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REMOVAL OF TOXIC METALS FROM METAL FINISHING WASTEWATER BY SOLVENT EXTRACTION



**Industrial Environmental Research Laboratory
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REMOVAL OF TOXIC METALS FROM
METAL FINISHING WASTEWATER BY SOLVENT EXTRACTION

by

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-CI) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is a product of the above efforts. These studies were undertaken to perform a laboratory-scale investigation at Texas Southern University to ascertain the feasibility of utilizing solvent extraction techniques to develop economical methods for removing cadmium, chromium, copper, nickel and zinc ions from metal finishing wastewater.

Such information will be of value both to EPA and to the industry itself. Within EPA's R&D program the information will be used as part of the continuing program to develop and evaluate improved and less costly technology to minimize industrial waste discharges. Besides its direct application to metal-finishing wastes from electroplating, this technology may find application in the control of toxic metals generated by a host of other industries.

For further information concerning this subject the Industrial Pollution Control Division should be contacted.

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ABSTRACT

This report describes a study on the removal of chromium, cadmium, copper, nickel and zinc from metal finishing wastewater using the high molecular weight amine Alamine 336. The study consisted of an initial phase in which the extraction of the metal ions of interest was studied using synthetic solutions. The second phase of the study involved extraction from actual metal finishing wastewater samples.

The results of the study indicated that chromium, cadmium and zinc ions can be extracted simultaneously or selectively using a 100-to-1 wastewater to Alamine-336-xylene solution. The simultaneous extraction procedure appears to have some promise for adoption at the industrial scale. Copper and nickel could not be satisfactorily extracted using this procedure.

Chromium, cadmium and zinc can be stripped from the organic phase with better than 99.5 percent efficiency using 4M NaOH. The regenerated reagent can be recycled and reused without any loss of extraction efficiency. The procedures are reproducible, rapid and relatively simple.

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SECTION I

INTRODUCTION

As a result of our increased awareness in recent years of the importance of protecting and improving the quality of our water, there has been considerable interest in treating polluted waters generated by various industrial processes. Due to this concern, new technology has been developed and is currently available to remove toxic materials from polluted water at reasonable cost for many industrial processes; thereby preventing the pollution of our rivers, streams and municipal sewer systems.

The metal-finishing industry is one in which sufficient technology is not generally available for the economic removal of toxic materials from the wastewater it generates. There are more than 15,000 metal-finishing facilities in the United States. Of these, more than 10,000 can be classified as small shops. Ample technology is available at reasonable costs for huge operations such as large independent plants and captive facilities. The captive facilities are generally subsidiaries of automobile, home appliance, or plumbing manufacturing companies. The technology currently available to remove toxic metals from metal-finishing wastewater requires a capital outlay that poses a financial burden for equipment on the small shops. Since the vast majority of the metal-finishing facilities are in the small shop category and are generally concentrated in industrial areas within cities, they pose a serious pollution problem for municipal sewer systems.

This report describes the use of solvent extraction procedures using high-molecular-weight amines to detoxify metal-finishing wastewater. Solvent extraction methods using high-molecular-weight amines for the removal from aqueous solutions of the toxic metal ions generally found in metal-finishing wastewater, such as cadmium, chromium, copper, nickel, and zinc, have been extensively investigated (1-10). Some extraction processes have been recommended for utilization by various industries for water detoxification (11,13). Several industrial processes utilizing solvent extraction procedures have recently been employed in Europe (14). The Gullspang process utilizes the high-molecular-weight amine Alamine 336 to remove molybdenum, tungsten, chromium, iron, cobalt, and nickel from solid waste such as scrap lathe turnings, and mill shavings. The Soderfors process is used to recover metals and acids from a stainless steel pickling bath. The Valberg process is currently being used to recover zinc from effluent water generated by the manufacture of rayon. All of these processes utilize solvent extraction procedures on an industrial scale.

SECTION 2

CONCLUSIONS

1. Chromium, cadmium and zinc ions can be extracted simultaneously from metal finishing wastewater using a 25 percent Alamine-336-xylene solution. Using a 100 to 1 wastewater to Alamine-336 ratio, 90 percent of the chromium, 98 percent of the cadmium and 83 percent of the zinc can be removed with a single extraction.
2. Chromium, cadmium and zinc ions can be extracted somewhat selectively from metal-finishing wastewater using the 25 percent Alamine-336-xylene solution by carefully controlling the hydrochloric acid concentration. Using the 100 to 1 wastewater to extractant ratio, 89.8 percent of chromium can be extracted without removing any cadmium, zinc, copper or nickel. At higher hydrochloric acid concentrations, cadmium and zinc can be removed successively.
3. Neither copper nor nickel can be efficiently extracted from the metal finishing wastewater using 25 percent Alamine-336-xylene solution.
4. The high molecular weight amines, Alamine-336, Aliquat-336-S, Primene JMT, Primene 81R and Amberlite LA1 proved unsatisfactory as extractants for removing chromium, cadmium, copper, nickel and zinc from metal finishing sludge.

SECTION 3

RECOMMENDATIONS

1. The Alamine-336-xylene system for simultaneously removing chromium, cadmium and zinc merits further investigation. A pilot plant scale study is needed to determine the economic feasibility of the process.
2. Fundamental research needs to be undertaken on the utilization of commercially available high molecular weight amines in the relatively new foam and liquid membrane separational techniques to ascertain the potential of using these new methods for removing toxic metal ions from metal finishing wastewater.

SECTION 4

MATERIALS AND METHODS

Apparatus

A NaI(Tl) well type scintillation counter, 1.75 x 2.0 inches, consisting of a high voltage power supply, a discriminator and a timer scaler was used for gamma counting.

A Perkin Elmer Model 360 atomic absorption spectrophotometer equipped with digital display and a Houston Instruments OmniScribe recorder was used to analyze both phases for the metals. Dry air and acetylene gases were used for the flame.

A Dornmann Model DC-50 Total Organic Carbon Analyzer was used to analyze the aqueous phases for loss of reagent from the organic phases during the extraction processes.

A Sargent Welch Model 119NX digital pH meter was used to make the pH measurements.

High speed motors equipped with glass paddle stirrers were used to mix the phases.

A clinical centrifuge with 50 ml heavy walled glass centrifuge tubes was used for phase separation.

Reagents

Primene JM-T is a mixture of primary amines, principally in the C₁₈₋₂₂ range. Primene 81-R is a mixture of primary amines principally in the C₁₂₋₁₄ range. Amberlite LA-1 (impure n-dodecenyldimethylamine) is a secondary amine. Amberlite LA-1 and the primary amines listed above are available from Rohm and Haas Chemical Company, Philadelphia, Pennsylvania.

Alamine 336 (impure tricaprylmethylammonium chloride) is a quarternary ammonium salt, available from General Mills.

Extractant solutions were made of the high-molecular-weight amines by dissolving the appropriate quantities in xylene.

Aqueous standards (1000 ppm) for atomic absorption spectrophotometric analysis were obtained from Curtin-Matheson Company. The appropriate organo-

metallic compound was purchased from Curtin-Matheson and dissolved in xylene for use as standards for the nonaqueous phase analysis.

All of the aqueous solutions were prepared using deionized water.

Metal Finishing Wastewater

The metal finishing wastewater was obtained from the Dixie Metal Finishing Plant, Houston, Texas. It is a medium sized plant which generates between 40,000 and 50,000 gallons of wastewater a day. The plant is diversified, utilizing many metal finishing procedures. The wastewater from the various processes after appropriate pH adjustments is combined to leave the plant at a single outlet and then treated by an ion exchange system.

Samples of the untreated wastewater were collected for investigation. They contained all of the metallic ions of interest; cadmium, chromium, copper, nickel and zinc. Their composition varied widely depending on when the sample was taken. This apparently depended on the metal finishing process which was taking place at the time of the sampling operation. Generally, the wastewater content was; chromium 12 to 60 ppm, cadmium 2 to 8 ppm, copper 0.5 to 5 ppm, zinc 2 to 14 ppm, and nickel 2.2 to 2.5 ppm. The pH usually ranged between 4 to 5. The water was somewhat turbid and a brown gelatinous sludge formed in the bottom of the vessel on settling.

Sludge Samples

Sludge Samples were obtained through the U.S. EPA from a job plating company in Iowa.

Method

Screening studies were performed on synthetic solutions of cadmium, chromium, copper, nickel and zinc using Primene 81-R, Amberlite LA-1, Alamine 336 and Aliquat 336-S as extractants. In a typical screening study, 5 ml of a 5 percent solution of the high-molecular-weight amine in xylene was placed in a 50 ml heavy wall centrifuge tube with an equal volume of 10 ppm metal ion solution. The phases were mixed for 3 minutes using a small motor stirrer equipped with a glass paddle. The phases were separated using a clinical centrifuge. After phase separation, each was analyzed for its metal content using an atomic absorption spectrophotometer. In some cases the cadmium and zinc were analyzed using a gamma scintillation counter with cadmium-109 and zinc-65 as tracers.

SECTION 5

RESULTS AND DISCUSSION

Extraction of Chromium

The screening studies indicated that Alamine 336 and Aliquat 336-S showed promise as satisfactory extractants for chromium. Generally, Alamine was effective in acid media and Aliquat 336-S effective in slightly alkaline solution. Both removed more than 99 percent of the metal with a single extraction when carried out under optimum conditions. Alamine 336 was chosen for further investigations, since the pH of the wastewater was usually between 4 and 5. In addition, raising the pH will cause some of the metals to precipitate out as the hydrous oxides and cause unwanted sludge.

Attempts were initially made to extract the chromium from the wastewater as received from the plants by vigorously shaking the water and analyzing rapidly. This proved unsuccessful due to the clogging of the aspiration system of the spectrophotometer and the frequent necessity for cleaning the burner head. Clogging problems were also encountered when the mother liquor from settled wastewater was used. Filtered wastewater samples were used in all subsequent investigations.

The pH was generally in the range of 4 to 5 when received from the plant. If the pH was higher than 5, it was lowered prior to filtration to prevent loss of the metals as hydrous oxides.

A high aqueous phase to organic phase ratio is desirable in order to concentrate the chromium into a small volume. Ratios up to 100 to 1 proved satisfactory. Higher ratios increased settling time due to formation of emulsions. The high aqueous to organic phase ratios caused a need for a higher Alamine 336 concentration than was used in the screening studies. The 5 percent Alamine 336 solution did remove the chromium efficiently with a single extraction, but on standing, the solutions turned green, and the chromium content of the aqueous phase increased. This situation did not arise if a 25 percent reagent solution is used.

At a chloride ion concentration of $2 \times 10^{-3}M$ (as hydrochloric acid) or higher, 90 percent of the chromium can be removed from the wastewater. The pH of the $2 \times 10^{-3}M$ chloride solution varied from about 2.5 to 3.0 depending on the initial pH and composition of the samples. Some waste water samples showed considerable buffering actions presumably due to phosphates and/or borates used in the plating operations. Improving the extraction efficiency substantially above 90 percent was difficult. Increasing the

Alamine 336 concentration or reducing the aqueous to organic phase ratio did not materially improve the degree of extraction. Carrying out a second extraction on the raffinate from the first extraction removed only one to two percent of the remaining chromium. It appears that only about 90 percent of the chromium is in the hexavalent state under the conditions of the extraction. The remaining 8 to 10 percent appears as trivalent chromium which cannot be extracted into the organic phase. In the screening studies in which K_2CrO_4 was used as the source of chromium, 99 percent of the chromium was removed under the same conditions. The Chromium III was oxidized to chromium VI by acidifying the wastewater, adding potassium permanganate and heating. On extracting the oxidized wastewater, more than 99 percent of the chromium was removed.

Further studies indicated that chromium can be extracted selectively (about 90 percent of the chromium) by controlling the chloride ion concentration. At a chloride ion concentration of $2 \times 10^{-3}M$, no detectable quantities of cadmium, copper, nickel, or zinc are extracted, when the extractions are carried out with 25 percent Alamine 336 in an aqueous to organic phase ratio of 100 to 1.

Extraction of Cadmium

Screening studies indicated that Primene JM-T, Alamine 336, Aliquat 336-S can remove more than 95 percent of the cadmium from synthetic solutions with a single extraction. Of the three reagents, Alamine 336 appeared to be superior and was chosen for further investigations. If sufficient hydrochloric acid is added to the metal finishing wastewater sample (after removing the chromium) to make the solution 0.03M in chloride ions, more than 90 percent of the cadmium can be removed from the solution. This extraction is again carried out using 25 percent Alamine 336 and an aqueous phase to organic phase ratio of 100 to 1. Unfortunately, about one percent chromium and about 8 percent zinc is also extracted. No copper or nickel was extracted under these conditions.

Extraction of Zinc

If the wastewater raffinate after removal of both chromium and cadmium is further acidified with hydrochloric acid such that the chloride concentration is 0.4M, approximately 85 percent of the zinc is removed from the solution. The extractions were again carried out using 25 percent Alamine 336-xylene solutions and aqueous to organic phase ratio of 100 to 1. A single extraction was used as in the other studies.

Extraction of Copper and Nickel

In the screening phase of the study, copper and nickel showed some promise of being extracted with Aliquat 336-S. The extraction efficiencies were low except in alkaline solutions. No detectable quantities of copper or nickel were extracted with Alamine 336 under the optimum conditions described for chromium, cadmium, and zinc.

Selective Extraction of Chromium, Cadmium and Zinc

In a typical laboratory extraction, the metal finishing wastewater was filtered through a no. 1 fluted filter paper. To one liter of the filtered solution was added 5.0 ml of 0.4M hydrochloric acid. A 25 ml sample of the wastewater was removed and analyzed for chromium, copper, cadmium, nickel and zinc with an atomic absorption spectrophotometer. To the remaining solution was added 10.0 ml of 25 percent Alamine 336-xylene solution. The phases were then stirred in a 2 liter beaker for three minutes using a motor driven stirrer. The resulting mixture was transferred to a liter separatory funnel and allowed to settle for twenty minutes. The phases were then separated. A 25 ml sample of the aqueous phase was analyzed for cadmium, chromium, copper, nickel and zinc.

To the raffinate from the first extraction was added 25 ml of concentrated hydrochloric acid and 10.0 ml of 25 percent Alamine 336-xylene solution. The resulting mixture was again extracted and its raffinate analyzed for the five metals.

To the remaining raffinate from the second extraction was added 30 ml of concentrated hydrochloric acid and 10.0 ml of 25 percent Alamine 336-xylene solution. The resulting mixture was extracted and its raffinate analyzed for cadmium, chromium, copper, nickel and zinc. The results from eight analyses are shown in Table 1. No copper or nickel was extracted in either of the extractions.

Simultaneous Extraction of Chromium, Cadmium and Zinc

To a liter of the filtered metal finishing wastewater was added 33 ml of concentrated hydrochloric acid. Twenty-five ml of the solution were removed and analyzed for chromium, cadmium, zinc, copper and nickel. To the remaining solution was added 10.0 ml of 25 percent Alamine 336-xylene solution. The phases were mixed using a magnetic stirrer for three minutes. The mixture was then transferred to a one liter separatory funnel and allowed to settle for ten minutes. The phases were then separated and the aqueous phase again analyzed for the five metals.

To the raffinate from the first extraction was added another 10.0 ml of the 25 percent Alamine 336-xylene in order to carry out a second extraction. The results of the ten analyses of the metal finishing wastewater of varying composition are shown in Table 2. No copper or nickel was extracted in either extraction.

Reagent Loss

A study was carried out to determine if any Alamine 336-xylene solution would dissolve in the aqueous phase during the extraction processes. A Dohrmann Model DC-50 Total Organic Analyzer was used in the investigation. The total organic carbon did increase during the extraction process. Generally, the TOC content increased approximately 50 ppm per extraction. The extractions were carried out using the usual 100 to 1 aqueous to organic

TABLE 1. SELECTIVE EXTRACTION OF CHROMIUM, CADMIUM AND ZINC

	CHROMIUM		CADMIUM		ZINC	
	Mean % Extd.	Std. Dev.	Mean % Extd.	Std. Dev.	Mean % Extd.	Std. Dev.
First Extraction 0.002M Chloride	88.6	4.0	0.0	0.0	0.0	0.0
Second Extraction 0.03M Chloride	0.65	1.09	94.1	1.65	8.1	2.1
Third Extraction 0.4M Chloride	0.55	0.87	4.8	1.3	80.9	3.5
Total Metal Extracted	89.8		98.9		89.0	

Composition of Wastewaters: Cr - 10.0 to 56.8 ppm

Cd - 4.1 to 5.9 ppm

Zn - 5.2 to 9.2 ppm

Cu - 0.3 to 0.5 ppm

Ni - 0.4 to 0.5 ppm

TABLE 2. SIMULTANEOUS EXTRACTION OF CHROMIUM, CADMIUM AND ZINC

	CHROMIUM		CADMIUM		ZINC	
	Mean % Extd.	Std. Dev.	Mean % Extd.	Std. Dev.	Mean % Extd.	Std. Dev.
First Extraction	90.6	1.2	98.0	0.11	83.3	0.11
Second Extraction	0.0	0.0	1.4	0.86	15.4	1.8
Total Metal Extracted	90.6		99.4		98.7	

Composition of Wastewaters: Cr - 8.0 to 9.0 ppm

Cd - 3.7 to 4.0 ppm

Zn - 4.8 to 5.2 ppm

Cu - 0.3 to 0.5 ppm

Ni - 0.4 to 0.5 ppm

phase ratio and 25 percent Alamine 336-xylene solution.

Stripping and Recycling

After extracting the toxic metal ions from the metal finishing wastewater into the organic phase it is desirable to recover the metal regenerating the Alamine 336-xylene solvent in order that it may be recycled.

This process generally called stripping is very important in developing economic cyclic industrial processes. A series of strippants were investigated including sulfuric acid, ethylenediamine, EDTA and sodium hydroxide. Of these, sodium hydroxide proved to be most effective.

In a typical stripping experiment, to 10 ml of the organic phase (Alamine 336-xylene) containing 3 to 5 mg/ml chromium, 0.6 to 0.8 mg/ml cadmium, and 1.0 to 1.5 mg/ml zinc is added 3.0 ml of 4.0M sodium hydroxide solution. The phases are mixed for three minutes in a 50 ml beaker using a magnetic stirrer. The mixture is allowed to settle for 15 minutes for phase separation. The organic phase was then analyzed for chromium, cadmium and zinc. Stripping studies were carried out on ten solutions. The results (Table 3) show that more than 99.5 percent of the chromium, cadmium and zinc were removed from the organic phase in a single stripping operation.

The regenerated Alamine 336-xylene solution was used again to extract the metals from the wastewater without loss of any efficiency. Fifteen cycles were carried out using the same solvent without loss of efficiency. No larger number of cycles were investigated.

Studies on Sludge

The sludge samples were pale aquamarine in color indicating the presence of copper or chromium. It was quite thick and had many lumps. It had to be stirred for several hours to get a homogeneous mixture.

The sludge was essentially insoluble under ordinary conditions. About 70 percent dissolved on boiling with concentrated nitric acid, concentrated hydrochloric acid or aqua regia. The chromium was not extracted with Alamine 336-xylene solution. Apparently it was in +3 oxidation state. After oxidizing the sludge with potassium permanganate it could be extracted. Use of potassium permanganate is cost prohibitive, moreover, it is pollutant itself. Attempts to remove cadmium and zinc were also unsuccessful. Thus, detailed studies on sludge were discontinued.

Chemical Reactions and Mechanism

The mechanism for the extraction of cadmium and zinc from the metal finishing wastewater is:

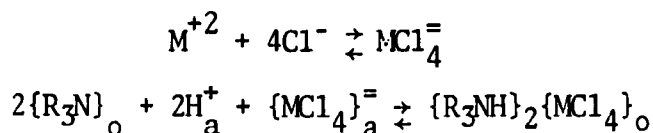


TABLE 3. STRIPPING STUDIES

	Mean % Stripped	Std. Dev.
1. Chromium	99.86	0.10
2. Cadmium	99.53	0.18
3. Zinc	99.95	0.03

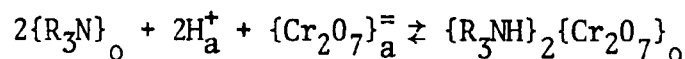
Stripping Solution: Cr - 3 to 5 mg/ml

Cd - 0.6 to 0.8 mg/ml

Zn - 1 to 1.5 mg/ml

Strippant - 4.0M NaOH

The mechanism for removing the chromium is:



Where R_3N = Alamine 336

M = Cd or Zn

o = organic phase

a = aqueous phase

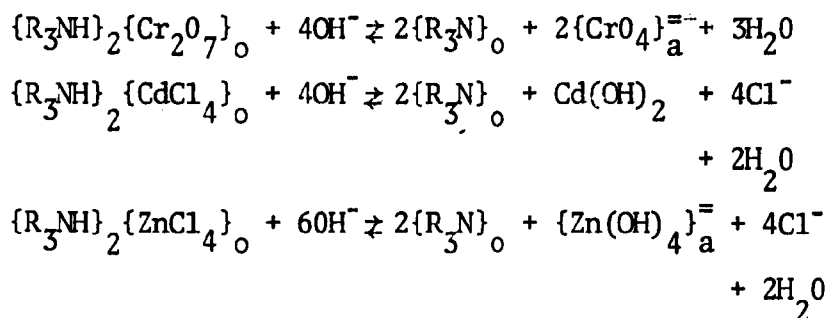
The complexes formed by cadmium, zinc and chromium with Alamine 336 are soluble in common organic solvents such as xylene, benzene and kerosene, etc.

The extraction parameters associated with the selective extraction of chromium, cadmium and zinc are somewhat critical. Chromium can generally be removed without contamination by cadmium and zinc. The chromium could be reclaimed and returned to the plating bath. There were some metal finishing samples in which each of the three metals could be extracted selectively without any contamination of the other two metals. A general procedure with industrial potential appears unlikely for the selective extraction of cadmium and zinc due to the great variation in wastewater.

The simultaneous extraction of all three metals appears promising if a second extraction is carried out.

The metals can be easily stripped quantitatively from the Alamine 336-xylene with 4 M sodium hydroxide. The amine solvent can be regenerated and reused repeatedly, making the process attractive for industrial utilization.

The reaction mechanisms for stripping with sodium hydroxide follows:



The procedures discussed here merit further study. Pilot plant studies should be carried out on the processes, particularly the simultaneous extraction method. It shows promise for utilization by small metal finishing plants.

REFERENCES

1. Pribil, R. and V. Vesely, The Extraction of Cadmium and Zinc and Their Complexometric Determination in the Presence of Other Elements, *Collect. Czech. Chem. Commun.*, 37, 13-21, 1972.
2. Mahlman, H., G.W. Leddicotte and F.L. Moore, Separation of Cobalt and Zinc by Liquid-Liquid Extraction, *Anal. Chem.*, 26, 1939-1941, 1954.
3. Singh, O.V. and S.N. Tandon, Extraction of Cadmium as Chloride by High Molecular Weight and Quaternary Ammonium Salts, *J. Inorg. Nucl. Chem.*, 37, 609-611, 1975.
4. Florence, T. and J. Farrar, Liquid-Liquid Extraction of Nickel with Long-Chain Amines from Aqueous and Nonaqueous Halide Media, *Anal. Chem.*, 40, 1200-1206, 1968.
5. McDonald, C.W. and T. Rhodes, Liquid-Liquid Extraction of Zinc with Aliquat 336-S-I from Aqueous Iodide Solutions, *Anal. Chem.*, 46, 300-301, 1974.
6. Maeck, W.J. et al, Extraction of the Elements as Quaternary Amine Complexes, *Anal. Chem.*, 33, 1775-1780, 1961.
7. McDonald, C.W. and F.L. Moore, Liquid-Liquid Extraction of Cadmium with High Molecular Weight Amines from Iodide Solutions, *Anal. Chem.*, 45, 983-985, 1973.
8. McDonald C.W. and T. Rhodes, Liquid-Liquid Extraction of Zinc with Aliquat 336-S-Br from Aqueous Bromide Solutions, *Separ. Sci.*, 9, 441-446, 1974.
9. McDonald, C.W. and T.S. Lin, Solvent Extraction Studies of Zinc and Cadmium with Aliquat 336-S in Aqueous Chloride Solutions, *Separ. Sci.*, 10, 499-505, 1975.
10. McDonald, C.W. and G.H. Pahlavan, Liquid-Liquid Extraction of Cadmium with Alamine 336 from Aqueous Chloride and Bromide Media, *Separ. Sci.*, 12, 271-279, 1977.
11. Moore, F.L., Liquid-Liquid Extraction of Zinc with High Molecular Weight Amines from Alkaline Cyanide Solutions, *Separ. Sci.*, 10, 489-497, 1975.

12. McDonald, C.W. and R. Bajwa, Removal of Toxic Metal Ions from Metal Finishing Wastewater by Solvent Extraction, Separ. Sci., 12, 435-445, 1977.
13. Reed, A.K., An Investigation of Techniques for the Removal of Chromium and Cyanide from Electroplating Wastes, Battelle Report # G-8925-2, 40-49, July 1970.
14. Reinhardt, H., Solvent Extraction for Recovery of Metal Waste, Chem. and Ind., 210-213, March, 1975.

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