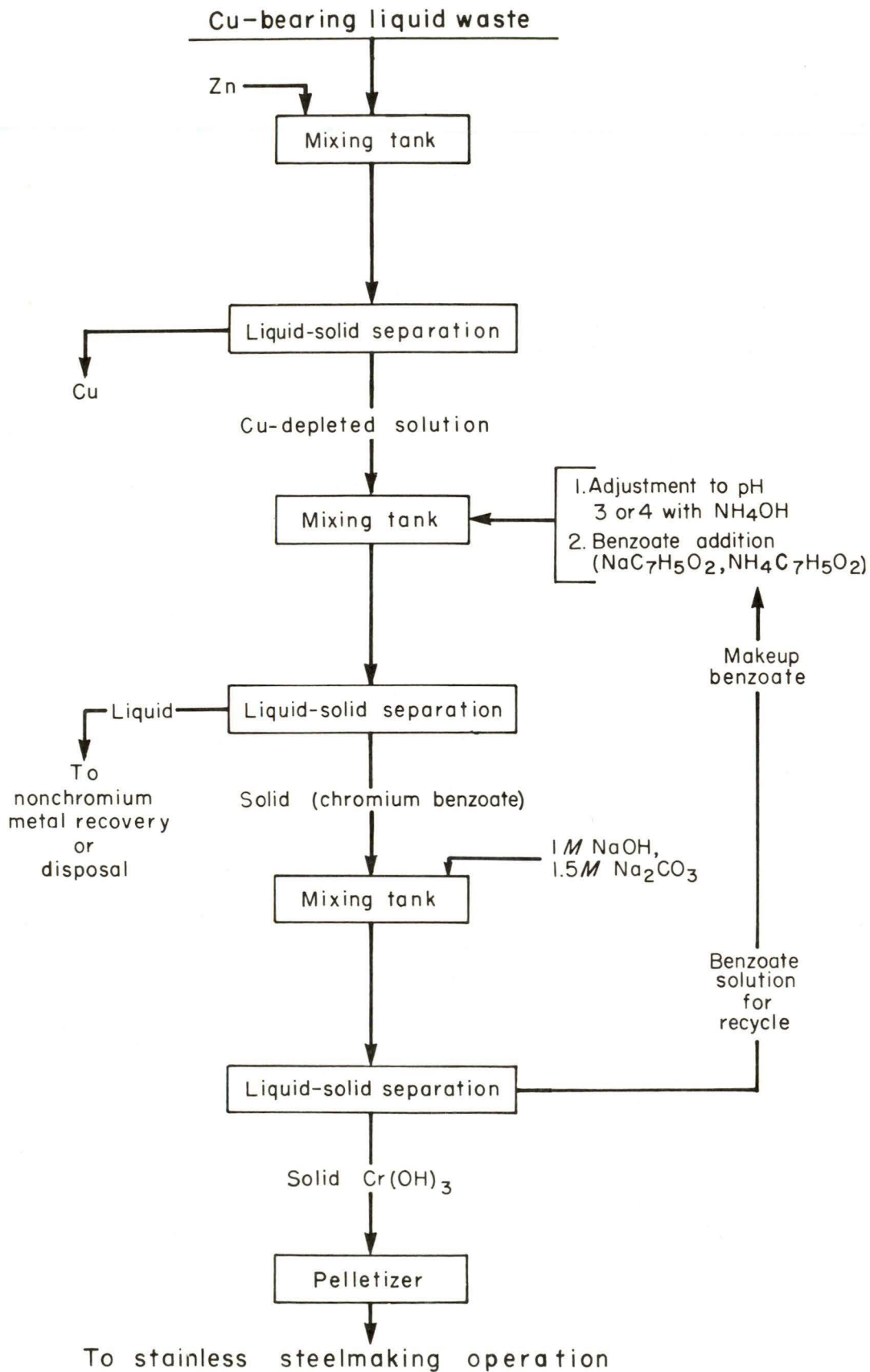


FIGURE 1. - Flow diagram for chromium recovery from waste.

CONCLUSIONS

The results of this investigation show that chromium and zinc can be separated from a variety of wastes. From 92 to 100 pct of the chromium can be recovered as a valuable hydroxide product while leaving 71 to 96 pct of the zinc in solution.

Sodium benzoate, the main precipitation reagent, can be reclaimed for recycle to the separation process. The chromium separation efficiency and effectiveness

was not affected when reclaimed or recycled sodium benzoate was used as the precipitation agent.

Because of its crystalline nature, the chromium benzoate precipitate can be easily filtered and washed, which facilitates separation of chromium from other metallic values. The chromium benzoate is readily converted to the hydroxide, which has several potential end uses.

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