

Permit By Rule for Treatment of Aqueous Wastes Containing Cyanides
Department of Toxic Substances Control Regulatory Number: R-96-48
INITIAL STATEMENT OF REASONS
Office of Administrative Law Notice File Number: Z-07-0605-12

EFFORT TO AVOID DUPLICATION OR CONFLICTS WITH FEDERAL REGULATIONS

Under Federal law, most onsite treatment of aqueous wastes containing cyanides is exempt from the authorization requirement and all hazardous waste regulatory standards (as wastewater treatment units), or is regulated under only the generator standards as treatment in tanks and containers within the allowed generator accumulation time. The federal exemptions for wastewater treatment units are found in 40 Code of Federal Regulations sections 264.1, 265.1, and 270.1. The permit exemption for treatment in generator accumulation tanks and containers was set forth in the Federal Register Notice establishing the Federal small quantity generator rules, (51 Fed. Reg. 10174 (Mar. 24, 1986).) These operations cannot be exempted under State regulations because Health and Safety Code section 25201 requires a permit for all but specified hazardous waste treatment. The federal exemption cannot be duplicated within the mandate of Health and Safety Code section 25201.

The proposed regulations do not conflict with federal requirements because the Resource Conservation and Recovery Act (RCRA) of 1976, as amended (42 U.S.C. § 6901 et seq.) allows states to be more stringent and/or broader in scope, but not less stringent. These regulations are both more stringent as regards treatment of cyanide containing wastewaters and broader in scope.

STUDIES RELIED ON

- a. The California hazardous materials incident reporting database archive:
<http://rimsinland.oes.ca.gov/rims.nsf/RIMS%20Archive%20Databases?OpenPage>
- b. The United States Environmental Protection Agency (U.S. EPA) incident reporting system.
- c. Google searches of the Internet for:
 - Cyanide release
 - Cyanide incident
 - Cyanide poisoning
 - Cyanide spill
 - Hydrogen cyanide release
- d. Capsule Report. Managing Cyanide in Metal Finishing December 2000, EPA/625/R-99/009

Permit By Rule for Treatment of Aqueous Wastes Containing Cyanides

- e. Permit by Rule for Treatment of Aqueous Wastes Containing Cyanides, Fiscal and Economic Analysis. Department of Toxic Substances Control. January 30, 2006.

ALTERNATIVES CONSIDERED

Chosen alternatives: Authorize the following types of cyanide treatment under a Permit by Rule (PBR):

- a. Authorize treatment of cyanide-containing wastewaters using oxidation by addition of hypochlorite or chlorine, oxidation by addition of peroxide or ozone, with or without the use of ultraviolet light, alkaline chlorination, electrochemical oxidation, and ion exchange.
- b. Authorize treatment of high concentration process solutions by bleeding into the rinsewater tanks.
- c. Authorize metals recovery from process solutions by electrowinning prior to offsite recycling or disposal.
- d. Authorize treatment of cyanide-containing wastes generated by regeneration of ion exchange resins used to recycle water at facilities that have eliminated industrial discharge of wastewaters (“zero discharge” facilities) using oxidation by addition of hypochlorite or chlorine, oxidation by addition of peroxide or ozone, with or without the use of ultraviolet light, alkaline chlorination, electrochemical oxidation, and ion exchange.

Alternatives considered:

Alternative 1: Do nothing. This alternative would require that businesses treating cyanide containing wastewaters onsite obtain a standardized hazardous waste facility permit or ship all cyanide containing wastewaters to offsite hazardous waste facilities for treatment and/or disposal.

This alternative was rejected because the standards and process for obtaining a standardized permit are not commensurate with the risks posed by onsite treatment of aqueous wastes with relatively low levels of cyanides.

Alternative 2: Authorize onsite cyanide wastewater treatment under a grant of conditional exemption or a grant of conditional authorization.

Permit By Rule for Treatment of Aqueous Wastes Containing Cyanides

This alternative was rejected because Department of Toxic Substances Control (DTSC) cannot add these wastestreams and/or treatment processes to the list of eligible wastestreams and treatment processes that can be authorized under conditional exemption or conditional authorization.

Alternative 3: Adopt the federal exemption for wastewater treatment units.

This alternative was rejected because Health and Safety Code section 25201 requires authorization for treatment of hazardous wastes unless that specific treatment activity is otherwise exempted from the authorization requirement. Therefore, DTSC cannot adopt the federal wastewater treatment unit exemption into State law.

Alternative 4: Authorize treatment of wastewaters containing cyanides and cyanide-containing process solutions diluted to similar concentrations under a PBR. This alternative was chosen because it is the most suitable grant of authorization for onsite treatment that is more complex than that allowed under a grant of conditional exemption or a grant of conditional authorization.

Alternative 5: Authorize direct treatment of all cyanide containing wastes under a PBR, including high concentration process solutions, in addition to wastewaters.

This alternative was rejected because direct treatment of the high concentration wastes like process solutions pose a much higher risk of hydrogen cyanide gas generation at levels that could pose a significant risk.

Alternative 6: Limit this grant of authorization to only 1500 parts per million (ppm) total cyanide. (Some calculations such as the recently withdrawn U.S. EPA guidance on reactivity have posited that the danger of hydrogen cyanide generation is minimal below this concentration.)

This alternative was rejected because it would not promote pollution prevention by authorizing treatment of higher concentration wastewaters generated by businesses that have implemented effective pollution prevention programs. Rather than promoting pollution prevention, this alternative could potentially increase water usage, wastewater flow to publicly owned treatment works (POTWs), and the mass loading of hazardous constituents in the discharges from the businesses to the POTWs.

Alternative 7: Allow treatment of high concentration process solutions by bleeding into the rinsewater tanks.

This alternative was chosen to allow onsite treatment of process solutions and to avoid

on-road transportation of highly toxic and reactive spent process solutions.

Alternative 8: Allow rinsing of housekeeping wastes into the rinse tanks followed by treatment in the treatment system. Housekeeping wastes would include:

- Filter units. The filters are used to remove insoluble particles of metal carbonates that form from reaction of atmospheric carbon dioxide with dissolved metals. When the filters are fully loaded, they have very high concentrations of cyanide. Authorizing rinsing of filters was rejected due to the very high cyanide and metal concentrations that could contribute to increased metal and cyanide loading in the facility's sewer discharge. Note that rinsing would not render the filters non-hazardous; they would require management as hazardous wastes even after rinsing.
- Pumps, hoses, and containers used to transfer process solutions. These devices will retain residual process solutions after transferring process solutions in or out of process tanks. They must be rinsed prior to use for the next solution both to avoid cross-contaminating solutions and to avoid combination of incompatibles (like cyanide combining with acids). Because the equipment must be rinsed and there is a high degree of dilution inherent in rinsing it, DTSC is proposing to authorize treatment of cyanide solutions rinsed from pumps, hoses, and containers used to transfer process solutions.
- Anode bags. Metal plated out of solution is often replenished by dissolving soluble anodes during the electroplating process. To avoid contaminating plated surfaces with particulate released from the anodes, they are used inside tightly woven synthetic bags. When the bags are plugged with particulate or damaged, they must be replaced. DTSC rejected authorizing rinsing and subsequent treatment of anode bags for the same reasons as filter units.
- Cleaned up spills. Spills of process solutions produce both recovered liquid wastes and liquid filled absorbent materials such as spill pillows, absorbent berms, and contaminated "kitty litter" type materials. All of these wastes will be high concentration. DTSC rejected authorizing treatment of spill cleanup materials for the same reasons as for filter units.

DTSC is proposing authorizing treatment of only one of these wastestreams under the PBR. The regulations would allow treatment of cyanide containing wastewaters generated by rinsing pumps, hoses, and other transfer equipment into a rinse tank. This equipment is rinsed out to prevent cross contamination of process solutions and combination of incompatibles, then reused. The regulations would not authorize rinsing of other housekeeping wastes that are then disposed.

Alternative 9: Authorize metals recovery from waste process solutions by electrowinning prior to offsite recycling or disposal, or further treatment under this PBR.

Many metals can be plated from solution onto a polished cathode such as a thin piece of stainless steel. When the plated cathode is bent, the plated metal spalls (flakes) off. This process is called “electrowinning” and is often used to recover precious metals from waste process solutions prior to disposal. Electrowinning is identical to the electroplating process both in the physical process and the hazards posed. Electrowinning does not offer any significant hazards beyond the actual production process. Note that some cyanide is incidentally destroyed by electrochemical oxidation during electroplating and electrowinning. DTSC proposes to authorize electrowinning under this PBR.

Alternative 10: Authorize treatment of aqueous wastes generated by regeneration of demineralizer (ion exchange) columns that were used for recycling of wastewaters at facilities that have eliminated the discharge of wastewaters (other than sanitary discharges.)

Chosen alternatives: DTSC is proposing to adopt regulations implementing alternatives 4, 7, 9, and 10, and the pumps and hoses portion of alternative 8.

GENERAL STATEMENT OF REASONS

Cyanide Toxicity: Hazardous wastes containing cyanides are generally identified as “toxic” hazardous wastes. They are hazardous due to their oral toxicity and due to their toxicity to aquatic organisms. Additionally, most of the wastewaters addressed by this rulemaking contain various metals dissolved in the solution that add toxicity and can often identify these wastes as hazardous wastes independent of cyanides.

Cyanides in aqueous solution are often bound up in “complexes” where the cyanide ions are bonded to metals in solution with varying degrees of tenacity. Some metal-cyanide complexes are bonded very tightly greatly reducing the toxicity of the cyanides in those solutions. Others are bound very loosely having little effect on the toxicity of the solution. Alkali metals like sodium and potassium do not form complexes with cyanides in solution and do not affect the toxicity. All solutions with cyanides also produce amounts of hydrogen cyanide, a compound which is a product of the complex equilibria found in aqueous cyanide solutions. Hydrogen cyanide can be emitted as a gas from cyanide solutions. A sampling of cyanide toxicity follows:

Compound	Formula	Physical State	LD₅₀
Hydrogen Cyanide	HCN	Gas	1 mg/kg (human)
Potassium Cyanide	KCN	Solid	2.85 mg/kg (human)
Sodium cyanide	NaCN	Solid	2.85 mg/Kg (human)

Compound	Formula	Physical State	LD₅₀
Potassium Ferricyanide	K ₂ [Fe(CN ₄)]	Solid	1600 mg/kg (rat)

Human health effects from cyanide can be caused by two different types of exposure. First and most important, inhalation of hydrogen cyanide gas evolved from cyanide solutions can affect workers and others in the vicinity of cyanide solutions. A second pathway is direct ingestion of the solutions. This type of exposure would result from releases of cyanide solutions from leaking tanks or containers or from catastrophic failure of a tank system or a transportation vehicle. The risk of hydrogen cyanide release is addressed both by DTSC's limitations on the types of waste treated and by other laws that address such releases. Actual chemical treatment (cyanide removal or destruction) authorized by this PBR would be limited to dilute wastestreams and more concentrated wastestreams diluted to wastewater concentrations rather than direct treatment of concentrated process solutions and other non-aqueous wastes.

Note, however, that concentrated process solutions can be treated under this proposal by metal recovery, a process identical to the business's normal electroplating operations.

Additionally, businesses must control worker exposure to hydrogen cyanide ensuring that exposure to the workers, the closest and most effected receptors of any released hydrogen cyanide, is kept to a safe level (required by both the State and Federal Occupational Safety and Health Administrations' regulations.) The California Occupational Safety and Health Administration (Cal/OSHA) regulations are found in California Code of Regulations, title 8, division 1, chapters 3.2 and 4.

Further protection is afforded by the California Accidental Release Prevention (Cal ARP) Program which requires all businesses with significant quantities of cyanide on hand (>100 pounds at any one time) to conduct a safety analysis including offsite consequence analysis and adoption of mitigation measures. The Cal ARP Program is found in California Code of Regulations, title 19, division 2, chapter 4.5.

The general tank and container standards address the second pathway by ensuring that tanks and containers are sound and capable of holding the solutions and are managed properly. Ingestion of cyanides is prevented by the general tank and container standards because these standards are crafted to preclude and/or contain leakage of cyanides to groundwater or surface waters that would later be extracted and used as drinking water.

Wastestream s: There are several types of cyanide-containing waste generated by the State's businesses and are generated by various State industries. Use of these

solutions generates rinsewaters containing cyanides, referred to herein as “wastewaters”. These wastewaters can be treated onsite to first destroy the cyanides and then remove other hazards such as heavy metals. Wastewaters are generally relatively dilute, but are generated in large volumes on a daily basis. The best management practices for these wastes are to treat them onsite, discharge non-hazardous water, and properly manage any sludges left after treatment.

There are high concentration wastes including spent plating baths, heat treating wastes, precious metals stripping solutions, and others. These wastes have concentrations of cyanide measured in whole number percents. Direct treatment of these concentrated wastes by cyanide destruction is not addressed in this project. The more concentrated wastes may be treated by dilution prior to cyanide destruction or by electrowinning to recover metal content.

Note that concentrations of hazardous constituents in wastewaters is properly measured for the purposes of the Hazardous Waste Control Law at the exit from the generating process (i.e.: the rinse tank), rather than at the actual treatment tank where combination with other wastewaters has reduced the concentration. A discussion of cyanides in industry, types of industries, and the particular hazards of cyanides follows.

Wastestream A

Cyanide-Containing Aqueous Waste (wastewaters): This project addresses treatment of wastewaters containing cyanide. Wastewaters are generated by rinsing of objects removed from higher concentration plating, stripping, and other “process” tanks. Because the wastewaters rinse off only the traces of the process solutions that remain on the surface of the objects removed from the process baths, the cyanide concentrations are much lower and are typically measured in the parts per million (ppm) range. The Surface Treatment Association has told DTSC that the maximum cyanide concentrations in rinsewaters at plating facilities that practice best management practices for wastewater range from 3000 ppm to 5000 ppm. Other facilities with less rigorous wastewater management practices will produce greater volumes of rinsewater with lower cyanide concentrations.

The Surface Treatment Association developed the concentration data in 1998 in response to an earlier proposal for a cyanide wastewater PBR that proposed limiting treatment to wastewaters with 1000 ppm total cyanide or less. Members of the association reported wastewater concentrations up to 5000 ppm with the most sophisticated shops reporting the highest concentrations due to better rinse water management practices. Because the poll was verbal, no written documentation exists.

Wastestream B

Cyanide-Containing Aqueous Waste (wastewaters): Cyanide containing wastes from the

regeneration of ion exchange resins used for recycling water at facilities with that have eliminated the discharge of wastewater (“zero discharge” facilities). Zero discharge facilities recycle all process waters used. They are the best facilities from an environmental point of view because they make maximum use of water and discharge no process wastes to the sewer. It is important to promote such water resource conservation and protection of the waters of the State by allowing treatment of the wastes from regenerating the ion exchange columns used to recycle the facility’s wastewaters.

This wastestream is generated when zero discharge facilities regenerate ion exchange columns used to purify water for reuse. All the contaminants in the water adhere to the ion exchange columns; when the columns are saturated with contaminants, they are flushed with acid and alkali to remove the contaminants and return the columns to service. The acid and alkali are combined to form a relatively neutral aqueous solution (the “regenerate”) that contains the contaminants removed from the columns. This resulting wastestream would be treated to destroy cyanides under the PBR.

Currently, most zero discharge facilities put regenerate into drums for shipment to an offsite treatment facility. Because all existing treatment activities at zero discharge facilities are part of the water recycling process, they are exempted from the authorization requirement by Health and Safety Code section 25143.2. DTSC is including treatment of this wastestream to encourage the maximum number of facilities to convert to zero discharge status by allowing the facilities to choose from a wide range of management options for the only wastestream that cannot be recycled onsite.

Wastestream C

Cyanide-Containing Aqueous Waste (wastewaters): Rinsate from pumps, hoses, and containers used to transfer cyanide containing materials into and out of tanks and other holding devices. The equipment must be rinsed prior to reuse to avoid cross-contamination of process solutions and potential reactions between incompatible materials. Rinsing the equipment produces lower concentration cyanide solutions that would be added to the rinse tanks or the equipment would be rinsed directly into the rinse tanks to be treated with rinsewaters.

Note that rinsing materials directly into a production tank where they would be used in production work would be exempt from the authorization requirement under Health and Safety Code section 25143.2.

Wastestream D

Spent Process Solutions treated by electrowinning: These are high concentration wastes including spent plating baths, heat treating wastes, precious metals stripping solutions, and others. These wastes have concentrations of cyanide measured in whole

number percents.

Electrowinning is essentially electroplating onto a polished metal surface rather than onto a product for sale. Electrowinning is used to recover metals from solutions prior to shipment to a recycling or treatment facility. It is mostly used to recover precious metals due to their high intrinsic value. Electrowinning offers no hazards beyond those of the electroplating process which is the prime business of electroplating firms.

Note that a small amount of cyanide is incidentally destroyed through electrochemical oxidation during the electrowinning process.

Wastestream E

Spent Process Solutions added slowly to a rinse tank and treated in the wastewater treatment system: Spent plating baths, heat treating wastes, precious metals stripping solutions, and others would be added very slowly to keep the cyanide concentration in the rinse tank within the concentration range for cyanides in rinsewaters.

Note that rinsewater treatment is the intended scope of this rule. Specified conditions would be placed on this treatment; see the detailed statement of reasons.

Cyanide generating businesses in California: There are a number of industries that use cyanides for a number of purposes in California. These purposes include:

1. Electroplating: Cyanide solutions electrodeposit layers of metals on pieces to be plated. Metals commonly plated from cyanide baths include cadmium, copper, gold, silver, platinum, and zinc. Industries include aerospace, electronics, circuit board manufacture, metal fabrication, plumbing fixtures, automotive parts, appliances, and jewelry manufacture.
2. Stripping: Cyanide solutions are used to dissolve and remove precious metals from various products. Industries involved include aerospace, jewelry manufacture, electronics, and circuit board manufacture.
3. Cleaning: Cyanides are combined with hydrogen peroxide to form an aggressive cleaning solution for cleaning jewelry castings. The process is called "cyanide bombing".
4. Heat treatment: Metals are heated to specified temperatures and quenched in cyanide powders in a "case-hardening" process. The cyanides are used to maintain a reducing atmosphere during heat treatment. Cyanide containing wastewaters are generated from rinsing the work pieces after heat treatment.

5. Primary metals production: Huge quantities of cyanide solutions are sprayed over piles of ores acres in extent to remove metals in the mining industry. The process is called "heap leaching". Note that most of the wastes from heap leaching are exempted from classification as hazardous wastes by Health and Safety Code section 25143.1. Treatment of cyanide wastes from mining is outside the scope of this rule.

Physical Locations: Many of the businesses that must obtain authorization for their cyanide treatment are industrial businesses. There are no agricultural uses of cyanides that must obtain authorization for wastewater treatment. Industrial businesses are located in urbanized areas and in industrial parks. The areas are already developed because these businesses not only already exist, they are already generating and treating these cyanide containing wastewaters. Jewelry businesses are located both in industrial areas (larger manufacturers) Jewelry Marts (in Los Angeles and San Francisco) and in jewelers in retail areas; those jewelry businesses likely to notify under this PBR will be manufacturers rather than retail businesses.

The sole user of cyanides that is located outside of developed areas is the mining industry that uses large volumes of concentrated cyanides in open pits and heaps of ore in deserts, forests, and other otherwise natural areas. However, mining wastes containing cyanide are exempted from regulation under the hazardous waste program and do not require the grants of authorization addressed by this project.

Cyanide Treatment: Any hazardous waste containing cyanides can only be treated under a grant of authorization (outside of specified narrow exemptions like the onsite recycling exemption.) With some stated exceptions, "treatment" means any method, technique, or process which is not otherwise excluded from the definition of treatment by chapter 6.5 of the Health and Safety Code and which is designed to change the physical, chemical, or biological character or composition of any hazardous waste or any material contained therein, or which removes or reduces its harmful properties or characteristics for any purpose (Health and Safety Code section 25123.5, the definition of "treatment"). Thus, actions such as diluting a waste, destroying cyanides, precipitating metals, changing the pH, and other actions constitute "treatment" that requires authorization.

The types of treatment for cyanide containing wastes that are proposed to be authorized under a PBR include the following:

- Cyanide destruction. This is a treatment activity wherein the cyanide component of the wastestream is oxidized ultimately ending up as nitrogen and carbon dioxide; there is no cyanide left in the solution.
- Cyanide removal. The ion exchange process removes the cyanide ions from solution leaving the wastewater virtually cyanide free.
- Dilution. The regulations would allow spent process solutions to be diluted by

addition to the rinsewater stream. After dilution, the cyanides would be destroyed as in the first treatment type above.

After cyanide destruction or removal, wastewaters would generally be further treated under existing PBR authorization to remove dissolved metals and/or organics and to adjust the pH for sewer disposal.

Hazards of cyanide treatment: Cyanides in general are toxic materials. Pure uncomplexed cyanide ions in water (such as derived from sodium or potassium cyanide) have an oral LD50 of 3.2 mg/kg making most pure cyanides extremely hazardous wastes. However, treatment authorized by this project would be limited to cyanide concentrations in the range of hundredths of a percent and none of these solutions would be extremely hazardous due to their cyanide concentration.

Note also that the toxicity of cyanide solutions is a property that is particular to the waste rather than the treatment operation. This hazard is the same for wastes that are merely accumulated by generators for offsite shipment as it is for persons treating the waste.

Other constituents in the solution provide additional toxicity. Cyanide is often accompanied by metal ions, some of add significantly to the toxicity of the solution. Conversely, the tendency of many metals to form strongly bonded complexes with cyanides can lead to much lower toxicity levels for those solutions with strongly complexed cyanides. Once these regulations allow the destruction of cyanides, most other treatment, such as treatment of metal ions, pH adjustment, or neutralization, necessary to dispose of the hazardous waste or the aqueous residuals would be authorized by the pre-existing PBR program.

There is one particular hazard posed by both the treatment of cyanide bearing wastes, including the wastewaters addressed by this project, and the use of cyanides in commercial processes (not addressed by this project). That hazard is the generation of hydrogen cyanide gas. Hydrogen cyanide is a toxic gas that has been used as a war gas and has been used to administer capital punishment. Generation of hydrogen cyanide is the primary hazard considered in developing this proposal.

Other laws governing cyanide use and treatment: A number of different agencies regulate various aspects of cyanide use and cyanide treatment. These laws combine with the hazardous waste treatment permit program to protect workers, the public, and the environment from the hazards of cyanide.

- Worker safety programs: The federal Occupational Safety and Health Administration (OSHA) and the California Occupational Safety and Health

Administration (Cal/OSHA) have specific rules for working with cyanides. Most importantly, the OSHA and Cal/OSHA rules limit workplace exposure to hydrogen cyanide and require specific precautions to avoid generating hydrogen cyanide. Because the workers are in the closest proximity to the cyanide waste treatment system for up to 12 hours in a workday, they would be the most exposed humans to any significant release of hydrogen cyanide. Thus, the OSHA and Cal/OSHA rules provide comprehensive protection against hydrogen cyanide for the public since members of the public will be further from the waste treatment operation and exposed to lower cyanide concentrations in the case of an air release. This rulemaking does not need to address that issue separately.

- **Clean Water Act programs:** The federal Clean Water Act and the California Porter Cologne Act protect the waters of the State from pollution including from cyanide solutions. Both acts govern the composition of wastewaters disposed to the waters of the State by issuing permits to dischargers that specify types and concentrations of pollutants allowed. In practice, most industrial businesses discharge to sewer systems and rarely discharge directly to the waters of the State. Sewer agencies maintain pretreatment regulation systems that establish discharge limits for all persons discharging to the sewer system. The discharge limits control pollutants in the discharge to the sewers. The local limits and other types of discharge standard are calculated to ensure that the POTW meets its own permit standards in its own discharge. Thus, the Clean Water Act programs adequately regulate the chemistry of sewer discharges and this rulemaking need not address that issue separately.
- **Clean Air Act programs:** The California Air Resources Board, working through local air pollution districts, governs discharges to the air. Cyanide emissions are controlled and limited; however, permits are needed for only the largest dischargers and the most polluted air basins.

The Clean Air Act also contains the Cal ARP program in this State which requires pre-planning for businesses with larger quantities of very hazardous chemicals, including cyanides. This program is implemented at a statewide level by the California Office of Emergency Services and directly implemented by the Certified Unified Program Agencies (CUPAs). All businesses that have over 100 pounds of cyanide onsite at any one time are subject to the Cal ARP program. Cal ARP requires complex analysis of cyanide using operations to identify potential process upsets and other types of accidents that can cause release of cyanides to the environment. This analysis includes offsite consequence analysis of worst case releases and mitigation measures to minimize the chances of such releases and the consequences of these releases. The Cal ARP program is implemented in California by the CUPAs, the same agencies

that implement the PBR program, providing a seamless continuum of protection from cyanide releases.

Philosophy of the PBR Program: The tiered permitting system offers a tiered system for authorizing hazardous waste treatment where the regulatory requirements of each tier roughly mirror the relative hazard of the activities authorized. For instance, solvent recyclers managing large volumes of toxic, ignitable, and even explosive solvents are authorized by the full hazardous waste facility permit with the highest level of review and public participation. On the other hand, separation of oil from aqueous wastes that are hazardous solely due to the presence of oil is authorized under the simple self-implementing Conditional Exemption tier.

PBR is the most complex of the three self-implementing tiers for generators treating their own hazardous waste onsite. PBR facilities are subject to more stringent regulation because the wastes they treat and, sometimes, the treatment processes they operate, offer a higher level of risk to human health and the environment. However, PBR does not authorize all onsite hazardous waste treatment; many operations cannot be authorized through a PBR but must be authorized under a more review intensive and discretionary full or standardized permit. Some treatment operations may even be denied authorization and effectively forbidden due to unacceptable levels of risk.

PBR was adopted into regulation in 1991. A limited subset of wastestream/treatment processes were chosen that met the following criteria:

- The wastestream/treatment processes were well characterized. That is, the operator can understand how to treat the wastes successfully and which actions or other errors would cause failure to properly treat the waste or process upset and emergency conditions. Processes are shown to be well characterized when they are widely used in industry and appear in numerous journal articles and textbooks.

The majority of the metal finishing businesses in the United States plate metals from cyanides and generate cyanide containing wastewaters. Under the federal Clean Water Act and parallel state laws, these businesses are required to treat these wastewaters to meet concentration based limits for metals, cyanides, fluorides, pH, and other contaminants and properties. Cyanide destruction is one of the most common treatment processes. It precedes metal precipitation and removal and final neutralization or adjustment of pH prior to discharge of the wastewaters to the sewers. The vast majority of cyanide destruction utilizes a chlorine based oxidizing agent in an alkaline environment, generally chlorine gas bubbled into solution or addition of sodium hypochlorite. A smaller number of businesses use ozone and peroxide oxidation and electrochemical oxidation systems to destroy cyanides. All of these systems use reactive oxygen to oxidize the cyanide. Ultraviolet light is also used with ozone and

peroxide to break apart tightly bound cyanide complexes such as iron cyanides (ferricyanide) and free the cyanide for destruction.

The other treatment processes proposed for authorization under this PBR also commonly used throughout the electroplating industry. This PBR would authorize removal (rather than destruction) of cyanides from rinsewater using ion exchange systems similar to water softeners. Ion exchange systems are used for a wide variety of waste treatment and industrial processes such as demineralization of incoming water. Because the ion exchange resins only remove cyanide rather than act chemically on it, ion exchange poses no threat at all of hydrogen cyanide generation. The last treatment process that would be allowed is electrowinning to remove metals from process solutions for metal recovery. Electrowinning is simply electroplating onto a metal electrode where the plated metal does not adhere tightly and can be removed for recycling. Electrowinning is clearly well understood and well documented since it is merely the same plating process as the primary business of a plating shop.

- The wastestream/treatment processes could reliably be operated safely. A relatively clean track record demonstrates that commonly used treatment processes can be operated safely over time. However, many treatment processes that would meet this standard may have caused incidents over time due to improper operation. “Well characterized” and “reliable” mean that the processes can be operated safely, not that they always will be operated safely. Promoting safe and effective operation is the reason that hazardous waste treatment operations must obtain authorization and are inspected for compliance with regulatory standards.

Searching the State and federal emergency response databases and the general internet, DTSC has been unable to find any record of process upset or accident involving the kinds of waste treatment proposed for authorization under this PBR. Given the number of businesses engaging in cyanide destruction on a daily basis, the lack of documented accidents shows that the processes proposed here can clearly be and are operated safely.

- The wastestream/treatment processes did not have a track record of treatment upset or treatment failure. That is, the treatment processes have a good reputation, both in print and in verbal knowledge of skilled practitioners, and are not known to frequently fail or go into upset conditions.

Again, searching available records of emergency response and accidents does not reveal any accidents involving cyanide wastewater treatment.

In conclusion, the wastestreams and treatment processes proposed for this rulemaking

meet the criteria that DTSC has used to designate PBR wastestreams and treatment processes. There are other cyanide containing wastestream and treatment process combinations currently in use that have not been proposed for inclusion in this rulemaking; some of the treatment processes are commercially available. None of these non-included treatment processes has been judged to be widely enough used to be “well characterized” or the wastes have not been included in the scope of this rulemaking. DTSC has chosen wastestreams for inclusion in this rulemaking based on the need for authorization for onsite treatment and the desirability of treating these wastes onsite.

Yet another consideration that DTSC took into account in proposing these regulations is the web of other agencies’ standards that provide additional safeguards. As discussed above, strict Cal/OSHA worker safety rules limit the exposure of the closest receptors to any process emissions or upset conditions in a manner that protects them from the toxicity of the hydrogen cyanide gas. Any other receptors, for instance neighbors, will be much further from the source of hydrogen cyanide and will be exposed to much lower concentrations.

The cyanide waste treatment operations and, more importantly, the cyanide using operations, at each facility will also be subject to the stringent analysis of the California Cal ARP.

DETAILED STATEMENT OF REASONS/NON-CONTROLLING PLAIN ENGLISH SUMMARY

The regulations modify California Code of Regulations, title 22, section 67450.11 by adding separate new wastestream and treatment process combinations.

Section 67450.11(d)(1): This section is added to provide applicability for the new wastestreams. It repeats the general applicability for this section, but does not include the prohibition against treatment of reactive hazardous wastes and eliminates the prohibition on treatment of extremely hazardous wastes for electrowinning of spent process solutions and for slow addition of spent process solutions to the wastewater stream (rinsates). The applicability is necessary because it establishes the basic limits on treatment suitable for PBR.

Note that the prohibition on treatment of reactive hazardous waste found in section 67450.11(a) is not being repeated in this applicability section. It is not being added because many of the wastestreams that will be treated under this authorization may exhibit the characteristic of reactivity. The germane criterion of the reactivity characteristic reads:

“§66261.23. Characteristic of Reactivity.

(a) A waste exhibits the characteristic of reactivity if representative samples of the waste have any of the following properties:

(1) ...

* * * *

(5) it is a cyanide or sulfide bearing waste which, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors or fumes in a quantity sufficient to present a danger to human health or the environment;

(6)...”

Cyanide-containing wastes can clearly exhibit the characteristic of reactivity under the narrative standard in section 66261.23(a)(5). However, the narrative standard offers no guidance that can establish a clear level above which cyanide-containing wastes would be hazardous. Previous guidance published by the U.S. EPA presented a test method that could be used to determine if a waste was a reactive hazardous waste. That test method has been withdrawn leaving only the narrative criterion to judge whether a hazardous waste is a reactive hazardous waste. When applied to the wastestreams authorized for treatment under this regulation, application of the narrative leads to the following conclusions:

1. Cyanides in waste process solutions would generally be sufficiently concentrated so that these solutions would be classified as reactive. Cyanides are found in these wastes at concentrations up to 40% to 50% (up to 400,000 ppm to 500,000 ppm). These wastes would be eligible for two types of treatment under this regulation:

The wastes could be diluted to a much lower concentration by slow addition to rinse tanks that would maintain the concentration of cyanides in the rinse tanks at a wastewater level. Simple dilution of process solutions does not increase the risk of process upset and hydrogen cyanide generation making a ban on reactive wastes unnecessary for the proposed allowance to dilute and treat waste process solutions. The wastes could be treated by further electroplating metals out of the process solution (electrowinning) prior to further treatment or offsite disposal. The electrowinning process is identical to the plating process except that a stainless steel cathode is plated onto rather than workpieces. Thus, electrowinning poses no additional risk of hydrogen cyanide generation in spite of the reactive nature of many waste process solutions.

2. The other wastes proposed for treatment under this regulation are orders of magnitude more dilute than the process solutions. These wastes may or may not be

Permit By Rule for Treatment of Aqueous Wastes Containing Cyanides

reactive and the lack of an objective test method makes a definitive statement impossible for a regulation that addresses generalized rather than specific wastestreams. That is, the narrative description of reactivity can be applied on a wastestream/facility specific basis considering the individual properties of a generator's waste and other factors that would influence the toxicity of any hydrogen cyanide generated such as ventilation rates, distance to receptors, temperature, and others. However, for wastestreams near the concentrations where they might or might not be reactive, no general statement can be made without specifying each individual factor relevant to the waste and its generation. Thus, no generalized statement concerning reactivity can be made about the dilute wastestreams approved for cyanide destruction in this regulation.

Section 67450.11(d)(1)(A): Treatment of the waste is not regulated under the federal Resource Conservation and Recovery Act of 1976, as amended (42 U.S.C., section 6901 et seq.). This limitation is necessary because treatment that is regulated under the federal act must obtain a full hazardous waste facility permit, not a simplified permit under a PBR. Cyanide waste treatment operations not regulated under the federal Hazardous Waste Facility Permit program include:

- Treatment of non-RCRA hazardous waste (Defined in section 66261.101)
- Treatment in a wastewater treatment unit or totally enclosed treatment unit (exempted from the federal permit requirement in 40 CFR sections 264.1, 265.1, and 270.1)
- Treatment in a generator accumulation tank or container within the unpermitted generator accumulation time (51 FR 10174, Mar. 24, 1986)

Section 67450.11(d)(1)(B): The waste is not extremely hazardous pursuant to sections 66261.107 or 66261.110. This limitation is necessary to ensure that self-implementing authorization is not granted for the most toxic hazardous wastes and/or the most hazardous treatment processes. Wastestreams listed in paragraph (2)(D) and (2)(E) of this subsection are excluded from this condition provided the owner or operators that treat these waste comply with the limitations specified in subsections (d)(6) and (d)(7). These limitations will act to prevent treatment of some cyanide solutions where the concentrations of other constituents would create toxicity sufficient to meet the criteria for an extremely hazardous waste. This limitation is conditioned in two ways:

- It does not apply the treatment allowed in subsection (d)(6), electrowinning to recover metals from spent process solutions prior to offsite shipment or other onsite treatment of the spent process solutions. Electrowinning is virtually identical to electroplating operations that use the concentrated process solutions to coat workpieces as part of the facility's business. The sole difference between electroplating and electrowinning is that the electrowinning process plates metals

Permit By Rule for Treatment of Aqueous Wastes Containing Cyanides

onto a passivated thin metal cathode so that the plated metal can be easily mechanically removed for recycling. A passivated electrode is one where the surface has been oxidized so that metal can be plated onto the surface but adheres loosely so that it can be easily flaked off for recycling. In electroplating, cathodes (parts to be plated) are prepared to make the surface active so that the plated metal will stick effectively.

- It does not apply to treatment allowed in subsection (d)(7). This wastestream, spent process solutions, is likely to be extremely hazardous due to the high cyanide and dissolved metal concentrations. However, the spent process solution is being added slowly to a rinse tank prior to cyanide destruction and the only treatment allowed in this subsection is dilution to a level where the subsequent cyanide destruction step poses a risk equivalent to treatment of other lower concentration wastes. Thus, while diluting extremely hazardous waste below the threshold for extremely hazardous waste classification does require authorization, the exception above from the prohibition on treatment of extremely hazardous wastes is necessary and appropriate to protect human health and the environment.

Section 67450.11(d)(1)(C): The waste to be treated is a hazardous waste only because it contains cyanide or a combination of cyanide and metals listed in section 66261.24(a). This limitation is necessary to ensure that treatment under a PBR remains well characterized and predictable. Treatment of wastestreams that have not been chosen as appropriate for PBR or the use of processes that have not been demonstrated to be well characterized and predictable would require the careful pre-analysis that is part of the full and standardized permit review process.

Section 67450.11(d)(1)(D): This condition limits the intent of the treatment solely for the purpose of treating the constituents listed in this subsection. The only treatment technologies allowed for cyanide-containing aqueous waste to those listed in subsection 67450.11(d)(3). Spent process solutions are limited to treatment by electrowinning for the recovery of metals and the incidental treatment of cyanide. Spent process solutions may be diluted to eliminate or greatly reduce generation of hydrogen cyanide prior to cyanide destruction treatment in accordance with subsection (d)(7).

Section 67450.11(d)(1)(E): This condition requires that any owner or operator of a TTU or FTU allowed to treat cyanide-containing waste under PBR comply with source reduction requirements specified in subsection (d)(4). This limitation is required to further reduce the amount of waste generated and minimize or eliminate releases to work areas and the environment.

Section 67450.11(d)(1)(F): All treatment is conducted in tanks or containers. This

limitation is necessary to ensure that treatment is not carried out in units that would pose a higher level of threat to the environment through groundwater contamination. Other types of units where such treatment could occur include waste piles, surface impoundments, and land treatment facilities. All of these types of units involve waste placed directly on the ground with enhanced threats of release to the environment; thus, they are not addressed by these regulations. Additionally, treatment in units other than tanks and containers would require a full hazardous facility permit under the federal act if the treatment involved RCRA hazardous waste, as is usually the case with cyanide containing solutions.

Note that the limitation to treatment in tanks and containers is not as narrow as it first appears. Many different types of equipment can meet the definitions of tanks and containers. For instance, a filter press would generally meet the definition of a container. Roll off bins meet the container definition. Sumps and oil/water separators generally meet the definition of tanks.

Section 67450.11(d)(1)(G): All discharges to air comply with applicable federal, state and local air pollution control and worker safety statutes and regulations. This limitation is necessary because treatment of hazardous wastes can lead to air releases directly from treatment tanks and containers. This rulemaking is not creating new air or worker safety standards, but it is requiring compliance with these standards as a condition for obtaining authorization under this section.

Note that the primary hazard posed by management of cyanide containing wastes is air releases of toxic hydrogen cyanide.

Section 67450.11(d)(2): This subsection introduces the list of wastestreams that may be treated under this PBR and requires that they be treated only by the list of processes found in subsection 67450.11(d)(3). It is necessary both to introduce the wastestreams and to ensure that only those treatment processes considered for this grant of authorization are used for treating them.

Section 67450.11(d)(2)(A): This subsection establishes the wastestream entry for rinsewaters containing cyanides. Wastewaters of this type are the primary focus for these regulations because they are relatively lower hazard (than concentrated process solution wastes) and because they are generated in very large volumes on a frequent basis. Producing rinsewaters is a necessary part of industrial processes that use chemical baths like plating or stripping solutions. Parts are mounted in fixtures (“racks”) and dipped into various process solutions, often with impressed electrical currents. Rinsing removes residues of the process solutions so that the parts and fixtures can be moved to the next chemical bath in the process of plating, stripping, etc. Often industrial processes require use of many different process solutions with multiple rinses

between each solution.

Rinsewaters from cyanide solutions contain dissolved metals, cyanides and other anions, surfactants, buffering salts, and other additives. Prior to removing metals and organics from the solution and adjusting the pH to a level acceptable for sewer discharge, cyanides must be destroyed. The treatment (destruction or removal) of cyanides specifically will be authorized by this wastestream entry. After cyanide destruction, existing PBR wastestream and treatment process combinations are used to remove dissolved metals and organics and adjust the pH for sewer disposal.

Cyanide concentrations in rinsewaters range up to 5,000 ppm. The Surface Treatment Association developed concentration data in 1998 in response to an earlier proposal for a cyanide wastewater PBR that proposed limiting treatment to wastewaters with 1000 ppm total cyanide or less. Members of the association reported wastewater concentrations up to 5000 ppm with the most sophisticated shops reporting the highest concentrations due to better rinse water management practices. Because the poll was verbal, no written documentation exists. The highest cyanide concentrations are found in rinsewaters at facilities that use best management practices for wastewater management due the reduction of water use, the resulting wastewater generation is more concentrated.

Section 67450.11(d)(2)(B): This wastestream entry is both very specific and open-ended. It specifically applies to a specific category of industrial wastewater dischargers that have eliminated discharge of wastewater from their facilities. To eliminate wastewater discharge, these facilities use standard methods for destroying cyanides, precipitating metals, and removing other hazardous constituents. After this treatment, the wastewaters are “polished” by ion exchange columns that remove residual contaminants yielding water that is equal to or better than the incoming water to the facility. Virtually all the waste waters at these facilities are recycled.

There is one wastestream that cannot be recycled by the facility. This is the wastewaters produced when the ion exchange columns used to recycle wastewater into process water are flushed with acid and alkali. The wastewaters resulting are relatively concentrated with up to 10,000 ppm cyanides and more concentrated metals, but are of low volume - typically 200 - 600 gallons.

This wastestream has been included to allow zero discharge facilities to treat the wastewater from flushing ion exchange columns and render it non-hazardous. It is often then evaporated and the residual solids are manifested offsite as hazardous waste. Cyanides must be destroyed prior to any evaporation steps to avoid production and release of hydrogen cyanide. Zero discharge facilities are the most desirable

businesses environmentally because they use the least amount of water resources and because they send very little (only sanitary wastes) to the POTW for treatment. They are conserving both scarce water resources and expensive POTW treatment capacity and keeping metals out of the sewage sludge and the waters of the State.

Note that, while the higher cyanide concentrations would suggest a higher level of hazard, the small volumes produced mitigate that increased tendency towards hydrogen cyanide generation.

67450.11(d)(2)(C): This wastestream consists of sporadically generated rinsate from rinsing equipment used to transfer aqueous solutions containing cyanides. It includes transfer equipment such as containers, pumps, and hoses. The equipment must be rinsed after being used to transfer process solutions, replenishing solutions, or additives into process tanks or out of process tanks into drums or tank trucks for shipment to an offsite hazardous waste treatment facility. Rinsing is necessary between uses to ensure that solutions are not contaminated by residues left from the last use of the equipment and to ensure that incompatible materials, such as acids and cyanides, are not mixed in the equipment.

Note that no separate grant of authorization is needed for the pump transfer equipment rinsing process itself. That process can be considered to be either “equipment maintenance” or “onsite recycling” of the transfer equipment; neither category of action requires authorization from DTSC. Equipment maintenance is not a regulated activity under the hazardous waste laws because the equipment is not a waste. Onsite recycling is exempted from the authorization requirement under Health and Safety Code section 25143.2. The wastestream generated from rinsing, process solutions diluted with rinse water, is the wastestream that requires authorization for treatment.

However, process solutions may be rinsed into process tanks for use directly in the facility’s industrial process (such as electroplating and stripping) without obtaining authorization as allowed by the State’s statutes for recycling exemptions, Health and Safety Code section 25143.2.

Section 67450.11(d)(2)(D): This wastestream is spent processing solutions which contain recoverable amounts of metals. Electrowinning metals from the process solution makes the solution more amenable for further treatment and is predominately used for recovering precious metals. The limitations of the eligibility of this wastestream is detailed in subsection 67450.11(d)(6).

Section 67450.11(d)(2)(E): This wastestream consists of spent process solutions that are treated by adding them slowly to a rinse tank, a practice known in the industry as “bleeding”, “co-treatment”, or “in-line” treatment. The rinse tank waste is then treated by

cyanide destruction along with other wastewater generated by rinsing workpieces and fixtures. Because these spent process solutions contain very high concentrations of cyanides and dissolved metals, DTSC is not proposing to allow direct treatment. The very high concentration of cyanides in process solutions, up to 30% to 40% by weight, greatly increases the risk of hydrogen cyanide generation if the solutions are improperly treated. Direct treatment of such high cyanide concentrations may or may not be suitable for authorization under a PBR, but it is clearly outside the intended scope of this rule: authorizing treatment of lower hazard wastewaters generated by cyanide using industries.

Section 67450.11(d)(3): This subsection introduces the five cyanide destruction or removal treatment processes proposed for this grant of authorization. All five of these processes are well understood and predictable having been used for many years to destroy or remove cyanides all over the world. The five treatment processes are:

Section 67450.11(d)(3)(A): Oxidation by addition of hypochlorite. In this process, one of the specified oxidizing agents is added to a cyanide bearing wastewater with the pH adjusted to about 10.5. The oxidizing agent oxidizes the cyanide to cyanate. When the oxidation reaction is complete, the pH is adjusted to a slightly acid pH where the cyanate ion decomposes into carbon dioxide and nitrogen. After this treatment, the wastewater can be treated to remove metals or organic compounds and/or the pH can be adjusted to make the solution amenable for sewer discharge.

Note that the solution must be made non-hazardous prior to sewer discharge or discharge to the waters of the State.

Section 67450.11(d)(3)(B): Oxidation by addition of peroxide or ozone, with or without the use of ultraviolet light. This process is essentially identical to the process above, except that the oxidizing agent used is peroxide or ozone instead of hypochlorite. This process is often used with ultraviolet light that breaks apart strongly bonded metal/cyanide complexes like ferricyanide or gold cyanide and is the preferred process for treating strongly bonded metal/cyanide complexes. After oxidation, the remaining steps in the first process are carried out.

Section 67450.11(d)(3)(C): Alkaline chlorination. This process is similar to the process above, except that chlorine gas is bubbled into the solution forming hypochlorous acid that then oxidizes the cyanide. After oxidation, the remaining steps in the first process are carried out.

Section 67450.11(d)(3)(D): Electrochemical oxidation. In this process, an electrical current passed through the solution oxidizes the cyanide. After oxidation, the remaining steps in the first process are carried out.

Section 67450.11(d)(3)(E): Ion exchange. In this process, cyanide containing wastewaters are pumped through columns containing ion exchange resins. The resins have hydroxyl groups (OH-) attached to the resin. The cyanide replaces the hydroxyl groups on the resin and is thus removed from the wastewater. Additional treatment follows to remove other hazardous properties prior to discharge to the sewers or the waters of the State.

Section 67450.11(d)(4): In addition to the existing PBR requirements for generators found in section 67450.3, this section establishes source reduction and pollution prevention practices to reduce the generation of hazardous waste. Minimizing rinsewater generation (and generating rinsewater with higher cyanide concentrations) has the following benefits:

- It minimizes use of fresh water, a vital and limited resource in this arid state.
- It minimizes the volume of water that must be accepted and treated by the local POTW, a public agency with limited resources.
- By minimizing the volume of water sent to the POTW, it in turn minimizes the total mass of metal and other regulated contaminants sent to the POTW. Because most POTW discharge standards are concentration limits rather than mass limits, doubling the amount of wastewater would double the amount of contaminants sent to the POTW degrading both the POTW's own discharge and the biosolids produced by the POTW process.

Source reduction includes best management practices which can be prescriptive, such as:

- Designing fixturing and orienting workpieces so that they trap minimal volumes of process solution.
- Spray rinsing workpieces and fixturing over the process solution tank to rinse as much solution as possible back into the process solution, limited by the amount of water that can be added to the solution.
- Segregating cyanide processes, pretreatment, storage, and other operations from non-cyanide operations in a separate secondary containment system.

Best management practices also include health or performance based standards to reduce risk, such as:

- Developing a cyanide management plan, and integrating it with the environmental and safety management plan.
- Developing rinsewater quality standards for all cyanide processes and pre-cyanide processes.
- Monitoring work areas for hydrogen cyanide.

Section 67450.11(d)(4)(A): This subsection establishes the standards needed to reduce spills and prevent releases. Modifying the procedure to drain work pieces by using holding racks and drain boards so that drag-out solution is reused helps maintain bath chemistries and minimize spills. This procedure will minimize drag-out waste, extend bath life and reduce the amount of concentrated spent bath waste that needs to be treated by “bleeding”.

Section 67450.11(d)(4)(B): This subsection establishes pollution prevention measures for metal finishing processes.

Section 67450.11(d)(4)(B)(1): This subsection establishes the requirement to use countercurrent rinsing techniques to reduce water use and wastewater generation. Using countercurrent rinses involves rinse tanks plumbed so that the outfall from the last rinse tank feeds the second to the last rinse tank which feeds the third from the last rinse tank, and so on. With countercurrent rinses, the first rinse tank after the process solution has the highest concentrations of metals and cyanides and is the wastewater sent to the treatment system. Three rinse stages are generally most effective. The operators should use countercurrent rinsing to improve rinsing effectiveness and facilitate batch treatment of wastewater when the flow is sufficiently reduced.

Section 67450.11(d)(4)(B)(2): This subsection establishes the requirement to review the use of cyanide containing process baths to determine if a non-cyanide alternative with equivalent results is available at least every four years. This review may be integrated into the facility’s Source Reduction Evaluation Review and Plan, or into an Environmental Management System, or any other environmental performance evaluation completed by the owner or operator of the site or facility. Some operators may be able to eliminate cyanide bearing wastestream and treatment in their current process. For some plating processes, such as precious metals plating, the existing alternatives to cyanide containing baths do not provide good production results. Improvements in plating chemistry will continue in the future making this periodic review necessary.

Section 67450.11(d)(4)(B)(3): This subsection establishes training requirements for employees handling process and rinse solutions. Existing PBR regulations (sections 667450.3(a)(10)(C) and 667450.3(c)(8)(C)) require that owners or operators maintain training documents at the site or the facility where the TTU or FTU is operating. These training documents must describe the type and amount of both introductory and continuing training that will be given to employees handling hazardous waste.

This additional training for source reduction practices is necessary for several reasons:

- To ensure that cyanide processing solutions are handled in a manner that reduces waste in the production areas.

- To inform the employees about good operating procedures.
- To ensure employees are aware of source reduction.

The proposed regulations require that the training include a number of topics described below:

Section 67450.11(d)(4)(B)(3)(i): This subsection requires that employees be trained in procedures on how to reduce drag out.

Section 67450.11(d)(4)(B)(3)(ii) : This subsection requires that employees be trained in procedures to minimize contaminants in process baths.

Section 67450.11(d)(4)(B)(3)(iii) : This subsection requires that employees be trained in procedures on how to extend the bath life.

Section 67450.11(d)(4)(B)(3)(iv) : This subsection requires that employees be trained in procedures on how to reduce chemical spills and splashes from process and rinse solution handling practices.

Section 67450.11(d)(4)(B)(3)(v) : This subsection requires that employees be trained in procedures on how to respond to chemical spills in a manner that reduces waste and minimizes releases from process and rinse solution handling practices.

Section 67450.11(d)(5): This subsection prohibits treatment of non-aqueous cyanide containing wastes under the authority of this section. While there may be many non-aqueous cyanide wastes that can be treated safely and effectively using a variety of treatment processes, the scope of this rule is limited to aqueous wastes.

Section 67450.11(d)(6): This subsection creates a separate wastestream/treatment process listing for electrowinning metals from process solutions that are being discarded. Electrowinning is essentially electroplating onto a polished metal surface rather than electroplating onto a product for sale. Electrowinning is used to recover metals from solutions prior to shipment to a recycling or treatment facility. It is mostly used to recover precious metals due to their high intrinsic value. Electrowinning offers no hazards beyond those of the electroplating process which is the prime business of electroplating firms.

Note that a small amount of cyanide is incidentally destroyed through electrochemical oxidation during the electrowinning process. Electrowinning is being included here to allow economic recovery of metals by the waste generator because the electrowinning operation offers no risks beyond the industrial plating process that is the core business of the facility.

Subsection 67450.11(d)(7): This subsection authorizes the slow addition of spent process solutions to the wastewater stream for subsequent cyanide destruction and other treatment. It must be added because diluting a hazardous waste meets the definition of “treatment” in Health and Safety Code section 25123.5 and thus requires authorization from DTSC. The rinsewaters are limited to the rinsates identified in subsection 67450.11(d)(2)(A) and (C) which are the authorized wastestreams for treatment.

To ensure that treatment of process solutions diluted in the rinse tanks is similar in risk to treatment of rinsewaters, to avoid negative environmental impacts from the treatment operation, and to allow enforcement of the conditions placed on this wastestream, conditions and document retention requirements are proposed in this subsection for authorizing treatment of process solutions bled into the rinse tanks.

Section 67450.11(d)(7)(A): This subsection requires that the solutions be added to the rinse tank at a rate that keeps the concentration of cyanides in the rinse tank within the expected range of cyanide concentrations normally found in rinsewaters. The Surface Treatment Association (formerly the Northern California Association of Metal Finishers) has stated that facilities practicing best management practices for rinsewater management generate the highest cyanide concentrations in their rinse tanks with the maximum concentration being 5000 ppm cyanide. Thus, the upper limit of 5000 ppm is chosen as the limit for cyanide concentrations in the rinse tank where the process solution is being slowly added. This number was not chosen because DTSC has demonstrated scientifically that higher concentrations cannot be safely and effectively treated; it was chosen to conform the concentration limits for this wastestream with the stated scope and intent of this rulemaking which is to address treatment of cyanides in rinsewaters (or at rinsewater concentrations).

Inclusion of this wastestream is also necessary because treatment of the waste in the generating facility means that only solid and semi-solid treated residuals from the process solutions will be transported to offsite facilities. If treatment of this wastestream is not included in the proposed PBR, large volumes of highly mobile, highly reactive, and highly toxic cyanide solutions will continue to be transported on the streets of our most populous cities. Given the increasing congestion of these streets and highways, there is considerable potential for transportation accidents and uncontrolled release of process solutions during transport.

Note that accidents with vehicles transporting treated residuals aren't nearly as serious because the wastes are solid or semi-solid and the highly reactive and toxic cyanide has already been destroyed during treatment.

Section 67450.11(d)(7)(B): This subsection requires that the solid residuals from treatment of process solutions be recycled at an offsite recycling facility rather than disposed to land. This solid residue consists of sludges removed from clarifiers and treatment tanks and filtercakes removed from filter presses used to dewater waste treatment sludges.

This condition is necessary to avoid the negative environmental impact that would arise if the wastes were land disposed and new materials were mined to replace the metal content disposed to land. Currently, spent process solutions are trucked from the facility to offsite treatment facilities. These facilities receive plating and other aqueous wastes containing metals from many businesses and the solid residues are combined into larger volumes. The offsite facilities almost uniformly send the solid residues from treatment of these process solutions to primary metals smelters for metal recovery. By doing so, they not only avoid the cost of disposing of the residues, they also enjoy exemption from the hazardous waste requirements because the residues are used in an industrial process as a substitute for an industrial product (exempt under Health and Safety Code section 25143.2) avoiding use of a hazardous waste manifest and a registered hazardous waste transporter.

Section 67450.11(d)(7)(C): This subsection establishes documentation requirements for facilities treating process solutions by slow addition to the rinse tanks. There are three reasons why document preparation and retention is necessary:

- Document preparation and retention allows DTSC and CUPA inspectors to confirm that the facility is in compliance with the conditions specified for treating this wastestream. That is, first that the facility has developed a reasonable and effective method to limit the cyanide concentrations in the rinse tank making the concentration limit more easily enforced and ensuring that the treatment operation will not address wastes with more concentrated cyanides than those considered for this rulemaking.
- Secondly, the inspector is able to confirm that the facility is indeed recycling solids and semi-solid wastes that are generated are recycled.
- Preparation of a written method gives facility personnel involved in bleeding wastes into the rinse tanks an established and effective guideline for the operation allowing consistent safe and compliant operations.

The following subsections contain the documentation requirements:

Section 67450.11(d)(7)(C)1.: This subsection requires that the facility obtain written approval from the appropriate POTW for adding spent process solutions to the rinse tank for treatment. Bleeding process solutions can affect the discharge sent to the POTW by increasing metal loading. Since most POTWs establish concentration based standards for metals and cyanides in sewer discharges, anything that increases the

amount of metal and/or cyanide entering the treatment works can increase the total amount of metal or cyanide that the treatment works receives. Excess cyanide that is not completely destroyed will remain dissolved in the POTW's own discharge to the waters of the State both degrading those waters and potentially causing the POTW to violate their own discharge permit. Excess metals discharged to the POTW will end up in the biosolids (sewage sludge) produced by the POTW's own waste treatment process. Metals degrade the quality of the biosolids potentially making them unusable as fertilizer and potentially classifying them as hazardous waste.

DTSC asked POTWs in areas with concentrations of cyanide using businesses whether they allow bleeding. Two POTWs replied. The Los Angeles Sanitation District allows bleeding because they use mass-based discharge limits for industrial dischargers. The Palo Alto Sanitation District does not allow bleeding except on a case-by-case basis. The mixed response from POTWs leads DTSC to ensure that the POTW is both notified about a proposed bleeding operation and approves of it.

The document retention requirement allows DTSC and CUPA inspectors to quickly assess a business's compliance with this requirement.

Section 67450.11(d)(7)(C)2.: This subsection requires the facility to prepare a method for ensuring that the cyanide concentration in the rinse tanks never exceeds 5000 ppm, the upper limit for cyanide concentration in rinsewaters. It is necessary to develop a written plan for the stated reasons above in the discussion of proposed 67450.11(d)(7)(C)3.

The requirement is left open deliberately because the variety of different types of rinsewater and treatment system are better addressed by the flexibility of a performance standard rather than a series of prescriptive standards. There are many ways to add a process solution gradually to the rinse tank for treatment, including, but not limited to the following:

- A metering pump can be used that pumps a constant flow of process solution into the rinse tank. The facility would use the normal water flow through the rinse tank and the cyanide concentration in the rinse tank and the process solution to choose the proper flow rate for the metering pump.
- The process solution can be manually added to the rinse tank using containers added at specified intervals. The intervals would be calculated using the volume of the container, the flow rate of water through the rinse tank, and the cyanide concentrations in the rinse tank and the process solution.

Development of this method will not be unduly difficult because the industries that use aqueous cyanides are familiar with considerations such as flow rates and concentrations and knowledge of how to move, add, and treat solutions is integral to

operating such a business.

Section 67450.11(d)(7)(C)3.: This subsection requires that the business retain records demonstrating that they have sent their residual solids and semi-solids for recycling. It allows DTSC and CUPA inspectors to assess compliance with 67450.11(d)(7)(B) on inspection. The requirement can be satisfied by a manifest showing that the residual materials were handled with a recycling handling code, a certificate of recycling from the recycling facility, or any other document that unambiguously establishes that the residual materials were sent to a recycling facility.

Changes to the Authority and Reference Citations:

Authority: An incorrect authority citation, Health and Safety Code section 58004, is being deleted. This section does not give DTSC authority to adopt regulations.

Changes to Title 27, California Code of Regulations:

Changes are being made to the Unified Program Consolidated Forms in title 27, California Code of Regulations to conform to the changes made here. Those changes will modify the form to allow businesses to notify their local CUPA of treatment under this PBR.

The following statements of reason pertain to proposed regulation text in title 27, division 3, subdivision 1.

Chapter 4, Hazardous Waste

C. Onsite Tiered Permitting - Waste and Treatment Process Combinations.

Add ‘, except that items 630-14a through 630-17 cannot be treated under CESQT.’ to the ‘INFORMATION DESCRIPTION’ note. This addition is per proposed regulation (DTSC R-96-48) that allows treatment operations for small quantities of the proposed PBR wastestreams. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add ‘630-14a’, ‘Cyanide Rinsewater, Cyanide Destruction – Oxidation by Addition of Hypochlorite’, ‘Y or N’, ‘1’, ‘AN’. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add ‘630-14b’, ‘Cyanide Rinsewater, Cyanide Destruction – Oxidation by Addition of Peroxide or Ozone, with or without Ultraviolet Light’, ‘Y or N’, ‘1’, ‘AN’. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add ‘630-14c’, ‘Cyanide Rinsewater, Cyanide Destruction – Alkaline Chlorination’, ‘Y or N’, ‘1’, ‘AN’. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add ‘630-14d’, ‘Cyanide Rinsewater, Cyanide Destruction – Electrochemical Oxidation’, ‘Y or N’, ‘1’, ‘AN’. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add ‘630-14e’, ‘Cyanide Rinsewater, Cyanide Removal – Ion Exchange’, ‘Y or N’, ‘1’, ‘AN’. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add ‘630-15a’, ‘Demineralizer Regenerate with Cyanides, Cyanide Destruction - Oxidation by Addition of Hypochlorite’, ‘Y or N’, ‘1’, ‘AN’. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Permit By Rule for Treatment of Aqueous Wastes Containing Cyanides

Add '630-15b', 'Demineralizer Regenerate with Cyanides, Cyanide Destruction - Oxidation by Addition of Peroxide or Ozone, with or without Ultraviolet Light', 'Y or N', '1', 'AN'. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add '630-15c', 'Demineralizer Regenerate with Cyanides, Cyanide Destruction - Alkaline Chlorination', 'Y or N', '1', 'AN'. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add '630-15d', 'Demineralizer Regenerate with Cyanides, Cyanide Destruction - Electrochemical Oxidation', 'Y or N', '1', 'AN'. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add '630-15e', 'Demineralizer Regenerate with Cyanides, Cyanide Removal - Ion Exchange', 'Y or N', '1', 'AN'. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add '630-16a', 'Transfer Equipment Rinsate with Cyanides, Cyanide Destruction – Oxidation by Addition of Hypochlorite', 'Y or N', '1', 'AN'. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add '630-16b', 'Transfer Equipment Rinsate with Cyanides, Cyanide Destruction – Oxidation by Addition of Peroxide or Ozone, with or without Ultraviolet Light', 'Y or N', '1', 'AN'. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add '630-16c', 'Transfer Equipment Rinsate with Cyanides, Cyanide Destruction – Alkaline Chlorination', 'Y or N', '1', 'AN'. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add '630-16d', 'Transfer Equipment Rinsate with Cyanides, Cyanide Destruction – Electrochemical Oxidation', 'Y or N', '1', 'AN'. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add '630-16e', 'Transfer Equipment Rinsate with Cyanides, Cyanide Removal – Ion Exchange', 'Y or N', '1', 'AN'. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add '630-17a', 'Process solutions with Cyanides added slowly to rinse tanks, Cyanide Destruction – Oxidation by Addition of Hypochlorite', 'Y or N', '1', 'AN'. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add '630-17b', 'Process solutions with Cyanides added slowly to rinse tanks, Cyanide

Permit By Rule for Treatment of Aqueous Wastes Containing Cyanides

Destruction – Oxidation by Addition of Peroxide or Ozone, with or without Ultraviolet Light’, ‘Y or N’, ‘1’, ‘AN’. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add ‘630-17c’, ‘Process solutions with Cyanides added slowly to rinse tanks, Cyanide Destruction – Alkaline Chlorination’, ‘Y or N’, ‘1’, ‘AN’. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add ‘630-17d’, ‘Process solutions with Cyanides added slowly to rinse tanks, Cyanide Destruction – Electrochemical Oxidation’, ‘Y or N’, ‘1’, ‘AN’. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add ‘630-17e’, ‘Process solutions with Cyanides added slowly to rinse tanks, Cyanide Removal – Ion Exchange’, ‘Y or N’, ‘1’, ‘AN’. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

Add ‘630-18’, ‘Electrowinning Process Solutions with Cyanides, Metal Recovery’, ‘Y or N’, ‘1’, ‘AN’. Proposed regulation (DTSC R-96-48) will allow this information to be collected.

**Chapter 6. Unified Program Consolidated Forms,
ONSITE TIERED PERMITTING PERMIT BY RULE PAGE**

Add ‘14. Aqueous wastes generated by rinsing products and fixtures holding products that were processed in cyanide containing solutions may be treated by the following technologies:’, Oxidation by addition of hypochlorite’, Oxidation by addition of peroxide or ozone, with or without the use of ultraviolet light’, Alkaline chlorination’, Electrochemical oxidation’. This addition corresponds to proposed regulatory requirements.

Add ‘15. Aqueous wastes generated by regeneration of demineralizer (ion exchange) columns that were used for recycling of wastewaters at facilities that have eliminated the discharge of wastewaters (other than sanitary discharges) may be treated by the following technologies:’, Oxidation by addition of hypochlorite’, Oxidation by addition of peroxide or ozone, with or without the use of ultraviolet light’, Alkaline chlorination’, Electrochemical oxidation’.
This addition corresponds to proposed regulatory requirements.

Add ‘16. Rinsate from rinsing equipment used to transfer aqueous solutions containing cyanides such as containers, pumps, and hoses may be treated by the following technologies:’, Oxidation by addition of hypochlorite’, Oxidation by addition of

Permit By Rule for Treatment of Aqueous Wastes Containing Cyanides

peroxide or ozone, with or without the use of ultraviolet light', Alkaline chlorination', Electrochemical oxidation'. This addition corresponds to proposed regulatory requirements.

Add '17. Process solutions containing cyanides added slowly to a rinse tank at a level that never exceeds 5000 ppm cyanide in the rinse tank may be treated by the following technologies:', Oxidation by addition of hypochlorite', Oxidation by addition of peroxide or ozone, with or without the use of ultraviolet light', Alkaline chlorination', Electrochemical oxidation'. This addition corresponds to proposed regulatory requirements.

Add '18. Process solutions with recoverable amounts of metal may be treated by the following technology:', Electrowinning to recover metals prior to further treatment, including destruction of incidental amounts of cyanide by electrochemical oxidation resulting from the electrowinning process'. This addition corresponds to proposed regulatory requirements.

Delete '(1/99)' and 'Formerly DTSC 1772D' from all footers of the 'ONSITE TIERED PERMITTING PERMIT BY RULE PAGE' form. The date and former form name are no longer valid.

Add '(XX/07)' after 'UPCF' in all footers of the 'ONSITE TIERED PERMITTING PERMIT BY RULE PAGE' form. This is a reference to the new revision date.