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# Environmental Aspects of the Metal Finishing Industry :

A Technical Guide



**ENVIRONMENTAL ASPECTS  
OF THE METAL FINISHING INDUSTRY:  
A TECHNICAL GUIDE**



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As before, the Technical Report Series aims to meet the needs of a wide range of government officials, industry managers and environment protection associations, by providing information on the issues and methods of environmental management relevant to various industrial sectors.

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## OVERVIEW AND SUMMARY

Surface treatment of metals is an operation that is an important source of pollution when compared with some other manufacturing operations. The toxic nature of many of the chemicals involved in such treatment, and perhaps even the toxic nature of the metals being coated themselves, means that any release of materials has potentially serious effects on the environment.

Metal finishing may cover a potentially vast number of operations in which metals are cleaned, prepared, treated and coated. Intermediate operations may be carried out to make the surface receptive to the final coating. The coatings themselves can have a variety of compositions and consistencies. This Guide focusses principally on the traditional metal plating operations which have a long history of use, and are in widespread use around the world. They are significant in terms of environmental impact on account of the metals, chemicals and processes they involve. Nevertheless, the principles elaborated in this Guide will also be applicable to many other processes, and the Guide should be of value to a wide audience in government and industry.

### Environment

Environmental issues relevant to the industry now go considerably beyond the traditional one of water pollution from untreated wastewaters. Workplace safety, outside air emissions, soil and groundwater pollution, and excessive noise have all assumed greater importance in the minds of regulators in recent years. Solid waste disposal, disposal of treatment sludges, and prevention of industrial accidents have become high priorities within our crowded communities. The cost to clean-up historic dumpsites and present-day

spills involving persistent chemicals has become an unacceptable burden on the public purse.

These issues have all found their way into regulatory programmes in industrialized countries. The control programmes are often a high priority in the minds of politicians. With such rapid evolution it is important that industry remains in touch with contemporary environmental affairs so as to be able to monitor trends, and thereby anticipate the impact of new regulations that have been framed to address these issues.

### Pollution Control Strategies in the Metal Finishing Industry

As environmental issues have become more complex, so the resulting strategies for pollution control have had to become more systematic, and more integrated. The value of preventive rather than curative approaches has become more widely appreciated. Responsibility for environmental control tends now to be taken at higher levels within a company, and practical contributions are expected of all operational and managerial personnel.

The most useful approach to environmental control for metal finishing enterprises follows that which has been adopted for industry in general. Avoidance of waste generation and reduction wherever possible of pollution loads is the first priority. Recovery and recycling of waste streams is the next consideration. Only then should treatment be considered. (There is unfortunately still a common mentality that assumes treatment is the only option). In following the above scheme it is important to remember that all environmental impacts listed above are taken into account. An attempt to reduce a particular waste stream

should not result in merely shifting the hazardous residues to another environmental medium, or another location.

The final consideration for an enterprise is disposal: disposal of treated effluents, of surplus stock, of treatment residues, of contaminated objects and soil. If avoidance, recycling and treatment have been effective there should be relatively little material requiring disposal. Nevertheless this must still be carried out without undue impact on the environment, and without risk to workers or the community.

For a metal finishing enterprise four broad considerations will be particularly important in contributing to a pollution control strategy:

- (i) use of low and non-waste production technology;
- (ii) installation of properly designed treatment plants;
- (iii) competent operation and maintenance of (i) and (ii);
- (iv) adequate information and training of shop floor personnel to avoid mis-handling and accidents.

The relative emphasis on these four areas will vary from one enterprise to another. Older established plants for example will need to rely more heavily on end-of-pipe treatment than newer plants where cleaner technologies can be more easily built in. It is clear that if less emphasis is given to one of the above areas, then the others need to make a proportionately greater contribution in order to achieve the same goals.

### **About this Guide**

The present Guide deals in some detail with the technical options indicated above - low

and non-waste production processes, and treatment technologies. There are many options available for reducing harmful effluents. They may involve reducing effluent volume, or its strength, or both.

Reducing rinsewater consumption, recycling rinsewaters within the plant, extending the working life of active solutions and baths, and avoiding spills and overflows should all be important management objectives. These initiatives generally achieve economic gains alongside environmental ones. A lower volume of effluent can be dealt with by a smaller, cheaper treatment plant using fewer chemicals.

Lowering the concentration of pollutants in the effluent relies on many of the same concepts, ie. reducing loss of chemicals by recycling spent solutions, extending the service life of baths by improved maintenance, adopting processes that use lower active concentrations, avoiding the use of some toxic chemicals altogether, preventing spills, and preventing accidental contamination of baths that would then need to be discarded. Such actions again, often give an economic return through lower chemical consumption, and lower incurred treatment costs.

Having arranged the production process so as to generate the smallest possible amount of waste it then becomes necessary to optimize the treatment stage. Segregation and separate pretreatment of certain effluents is more efficient than trying to treat a complex mixed wastewater stream. Various options exist for treatment, and should be carefully assessed for each enterprise. In choosing among the options, considerations of subsequent effluent and sludge disposal should be taken into account. Ease of operation and maintenance, and cost of treatment chemicals are also



important. In all cases, it is beneficial to have a suitably equipped laboratory, and trained technical staff so as to monitor the performance of the treatment plants (and of the surface treatment process itself).

The problem of residue disposal is becoming more acute in many countries. Special procedures and special facilities are often required to deal with toxic sludges. Accordingly, further dewatering, drying and perhaps even chemical stabilization is becoming more common as a follow-up to wastewater treatment.

The level of treatment itself will be determined by the prevailing discharge standards in the country concerned. Both discharge to sewers and to natural waterways are becoming subject to increasingly stringent standards. Workplace air concentrations are also limited by regulation in many countries.

Chapter 5 recapitulates some of the broad considerations that are necessary to achieve good environmental performance by the industry. The replacement of process chemicals by less toxic alternatives, and process modifications so as to consume fewer chemicals is an important first step. The recovery of spent or discharged materials is a useful adjunct to this. The importance of good housekeeping and safe working procedures cannot be overstated if consistent good environmental results are to be achieved. The proper design of factory layout, and sound construction of equipment is an essential prerequisite to effective housekeeping. Careful operation, in accordance with clear instructions from supervisors will reduce the incidence of accidents and

spills, thereby avoiding significantly the need to dispose of waste materials.

There is often a great need to make more information available to shop floor personnel. This should include information on the surface treatment processes themselves, and the options for reducing pollution loads. In particular, safety information regarding the chemical substances used should be more widely known by operational personnel and by supervisors. Material Safety Data Sheets are available for most substances used in the industry. They can be obtained from the chemical supplier, or from commercial publishing houses. Basic information is also available in chemical handbooks. Several UN agencies operate information services on occupational and chemical safety, and on environmental questions.

The present Guide is intended for readers with several different responsibilities:

- for industry, an outline of common processes is presented with respect to environmental implications. Costs, energy consumption, process efficiencies, maintenance questions, operational and process control factors are discussed;
- for regulators, an outline of environmental considerations, infrastructure, supervision and control needs is given;
- for operators, process and maintenance details, environmental implications, and possible legal requirements are presented.

## I. INTRODUCTION

«The demand for natural resources and environmental amenities in the ASEAN region is bound to increase sharply for three reasons. First, the population which was 273 million in 1982 is expected to increase to 380 million in the year 2000. Second, the expected annual growth rate of economic activity is at about 5 percent. This growth rate is likely to continue, doubling the demand on natural resources, *ceteris paribus*, every 15 years or so. Third, the process of production inevitably becomes more capital and technology intensive. Consequently, pressure on the natural resources will continue to increase.»

Prof. Dr. Emil Salim, State Minister For Population and Environment, Indonesia, 30th October, 1987

What Minister Salim stated for the ASEAN region is also true for much of the rest of the world. One of the goals of the Industry and Environment Office of the United Nations Environment Programme is to offer practical help to those industries which are particularly prone to contribute to environmental pollution, and thus increasingly come under pressure to change their ways of operation.

Metal finishing is an activity which is introduced early in the process of industrialization. It contributes significantly toward offering pleasing and non-corroding objects at affordable prices without placing too large demands on skilled labour or sophisticated equipment. However for many processes the consequent consumption of water and chemicals can be astoundingly high, and constitu-

tes, unless reasonably controlled, a major threat to health of people and the environment.

Metal finishing processes can give rise to several environmental problems. The soil around the premises may be contaminated through spills and careless dumping of residues, thus leading to the contamination of ground and surface water. Wastes carried in the discharged wastewater may pollute streams. Hazards may arise from the improper storage and transportation of residues containing toxic chemicals. The unsafe handling of process chemicals may cause workplace accidents and illness from direct contact and inhalation of fumes.

The chemicals involved in metal finishing processes are generally long lived. This means that the problems do not disappear with time. Homes built on the soil of an abandoned metal finishing shop may endanger the health of residents long after the industrial operations have ceased. Chemicals leaving the premises as wastewater or in the form of sludge may well affect people or the environment far downstream.

It is important to stress that the factory owner has the prime responsibility for avoiding such impacts. However improvements as regards environmental pollution also require the involvement and co-operation of people beyond the owner. They require for example proper residue transportation and adequate waste deposit or treatment facilities. Competent organizations must become involved in providing, supervising, and controlling appropriate services and infrastructures.

## 2. ENVIRONMENTAL IMPACT OF THE METAL FINISHING INDUSTRY

### 2.1 SOURCES OF POLLUTANTS

Metals and chemicals are the basis of the metal finishing industry. The thoughtless use, release or dumping of chemical residues and effluents can affect a wide range of environmental species, as well as causing serious human health effects. Some effects occur immediately, others may take some years to manifest themselves. Often pollution and health effects are closely linked.

Common processes, and the chemicals used are summarized in Annex C. It is important to stress that irrespective of their measured levels of toxicity, all chemicals must be treated with respect. Most chemicals are toxic if their exposure is high enough, and all chemicals will cause environmental pollution if released in large amounts. Information on chemical hazards, on pollution, and on management options to avoid these effects is now available through handbooks and information networks.

Most processes which involve the use of chemicals should be examined for their propensity to cause pollution. Loss of chemicals can occur from rinsing operations, from spills, or the discarding of spent solutions. In a few instances even the products from the industry may be of environmental concern, eg. objects plated with cadmium.

While wastewater treatment will greatly reduce the quantities of pollutants reaching the environment, it is also now realized that such treatment can itself lead to some environmental problems if not carefully done. In some cases the sludges resulting from wastewater treatment are considered «hazardous wastes» by regulatory authorities, due to their high metal concentrations. Reduction of such secondary sources of pollution can only be

achieved when a comprehensive approach to waste management, preferably based on waste avoidance principles, is adopted within a company.

A number of ancillary operations may also give rise to loss of chemicals to the environment. These include:

- storage of chemicals;
- transfer and handling of chemicals;
- wastewater treatment and discharge;
- discharges from process control laboratories;
- disposal of residues;
- re-use or disposal of empty chemical containers.

### 2.2 ENVIRONMENTAL EFFECTS

Chemical pollutants can cause a wide variety of environmental effects. These effects may vary from one target species to another, and also depend on the particular pathway that a chemical takes in the environment. Humans are particularly important targets of course, but many other parts of the environment are also susceptible to the toxic effects of chemicals.

With respect to the workplace it is useful to identify a number of common hazards. Corrosive chemicals such as acids and alkalis eat away at tissues and materials, eg reaction tanks. Strong oxidizing agents may cause burns, or cause fires if they come into contact with paper, packaging materials, timber, or textiles. Large quantities of flammable materials are a fire hazard and sometimes cause explosions. Many solvents are flammable.

With respect to human health and animal and plant life, the following terms are often

encountered: toxicity refers to poisoning of living things and can be immediate (acute), or can manifest itself after long periods of time (chronic). Many chemicals such as heavy metals tend to gradually accumulate the body and may begin to show effects only years after exposure has begun. Only rarely can sickness then be prevented from proceeding. Cancer producing properties of chemicals (carcinogenicity) and their potential to alter genetic codes (mutagenicity) are normally counted among the toxic properties.

With respect to the environment it is useful to have an understanding of the following terms: pollution refers to damage to the environment, or upset of ecological systems. The routes in the environment through which chemicals are distributed are called environmental pathways. Chemicals can migrate in the environment from one «compartment» to the next: eg. from soil into water, or from water into air. Some materials and chemicals tend to degrade rapidly in the environment; others are more or less persistent and can, over time, migrate to new locations under the influence of natural forces. Metals tend to adsorb easily on surfaces like soil or sediments and show a considerable tendency to geo-accumulate. Many metals also have the ability to bio-accumulate in plant or animal tissue. Sometimes they can reach such high concentrations there that the consumption of the contaminated foodstuffs has to be regulated for reasons of health.

The discharge of untreated metal finishing wastewaters to natural waterways has contributed to water pollution in many industrial regions. As well as damaging natural ecosystems, the water has often become unfit for drinking. Fisheries may be directly destroyed, or their products rendered unfit for eating.

Purification of water to restore its use is generally expensive.

To reduce problems of local pollution, many authorities provide a public sewerage system for wastewaters. However if such wastewaters are too concentrated, the discharge into public drains and sewers can still cause problems. Toxic chemicals can interfere with the purification process of treatment systems. Heavy metals contained in effluents often accumulate in the biological sewage sludge. If used as soil conditioners on farms, the contaminated sludge can pass the chemicals on to food plants or to animal feed. Many public authorities now regulate the discharge of effluents into the public sewerage system to avoid such effects.

The storage and transportation of heavily contaminated sludges or wastewaters may also pose some difficulties due to the composition or consistency of the materials. Hauling equipment and transfer operations should therefore pay particular attention to these needs.

Although many reagents in metal finishing are relatively non-volatile, air pollution problems may still be important. Substantial quantities of acid fumes and mists may be released from some operations. Certain hazardous gases may be released from process reactions.

The dumping of treatment sludges and chemical wastes into poorly located, badly constructed or carelessly managed landfill sites can lead to groundwater pollution problems. Obviously health and safety problems for workers can also result from such practices.

Hazards from old waste dumps, abandoned storage and plant sites are now well known and documented in many parts of the world.

The high concentrations of toxic chemicals sometimes found there have led to costly excavation programmes in order to prevent continued damage to health and the environment.

Accidents involving chemicals can be a very serious matter. Prevention of accidents is far more effective and less costly than paying for the clean-up and damage after they have occurred. Prevention means installing equipment that is not accident prone, ensuring safe operating procedures, and having suitable emergency response procedures in place. Pro-

per training of personnel is essential to ensure safe operating procedures. Recruitment of shop floor personnel should pay due regard to their need for safety training.

Direct exposure of workers to chemical reagents and fumes can cause a number of long-term illnesses, some of which may be irreversible. Severe exposure may cause acute illness, or even death. Unhygienic conditions at work, and eating and smoking in the workplace greatly contribute to the chance of exposure.

### 2.3 ASSESSMENT OF POTENTIAL IMPACTS

The potential environmental impacts will vary from situation to situation, depending on the type of industrial process, location, local environmental conditions and so on. Professional judgement of experts experienced in both process technology and in environmental control should be sought prior to making decisions about the future of a metal finishing plant. As an aid in decision making, formal Environment Impact Assessment (EIA) procedures are often recommended. Such procedures are designed to systematically search for and identify possible environmental problems so that they can be addressed at the outset.

Some references to the EIA process are included in Annex A. The use of checklists or interaction matrices is a common feature of EIA processes. Both methods can be applied in simplified form to medium or small projects. Table 1 gives an example of a simple checklist which can be used as a basis for assessing individual plants. Some of the

environmental effects that can be expected from the chemicals used in, and the wastes generated by, metal finishing processes are indicated in the text. Annex C lists chemicals commonly used for a number of processes. Potential effects of chemicals are also found in Material Safety Data Sheets, and through the information services shown in Annex D. The EIA process would use such information, together with project-specific information, to evaluate the overall impact of a proposed development. It can also be carried out for an existing facility to guide further investigations.

For industrial activities that involve significant quantities of hazardous materials, a preliminary stage to the EIA is now often a risk assessment of the plant. This assessment evaluates plant design and operation, and of course safety procedures, so that the likelihood of an accident can be established.

A variety of techniques is available for carry-

ing out a risk assessment, but in all cases professional judgement plays a large part. For small installations professional judgement may be all that is possible, as an expensive quantitative modelling exercise may not be justified. Such assessment should of course be

carried out by an independent expert, not by the proponent of the proposal. The proponent may carry out a study for his own use. For larger projects formal procedures have been developed, and are described in a number of manuals and handbooks.

### ENVIRONMENTAL CHECKLIST FOR METAL FINISHING

Environmental considerations to be included in a first assessment:

- occupational exposure of workers to process chemicals;
- occupational exposure of workers to waste residues;
- water pollution from wastewaters, washwaters;
- discharge of chemicals to drains streams, or to soil;
- impact on public sewer systems, leading to damage to the sewer itself, to the sewage treatment process, and to the environment near the sewage outfall; as well as presenting danger to sewer maintenance personnel;
- contamination of sewage sludge by persistent, bio-accumulative, and toxic residues;
- groundwater contamination through seepage;
- disposal of surplus chemicals and/or treatment sludges;
- soil contamination from spills, at chemical and waste storage areas;
- transport accidents involving chemicals transported to or from the plant;
- accidents in the plant involving the release of chemicals;
- energy and resource consumption.
- air emissions of chemicals and subsequent workplace and public exposure;
- unsafe re-use of chemical containers;
- accumulation of surplus chemicals with subsequent risk of deterioration and need for disposal;
- on-site disposal of wastes;
- excessive noise and vibration from machinery.

Table 1 : A simple checklist for assessing the potential impact of metal finishing plants. For large plants, or those using advanced technologies, additional factors may have to be considered.

A comprehensive assessment can in general only be performed by someone experienced with the process being studied. Special assessment techniques may be required to ensure that common-cause failure modes are adequately considered, for example.

## 2.4 MANAGEMENT TO REDUCE ENVIRONMENTAL IMPACTS

As can be seen from Annex C, a range of chemicals and processes contributes to the hazards discussed above. Avoiding such risks is partly a matter of choosing appropriate

technology, and partly appropriate management. Fig. 1 shows the principal pathways by which chemicals can reach the environment as solutions, solids or vapours.

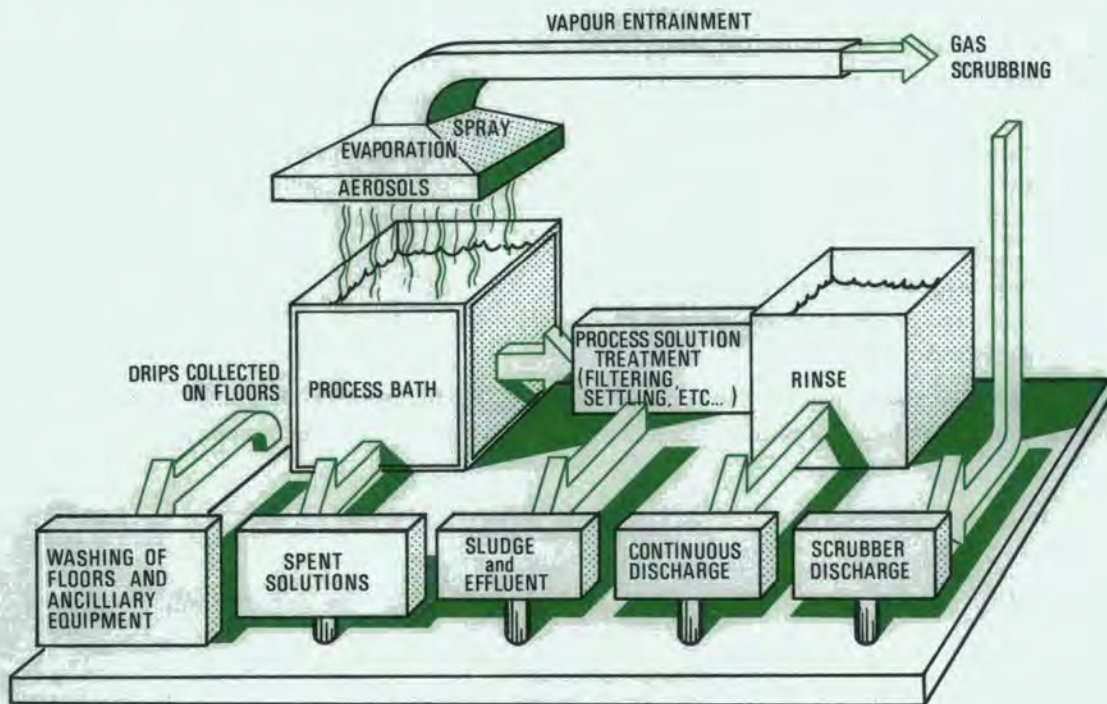


Figure 1 : Schematic illustration of losses of chemicals in a generalized plant.

The following objectives are important in ensuring that such losses do not cause undue impacts:

- avoid the generation of effluents, residues and wastes wherever possible;
- avoid accidents, spills, contamination and abandoned residues;
- try to recover, recycle, reclaim and exchange wastes as far as is technically feasible;

- ensure adequate treatment of any remaining waste;
- ensure safe disposal of all final residues;
- prevent runoff of polluted stormwaters.

The proper choice and design of production equipment, and of treatment plant, is indispensable in achieving these objectives. However it must be stressed that training of operating personnel, regular maintenance of equip-

ment and vigilant supervision are also necessary to allow such equipment to perform properly. Management's dedication to good housekeeping practices must be maintained throughout the life of the plant.

Ignorance of the potentially toxic effects of process chemicals contributes to their careless handling and release. Before purchasing chemicals, operators should insist on obtaining from the dealer or distributor the Material Safety Data Sheets for each chemical or mixture of chemicals purchased. These Data Sheets are provided by the manufacturers in many languages and describe in clear and concise form the properties of the chemical or mixture. They also contain information on health and environmental effects, handling, use, disposal, and on what to do in cases of emergency (see Annex E).

The safe use of chemicals requires the application of management practices that are now

routinely applied in the chemical industry. In particular:

- sufficient information on each chemical must be available;
- safety and hazard information should be close at hand and its location made known to all workers;
- all storage and chemical distribution systems (tanks, pipes etc) should be labelled and marked;
- emergency response procedures for accidents and spills should be worked out, put into place and be exercised regularly;
- equipment should be safe or, where necessary, fenced off;
- all workers handling chemicals and wastes must be properly trained.



### 3. IMPROVING METAL FINISHING TECHNIQUES IN REGARD TO ENVIRONMENTAL PROTECTION

In view of the many possible sources of pollutants, and their multiple origins, a systematic, organized approach to pollution control is required in the industry. The selection of process technologies that achieve an intrinsically low rate of waste generation is a vital part of such an approach. Additional treatment technology to reduce the effect of the remaining residues is a subsequent step. Recycling and recovery are usually included within these two areas of consideration.

Considerable economic advantages can be expected to accompany the environmental benefit that flows from such a systematic approach to pollution control. The application of more advanced levels of technology can improve process control so as to achieve:

- saving in raw materials;
- decrease in rinsewater consumption;
- decrease in the consumption of reagents for effluent treatment;
- decrease in the size of effluent treatment facilities.

Many improvements will of course require an initial investment, such as new equipment (cost, setting up time, extra floor space), retraining of staff, possible higher energy consumption, and extra supervision. Nevertheless the environmental benefits can be substantial, and even from a purely economic point of view, the resulting improvements in throughput and product quality are often enough to justify investments in cleaner processes.

Every plating shop needs to evaluate its own situation, so as to be able to select the best package of measures. This evaluation should include: consumption of process chemicals, water and energy; assessment of the production methods in use from the standpoint of

environmental impact, and the need and options for waste treatment and disposal.

For most establishments, a proper process control laboratory will do much to help the owner/manager in the efficient operation of his plant. A laboratory will help in:

- control of finishing processes within narrower and lower operating ranges. Lower operating ranges means savings in chemicals dragged out, reduced need for treatment, and less sludge for disposal;
- trouble shooting to reduce rejects caused by out-of-control situations;
- efficient operation of treatment baths, determination of dumping frequencies by test rather than habit, control of additions to processing baths;
- determining effectiveness of treatment.

#### 3.1 MINIMIZING EFFLUENTS

Both the volume and strength of effluents are important in regard to environment impact. As well as having a greatly diminished pollution potential, there is a concomitant saving in requiring a smaller effluent treatment plant. A number of effluent reduction options are discussed below.

##### 3.1.1 Drainage and Dragout

Most of the contaminants in rinses come from the dragout of chemicals when work pieces (and the work carriers) are transferred from the treatment bath to the rinse tank. Volume of dragout depends on the drainage procedure, in particular:

- the speed of withdrawal;
- the shape of the work pieces;

- details of barrel perforations;
- the dripping time;
- the concentration of the bath chemicals;
- the viscosity of the bath;
- the temperature of the bath;
- the position of the work piece on the rack.

The reduction in dragout is a particularly useful first step to pollution reduction as substantial benefits can be achieved for almost no additional investment. The following suggestions should be helpful in minimising dragout.

If barrels are used for the rinsing operation, they should be immersed twice in the rinse-tank, with a complete rotation over the tank between immersion to improve drainage.

Barrels create more difficulties than racks because of entrapments in and on the barrel itself. Barrels containing simple parts that do not collect solution should not normally be rotated during drainage, since rotation will hold the solution on the surface of the pieces. However rotation of barrels for cup-shaped components is necessary to effect proper drainage.

A simple test for the effectiveness of any barrel-parts combination is to measure the amount of solution recovered after allowing the liquid to drain into a dry container for various combinations of operation. A more thorough test is to measure, by chemical analysis, the amount of chemical carried over into a tank of clean water. (The volume of the tank needs to be known, of course, to permit the calculation). This method measures the total carry-over, not just the amount lost by dripage.

It is important to inspect barrels frequently to ensure that the holes remain clear. Barrel

holes in polypropylene cylinders for example, are subject to peening over when heavy parts are run.

With rack systems, the rack and the work pieces should be placed above the plating tank for dripping (see Fig. 2).

In all cases, sufficient dripping time should be allowed. With chrome plating, for example, this time should at least be 20 seconds for each work piece.

By draining the work pieces carefully, about 70 % of the dragout problems can be eliminated. (For hot solutions caution must however be exercised to avoid the solution drying out onto parts, as this makes rinsing more difficult subsequently).

Draining of work pieces can be further improved by additional equipment. Air stream dripping (see Fig. 3) reduces the required time significantly. Other techniques include the removal of solution drops by vibrations or ultrasonic treatment. In some cases the addition of surfactants to the bath may improve drainage, provided that these substances do not themselves create problems at subsequent operational steps, or themselves constitute a pollution problem.

### 3.1.2 Reduction of Rinsewater Consumption

Traditionally, the metal finisher has used water generously for rinsing purposes, often without attempting to measure the amounts really required. This practice is now being increasingly questioned because of the cost of treating the resulting large volumes of wastewater. The high price of water in urban areas is a contributing factor in many places.

Where water is still being used freely without any attempt at control, it is usually quite easy

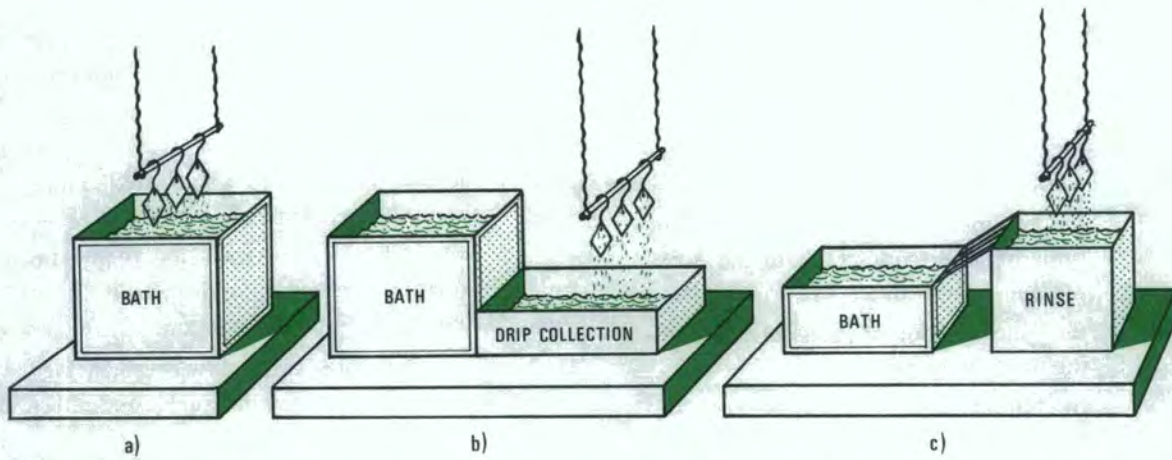


Figure 2 : Allowing sufficient dripping time for treated work pieces is the simplest and most cost-efficient method of pollution control : (a) over the treatment bath, (b) over a special drag-out recovery tank and, (c) after every rinsing over the rinsing bath. Baths which are close together reduce the opportunity for spillage. The use of drain-boards made of corrosion resistant material helps to return drips to the baths when parts are transferred between tanks.

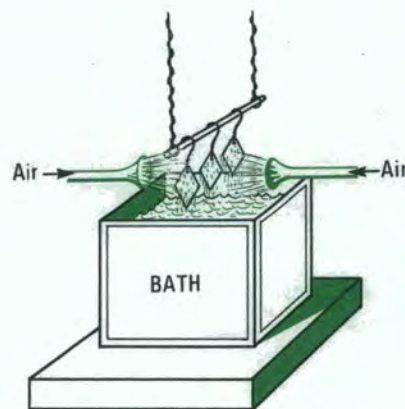


Figure 3 : Principle of improved dripping of the work pieces by air stream or fog spray treatment above the bath. When applying this technique, care must be taken that air velocity is not excessive and that drops are collected in the bath tank. Air must be oil-free to avoid deterioration of the finish.

to reduce consumption by at least 50% and, in some instances, by as much as 90%. The consumption of rinsing water is governed by:

- the arrangement of the rinsing tanks;
- the length of time during which the work piece is being rinsed;
- the volume of rinse water that can be brought into contact with the work piece in a given time;
- the concentration of the solution adhering to the work piece;
- the temperature of the work piece and the water;
- the shape of the work piece, and the turbulence of the solution;
- the position of the work piece on the rack;
- the draining time required over the process tank prior to rinsing.

### Minimizing Water Consumption

The first step, both in new and existing plants, is to find out how much rinsing is required. This question has been the subject of much study, and theoretical calculations are available from handbooks (e.g. 9, 12). Most metal finishers, however, prefer to work out the actual requirements on their own as follows:

1. run the process with those pieces which are the most difficult to rinse, e.g. due to form;
2. run the procedure with the bath where the rinsing procedure is the most complex;
3. determine the water flow rate for that bath. This can be done with a bucket and a stop watch or by measuring how long it takes to fill a tank to a given depth;

4. gradually reduce the flow of water until the rinse becomes inadequate because of contamination of subsequent baths or because stains are remaining on the work pieces;
5. increase the flow to about 10% more than the level in step 4;
6. install flow restrictors to keep the flowrate constant, and permit only supervisors to make changes.

Automatic control of water flow can be achieved with a controller that measures conductivity in the rinse tank.

While rinsewater minimization is an important goal, care must be taken that this does not increase the carry-over of contaminants, which cause defects in the work, or rejection of contaminated baths. Chemical analysis should corroborate the visual inspection of rinsewaters.

### Improvement of Rinsing Effectiveness

A significant improvement in water consumption can be obtained by optimizing the rinsing quality of the baths. Possibilities to improve the rinsing efficiency include:

- air agitation of the rinse water, or agitation by hydraulic, mechanical or ultrasonic methods (note that air agitation, while simple, is energy intensive, and requires a clean, oil-free air supply);
- agitation of work pieces during rinsing;
- raising the water temperature;
- introduction of fresh water at the bottom of rinse tanks, using a spreader, or even better, an eductor;
- use of spray rinsing techniques.

A well equipped bath is shown in Fig. 4.

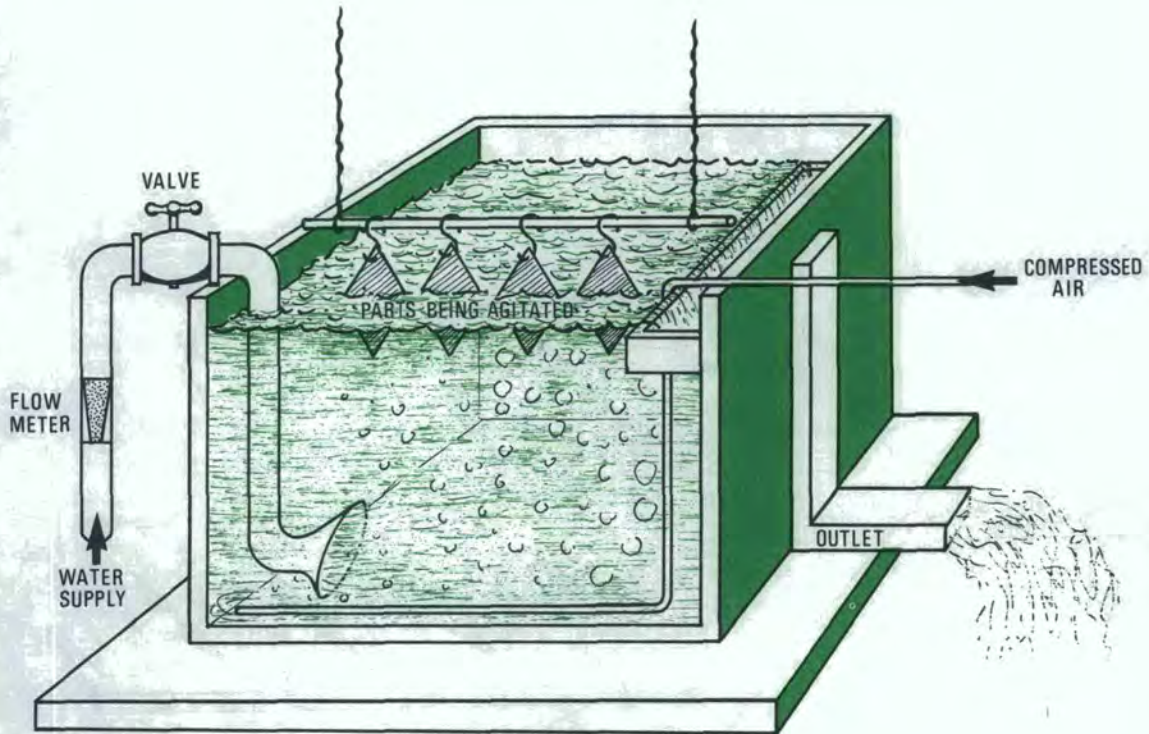


Figure 4 : Control of water flow and improvement of rinsing efficiency.

### Flow Rinsing, Static Rinse Baths, and Cascade Rinsing

The simplest rinsing procedure uses simple flow rinsing in a single rinse bath with a continuous high water flow to clean the work piece. Chemicals dragged out into the rinse tank are lost. Improvements in water consumption, chemical loss, and final treatment can be achieved by using one or more intermediate static rinse baths in sequence before the final continuous flow rinsing tank (see Fig. 5). The water in the static rinse baths is periodically replaced.

The highest efficiency is obtained by installing a counter-current rinse water cascade as

shown in Fig. 6. For most tank designs, the best efficiency will be obtained with a bottom water supply and a top water run-off for each bath, as shown earlier in Fig. 4.

In existing plants where multiple cascade rinsing is not already in use, at least two counter-flow tanks should be installed wherever possible. Their introduction will dramatically reduce water consumption (up to 90%) while not changing the rinsing effect. A third tank would allow a further reduction. New installations should be equipped with multiple cascade rinsing from the start.

Annex B contains some tables for calculating cascade rinsing effects.

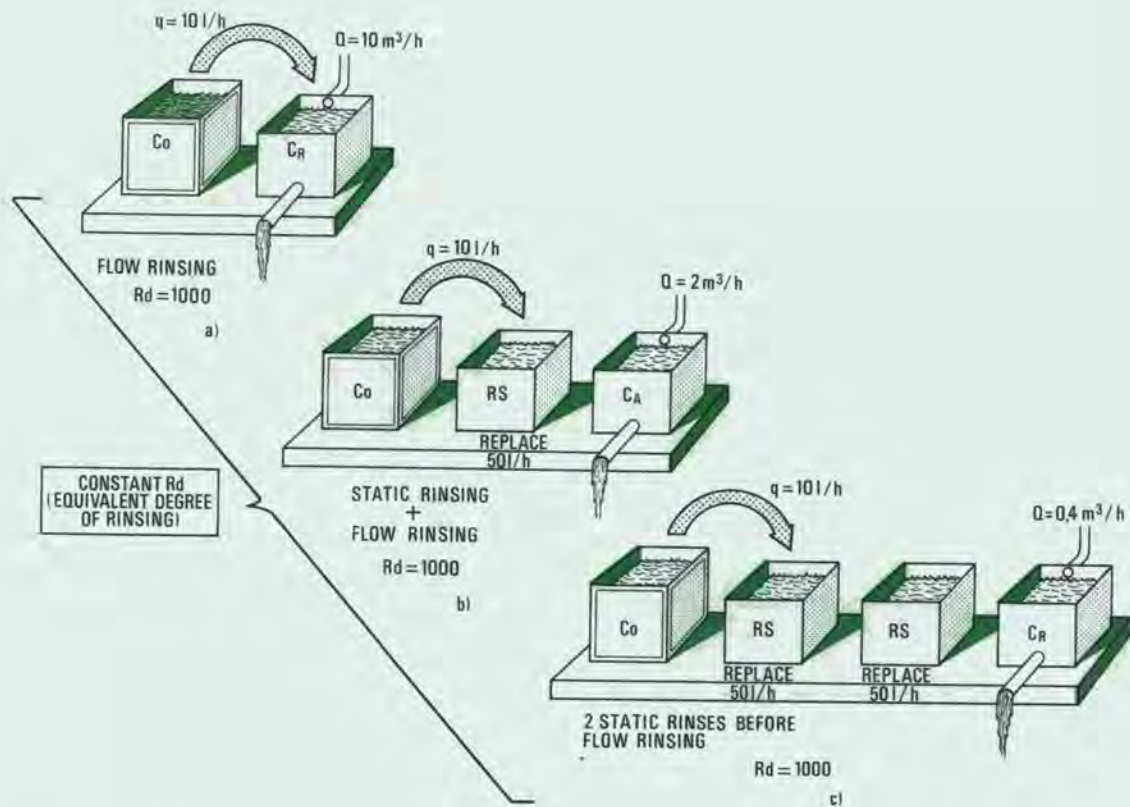


Figure 5 : Effect on rinse water consumption by use of intermediate static rinse baths to achieve an equivalent degree of rinsing.

### Static Recovery Rinse

An alternative to flow rinsing arrangements is to use one or more static rinse tanks. With such a system the dragout accumulates in the rinse tanks, and can therefore be recovered. The solution contained in these tanks can be used to make up the plating bath losses caused by evaporation and dragout (see Fig. 7).

Under some circumstances the bath chemicals can be recovered almost completely.

The following are particular advantages of the static recovery rinse:

- lower costs due to recovery of the bath chemicals;
- decrease in labour for bath maintenance.

Disadvantages of this process are:

- the increase in plating operations by an increased number of rinse tanks;
- the increase in floor space requirement for these rinse tanks.

### ECO-Rinse

ECO (ie. « economical ») rinses are static rinses in which the workpieces are immersed in

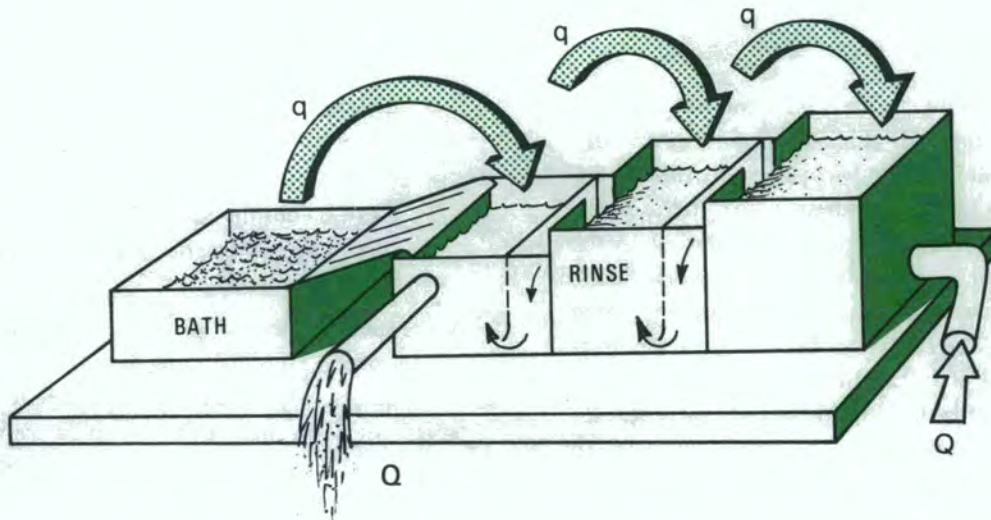


Figure 6 : Schematic design of cascade rinsing. Water consumption is reduced by use of the counter-current principle : the effluent of the downstream rinse bath serves as water supply;  $C_0$  = concentration of the treatment bath,  $C_1, C_2, \dots, C_n$  = concentrations of the 1st, 2nd, ...and last rinsing bath within the cascade;  $q$  = drag out ratio specified as volume per hour;  $Q$  = water flow rate.

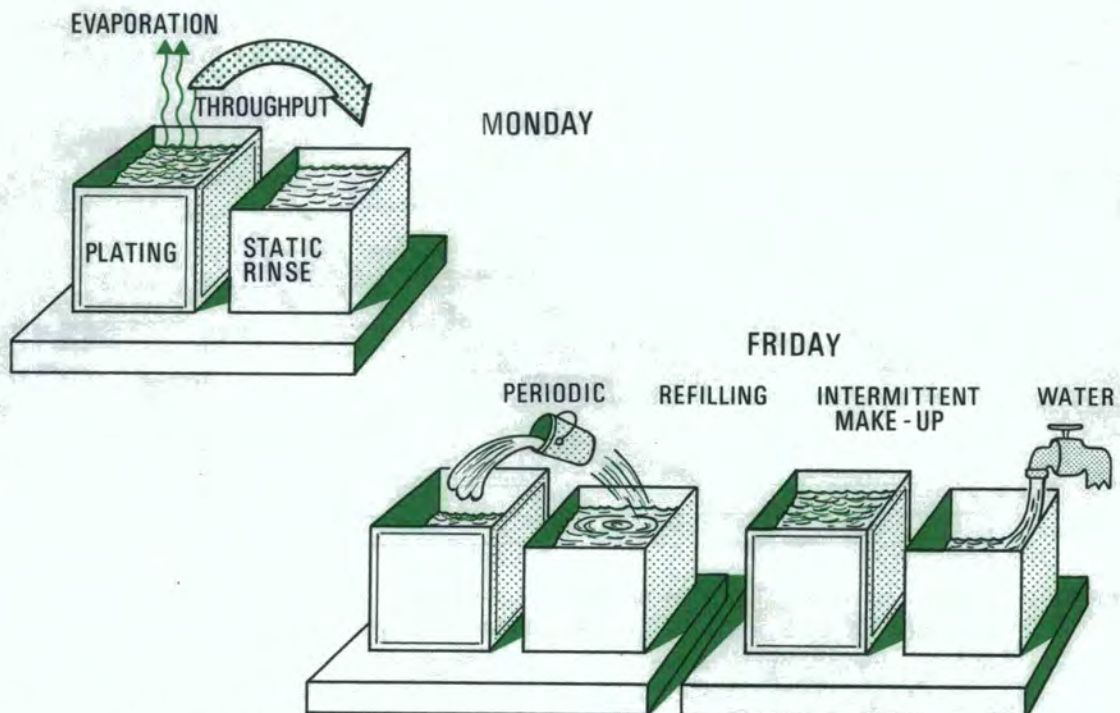


Figure 7 : Schematic design of a static recovery rinse

the rinse tank before and after treatment in the plating bath (Fig. 8). The term dragin/dragout may also be applied to this procedure. Dragout is lowered to 50% because the same quantity of liquid is transferred to the treatment bath (by the untreated work pieces) as to the subsequent rinse tank (by the treated pieces). The recovery of chemicals is optimized by use of an ECO rinse followed by cascade rinsing; effluent carried over compensates for the evaporation from the treatment bath. In using this procedure care must be taken that contaminants do not build up in the rinse tanks over time. Organic contaminants can be removed by passing the solution periodically through a carbon filter.

### Spray Rinse

Spray or jet rinse offers some advantages, especially for zinc, copper or nickel plating in the barrel:

- a decrease in water consumption;

- the cost of concentrating the solution prior to recycling into the plating bath is reduced;
- there is considerably less static recovery rinse: 99% of dragout can be recovered by spray rinse.

A number of different process configurations are possible. Thus dripping liquid from the work pieces can be directly returned to the treatment bath, spray effluent can be trapped by an extra tank, or the spray solution is drained into the following rinse tank. A further possibility is to use several successive sprays over a series of counter-current flow tanks. The water from each succeeding tank is used for the preceding spray rinse stage.

### Reactive Rinse

Reactive rinsing is the use of rinsewater from one operation as the source for another. For example, rinsewater following chloride zinc plating may be used for the hydrochloric acid

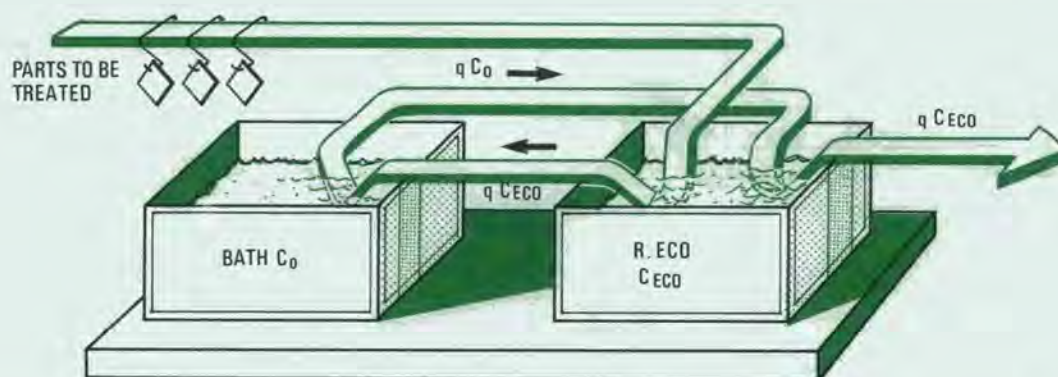


Figure 8 : ECO-rinse operation. The work pieces are immersed before and after the treatment bath in a static rinse tank; a smaller quantity of chemicals is concentrated in the rinsewater under steady state conditions because half of the dragout is transferred back into the treatment bath;  $q$  = dragout ratio,  $C_0$  = bath concentration,  $C_{ECO}$  = ECO rinse concentration;  $C_0 = 2 \times C_{ECO}$ , i.e.  $C_{ECO} = C_0/2$ .



rinse preceding the zinc plating, utilizing the wetters in the zinc to promote drainage. Any rinsewater dragged back into the zinc contains zinc solution just carried out. Rinse waters in rack operations may be able to be used in companion barrel plating operations for the same operations, where lower rinse ratios may be acceptable. Another method of accomplishing similar goals, is to simply dip a rack of barrels in the rinse immediately following a process before being immersed into the process itself, thereby dragging back in some of what had just been dragged out in a previous operation.

### 3.1.3 Regeneration of Baths

In order to keep solution strength constant, the chemicals lost to a process are periodically replaced. However the accumulation of by-products (which may consist of precipitated, suspended or dissolved substances) will eventually result in a deterioration of the finishing quality. The replacement of baths yields a significant quantity of waste to be disposed of, and the process which maintains the baths in the best condition for as long as possible is the most desirable. Some regeneration methods are described in the following pages. Operators are advised to consult their suppliers for individual applications and the installation of suitable equipment.

A related consideration to the above is bath re-use for an application where less exacting requirements exist. The progressive re-use of cleaning solutions from the rear of a series of baths to the front of the sequence where the highest levels of contamination exist is one application of this technique.

While bath regeneration and re-use are highly desirable from both economic and environ-

mental points of view, it is unwise not to have some spare capacity in the general waste treatment system so as to cater for spent baths if the regeneration system should one day fail. The lack of such back-up could otherwise cause severe complications, and perhaps lead to a temptation to illegally dump the bath contents.

### Filtration And Centrifugation

Filtration or centrifugation (Fig. 9) are effective methods for improving the life of a treatment bath. An activated carbon filter can be used to remove dissolved organic impurities in addition to its action in removing solids. The removal of oils from alkaline cleaners by ultrafiltration considerably prolongs the life of treatment baths, and reduces interference by oils with flocculation and settling steps during clarification. Separation of the grease film from degreasing baths is another example of the use of centrifugation or filtration (see Fig. 9). In addition to the above a number of newer technologies such as hydrocyclones, packed media filters, and electrolytically enhanced cross-flow membrane filters are being refined and should become more readily available in the future.

Filtration or centrifugation can be carried out during normal operation, either continuously or intermittently. The advantages of these techniques are:

- fast regeneration of the treatment bath with high efficiency;
- the working process does not have to be interrupted;
- resulting wastes are highly concentrated (and may thus be able to be recovered);
- disposal of residues may be easier than would be the case for concentrated liquid wastes.

Despite the advantages, the comparatively high investment and operating costs have tended to inhibit the use of these techniques. Nevertheless there are circumstances where filtration or centrifugation offer interesting alternatives to other approaches.

### Evaporation

Normal evaporation losses from hot treatment baths can often be compensated by re-use of effluent from the rinsing cascade as illustrated in Fig. 10. If the effluent rate equals the evaporation rate, a complete recovery of bath chemicals can theoretically be obtained. If the rate is inferior, the rinse bath can still be concentrated by forced evaporation to achieve the required strength.

In the case of cold baths, recovery of the bath chemicals is still feasible (Fig. 11), but forced evaporation requires additional investment in equipment, and higher energy costs. If a condenser is used, both dragout chemicals and water can be recirculated (Fig. 11 (a) and (b) for example).

If there is a possibility that dissolved minerals in the feed water will build up and interfere with the treatment process, it is recommended to use de-ionized water for makeup. Other contaminants that build up may need to be removed by cation exchange or similar techniques from time to time.

Forced evaporation techniques could be considered for processes involving highly toxic or expensive chemicals. Given the installation

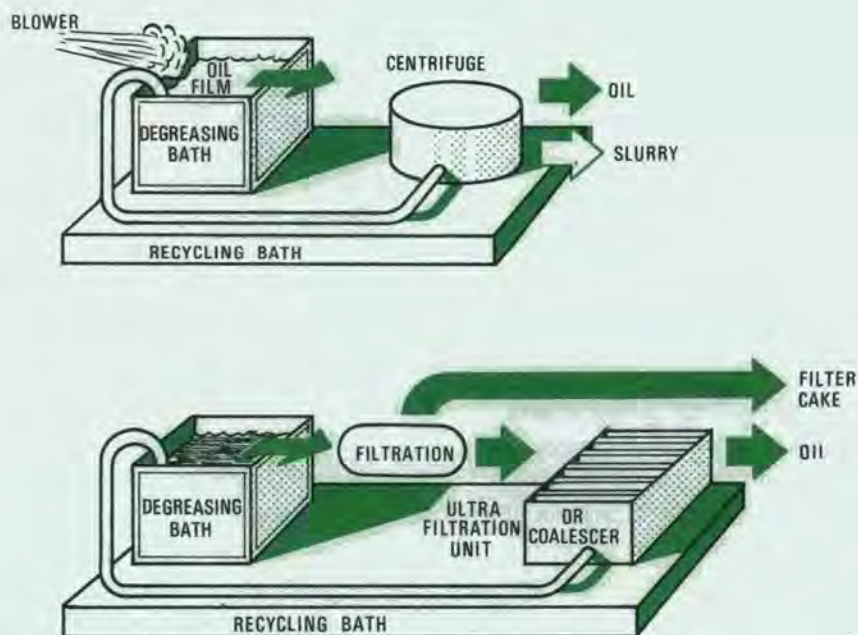


Figure 9 : Filtration or centrifugation of suspended or sedimented particles from treatment baths.

and operating costs, as well as the requirement for technical and chemical know-how, they are best suited to larger plants. They may nevertheless be also considered for advanced new plants of smaller enterprises where a high level of technology is desired. In suitable climates, solar energy may be a useful source of heat for evaporation. For a more detailed description of the necessary equipment the reader is referred to literature reference (12) or handbooks on this subject.

### Freeze Separation

The freezing of solutions may be used to concentrate and separate dissolved impurities. It can for example regenerate copper cyanide by removing the carbonates.

Thermodynamic energy requirements for separation by freezing are less than for evaporation (the theoretical values are 334 kJ/kg instead of 2257 kJ/kg) and this technique therefore has a lower operating cost than

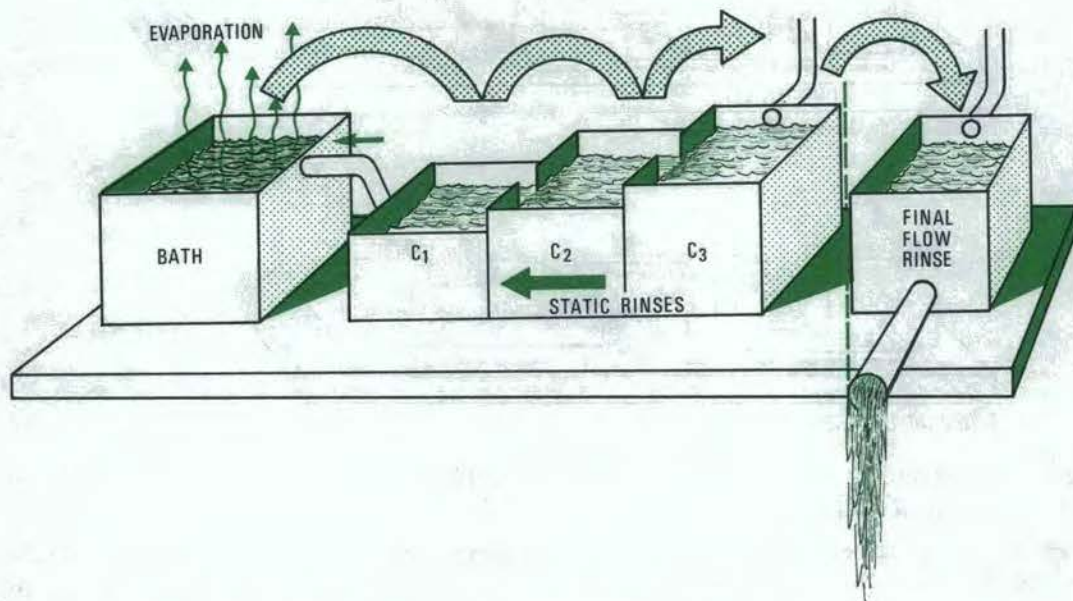


Figure 10 : Use of rinse effluent to compensate for evaporation loss in a bath.

Fig. 11 (c) illustrates an evaporation technique with practically complete recycling of rinse water and bath chemicals. Due to possible corrosion problems accompanying evaporation of strong electrolyte solutions in 11 (c) it is in fact more common to carry this out on the more dilute rinse solutions.

evaporation. Investment costs may be acceptable for larger metal finishing plants.

### Electrolytic Recovery

Electrolytic recovery of metals is a well developed technique. It can be recommended for

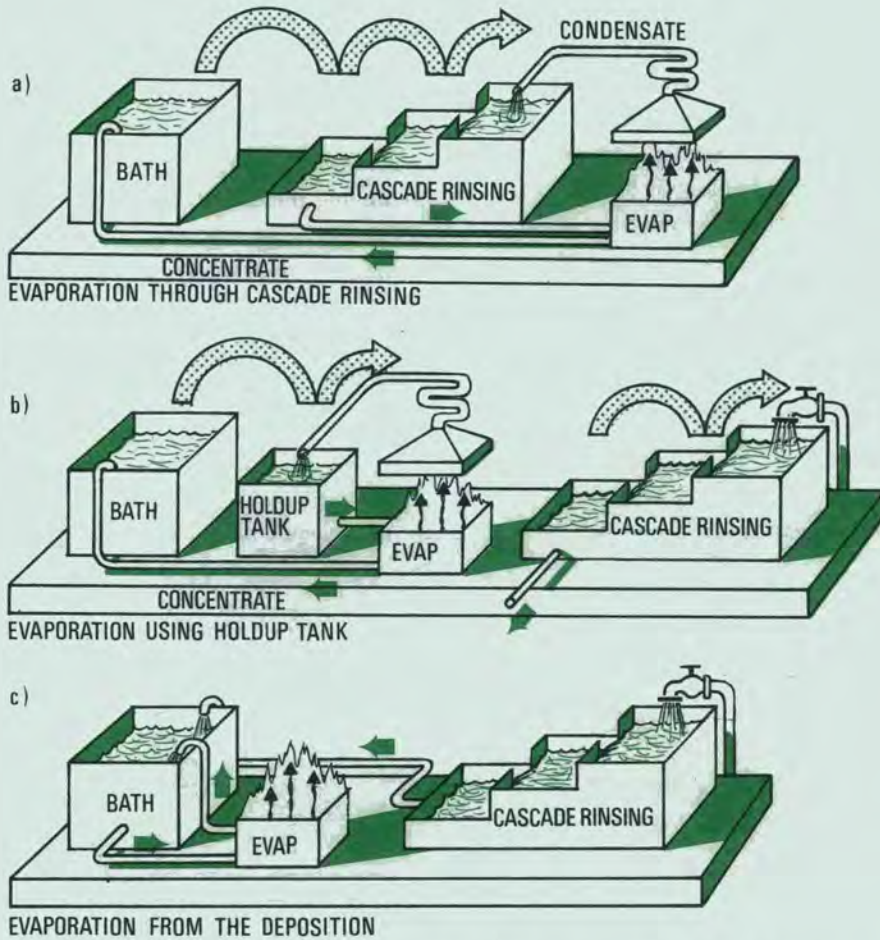


Figure 11 : Possibilities for the use of evaporation and condensation to avoid or minimize the loss of bath chemicals.

smaller as well as larger finishing facilities, especially in cases where the cathodically deposited metal can be re-used for metal plating within the plant.

It is characteristic of this technique that complete recovery of the metal from dilute solutions cannot be achieved. As the metal salt concentration reduces due to the metal extraction, the voltage must be increased in order to continue the cathodic deposition. Voltage enhancement is ultimately limited by secondary reactions such as water decomposition.

Electrolytic recovery can therefore only be one of several steps within a pollution control strategy. Nevertheless, the efficiency of traditional recovery methods is gradually being improved by the development of new electrochemical reactors incorporating for example magnetic activation or porous electrodes. Such new techniques should gradually find their way into more common use in coming years.

Fig. 12 shows how an electrolytic cell may be integrated into a treatment chain. Three

examples of the implementation of electrolytic copper recovery from pickling are shown. It should be emphasized that electrolytic recovery combined with metal concentration by evaporation (hot treatment bath, use of an evaporator), or by a cation exchanger, improves the recycling efficiency considerably. Chrome (III) recovery from chromic acid baths is also possible by electrolysis.

For ion exchange processes, columns filled with special resins are employed to extract specific anions or cations (eg. nickel) from liquids which pass through the columns.

Ion exchangers are effective for recovering materials from dilute solutions, but investment and processing is rather expensive. Furthermore their maintenance is not simple.

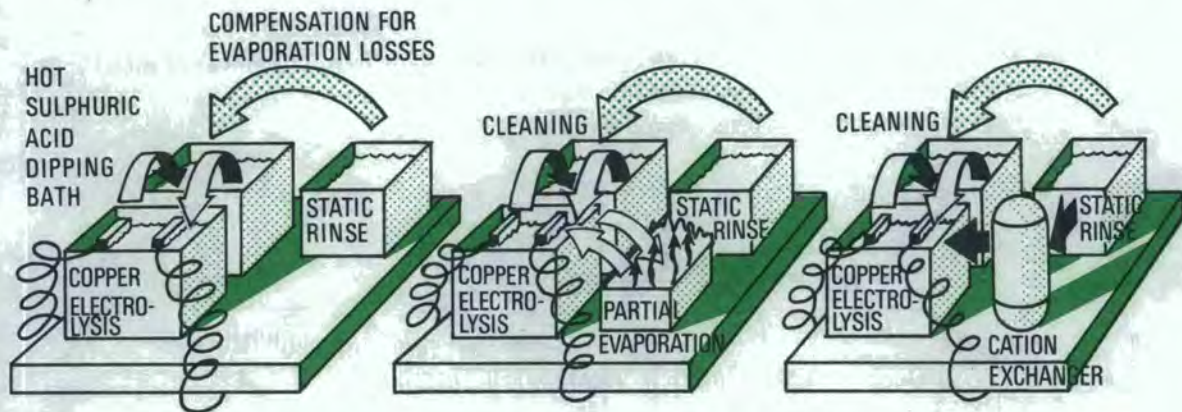


Figure 12 : Examples of electrolytic copper recovery from pickling baths combined with evaporation (hot bath or evaporator) or ion exchange techniques.

### 3.1.4 Recovery from Dilute Solutions

The preceding techniques will be useful in minimizing the loss of chemicals to the effluent stream. Only rarely however can the loss be totally prevented. A further consideration is then to attempt to concentrate the remaining inevitable losses so as to facilitate the subsequent recycling or treatment. Methods described below can be helpful in extracting chemicals which are present in low concentrations. Accordingly, while they have useful particular applications, they are not all equally suited for all types of baths or effluents. Further expert advice should be sought in order to make the best choice.

Regeneration has to be undertaken from time to time when the resin is saturated with ions. Ion exchange systems with automatic regeneration are now commercially available. Alternatively, resin cartridges may be sent off to a commercial regeneration facility.

Fig. 13 shows the installation of an ion exchanger. A more sophisticated system (Fig. 14) consists of three exchangers in sequence for the elimination of metal ions from a chromic acid bath. Here ion exchange is used for the regeneration of treatment baths to significantly enhance their service life.

In modern installations, ion exchangers are essential for the reduction of water consumption (rinse waters are used in a closed system

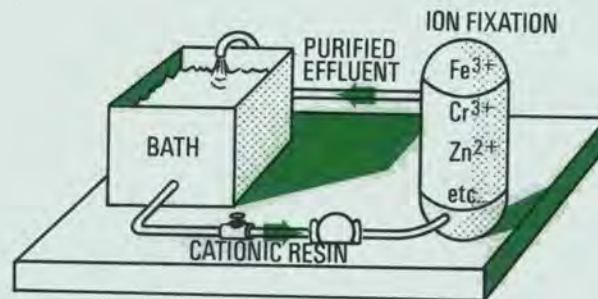


Figure 13 : Use of ion exchange : regeneration of a treatment bath by the removal of metal ions results in a significantly extended life time of the bath, reduced consumption of chemicals, and an enhanced level of product quality.

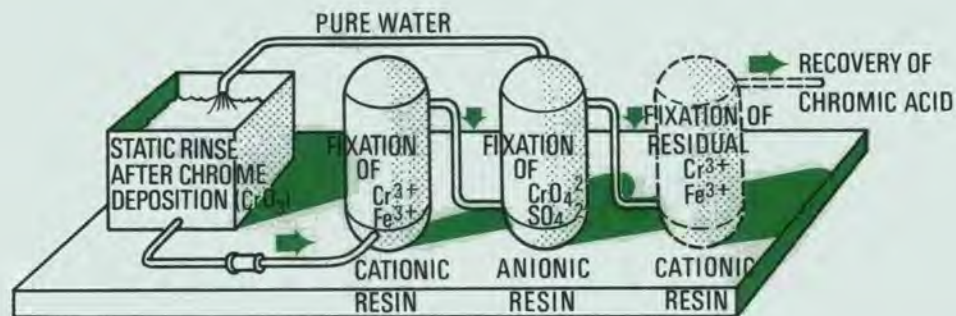


Figure 14 : Ion exchangers in sequence for the recycling of metal ions, of rinsing water, and of chromic acid.

without an effluent) and for the recycling of treatment chemicals. Recovery of other wastes by means of ion exchange will also become more significant in the future. For example it can be used to recover copper from process waters in the electronics industry

### Reverse Osmosis

Reverse osmosis can be used to concentrate a solution by using high pressures to force solvent molecules through a semi-permeable

membrane. The larger solute molecules cannot pass through the membrane and are left behind, becoming gradually more concentrated as the solvent is driven off. Eventually the concentrated wastewater is bled off for further treatment, or for recovery. Equipment is rather specialized, requiring special membranes and high pressures of 20 to 30 bars. Accordingly reverse osmosis is expensive, and the maintenance of the membrane needs a skilled operator. It is suitable for large plants with access to technical skills.

Fig. 15 shows how a reverse osmosis unit can be integrated into a process line.

### Ultrafiltration

Ultrafiltration employs larger membrane pores than reverse osmosis, and therefore can operate with lower applied pressures (from 1 to 8 bars). Ultrafiltration is useful for the separation of chemicals of larger molecular size, such as oils and dissolved organic substances.

It can for instance be applied to remove emulsions or colloids from degreasing or amorphous phosphatation baths, or for the separation of smaller contaminating molecules from larger sized particles.

Due to the nature of materials likely to be recovered, it is more applicable as a pretreatment in waste water treatment than as a method of recovery of useful chemicals.

Water treated by ultrafiltration is less pure

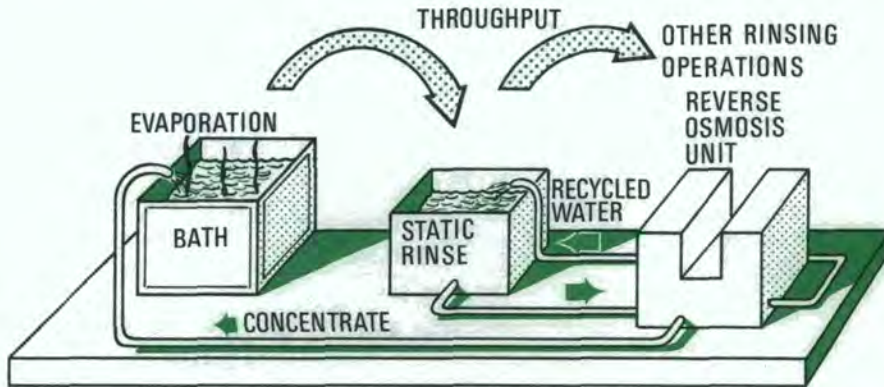


Figure 15 : Application of reverse osmosis : the dragged out chemicals are re-cycled to the treatment bath.

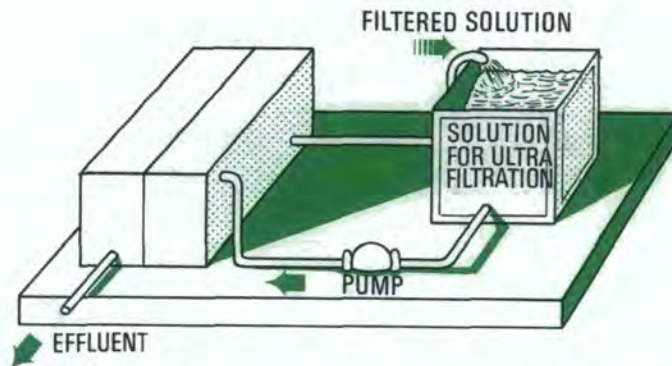


Figure 16 : Ultrafiltration system for the separation of colloids, and particles or dissolved substances with large molecular sizes (molecular weight between 1000 and 100 000).

than that obtained by reverse osmosis. Subsequent purification (e.g. by ion exchange) may be necessary. The specific advantage of ultrafiltration is to separate large molecular weight materials very effectively from solutions.

### Other Membrane Techniques

In electrodialysis the diffusion of ions across a membrane is accelerated by an electric potential. This method is useful for the concentration and purification of chromic acid baths as well as rinsewaters generally. It is useful in achieving recovery of bath materials, and is suitable for small as well as larger plants.

There are also other membrane exchange techniques under development. They pro-

mise to be suitable for the removal of heavy metals, but they are still in the experimental stage and are not yet routinely applied.

### 3.1.5 Combination of Different Technologies

Some of the technologies discussed so far can be used in combination so as to achieve higher efficiencies than would be individually possible. The selection of such a combination depends on a careful analysis of the production process, the purification objectives, and the relative cost factors under the conditions prevailing at each plant.

In some cases combinations are not only options, they are necessary. In the case of dec-

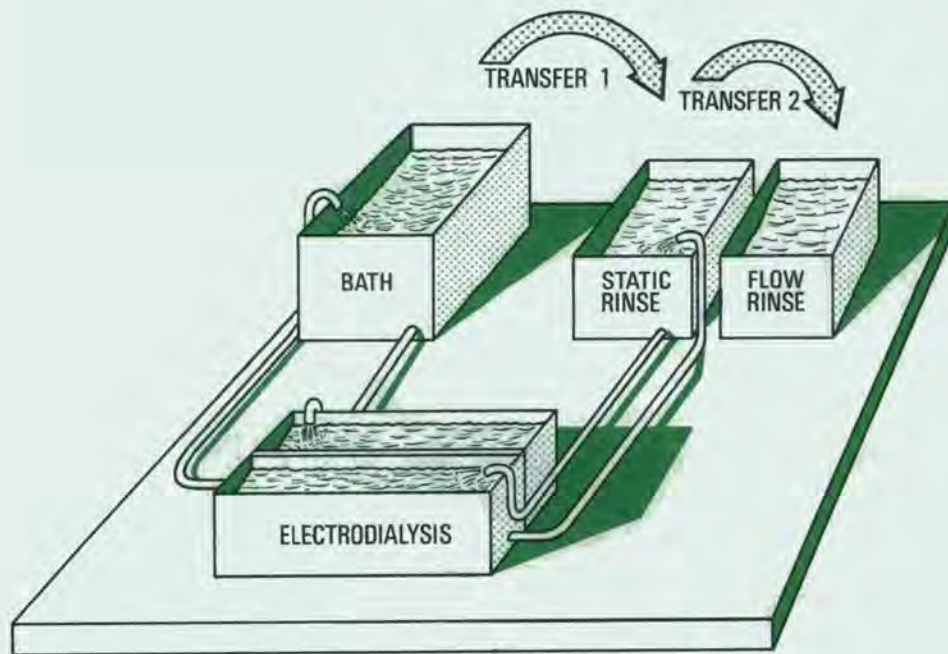


Figure 17 : Typical placement of an electro dialysis step in a low pollution operation.



orative chromium treatment for example, electro dialysis in connection with a static rinse requires a further concentration step (eg. evaporation) for the chromic acid solution from the electro dialyser before it can be usefully re-introduced into the plating bath. Another example concerns the cascade rinse effluent from a cold plating process. This must again be concentrated before it can be re-used.

Not all options can be discussed here. Table 2 shows a number of combinations that can be easily used to achieve the efficiencies shown. Other combinations must be investigated on a case by case basis.

### 3.2 WASTEWATER TREATMENT

Several different waste streams will usually originate from a single metal finishing plant. The different composition and concentrations of these waste streams will require different treatment procedures, and in many cases it is advisable to treat them separately so as to achieve the highest removal efficiency. Separate treatment (or at least pre-treatment) also avoids the possibility that incompatible wastes will undergo undesirable reactions in the storage tanks. Such reactions can be a hazard to personnel by generating toxic gases, or the wastes may combine to form complexes that are difficult to treat, eg. nickel cyanide.

In all cases the waste stream must be carefully evaluated before selecting a treatment scheme. Many enterprises have opted for treatment schemes that cater for their own wastes, but in some circumstances it may be economic and practical to arrange a centralized waste treatment facility for a group of enterprises close together.

It is also common in many cities for industries to discharge wastewaters to a public sewerage system. Public sewage treatment systems however usually rely on biological processes which cannot deal with heavy metal wastes. Accordingly many authorities only accept pretreated effluents in their system. Such a system then provides dilution, but little further treatment.

Figure 18 depicts the basic elements of a typical wastewater treatment system for metal finishing operations. In the following sub-paragraphs, specific parts of the overall system will be discussed.

For most heavy metals, precipitation as insoluble hydroxy or sulphide compounds is achieved by addition of simple reagents followed by pH adjustment and sedimentation. In the case of hexavalent chromium, it may be necessary to first chemically reduce the metal to a form where it will more readily form insoluble precipitates.

Cyanide removal is achieved by oxidation to harmless residues. A precipitation step may still need to follow the oxidation stage in order to remove the accompanying soluble metal ions.

For particularly hazardous substances such as cadmium a totally separate treatment system may be advantageous, including separate disposal procedures. In all cases, to ensure that treatment will be effective there is a need to distinguish between treatment of rinsewaters (high flow and low concentration) and discarded strong process solutions (cleaners, acid dips, plating solutions) of low volume and only occasional discharge, but of high concentration. A batch treatment system can cope with the two types of wastewater but a continuous flow system is likely to be overloaded by shock loads. Accordingly, a simple

Table 2

Specific Combinations of Pollution Reducing Technologies and their Efficiency in with Regard to Various Metal Finishing Processes

	Cyanide copper plating	Acid copper plating	Nickel plating	Decorative chromium plating	Thick chromium plating	Cyanide zinc plating	Acid zinc plating	Cyanide cadmium plating	Chromic passi- vation	Copper pickling	Acid pickling
Dripping . . . . .	x	x	x	x	x	x	x	x	x	x	x
Eco rinse . . . . .	x	x	x	x	x	x	x	x	x	x	x
Static recovery rinse	x	x	x	x	x	x	x	x	x	x	x
Ion exchange . . . . .	x	x	x	x	x	x	x	x	x	x	x
Electrolysis . . . . .	x	x	x	x	x	x	x	x	x	x	x
Electrodialysis . . . . .	x	x	x	x	x	x	x	x	x	x	x
Evaporation . . . . .	x	x	x	x	x	x	x	x	x	x	x
Pollution avoidance	98%	80%	98%	98%	70%	98%	98%	80%	80%	98%	98%

Adapted from "Disposal of Hazardous Waste-Metal Finishing Waste", NATO-CCMS, Study No. 121, 1981.

WASTEWATER TREATMENT

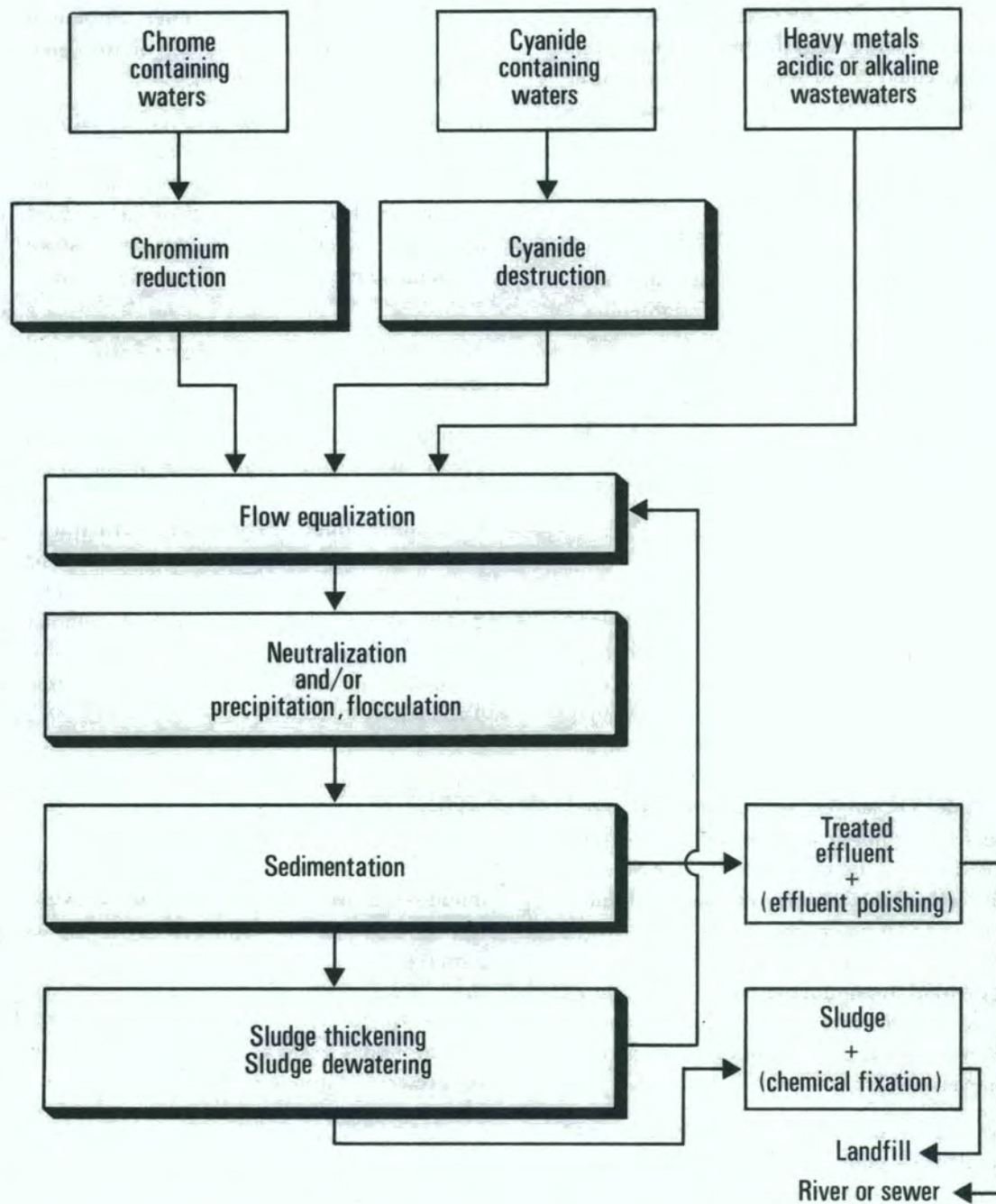


Figure 18 : Elementary block design of a wastewater treatment system for a typical metal finishing operation. In practice a number of additional treatment processes may be added to recover materials, and to enhance treatment effectiveness.

approach is to store any strong solutions and release them slowly into the treatment system. The flow equalisation stage is vital to ensure that the treatment process can function as designed.

### 3.2.1 Detoxification of Hexavalent Chromium

Hexavalent chromium compounds come from processes such as polishing and brightening, pickling, passivation, chrome plating, chromating, and plastic metallisation. Reduction of Cr (VI) to the more easily precipitated trivalent state can be achieved in a number of ways.

#### Chromate Reduction with Sulphur Compounds

Sulphur compounds are commonly employed for the reduction of hexavalent chromates. Advantages include short reaction times, the simple observation of the reactions by measuring the redox potential, and a low yield of sludge after neutralisation with sodium hydroxide. The sulphur compounds may conveniently be sulphur dioxide gas ( $\text{SO}_2$ ) (the gas is dissolved in the solution), metabisulphite ( $\text{Na}_2\text{S}_2\text{O}_5$ ), or normal sulphite ( $\text{Na}_2\text{SO}_3$ ). All these substances react with hexavalent chromium in the same way: in acid solution (optimum pH range: 2 to 3) they are dissociated and the bisulphite anion ( $\text{HSO}_3^-$ ) reduces the chromium to the trivalent state.

Stoichiometrically, for the reduction of 1 g of hexavalent chromium 0.92 g of S is required. From this the quantities of the appropriate reagent can be calculated, assuming the reaction goes quickly to completion.

Table 3 shows the yield of hydroxide precipit-

ation and of sulphur salt after chromium reduction to indicate the burden on the deposition site or the environment.

In view of the deleterious effects of sulphur compounds on concrete sewers and drains, the effect of the reaction products may need some evaluation. The requirements of the relevant authorities should be ascertained before installing and operating the reduction plant.

#### Reduction with Divalent Iron Salts

Iron salts are often used because they are cheap, and readily available as by-products from other processes (removed from waste water, for example). The theoretical requirement is 3.22 g Fe (II) and 6.60 g  $\text{H}_2\text{SO}_4$  (or 4.91 g HCl, respectively) for the reduction of 1 g of hexavalent chromium. The high volumes of sludge generated increases the cost of disposal compared to other methods (see Table 3).

#### Electrolytic Reduction of Chromate

The cathodic reduction of hexavalent chromium is performed in acid solution. pH control is achieved through acid addition as required (the theoretical value equals that of the iron salt reaction). The electrolytic efficiency is 95%, the practical energy consumption around 1.2 kWh/1 kg  $\text{CrO}_3$ . However the presence of iron or copper affects the efficiency of electrolytic reduction, and these metals may need to be removed first if they are present. The lowest concentration possible under practical conditions is 0.5 mg/l, but it is not recommended to run the process to this value, because at low concentrations the time requirements increase considerably. If the

CORRIGENDUM - Please note that Para 5, p 31 should be replaced by:

Hazards are best minimized by ensuring as rapid a hydrolysis as possible. This is achieved at a high pH of around 11.5 with a detention time of up to one hour to guarantee complete reaction. Good mixing is essential. In some countries the retention time may be set by regulation.

If no further oxidation is required from cyanate to nitrogen and carbon dioxide, then the overflow from the retention tank can be piped to an equalization tank for subsequent neutralization.

In a few cases the further oxidation of cyanate may be required. This is usually carried out at a pH of 8.0 to 8.5, again using hypochlorite. pH control must be highly reliable to avoid the risk of toxic gas formation under acidic conditions.

Good control of the above reactions is greatly facilitated by the use of automatic pH sensors and feed pumps. These should be meticulously maintained to guarantee reliable operation. The use of equalization tanks allows for easier flow regulation prior to subsequent treatment stages. Equalization tanks are a key to effective waste treatment for most metal finishing effluents.

chromium concentration is not high (100 to 1000 mg/l), other reducing methods can also be used. Higher concentrations should be pre-treated electrolytically, followed by other reducing processes.

In a first step, cyanides are oxidized by hypochlorite to cyanogen chloride, an extremely toxic gas. The second step, the hydrolysis of cyanogen chloride to cyanate, takes place virtually at the same time in the reaction ves-

Reducing Agent	Yield of Sodium Sulphate from Neutralization (kg)	Precipitated Hydroxides as Dry Matter (kg)
sulphur dioxide	4.1	1.98
sodium bisulphite	8.2	1.98
iron (II) sulphate	16.4	8.14

Table 3 : Precipitation of hydroxides and neutral salts from hexavalent chromium reduction by sulphites or iron salts (Table taken from 6)

### 3.2.2 Detoxification of Cyanides

Processes for the detoxification of cyanide have been thoroughly researched, as cyanide is one of the most toxic agents used in the metal finishing industry. The chemistry of cyanide detoxification is relatively complicated and in most cases degradation needs more than one reaction step.

#### Degradation with Chlorine

Large detoxification facilities work economically with chlorine gas addition or electrolytic chlorine production. The use of (12% to 15%) sodium hypochlorite solutions is recommended for smaller plants. If chlorine gas is used, the hydrochloride generated together with hypochlorite requires further neutralisation chemicals. This technique is suitable if the cyanide concentration ranges between 0.1 and 1.0 g/l. A disadvantage of using chlorine is the high production of salts from the subsequent neutralisation.

sel. Although cyanogen chloride is highly soluble in water, the temperature must not exceed 40°C to avoid degassing of solutions.

Hazards are best minimized by ensuring as rapid a hydrolysis as possible. However pH should not be too high if the further oxidation of cyanate to nitrogen and carbon dioxide is to be carried out. This third degradation step, not always required by the water authorities in industrialized countries, is again achieved by hypochlorite. A suitable pH for both reactions is around 8.5, and this should be very carefully maintained.

Alkaline, zinc or cadmium cyanides are destroyed rapidly. Under excess hypochlorite conditions, suitable pH and with solution turbulence, copper cyanides need about 30 minutes oxidation time. For safety reasons, three times the minimum reaction time should be allowed, i.e. 90 minutes. In some countries the times may be set by regulation. Complexed, other noble metal, iron or nickel cyanides

however need much higher hypochlorite excess and longer times for an adequate reaction. These cyanides should preferably be first separated by ion exchange. Regeneration then yields alkaline cyanides which are readily degradable. Recycling of the metals from the cation exchanger is also possible, and is a particular advantage for the expensive noble metals. Wherever possible unnecessary complexing of metals with cyanide should be avoided in the plating process.

The oxidation of 1 kg of cyanide ( $\text{CN}^-$ ) to cyanate theoretically requires 2.86 kg of sodium hypochlorite, or 2.6g kg of chlorine gas. If chlorine ( $\text{Cl}_2$ ) is used, neutralisation of the generated hydrochloride requires 3.08 kg of NaOH per kg NaCN.

For the oxidation of cyanates additional hypochlorite is required. In this case the theoretical amount for the complete degradation of cyanide to nitrogen and carbon dioxide is 7.12 kg sodium hypochlorite or 6.70 kg of chlorine gas (and 7.7 kg NaOH for neutralisation), per kg of cyanide.

Oxidation of cyanides has to be checked by chemical analyses in order to regulate the dosage of chemicals. Special electrodes for pH, cyanide or chloride are available. The addition of chemicals may be undertaken manually, or automatically by special equipment. There should be no free chlorine in the effluent in order to avoid the possibility of oxidizing chromium to the hexavalent state when effluent is mixed with other wastewaters.

### Cyanide Degradation by Active or Activated Oxygen

If oxygen is used for the degradation of cyanides, no additional salts are produced, and no

neutralisation of the treatment solution is necessary. There are several methods in use.

A suitable oxygen producing agent is hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). Theoretically 1.3 kg  $\text{H}_2\text{O}_2$  is sufficient per kg of cyanide. In practice an excess of  $\text{H}_2\text{O}_2$  is necessary to ensure a useful reaction rate. This process is not recommended with low initial cyanide concentrations (less than 500 mg/l). The reaction can be accelerated by addition of catalysts or formic acid, and may then be suitable for cyanide concentrations between 100 and 1000 mg/l. Persulphuric acid can also be used as the oxygen delivering substance. It hydrolyses to  $\text{H}_2\text{O}_2$  and sulphuric acid in aqueous solution. Direct ozonation is another possibility. Concentrated peroxide and persulphates are hazardous substances and must be handled with care.

The catalytic oxidation of cyanides by non-activated oxygen is also possible. Several carbon products have been tested as catalysts. Due to longer reaction times, these methods are recommended only for wastewaters containing low concentrations of cyanides, especially as aftertreatment.

### Other Cyanide Oxidation Processes

Electrolytic cyanide degradation can be carried out in the presence of chlorides. Cyanides can be oxidized by electrolytic splitting of oxygen from hydroxides. This technique works economically only with concentrated cyanide wastes.

### Precipitation of Cyanides

Iron ions form highly stable complexes with cyanides. A precipitation of divalent or triva-

lent hexacyanoferrates is possible as a detoxification step within the final wastewater treatment. But the resulting sediment is not suitable for a landfill waste deposit, because acids or photolytic reactions may under some circumstances release cyanides from the deposit. Disposal therefore should be by other means such as thermal destruction.

### Thermal Degradation of Cyanides

Thermal degradation of cyanide substances yields nitrogen or nitrates and carbon compounds (formates, carbonates), together with an inorganic residue from any associated metal cations. Burning at 1200 to 1400°C destroys cyanides completely, yielding nitrogen and carbon dioxide as products.

Thermal processes are applicable only for concentrated wastes. The equipment required is capital intensive and skilled maintenance is necessary. Metallic combustion residues may still pose a disposal problem. As a rule such techniques have a use only for solid residues which cannot easily be brought into solution for treatment in aqueous media.

### Comparison of Cyanide Degradation Techniques

The standard detoxification method for cyanides in small metal finishing plants is still oxidation by chlorine. Advantages are the reaction speed, the possibilities of analytical process control, low costs, and a relatively long experience in handling.

The precipitation of cyanides from concentrated wastewaters as hexacyanoferrates is suitable, if a thermal degradation step follows.

Peroxy-compounds have the general disad-

vantage of requiring long reaction times. These processes are useful where only small quantities of cyanide waters are to be treated. The content of salts in the effluent is low.

If cyanides are destroyed in a continuous flow stream, hypochlorite treatment may be the best choice because of its simple handling requirements. If concentrated or small volumes are to be treated, techniques should be chosen which yield a minimum of waste even if performance and maintenance is more complex.

### 3.2.3 Neutralisation and Precipitation

This step is the principal operation that converts dissolved metals to insoluble hydroxides and thus allows them to be removed from effluents. Neutralisation must in general be preceded by effective flow equalisation procedures to allow the system to operate effectively.

«Neutralization» of metal finishing waste waters is to be understood more as a traditional term than as a real neutralisation: it does not mean the adjustment to a pH of 7.0, but a precipitation of the metal hydroxides from alkaline media (see Fig. 19 for best ranges). In earlier times the elimination of metal hydroxides during neutralisation of the waste water was seen as a secondary effect of neutralisation, but since metal discharges are now recognized as serious ecological risk, the precipitation subsequently became as important as neutralisation itself.

As precipitation agents, sodium hydroxide, lime, and soda are generally used. Magnesium hydroxide is also sometimes used as it produces a better sludge. However the reaction is slower and pH range is limited. Alkaline



wastewaters are neutralized by technical sulphuric acid, subject to discharge limits for sulphates not being exceeded. Smaller facilities are advised to use sodium hydroxide solution (450 g/l), unless wastewaters contain fluorides. In larger factories, and in the presence of fluorides, lime solution treatment should be used — it is cheaper than applying NaOH and also removes the fluoride. On the other hand this treatment requires the installation of a lime milk preparation plant.

discharged quantities are large or the receiving waters are sensitive to alkaline effluents.

Neutralisation itself is rapid. The process should be carried out in two stages. In the first (or « pre-reaction ») tank either acid or alkali is added with vigorous agitation to a preset pH point controlled by pH electrodes. The retention time in this first tank is approximately 10 minutes. In the second stage final pH adjustment occurs. More acid (or alkali) is

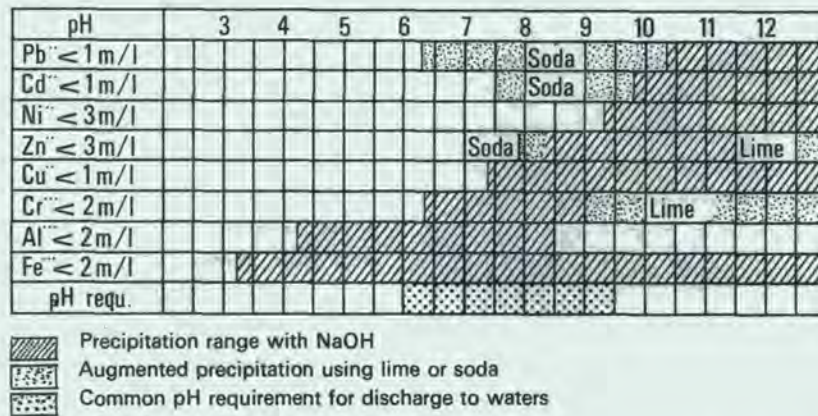


Figure 19 : For the precipitation of solid metal hydroxides the waste water has to be adjusted to specific pH ranges. (Figure taken from (6) )

The correct pH for the precipitation of the metal hydroxides varies with the metal ions under consideration. In Fig. 19 pH ranges are given for the precipitation of several metal hydroxides. For most cases, the pH will be within a range of 8.5 to 11. Unnecessarily high pH may interfere with the formation of a good settleable sludge, and accordingly a pH only slightly above minimum is recommended. For mixed metals in-situ tests should be carried out to determine the best pH. For discharge of the final effluent precise requirements may differ from one regulatory authority to another. Further adjustment of the pH to near 7 may be necessary before discharge if

added, still with vigorous agitation, and the pH is controlled to the optimum set-point for minimum solubility of the various metals present in the waste stream. Retention time in the second stage is 10 minutes as well. If alkalis other than sodium hydroxide are used, longer reaction times are necessary. A common configuration for effluent treatment involving neutralisation is shown in Fig. 22.

In special cases, for example if the metal ions are complexed by EDTA or NTA and a precipitation under the conditions mentioned above is not possible, there are more effective processes like sulphide precipitation, high pH

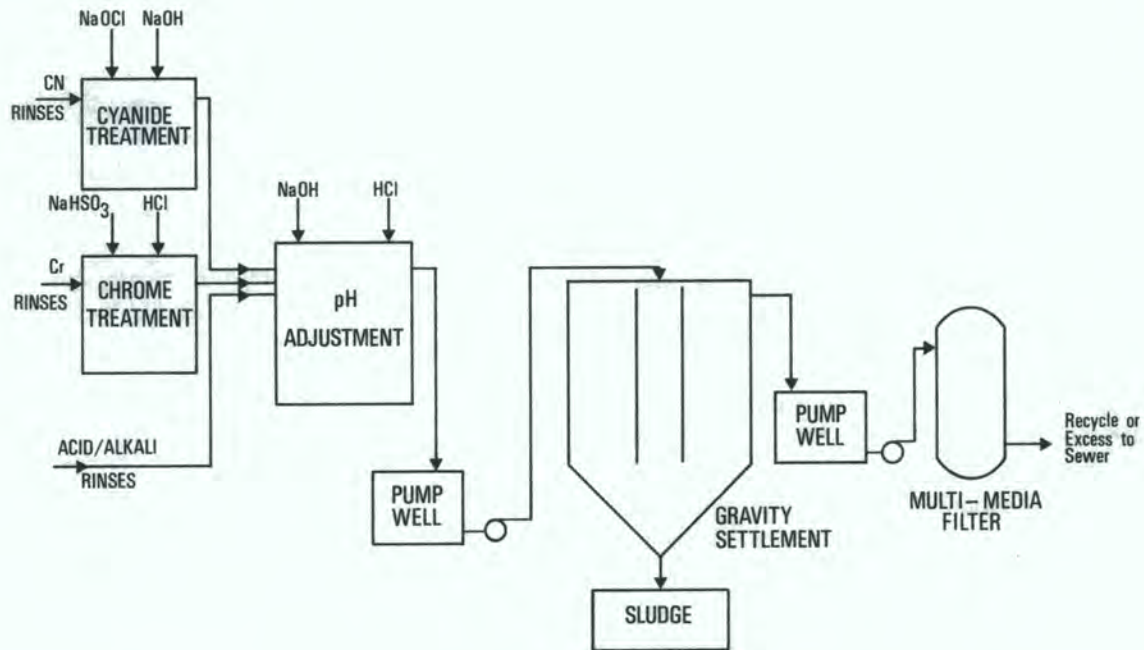


Figure 20 : Common Configuration for Effluent Treatment involving Neutralisation  
(Figure from W. Regan, Australia – private communication)

precipitation, solvent extraction, or starch xanthate extraction.

### 3.2.4 Sedimentation and Clarification

Following the precipitation stage, solids removal is normally achieved in gravity settlement systems such as is illustrated in Fig. 21. These are normally used as continuous flow devices, but where the waste volume is small a batch system may be used. Batch systems usually use two settlement tanks, one being filled while the other is emptying.

Solids removal is an important step in the treatment process since precipitated metals may under some circumstances re-dissolve if discharged to the aquatic environment.

Settlement effectiveness is affected by factors such as the size and density of particles, and the velocity of flow (in a continuous flow system). The presence of some chemicals may result in poor settlement due to the formation of a colloidal suspension that resists the coagulation into larger particles that fall out readily.

Ferrous and chromium hydroxide readily form colloidal suspensions. Chemicals such as

pyrophosphate, carbonates, organic brightening and wetting agents tend to promote such colloid formation. Conversely, ferric chloride and aluminium sulphate may aid settlement and their precipitation as hydroxides neutralises the electrical charge of colloidal particles and provides an opportunity for co-precipitation. Sedimentation may also be assisted by the use of flocculating agents such as long chain polyelectrolytes that entrap small particles and neutralise electrical charges. The use of lime as neutralising agent may also be effective in aiding sedimentation.

Some common types of sedimentation basins are shown in Fig. 21. The vertical flow basin has the advantage that it can be constructed of steel and mounted above ground, thus taking up a minimum of ground space. The conical bottom allows easy removal of settled solids. Settled solids will usually require further dewatering before disposal. Dewatering may be accomplished by further settlement, drying beds, filter or centrifuge.

The critical design parameter for sedimentation basins is « surface loading », defined as flow rate divided by surface area of the basin (units are metres per hour).

In horizontal flow basins the velocity along the tank may exceed the settlement velocity provided that the tank is long enough. In the case of vertical flow basins however the upflow velocity must be less than the settling velocity, otherwise sedimentation will not occur.

Detention time in basins is normally recommended to be 4 hours or more. If space is a problem a device known as a « lamellar » or « inclined tube » separator may be used. This is illustrated in Fig. 21 (b). The principle of the design is that particles only have a very small distance to settle between a series of parallel plates or tubes. The angle of the pla-

tes or tubes allows the accumulated solids to move down the slope to a sludge removal point. Detention time may be reduced to 1 to 2 hours.

Dissolved air flotation is another method of solids removal that may be more effective with solids of low density. Fine air bubbles are introduced to the liquid by various methods, for example by dissolving air in water under pressure followed by pressure release. Solids are carried to the surface by air bubbles that expand as they rise and are removed by a surface skimming device. Detention time may be of the order of 20 to 30 minutes.

A conical vertical-flow designed basin allows easier collection of sludge than a horizontal-flow basin. Conical or square vertical flow basins are rather easily upset by changes in loading, and in some regions there is increasing use of lamellar flow units. These in turn are however relatively sensitive to overloading, so good process control is still required. In all sedimentation basins it is vital that the inlet and outlet zones be designed to ensure smooth and gentle flow.

Where very high standards of solids removal are required some form of filtration may need to follow sedimentation.

Vacuum or pressure filters can be used, although these are expensive and suitable only for large production plants. More suitable to the small operation is the use of low-cost sand or multi-media filters. The latter are similar in construction to a sand filter but use media of different sizes and densities such as gravel, silica, or anthracite together in a mixture. As it blocks up, back-washing of the filter is required, with the back-wash water being returned to the sedimentation basin. These filters are used in addition to sedimentation basins; they are not substitutes.

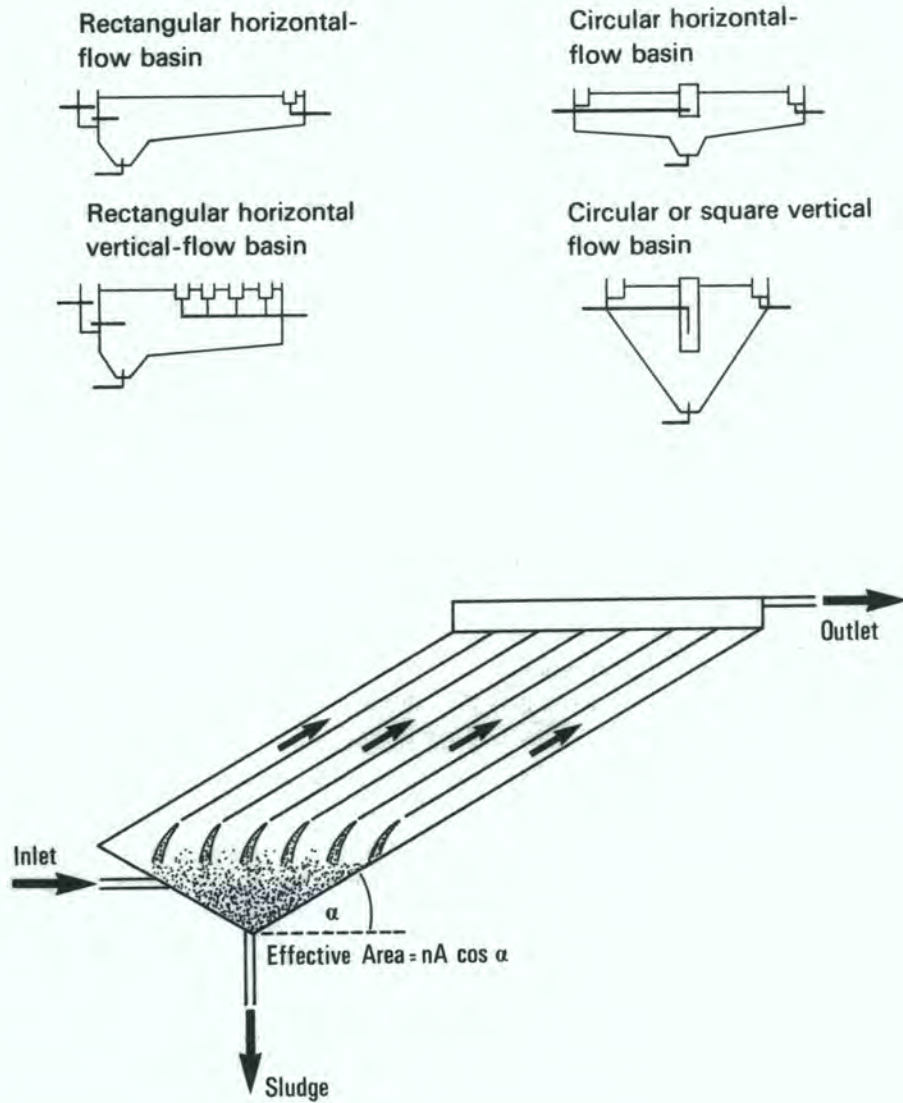


Figure 21 (a) Shapes of some sedimentation basins (From (14) )  
 21 (b) Lamellar Flow Separator (From W. Regan)

### 3.2.5 Sludge Dewatering

In order to facilitate the disposal of sedimented material, it is advantageous to dewater the sludge to a more solid form (in many

places the disposal of liquid sludge is now severely restricted). A number of techniques are available for such dewatering.

Prior to dewatering sludge thickening is

becoming an increasingly common step. A typical sludge thickener is a cone-bottomed cylindrical tank in which further compaction of sludge occurs under the influence of gravity, prior to it being withdrawn.

If chemical fixation with cement or silica is carried out to ensure that the sludge remains stable in subsequent landfill, then this is best achieved with thickened sludge.

### **Ambient Air Drying, Natural Evaporation**

The simplest, but still a very effective, sludge dewatering method, mentioned already in Section 3.2.4 is the technique used normally by small finishing factories, particularly in warmer countries.

If sufficient ground near the sedimentation pond is available, a suitable drainage basin is constructed and used for drying the sludge by natural evaporation. Construction of the basin must however be controlled by the authorities since the environment can be severely impacted otherwise. Precautions need to be taken against wind or rainfall dispersing the material, and to prevent access by wildlife and unauthorized persons. From time to time the solid earthy-looking sludge has to be transported to a deposition site suitable for industrial wastes. The need for better control over the dewatering process has led most establishments to adopt more mechanized processes.

### **Filterpress, Filterbelts**

**Filterpressing** reduces the volume of the sedimented sludge 15 times or more and yields about 30-35% solids content in the cake. The water pressed out of the filter by hydraulic forces is returned to the sedimentation pond.

The filter cake is peeled off the filter material and stored for transportation. Filter presses are relatively inexpensive and simple to operate, and do not require extensive maintenance.

**Beltfilters** in which the sludge is dewatered by progressively higher pressures on a moving belt are also in common use.

### **Other Dewatering Methods**

Several other dewatering techniques are occasionally used.

In vacuum filtration a horizontal drum rotates partly submerged in a vat filled with sludge. The surface of the drum is covered by the filter medium connected to a vacuum pump. The dewatered filter cake is lifted from the drum surface as it rotates. Investment and operating costs are higher than those of filterpresses.

Basket centrifuges are also sometimes used for compressible slurries that settle well. The collected effluent is returned to the sedimentation pond. This technique is not recommended for sludge dewatering in general because the costs are relatively high.

Following sludge dewatering, some companies practice sludge drying, utilizing various types of equipment. This process further dries sludge filter cake from approximately 35% solids content up to a virtually dry material. The volume reduction to be expected is in order of 4 to 1. Where sludge disposal costs are based on volume, the savings can be substantial.

### **3.2.6 Treating Oily Waters**

Oil and grease are common pollutants in the metal finishing industry. Oil has a high biochemical oxygen demand (BOD) of 1000 to

2000 mg per gramme of oil. BOD is a measure of the amount of oxygen consumed while the pollutant is being degraded in the aqueous environment: the higher the BOD, the more polluting is the material.

Wastewater with low quantities of free oil (less than 5 mg/l) is best treated using some form of filtration. Activated carbon, sand or kieselguhr are suitable filter media. Fine coalescer units or combined coalescer/filter units are also on the market. With any of these processes the oil content of the treated water can be lowered to less than 1 mg/l. Thus this method is suitable also for final stages in the treatment of oily waters. Ultrafiltration may also be applicable.

For larger concentrations of free oil, gravity separators are used. Water-oil emulsions must be broken before separation by gravity is possible. Oil separators are dimensioned on the basis of surface load and retention time. Compressed air blown into the incoming wastewater line improves the cleaning effect by lifting the oil to the surface in the separation basin. Some designs also work effectively without air, thus reducing considerably the energy consumption of the treatment.

Emulsion-splitting is normally carried out by adding salts (sodium-, calcium-, magnesium-, aluminium- or iron-salts) or acids. After emulsion splitting and sludge separation, the water usually contains between 1 and 50 mg/l of oil depending on the type of emulsion, the chemical additive etc., and should undergo a biological cleaning stage, or be filtered through an absorption agent.

Ultracentrifugation has only recently been introduced for treating oily industrial waste waters. Ultracentrifugation requires a relatively high level of investment, and skill for

operation and maintenance. Final results of about 1 mg/l oil in water can be obtained.

Absorption agents are on the market for treating water containing emulsified oil. They can be directly mixed with the wastewater to convert the oil to an easily removable solid phase. Silicic acid is frequently the active ingredient. Results are comparable to chemical emulsion splitting, however the treatment time is much shorter: only some 20 minutes. The technique requires little equipment but the price of the material required is relatively high, so that the treatment of large volumes of wastewater is uneconomical. Disposal of the resulting solids needs to be carefully controlled, and should occur only at preselected sites, perhaps after further stabilization and solidification of the solid phase.

### 3.3 CONTROL OF AIR EMISSION

A number of surface treatment operations generate acid mists, particulates and solvent fumes. These pollutants may be toxic to workers, as well as to the surrounding environment.

The control of air emissions can be approached in several different ways:

- substitution of less hazardous materials;
- removal of the pollutants from the collected air stream;
- dispersion of the pollutants to acceptable low concentrations.

Clearly the first alternative is the most preferred. Solvent substitution is a good example of this.

Exhaust hoods and good ventilation can reduce the level of air pollutants in the workplace. Open-tank operations from which mist, spray or volatile gases can escape are particu-

larly in need of such equipment. Every effort should be made to design hoods which enclose as much of the tank surface as possible. This will result in better ventilation using smaller ducts and fans, and lower power consumption.

It is necessary to consider the point at which such vented gases are discharged outside to ensure that no deleterious effects occur there. In many circumstances it will be necessary to treat the off-gases to remove the pollutants prior to discharge.

Particulate pollutants from mechanical surface preparation can be removed by cyclones, or by filters (fabric or bag). Cyclones have low capital and operating costs. Fabric filters are more expensive, but need to be considered for high efficiency filtration in low volume, low humidity gas streams. Mist eliminators should be fitted over acid cleaning baths and electroplating baths. Fume scrubbers are used on pickling, etching, bright dipping, plating, anodizing and phosphating lines. They are designed to handle high temperature and corrosive gas streams with high efficiency. Both capital and operating costs are relatively high.

## 4. RESIDUE DISPOSAL

As has been discussed already in Chapters 2 and 3, on account of their chemical composition, most residues from metal finishing processes should be considered potentially dangerous to health and the environment.

Residues generated in the metal finishing industry include:

- process waters of different kinds;
- spent process solutions and electrolytes;
- surplus chemicals;
- rubbish, packing materials etc.;
- sludges of different consistencies;
- filter cakes;
- debris and soil on abandoned sites.

### Process Waters, Spent Solutions

Chapter 3 already considered the minimization and treatment of pollutants. In Chapter 6 are presented examples of quality objectives, control guidelines and legally imposed restrictions that are applied to effluent release in some countries.

### Surplus Chemicals

Recycling, recovery of chemicals, or return to the supplier is the preferred option. Surplus chemicals should not normally be disposed of by discarding them into general waste bins or «washing them down the drain» unless this specifically permitted by the authorities for the chemicals in question. The precise conditions and/or degree of dilution required will be specified in each case. If off-site disposal becomes necessary, the staff at the appropriate waste disposal authorities can be consulted. In the final instance the operator of licenced hazardous waste disposal facilities could be contacted for advice and help. It is strongly recommended to call on the chemical supplier for

assistance if the shop personnel do not have sufficient information, disposal equipment or containers available.

### Rubbish, Packing Materials etc

Virtually anything in a metal finishing shop can become contaminated with toxic chemicals. Good management will ensure that materials, tools, and equipment will only be in those working areas where they are actually needed to run the operation. Duplicate sets of tools, equipment, shoes and working clothes for different places within the plant may later save costs for de-contamination.

All materials that are contaminated with chemicals can be considered to be toxic waste and have to be treated accordingly. This is true for clothes, waste paper, empty containers, as much as for defunct equipment. Separate waste bins for different kinds of waste should be placed on the shop floor and labelled clearly. If empty chemical containers are used as waste bins, all previous markings should be obliterated, painted over or removed to avoid confusion among shop floor personnel and at the waste disposal site. All chemical residues need to be cleaned from such bins prior to their use for rubbish.

Containers in which chemicals were delivered or stored should never be used for other purposes until declared safe by trained personnel. All markings and labels must be removed. They should not be discarded with normal rubbish until they have been expertly cleaned.

### Sludges and Filter Cakes

Disposal of sludges is now among the major environmental problems associated with the metal finishing industry.



Recognizing the need for environmentally safe disposal, many countries have enacted legal provisions for hazardous waste management that include metal finishing sludges. These provisions call for the analysis and identification of the wastes for the establishment of standards for generators and transporters of such waste, and permits for operators of waste disposal facilities. Treatment sludges containing heavy metals will often be regarded as hazardous until further treated by stabilization or cementation.

The disposal of sludges should always be carried out so that environmental contamination from such sludge or from leachate is avoided. This will invariably require disposal at a suitably sited, and managed, landfill site where precautions are taken to avoid remobilization of toxic substances in the sludge. Pretreatment and chemical stabilization of the sludge by the generator himself will also effectively reduce the risk of remobilization.

Many industrialized countries now require the use of special landfills for disposal of potentially harmful sludges. Such landfills are sited and designed to preclude the risk that toxic chemicals will leach into surrounding soil and into the groundwater. Relatively few landfill sites in each country are specifically licenced to accept hazardous waste. With only a limited number of sites accepting such waste relatively long distances for hauling may be necessary.

Designs for special landfills usually take advantage of natural geological barriers created by impermeable clays. Some sites add a flexible synthetic liner at the bottom as further protection against leaching of pollutants. A system of pipes for leachate collection may be buried in the bottom layer of the landfill. Leachate is recovered, and treated as neces-

sary. Monitoring stations are placed around the perimeter of the landfill for early detection of leachates escaping the landfill from a (hopefully unlikely) failure of the above system of safeguards.

To what extent such disposal sites will indeed stand the test over long periods of time remains to be seen. Accordingly, many authorities consider it prudent to also ensure that the wastes themselves are as inert as possible before they are disposed of. Thus toxic sludges from the metal finishing industry may have to be stabilized by chemical fixation or cementation so as to avoid leaching of metals. Several commercial processes are available for this purpose. Accelerated leaching tests (eg US Environmental Protection Test Procedures, US Federal Register 45 (98) : 33122, May 19, 1980) have been developed to indicate how the stabilized solids will stand up under actual landfill conditions.

Landfill disposal of wet or liquid sludges is now generally considered undesirable as this may allow soluble toxic components to escape more readily.

The waste generator has several means of lowering his costs for waste hauling and disposal. He can reduce the volume of residue and wastewater that must be treated. The solids can be concentrated with dewatering equipment to reduce the volume of water contained in the sludge. Minimizing wastes, implementing recycle and recovery modifications where possible, and using processes and reagents that generate less sludge can significantly reduce the amount of sludge requiring disposal.

The high price of sludge disposal may justify the purchase of dewatering equipment. Since the properties of sludges vary widely, some

form of pilot testing is recommended before equipment is purchased. This supposes that the subsequent sludge generation will be relatively uniform. If this is not likely to be the case equipment should be chosen which can realistically cope with a wide range of demands.

### **Abandoned Sites**

It has already been pointed out that metal finishing operations can under some circumstances lead to severe contamination of soils underneath the plant. The depth and severity

of such contamination depends upon the chemicals used, the quantities spilled, the period of time over which chemicals leaked into the soil, and the geological make-up of the site. It is not uncommon for chemicals used in metal finishing shops, including solvents, to have penetrated several metres into the soil. Many of these chemicals resist environmental degradation. Severe problems and high costs may be incurred if contaminated sites abandoned by metal finishing operators are to be re-used for other purposes, in particular if residential buildings are to be constructed.

## 5. PREVENTIVE MEASURES FOR POLLUTION AVOIDANCE

Previous chapters have examined the technical options for reducing environmental impact. Much also depends on the taking of preventive operational and management

measures so as to avoid problems in the first instance, and perhaps arrange the situation in the plant so that any necessary corrective action is readily taken.

### 5.1 REPLACEMENT OF HAZARDOUS CHEMICALS BY LESS TOXIC SUBSTANCES

In most cases, the metal finisher is not sufficiently experienced himself to search for and select among alternative chemicals. He will depend upon the dealer of chemicals and ultimately upon the manufacturer for help. Advice may also be available from relevant industry and professional associations. It is however advisable to also consult the relevant government authorities about the safety of the potential replacement products. As indicated earlier, in all cases the Material Safety Data Sheet or equivalent information should be consulted. Annex E shows an example of a typical Material Safety Data Sheet. Some safety information about product alternatives is also available from handbooks on hazardous materials (see Annex A), and from specialist international organizations (Annex D).

Opportunities for reducing or replacing process chemicals are shown below.

#### Cyanide

The greatest success so far in the reduction of cyanide has been in zinc plating. Because the higher concentrations of baths used traditionally also helped in the cleaning process, there has been some reluctance to go to weaker solutions. Nevertheless there is now some acceptance of lower strength cyanide formulations, which can reduce concentrations by up to 90%.

Some of the alternatives to cyanide in zinc plating are:

- sulphate acid baths where surface appearance is not critical;
- bright chloride zinc baths. These can have excellent performance characteristics. The need to use corrosion-proof equipment makes them particularly appropriate for new installations, however conversion of existing equipment has also been widespread in some regions;
- chelated zinc baths were among the first alternative processes to be introduced to the market. They have the problem that removal of zinc from the effluent is difficult;
- high alkaline zinc baths, not chelated, are now finding increased acceptance. As for some other alternatives, cleaning systems must often be upgraded as they contain no cyanide. The removal of zinc from effluents requires only a reduction of the pH to precipitate the metal as hydroxide. Increased workplace hazards from such baths need to be attended to through appropriate choice of equipment, and safety training of personnel.

Cyanide-free processes for other metals include:

- pyrophosphate copper as a substitute for cyanide copper. Good pH control is required to precipitate the copper from the effluent. When mixed with other metals, there may be a reduction in reaction efficiency;
- a cyanide-free cadmium bath is on the market but has not received a great deal of acceptance.

With the cleaners that are now available, there is no need to use cyanide in any cleaning operation. Similarly, there are substitutes for cyanide-containing stripping compounds. The materials suppliers should be consulted for a list of products available.

In plants where cyanide is only used occasionally, it could be eliminated completely by subcontracting when necessary.

### **Cadmium**

The high toxicity of cadmium in the workplace, and the contribution to its environmental dispersion from plated products, makes cadmium substitution a high priority with many authorities. Some countries have banned cadmium from non-essential uses, and discharge limits are often stringent (see Table 4).

The development of highly corrosion-resistant zinc plating has virtually eliminated the necessity to use cadmium except for special applications. For some uses aluminium coatings can also be employed.

### **Chromium**

As a substitute for hexavalent chromium, the less toxic trivalent chromium should prefer-

ably be used in making up baths. Trivalent chromium also rinses more freely and permits simpler waste treatment facilities. There is a slight difference in the colour of the plated metal compared to that plated from hexavalent chromium systems. Acceptance of this variation among customers should be promoted by industry itself.

### **Cleaners**

Non-biodegradable cleaners are difficult to remove in biological treatment systems. Most suppliers have voluntarily eliminated such compounds from their formulations, and many have also reduced or eliminated phosphates as well, although it may not be legally required as yet. Phosphates cause excessive nutrient enrichment in slow moving water.

## **5.2 RECOVERY OF CHEMICALS**

Recovery of process solutions provides a simple and economical way of avoiding the discharge of contaminants to the environment. Aspects of plant design and layout which assist in the recovery of process solution were discussed in Chapter 3. Recovery of process solutions has been standard practice for a long time by much of the metal finishing industry.

To fully exploit the recovery possibilities, it is advisable to always keep the bath solutions in as clean a state as possible. Accordingly it is useful to either reduce the entry of impurities into the baths, or to undertake more frequent purification procedures on the bath. Regular analyses and maintenance of process solutions is an essential part of such a programme.

The following practices can be used to reduce the impurities entering baths:

- improve the condition of plating racks by passing them through a cleaner and a chrome stripping process between rack cycles. This is the greatest source of chromium contamination in copper solutions, alkaline cleaning solutions and acid pickles;
- keep barrel holes clear to permit maximum drainage;
- improve the cleaning cycle before process baths;
- improve rinsing between process tanks;
- allow as much drainage time as feasible over the process tank from which the workpiece has been withdrawn;
- allow as much retention time as possible in the rinses before each process tank;
- design racks to prevent work pieces from falling into process tanks.

While these procedures may initially involve capital or increased operating cost, there are economic advantages that flow from the subsequent recovery of chemicals. The metal finisher should examine his consumption of chemicals to identify the potential for recovery.

Recovery may also be profitable from solutions or solids normally discarded. For example a considerable amount of solution is often left in the treatment tanks used to purify baths

and in filters when they are being cleaned. Significant quantities of solution can be lost if these are discarded.

Recovery of chemicals in dragout was touched on in Section 3.1.2. Work pieces should be allowed to drain directly back into the bath. Alternatively, recovery tanks can be used immediately after the process. This procedure is most successful where the contents of these tanks are used to make up for evaporative losses. Some recovery is possible on cold tanks if dragout can be reduced sufficiently. In extreme cases of dragout, two recovery tanks may be used, with the first making up the process solution losses and the second making up the first recovery tank.

Consideration should also be given to fog spraying of parts while they are suspended over the plating bath; this is a very effective way of carrying dragout directly back to the bath. The quantity of water used in the spray can be controlled to approximately equal the evaporation rate. This method is used, for example, to keep copper cyanide levels in effluent below 2 mg/l.

Good recovery techniques can lead to a build-up of carbonates in copper cyanide solutions (where these are still used). This can be limited by using de-ionized water for bath make-up, and in fog sprays. Failing this, freezing out of carbonates in cyanide baths is a possibility (see for example Section 3.1.3). They may be precipitated from potassium cyanide baths.

### 5.3 GOOD HOUSEKEEPING AND WORKPLACE SAFETY

Untidy, cluttered and chaotic working conditions constitute a safety hazard to personnel, and increase the number of unplanned discharges to the environment. Such conditions

also make it difficult to introduce many of the cost-saving measures described earlier.

Good housekeeping is a matter of attitude – essentially the attitude of management, and

the degree to which this is transmitted to the shop floor.

Materials losses can often be identified by simply observing chemical and water consumption. Spills can be reduced through careful handling and transfer of materials. Energy consumption can be reduced by switching off appliances not in constant use. General cleaning and maintenance of equipment improves its performance and prolongs its service life. Proper receptacles for wastes ensures that contamination of the surroundings of the plant is reduced. All of these matters depend on the willing good performance by shop floor personnel, and conscientious supervision by management.

The protection of workers, like the protection of the physical environment, relies largely on appropriate precautionary measures, aided by suitable organisational procedures. Such a combination of measures contributes to reducing exposure to chemical hazards, physical dangers from machinery and handling, and thermal, acoustic and vibrational stress. It should be stressed that the same conditions leading to workplace hazards often have an

impact on the environment and people surrounding the industry as well. Specialist bodies concerned with workplace hazard reduction should also pay attention to the external issues so as to support the initiatives of the environmental agencies.

Well planned organization to maintain safety and health in the workplace is the basis of prevention of occupational illnesses. Some essential aspects of such organisation are:

- management accepting its lead role in providing safe working conditions and procedures;
- participation by the workforce in ensuring safety at work;
- clear allocation of responsibilities for safety and health services;
- safety training and instruction, on induction and on-going;
- reporting, investigation and analysis of accidents and working conditions;
- dissemination of information on hazards and risks;
- co-operation with labour and safety inspections and reviews.

## 5.4 DESIGN OF BUILDING AND EQUIPMENT

### Design of Floors

The metal finishing industry brings together in a relatively small space a variety of corrosive and potentially contaminating materials.

To enable effective housekeeping, management must first turn its attention to the floor. Without floors that are properly designed and protected, many of the other recommendations will be more difficult, and perhaps impossible, to implement.

Finished new concrete floors should be covered with a corrosion-resistant material of brick or tile, with a resinous monolithic coating. The materials used should be easy to repair. In view of the brittle nature of bricks or tiles, it is advantageous to have a corrosion and leak-proof layer over the concrete itself, also.

Where changes to equipment permit an opportunity for re-layout, the floor should be

re-constructed with regard to the following:

- the specific chemicals to be used, susceptibility of concrete to chemical corrosion (consult the floor installer and handbooks or competent authorities before making decisions);
- type of traffic;
- thermal shock expected;
- mechanical shock expected; and
- capability for containing an accidental spill.

The base floor must be able to withstand the weight of tanks and equipment without movement or cracking. Cracking will permit penetration of chemicals through corrosion resistant materials applied over the floor.

Old floors must be thoroughly cleaned with detergent and all broken and uneven areas carefully repaired to a smooth surface.

New floors should be of reinforced concrete of high strength (in excess of 3000 psi) and homogeneous. Loadings of storage tanks on stands may be considerably higher than this, requiring a proportionally greater degree of strength in the floor. Sulphate resistance is also a useful attribute. Substantial curing should be allowed before corrosion proofing is applied. This may need to be as long as 30 days if the best bond between concrete and the proofing layer is desired. The concrete suppliers' advice should be sought on this point.

Expansion joints according to standard practice are satisfactory, but need to pay regard to process considerations as well as construction convenience. Pump foundations and other vibrating equipment should be isolated, along with structural columns. Joint sealing methods need to be carefully chosen.

The concrete surface should be finished in accordance with the recommendations of the supplier and/or installer of the corrosion resistant material used.

For drains, the use of plastic is preferred over glazed earthenware. Adequate fall should be designed for drains to facilitate rapid drainage. The same may apply to floors likely to be subject to spills or frequent washing. The joint between plastic gulley surround and the concrete needs to be constructed with particular care. Under conditions of extreme climatic variation, or if solvents or hot solutions are likely to be encountered special high performance plastics should be used. In all situations buried joints in pipes should be fused or solvent welded.

### Curbing

To ensure that the chemicals reaching the floor are confined or directed to the proper drain, curbing should be installed around each tank or piece of equipment. This curbing is most effective when it is installed with the flooring, since joints can then be eliminated. A common curbing can be used to collect any losses from a group of tanks used for the same treatment procedure. Curbing can also be installed in existing flooring, with proper attention to the sealing of joints.

Curbing should be sufficient to contain the contents of a ruptured tank, and preferably more than this. This allows the tank to be repaired and the spilt solution pumped back into the tank after repair. As a rule treatment systems for wastewater are unable to deal with the shock load from spills. The design of the drainage system must therefore be such as to contain spills rather than let them drain away.

## Protection of Equipment

Adequate protection must be given to equipment to ensure a reasonable operating life and to prevent accidental losses of hazardous chemicals. Every tank containing chemicals should be protected against corrosion. Time and money properly spent at the time when tanks are installed will always be repaid and, in the end, provide the easiest and least expensive protection against losses.

New installations today often use tanks made from non-corroding materials. Protection is usually provided by the supplier for the inside if the tanks are to carry corrosive materials. It is less common however to provide equivalent protection for the outside. Rinse tanks immediately adjacent to tanks containing corrosive chemicals should nevertheless be protected on the outside as well as on the inside. Coating the outside and bottom of tanks with half the coating thickness used on the inside and the flanges will usually give sufficient protection.

In addition, protection should be provided to the surfaces of hoists and other mechanisms, structural steel, utility connections and steel piping.

Hidden corrosion of lined tanks is always a matter of concern. Tanks should be inspected frequently for breaks in the lining, whether fully coated outside or not. A break in the lining of a tank coated inside and outside may lead to a sizeable but hidden corrosion of the steel tank. Eventually the lining may be all that is then holding the solution. Steady leaks

from pin holes can result in considerable loss of solution over time. Periodic spark testing or checking for electrical continuity between tank core and contents of critical tanks is a standard procedure with many metal finishers and is part of a wise maintenance programme, whether tanks have outside linings or not. The test equipment can usually be borrowed or rented.

Where it is too expensive or not convenient to purchase tanks which are lined on the outside, coatings may be applied which are similar to the monolithic resins used on the floors and which may be applied by brush or spray. They are nearly competitive in cost to most of the epoxy and vinyl paint systems and have superior shock and heat resistant, lower coefficient of expansion, and are more resistant to corrosion running out underneath.

No paints have been found which are truly satisfactory except as temporary protection. They are helpful in the short run and if re-applied annually will provide modest protection. This re-application is, of course, difficult in some cases, such as on the bottom of tanks.

In many instances, corrosion resistance is automatically provided when materials other than steel are chosen as the basic material of construction for the tank. Some of these materials might be:

- plastic, e.g. polypropylene or polyethylene;
- glass fibre reinforced plastic; and
- stainless steel.

## 5.5 MANAGEMENT OF SPILLS AND LEAKS

In addition to the running rinses that carry many of the pollutants to the effluent stream, large quantities are often lost to the environment through accidents and deliberate

dumps. In some instances, these two sources may account for as much as 80% of the heavy metal load to the environment. The shock effect of high concentrations of pollutants may



be far more drastic on sewage treatment plants and receiving waters than the same quantity discharged over a long period.

The following possible sources of accidental losses should be subject to stringent control and prevention measures:

- tank leaks;
- solutions remaining in filters, and in the bottoms of process tanks;
- equipment leaks, i.e. filters, pumps, heat exchangers, and their hoses and connections;
- overflows;
- accidental opening or rupture of a valve; and,
- spilling of chemicals in handling or in storage, or between process tanks.

Deliberate unauthorized release of solutions should never be permitted. It is usually illegal, and in any case quite irresponsible.

### Tank Leaks

Unprotected steel tanks should be shielded against stray currents with materials such as PVC. In barrel plating, when the tank is cathodic, insulation should be provided against arcing, which may occur between the anodes and the side of the tank.

In processes where there may be a buildup of chloride that is not itself deleterious to the process, there could nevertheless be accelerated corrosion of an unprotected tank. If improved rinsing does not correct the problem, it will be necessary to line the tank.

### Residual Solutions

These should generally be re-used, or if this is not possible, processed in the effluent treatment plant.

### Equipment Leaks

There is probably more loss of chemicals from equipment leaks than any other. The causes include carelessness, insufficient maintenance, or simple tolerance of a continuing condition. Filter hoses, heat exchanger connections, heating coils, pump hoses and connections are all prone to degenerate and permit leakage. Losses of 2.5 to 5 cm per day of solution from process tanks through any of these routes may be blamed on evaporation or dragout and go on for months. It is good economics to keep equipment in good condition.

Because filters probably cause the most trouble, curbing the area around the filter will allow leakage to be identified, and provide an opportunity for recovery. Some companies place the filter over a solution treatment tank so that all losses are recovered.

Heat exchangers and heating coils deteriorate slowly, and develop pinpoint breaks or cracks. When steam condenses, a vacuum is created and solution is drawn into the condensate. Since many metal finishers return the condensate to the boiler to save water and energy, there is the likelihood of corrosion damage to the boiler as well as solution loss.

An alarm system should be installed on the boiler condensate return line. Periodic examination of the waters should be carried out.

A similar problem may occur with cooling water, except that it is possible that both overflow of the bath and loss of chemicals to the cooling stream may take place. Where cooling water is used subsequently for rinsing (although this is not recommended as the flow need are mismatched and one or the other process is therefore not optimum), it is likely the break will be identified quickly.

## Overflows

Although completely avoidable, almost every shop experiences such events. Overflows usually occur during the «topping up» procedure and are the result of lack of attention.

The following steps minimize the possibility of overflows :

- fit all hoses for adding water with spring loaded nozzles;
- where water is added directly from piping, use float level controls;
- install back flow preventers where water is discharged below solution surface;
- supervise regularly.

## Accidental Valve Opening

This problem is best avoided by having no valves at all on the tanks holding concentrated solutions. If valves are already installed, they should be sealed off, making them impossible to open.

Valves are always a potential danger because they may be damaged by lift trucks, etc. and should be examined occasionally.

## Spillage of Chemicals

This is a problem which is primarily overcome by supervision, training, and the establishment of handling rules.

Chemicals should be stored by lift trucks in areas safe from damage and sudden flooding.

Many inexpensive methods are available for assisting an operator in the safe addition of chemicals. The easier and safer it is for him, the less he will waste. It is advisable to use equipment such as manual pumps, to avoid having to tip large containers. Chemicals which can react with each other should be kept well separated.

## General

Wherever possible and practical, a holding pit should be inserted between the plating plant and the discharge to the sewer. Alarms should be installed which automatically sound warnings in case of a sudden change in effluent. These alarms may also shut off the water supply.

The use of a holding pit is facilitated if the effluent flows are all piped above ground, or at least separately from general floor drainage. Such separation allows better monitoring, and control, and a greater degree of being able to intervene in case of unforeseen accidents.

## 6. EXAMPLES OF LEGAL PROVISIONS AND ADMINISTRATIVE ARRANGEMENTS

### 6.1 WATER QUALITY CONTROL

Many countries have enacted legal provisions or are otherwise applying recommended effluent limitations to protect the aquatic environment from pollution.

Within the European Communities, a number of Directives apply to metal finishing industries. Directives are legally binding on the 12 Member States, but the individual Member States may select their own legal and administrative means of implementation.

Discharge limits (Discharge Values) are normally prescribed in mass of pollutant per volume of water, for instance in milligrammes per liter (mg/l). However, since low effluent concentrations could be reached simply by diluting concentrated wastes with clean water, and also because in certain cases concentration limits cannot always be adhered to for technical reasons, regulations may also impose other restrictions. Such additional limits («limit values») can take the form of total mass of pollutants allowed per unit time (day or year), or they can be related to the material throughput in a given plant: eg. 0.3 grammes of cadmium released per 10 kilogrammes of cadmium processed (EEC Directive 83/513/EEC of 26 September 1983).

Monitoring and reporting procedures must be established and applied so as to ascertain that the quality objectives are being met. Obviously, monitoring must be performed or supervised by competent authorities.

This chapter contains examples of legal provisions and administrative guidelines of some countries to give the reader an overview of regulations and practices which are applied. Technically, the imposed requirements can all be met. While the selection of regulations shown is to some degree arbitrary, the pro-

visions illustrate well the stringent limitations now being increasingly placed on this industry.

### EEC

On 4 May 1976 the European Communities adopted Directive 76/464/EEC concerning the discharge of dangerous substances into the aquatic environment. For the chemicals listed in the Directive, zero emission into ground water applies, except for domestic effluents. Directive 80/68/EEC relates specifically to the protection of groundwater. For other waters, the Member States shall individually lay down emission standards and grant discharge permits on a temporary basis. The emission standards shall contain «Discharge Values» as well as «Limit Values» as discussed above. The Council itself has acted in the case of cadmium (Directive 83/513/EEC of 26 September 1983) for the electroplating industry, limiting the concentration permitted in the discharge to 0.2 mg/l of concentration, and 0.3 g of cadmium per kg processed.

### SWEDEN

A list of «Representative Discharge Values» was published in 1985 in the General Advisory 85 :1 by the National Swedish Environmental Protection Board. The pollutants listed are for outgoing treated wastewater.

If Representative Values are exceeded more than temporarily, measures must be taken in collaboration with the supervisory agency to prevent this from occurring again. A list of representative values is shown in Table 4.

### FRANCE

In 1985 France adopted Technical Instructions concerning the performance of surface

treatment facilities. The instructions contain the following discharge limits:

- zero discharge into ground waters;
- the total combined concentration of zinc + copper + nickel + aluminium + iron + chromium + cadmium + lead + tin, must not exceed 15 mg/l;
- no more than 0.3 g of cadmium may be discharged for every kg processed;
- the pH of effluents must be in the range of 6.5 to 9;
- the temperature must not exceed 30°C.

The values applied to individual pollutants are shown in Table 4.

With respect to controls, the following provisions have been laid down:

- official controls for discharges are on a case by case basis;
- action by the operator shall include:
- continuous measurement of pH;
- daily measurement of cyanide and hexavalent chromium;
- weekly measurement of metals;
- establishment of a representative 24-hour discharge curve for cadmium;
- records must be kept for at least 5 years.

## NORWAY

No national regulations or standards for discharge exist; each plant is given a separate permit limiting the quantity of effluent and the concentrations of the relevant chemicals. The quantity of effluent is reduced by prescribing countercurrent rinsing and recirculation of baths to the greatest extent possible.

## ALGERIA

On 19 July 1986, the Republic of Algeria published a Technical Instruction concerning the operation of metal surface treatment facilities (No. 211/675/DPPN/86). All waters from plants must be detoxified prior to release. Detailed instructions are laid down, such as:

- used waters must be collected separately according to the nature and concentrations of impurities;
- effluents containing cyanides may not be brought together with waters containing nickel salts or with acidic waste waters;
- cleaning water must be collected into a watertight basin, outside the plant, and subsequently treated like rinse waters;
- before discharge, the following minimum treatments must be performed: cyanides destroyed, chromates eliminated, metals co-precipitated, fluorides precipitated, sludges separated, and the pH adjusted;
- the detoxification equipment has to be installed under open air.

Discharge values are comparable to those in use in other countries.

## USA

Under the provisions of the Clean Water Act (Public Law 92-217) of 1977, every facility discharging into a waterway must apply for a permit which specifies what pollutants may be discharged, and a schedule for compliance, monitoring and reporting. If State water quality standards or other provisions of State or Federal law require more stringent pollutant limits, the permit-issuing authority must apply those limitations. The discharge values

Parameter	Discharge Values (mg/l) *		
	Sweden	France	USA (daily max)
Cadmium	0.1	0.2	0.11
Chromium (total)	1	2	2.77
Chromium (hexavalent)	0.1	0.1	
Cyanide (free)	0.1	0.1	0.86
Cyanide (total)	1	1.20	
Copper	1	2	3.3
Lead	1	0.2	0.6
Zinc	2	5	2.61
Nickel	1	5	3.98
Tin	1	2	
Silver	1		0.43
Iron	2	5	
Aluminium	2	5	
Fluorides		15	
Oil		5	5 <sup>2</sup>
Suspended Matter	10	15	60
COD		150	
pH range		6.5 - 9	6 - 9

\* refer to text for information on the way these values are applied.

Table 4: Discharge values applying in selected countries

applied after 30 June, 1984 are shown in Table 4.

Self-monitoring for cyanide must be conducted after cyanide treatment and before dilution with other streams.

## 6.2 SEWER DISCHARGE LIMITS

Many public authorities now specify standards for acceptance of pollutants into the sewerage system. These standards are designed to protect men working in sewers and manholes, as well as the sewers and sewage

treatment plants themselves, and to safeguard water quality around the sewer outfalls. Industrial installations must pretreat wastewaters to meet these standards.

Discharge standards vary widely from one local authority to another. The standards reflect the different conditions of environment and of sewage treatment in each place. Table 5 shows the standards that exist in several places around the world. It is common for the authority to issue a licence or permit to an industry prior to consenting to a discharge taking place.

Parameter	Discharge Limits to Sewer Systems (mg/l)			
	Baden Württemberg (FRG)	Melbourne * (Australia)	Italy	Singapore
Cadmium	1	10	0.02	1
Chromium (total)	2	10	4	5
Chromium (hexavalent)	0.5	0.2		
Cyanide	0.2	1	2	
Copper	2	10	0.4	5
Lead	2	10	0.3	5
Zinc	5	10	1	10
Nickel	3	10	4	10
Tin	5	10		
Silver	1	2		
Iron	10	30	4	50
Aluminium	10			
Sulphides	10	1		
Sulphates	400	300		
Phenols	100	100		
Oil & Grease	100	200		
pH	6 - 9.5	6 - 10	5.5 - 9.5	6 - 9
Temperature max	35°			
Total suspended solids	50	38°	80 - 200	

\* currently under review.

Table 5: Sewer discharge limits in selected countries.

### 6.3 WASTE DISPOSAL

Waste disposal practices for sludges and solids vary greatly between countries. The particular requirements will often depend on the composition of the waste to be disposed of. Consultation of an official list of contaminants (where this exists) will help to determine whether a residue is hazardous or is regarded as a normal industrial waste which can be disposed of by conventional means. Residues which contain cadmium, chromium, nickel, and other toxic materials in significant con-

centrations will usually be classed as hazardous. Such hazardous constituents must be rendered insoluble prior to disposal, and perhaps require disposal at special facilities.

In some situations there may be a commercial market for certain recoverable wastes, thus avoiding somewhat the need for disposal. If this is not possible then landfill procedures will have to be used.

Many authorities no longer permit the disposal of liquids or sludges into landfill, even if contained in drums. They must first be rendered solid by the waste generator. Either the

sludge itself can be dewatered and dried, or the liquid sludge can be further treated with setting agents. There now exist proprietary processes for such a procedure (15). Most are based on mixing the waste (after neutralisation) with cement, lime or silica which is then allowed to set. With a correct mixture of setting agent the heavy metal ions become chemically bound to the solid mass, and thus resist leaching. Where access to proprietary processes is not commercially available, the waste producer may be able to, with the involvement of local authorities, carry out some trials himself to determine the best conditions for solidification of his waste. The levels of extractable (i.e. leachable), toxic components in the resulting solid may be specifically laid down by some authorities.

Where stringent requirements for hazardous waste management apply, these will usually include the following:

- registration of the waste generator with the environmental authorities;
- obligation to use only transport services which are specifically licensed to carry hazardous waste;
- the use of a waste «manifest», (or certificate) system to keep track of the waste load until it is safely disposed of;
- an obligation to use only disposal facilities which have been licensed by the authorities;
- the use of specific labels and warning symbols for waste storage and transport.

Metal finishers should make themselves familiar with the requirements in their country.

Annex A includes some references which can assist in resolving technical questions regarding disposal options for specific substances.

#### 6.4 AIR EMISSION CONTROL

As the most significant impact of air emissions is in the workplace itself, exposure limits as established by occupational authorities are particularly significant.

Exposure limit values have been established by many authorities for some of the chemicals used in metal finishing. These values differ from country to country, and moreover the basis for setting such limits may also vary. Thus terms such as «maximum allowable concentration», «threshold limit value» (TLV), «time weighted average» (TWA), «short-term exposure limit» (STEL), and several other terms are regularly encountered in the literature. It is pertinent to note that such terms include two important concepts:

- (i) an average value of exposure which is regarded as acceptable;
- (ii) a maximum limit which must never be exceeded.

Many substances in the literature have both limits listed.

It is not possible to give here a useful comparison of the various limits applying to different chemicals which are in force in different countries. Readers are referred instead to standard reference works on chemical hazards (see Annex A), and information contained in Material Safety Data Sheets (Annex E) for particular chemicals which may be released.

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ANNEXES



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**ANNEX A**  
**RECOMMENDATIONS FOR FURTHER READING**

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## ANNEX B

### CASCADE RINSING TABLES

Table 1 may serve as a calculation aid for the metal finisher for estimating the economic and the ecological effects resulting from the installation of a rinsing cascade. This Table contains the rinse water consumption rates, depending on the numbers of baths per cascade, dragout of chemicals, and different dissolving factors (for explanations see legend). Different finish-

ing treatments have different rinse water requirements depending on the permitted degree of the remaining surface contamination of the piece, as shown in Table 2. Table 3 contains a comparison of water consumption rates for rinsing with one, two, three or four cascade steps.

Tables are taken from Ref. 9.

Drag Out D (l/m <sup>2</sup> )	Cascade Steps (n)	Dilution Ratio Rd = Co/Cr											
		100	500	1000	2000	3000	5000	7500	10000	12500	15000	20000	25000
.10	1	10	50	100	200	300	500	750	1000	1250	1500	2000	2500
	2	1.0	2.2	3.2	4.5	5.5	7.1	8.7	10.0	11.2	12.2	14.1	15.8
	3	.46	.8	1.0	1.3	1.4	1.7	2.0	2.2	2.3	2.5	2.7	2.9
.15	1	15	75	150	300	450	750	1125	1500	1875	2250	3000	3750
	2	1.5	3.35	4.7	6.7	8.2	10.6	13.0	15.0	16.8	18.4	21.2	23.7
	3	.7	1.2	1.5	1.9	2.2	2.6	2.9	3.2	3.5	3.7	4.1	4.4
.20	1	20	100	200	400	600	1000	1500	2000	2500	3000	4000	5000
	2	2	4.5	6.3	8.9	11.0	14.1	17.3	20.0	22.4	24.5	28.3	31.6
	3	.93	1.6	2.0	2.5	2.9	3.4	3.9	4.3	4.6	4.9	5.4	5.8
.25	1	25	125	250	500	750	1250	1875	2500	3125	3750	5000	6250
	2	2.5	5.6	7.9	11.2	13.7	17.7	21.7	25.0	28.0	30.6	35.4	39.5
	3	1.2	2.0	2.5	3.2	3.6	4.3	4.9	5.4	5.8	6.2	6.8	7.3
.30	1	30	150	300	600	900	1500	2250	3000	3750	4500	6000	7500
	2	3.0	6.7	9.5	13.4	16.4	21.2	26.0	30.0	33.5	36.7	42.4	47.4
	3	1.4	2.4	3.0	3.8	4.3	5.1	5.9	6.5	7.0	7.4	8.1	8.8
	4	.95	1.4	1.7	2.0	2.2	2.5	2.8	3.0	3.2	3.3	3.6	3.8
.35	1	35	175	350	700	1050	1750	2625	3500	4375	5250	7000	8750
	2	3.5	7.8	11.1	15.7	19.2	24.7	30.3	35.0	39.1	42.9	49.5	55.3
	3	1.6	2.8	3.5	4.4	5.0	6.0	6.8	7.5	8.1	8.6	9.5	10.2
	4	1.1	1.65	2.0	2.3	2.6	2.9	3.3	3.5	3.7	3.9	4.2	4.4
.40	1	40	200	400	800	1200	2000	3000	4000	5000	6000	8000	10000
	2	4.0	8.9	12.6	17.9	21.9	28.3	34.6	40.0	44.7	49.0	56.6	63.2
	3	1.9	3.2	4.0	5.0	5.8	6.8	7.8	8.6	9.3	9.9	10.9	11.7
	4	1.26	1.9	2.2	2.7	3.0	3.4	3.7	4.0	4.2	4.4	4.8	5.0
.50	1	50	150	500	1000	1500	2500	3750	5000	6250	7500	10000	12500
	2	5	11.2	15.8	22.4	27.4	35.4	43.3	50.0	55.9	61.2	70.7	79.1
	3	2.3	4.0	5.0	6.3	7.2	8.6	9.8	10.8	11.6	12.3	13.6	14.6
	4	1.6	2.4	2.8	3.3	3.7	4.2	4.6	5.0	5.3	5.5	5.9	6.3

Table 1: Computed rinse water requirement as a function of the number of cascade steps (n), dragged out chemicals (D = drag out from the treatment bath to the rinsing bath, depending on surface and shape of the working pieces, supports (frame or drum), production rate, dripping time, and bath viscosity; D is specified as volume per treated surface area), and dilution ratio (Rd = Co/Cr where Co = treatment bath concentration and Cr = mean concentration of the rinsing bath, in the case of multiple rinsing. Rd is the product of the dilution ratios of all cascade steps).

Bath type	Maintenance	Characteristic work pieces	Drag Out D (l/m <sup>2</sup> )	Dilution Ratio Rd = Co/C1	Rinsewater single bath	Requirement (l/m <sup>2</sup> )	
						- cascade steps - 2	3
Nickel bright	manual	ABS	.14	10 000	1 400	14	3.0
Nickel bright	manual	iron ware (brass)	.30	10 000	3 000	30	6.5
Nickel bright	semi-autom.	plumbing (brass, copper)	.18	7 500	1 350	16	3.0
Chrome decor	manual	iron and nickel ware	.45	10 000	4 500	45	10
Chrome decor	autom.	nickel plated tubes	.04	10 000	400	4	1.0
Acid copper	autom.	steel, Zamack	.24	5 000	1 200	17	4.0
Copper Cyanide	autom.	steel, Zamack	.19	10 000	1 900	19	4.0
Zinc cyanide	autom.	cartridges, lamp sockets	.25	10 000	2 500	25	5.4
Cadmium	manual	aircraft pieces	.16	10 000	1 600	16	3.5
Cadmium	semi-autom.	various	.06	10 000	600	6	1.3

Table 2 : Examples of rinse water requirements (litres per finishing surface area), depending on various treatment baths, and simple or cascade rinsing.

Dilution Ratio	Water Consumption (Rd)	Dilution Ratio	Water Consumption (Rd)
Rd = 100 to 1000	Q <sub>1</sub> = 20 to 200 l/m <sup>2</sup> for single rinsing Q <sub>2</sub> = 2 to 6 l/m <sup>2</sup> for 2 step cascade rinsing Q <sub>3</sub> = .9 to 2 l/m <sup>2</sup> for 3 step cascade rinsing Q <sub>4</sub> = .6 to 1 l/m <sup>2</sup> for 4 step cascade rinsing	Rd = 5001 to 10000	Q <sub>1</sub> = 1000 to 2000 l/m <sup>2</sup> for single rinsing Q <sub>2</sub> = 14 to 20 l/m <sup>2</sup> for 2 step cascade rinsing Q <sub>3</sub> = 3.4 to 4.3 l/m <sup>2</sup> for 3 step cascade rinsing Q <sub>4</sub> = 1.7 to 2 l/m <sup>2</sup> for 4 step cascade rinsing
Rd = 1001 to 5000	Q <sub>1</sub> = 200 to 1000 l/m <sup>2</sup> for single rinsing Q <sub>2</sub> = 6 to 14 l/m <sup>2</sup> for 2 step cascade rinsing Q <sub>3</sub> = 2 to 3.4 l/m <sup>2</sup> for 3 step cascade rinsing Q <sub>4</sub> = 1 to 1.7 l/m <sup>2</sup> for 4 step cascade rinsing	Rd = 10000	Q <sub>1</sub> = 2000 l/m <sup>2</sup> for single rinsing Q <sub>2</sub> = 20 l/m <sup>2</sup> for 2 step cascade rinsing Q <sub>3</sub> = 4.3 l/m <sup>2</sup> for 3 step cascade rinsing Q <sub>4</sub> = 2 l/m <sup>2</sup> for 4 step cascade rinsing

Table 3 : Examples of rinse water consumption (Q<sub>n</sub>) for various typical dilution ratios depending on the number of cascade steps (single bath, n = 2, 3, and 4 steps), and for a dragout of q = .2 l/m<sup>2</sup>. Data from Table 1.

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## ANNEX C

### TABLE OF COMMON PROCESSES AND CHEMICALS USED

This Annex lists the chemicals used in some common processes associated with metal finishing operations. It is these chemicals that present the environmental and occupational safety risks discussed in Chapter 2 when they are released.

The mere existence of a chemical in a process does not automatically indicate that it will be released to the environment. Conversely, additional chemical substances may be generated during the processing operations (eg. gases from electrolysis), or reagents may combine to form new compounds which find their

way to an effluent stream. The identification of all relevant chemical entities which can affect the environment is an important step in the assessment of environmental impact.

The discarding of spent solutions such as those listed here, together with chemicals carried away in washwaters, has traditionally represented the largest source of loss to the environment. Nevertheless the possibility of generation of fumes, gases and aerosol mists to workplace and ambient air should not be ignored. Many of the substances listed here can be carried over in spray and fumes.



## PROCESS: SURFACE PREPARATION

METHOD and TECHNIQUE	CHEMICALS, MATERIALS USED
<b>GRINDING</b>	
Cutting by means of grinding materials	<b>grinding material</b> : diamond, sand, flint, quartz, garnet, pumice, emery, corundum, aloxite, Si- and W-carbide, boron compounds, Si-compounds as additives for special cutting purposes <b>cementing substances</b> : ceramics, minerals, organic resin, rubber, poly-vinyl
<b>POLISHING, BRIGHTENING</b>	
Mechanical polishing	<b>polishing materials</b> : waxes, greases, oils, diatomite, Vienna or French chalk, oxides of Si, Al, Fe.
Electrolytic and chemical polishing and brightening	<b>polishing baths</b> : perchloric, nitric, acetic, phosphoric, sulphuric, chromic acids, glycerine, aniline, arsenates, alkaline baths for neutralisation
<b>PRE-CLEANING, STRIPPING</b>	
Mechanical cleaning by hand, machine or blasting techniques	HF (if sand blasting particles are removed chemically)
Chemical elimination of rust, tinter and oxide layers	<b>baths for</b> : - <b>iron and steel</b> : HCl, H <sub>2</sub> SO <sub>4</sub> , H <sub>3</sub> PO <sub>4</sub> , alkaline derusting salts, caustic soda, gluconates, heptonates, NaCN - <b>stainless steel</b> : HNO <sub>3</sub> , HF - <b>copper and alloys</b> : HNO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> accelerators, CrO <sub>3</sub> , NaCN, Na <sub>2</sub> CrO <sub>4</sub> -aluminium and alloys : H <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub> , HF, caustic soda - <b>magnesium and alloys</b> : H <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub>
Electrolytic descaling	<b>baths</b> : H <sub>2</sub> SO <sub>4</sub> , HCl, H <sub>3</sub> PO <sub>4</sub> , HNO <sub>3</sub> , HF, inhibitors (e.g. hexamethylenetetramine, thiourea, dibenzyl sulphoxide) Note : H <sub>2</sub> may be released during the process.
<b>FINAL CLEANING and DEGREASING</b>	
Chemical	<b>organic cleanser</b> : tri- and perchloroethylene, gasoline, kerosene, solvent naphtha, ethanol, emulsifying agents, amines, surfactants, dichloromethane, diethyl ether, glacial acetic acid, carbon tetrachloride <b>inorganic, alkaline cleanser</b> : NaOH, KOH, NaCN, Na <sub>2</sub> CO <sub>3</sub> , silicates, alkaline phosphates, pyrophosphates, carbonates, detergents, surfactants, soaps, Na-hexametaphosphate, borax
Electrolytic	H <sub>2</sub> , O <sub>2</sub> produced in process
Neutralisation	<b>neutralisation baths</b> : acids, alkaline solutions <b>neutralisation and pickling baths</b> : alkaline cyanides, KH-tartrate

**SURFACE ACTIVATION**

Pickling

**baths for :**

**-iron and steel :** HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, alkaline derusting salts, caustic soda, gluconates, heptonates, NaCN

**-stainless steel :** HNO<sub>3</sub>, HF

**-copper and alloys :** HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, accelerators, CrO<sub>3</sub>, NaCN, Na<sub>2</sub>CrO<sub>4</sub>

**-aluminium and alloys :** H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HF, caustic soda

**-magnesium and alloys :** H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>

note : Acid mists and vapours produced during process

Blasting

(see above under PRE-CLEANING)

**CORROSION PROTECTION  
AND HARDENING**

(aftertreatment)

Thermal

protective gases, metal oxides may be produced

Mechanical

dust, particulates produced

Chemical

oxidants, salts, soap, gloss oil, varnish

Passivation

**baths for Al, Fe :** HNO<sub>3</sub>, Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, H<sub>2</sub>SO<sub>4</sub>

## PROCESS : METALLIC COATING

METHOD and TECHNIQUE	CHEMICALS, MATERIALS USED
<b>ELECTROPLATING</b>	
Copper plating	<p><b>electrolytic solutions</b> : acids, alkalis, salts</p> <p><b>buffer</b> : <math>\text{NH}_4\text{OH}/\text{HCl}</math>, acetic acid/Na-acetate</p> <p><b>baths</b> : <math>\text{CuSO}_4/\text{H}_2\text{SO}_4</math>, <math>\text{Cu}(\text{BF}_4)_2/\text{HBF}_4/\text{H}_3\text{BO}_3</math>, alkaline baths of <math>\text{CuSO}_4</math>, wetting agents; <math>\text{Cu}(\text{CN})_2/\text{NaCN}/\text{KCN}</math> with alkali carbonates and hydroxides, Na-K-tartrate; hydroxides, sulphides, NaCNS (brightening agent); <math>\text{Cu}_2\text{P}_2\text{O}_7</math>, <math>\text{K}_4\text{P}_2\text{O}_7</math>, <math>(\text{NH}_4)_2</math>-oxalate, <math>\text{NH}_4\text{OH}</math>, <math>\text{KNO}_3</math></p> <p><b>polishers</b> : thiourea, gelatine, cellulose, organic sulphonc acids</p> <p><b>bath filtration</b> : asbestos, charcoal</p>
Nickel plating	<p><b>baths</b> : <math>\text{NiSO}_4</math>, <math>\text{NiCl}_2</math>, <math>\text{H}_3\text{BO}_3</math>, Ni-citrate, organic wetting and polishing agents e.g. cumarine, <math>\text{H}_2\text{O}_2</math>, emulsifier</p> <p><b>surface hardening bath</b> : <math>\text{NiSO}_4</math>, <math>\text{NH}_4\text{Cl}</math>, <math>\text{NiCl}_2</math>, <math>(\text{NH}_4)_2\text{SO}_4</math>, <math>\text{H}_3\text{BO}_3</math>, Ni-acetate</p>
Chrome plating	<p><b>baths</b> : <math>\text{CrO}_3</math>, <math>\text{H}_2\text{SO}_4</math>, <math>\text{Cr}_2\text{O}_3</math>, HF, <math>\text{H}_2\text{SiF}_6</math>, <math>\text{Na}_2\text{SO}_4</math>, Cr sulphate, chloride, fluoride, nitrate</p> <p><b>catalyst</b> : <math>\text{SrSO}_4</math>, <math>\text{K}_2\text{SiF}_6</math></p> <p><b>anodes</b> : Pb, Sb, Te, Sn, Ag</p> <p><b>coating of bath walls</b> : Pb</p>
Zinc plating	<p><b>electrolytes</b> : <math>\text{ZnSO}_4</math>, <math>\text{Na}_2\text{SO}_4</math>, <math>\text{Al}_2(\text{SO}_4)_3</math>, <math>\text{H}_3\text{BO}_3</math>, <math>\text{ZnCl}_2</math>, NaCl, NaF, <math>\text{AlCl}_3</math>, <math>\text{Zn}(\text{BF}_4)_2</math>, <math>\text{NH}_4\text{Cl}</math>, <math>\text{NH}_4\text{BF}_4</math>, glycyrrhizine</p> <p><b>alkaline electrolytes</b> : <math>\text{Zn}(\text{CN})_2</math>, NaCN, NaOH, ZnO, gelatine, piperonal, triethanolamine, hexamethylenetetramine, Mo-oxide, fatty alcohol sulphonates (wetting agents); <math>\text{Zn}_2\text{P}_2\text{O}_7</math>, <math>\text{K}_4\text{P}_2\text{O}_7</math>, K-citrate</p> <p><b>brightening agents</b> : polymers or heterocyclic compounds</p> <p><b>aftertreatment</b> : <math>\text{H}_2</math> degassing of metal layer by boiling water or hot air and neutralisation</p>
Cadmium plating	<p><b>electrolytes</b> : <math>\text{Cd}(\text{CN})_2</math>, NaCN, CdO</p>
Silver plating	<p><b>electrolytes</b> : AgCN, KCN, NaCN, <math>\text{K}_2\text{CO}_3</math>, brightening agents (polymers, heterocyclic compounds), wetting agents</p>
Alloy plating	<p><b>electrolytes</b> : <math>\text{NH}_4\text{SO}_3\text{NH}_2</math>, Fe-, Co-, Ni-, Cd-, Zn-, Rh-, Ag- or Pb-sulphate, NaOH</p>
Metallisation of plastics	<p><b>degreasing</b> : weak alkaline liquids without NaOH</p> <p><b>pickling</b> : <math>\text{CrO}_3/\text{H}_2\text{SO}_4</math>, <math>\text{H}_3\text{PO}_4</math>, precious metals</p> <p><b>surface activation</b> : HCl, <math>\text{NH}_4\text{OH}</math>, hydroquinone, <math>\text{PdCl}_2</math>, <math>\text{SnCl}_2</math>, Zn, Ag/Pd, <math>\text{H}_2\text{SO}_4</math>, stabiliser, reducing agents</p> <p><b>conductive coating</b> : graphite, Cu, bronze or Ag</p> <p><b>chemical copper or nickel deposition</b> : (see Cu-, Ni-plating)</p> <p><b>chemical deposition of other metals</b> : Na-K-tartrate, NaOH, formaldehyde, <math>\text{CuSO}_4</math>, <math>\text{Na}_2\text{CO}_3</math>, chelating, brightening and wetting agents; borazanes; <math>\text{AgNO}_3</math>, <math>\text{NH}_4\text{OH}</math>, hydrazine, formaldehyde</p>

## SOLUTION DEPOSITION

Ion exchange techniques

**deposition materials** : Cu, Zn, Sn, Ni, Ag, Au, Pt  
**exchanged ions** : Zn, Al, Fe, Cu

Reduction processes

**deposition materials** : Sn, Ni, Cu, Ag, Au  
**reducing agents** :  $\text{NaH}_2\text{PO}_4$ ,  $\text{NaH}_2\text{PO}_3$ , boron compounds, formaldehyde  
**stabilizer** : chelating agents, organic acids  
**buffers** : ammonium salts, acetates, borax, wetting agents  
**catalysts** : Fe, Ni, Ag

## HOT DIP DEPOSITION

Galvanizing

**bath** : melted Zn, fluxes  $\text{ZnCl}_2$ ,  $\text{NH}_4\text{Cl}$ 

Other Zn deposition methods

**baths** : cyanides,  $\text{H}_2\text{SO}_4$ , fluoroboratesHot-tinning,  
electro-tinning,  
other techniques**bath** : melted Sn, flux agents, fluoroborates, stannates, oil, cyanidesHot lead coating  
and other techniques**bath** : melted Pb, additives for better surface adhesion (Sn, Ni, As, Cd, Sb), fluoroboratesHot aluminium  
coating**bath** : melted Al, flux agents : KCl, NaCl

## DIFFUSION DEPOSITION :

Chrome evaporation

Chromium, chromium compounds

Sheradizing processes

Zinc dust, sand, coal, chalk, pumice

Peen plating

**process chemicals** : Zn, aqueous solution of chemicals, impact bodies, Sn

Alitizing

**process chemicals** : carrier of Al (e.g. Al/Fe), SiOther diffusion  
techniques (corrosion  
protection, hardening)

**diffusion materials** : Si (trichlorosilane,  $\text{H}_2$ , high temperatures, mainly combined with alitizing); B (diborane,  $\text{H}_2$ , 550 to 1050 °C reaction temperature, boron trichloride; boron carbide in ethylsilicate paste, high frequency heating); Ti (hardening of Mo and graphite); W (W-hexafluoride)

THERMAL SPRAYING  
TECHNIQUES

Gas spraying

**carrier gases** : acetylene, city gas, propane  
**spraying materials (inductive heated)** : metal wires or powders

Arc spraying

**carrier gases** : protective gases  
**spraying materials** : Zn, Al

Plasma jet spraying

**spraying material** : W, Mo, ceramics, plastics  
**plasma torch material** : Th, W, Cu  
**carrier gases** : Ar,  $\text{N}_2$  (protective gases)

Vacuum deposition	<b>coating substances :</b> Al, Ag, Au, Pt, Cu, Cr, Zn, Cd, SiO, SiO <sub>2</sub> , CaF <sub>2</sub> , ThF <sub>2</sub> , MgF <sub>2</sub>
Electric vaporisation (small range deposition)	<b>deposition material :</b> melted metals
Inductive vaporisation (treatment of larger quantities)	<b>deposition material :</b> melted metals
Electron beam deposition (large scale coating)	<b>deposition material :</b> various materials, especially if high melting temperatures are required for coating

## PROCESS : NON-METALLIC COATING

METHOD and TECHNIQUE	CHEMICALS, MATERIALS USED
<b>CONVERSION LAYERS</b>	
Phosphatizing in aquatic solution	<p><b>methods</b> : dipping, spraying, electrolytic, jet stream phosphatizing, roller feeding</p> <p><b>reaction acceleration chemicals</b> : nitrates, nitrites, chlorates, chromates, sulphates</p> <p><b>grain size reduction substances</b> : pyro-, polyphosphates, organic chemicals (e.g. EDTA), primary Ca- orthophosphate</p> <p><b>nucleation enhancement</b> : grinding, emulsion degreasing, titanophosphate, oxalic acid</p>
Thin-layer phosphatizing (primer for painting)	ortho-phosphates of Fe, Mg, Zn, primary Na-phosphate, wetting agents, oxidants, Mo-compounds
Phosphatizing in non-aquatic solution	<p><b>baths</b> : <math>H_3PO_4</math>, chlorinated hydrocarbons, butanol, amyl alcohol, other solutions,</p> <p><b>accelerators</b> : organic nitrogen compounds</p>
KEPHOS-process	<b>bath</b> : $H_3PO_4$ , epoxy resin, organic solvents
Aftertreatment	<b>passivation</b> : $Na_2Cr_2O_7$
Antique finishing of copper alloys	<b>bath</b> : chromic acid, acids
Dichromate treatment of magnesium alloys	<b>bath</b> : chromic acid
Alkaline oxidation of steel	<b>bath</b> : strong alkali
Chromating (yellow colour)	<b>bath</b> : $CrO_3$ , complex fluorides (activation by pickling),
(green colour)	<b>bath</b> : phosphoric and chromic acid, fluorides
<b>CHEMICAL OXIDATION</b>	
Passivation	<p><b>agents</b> : boiling water or steam (oxide layer)</p> <p><b>pretreatment (pickling)</b> : NaOH or acid mixture (<math>HNO_3/NaF</math>)</p> <p><b>agents</b> : <math>Na_2CrO_3</math>, waterglass (boiling)</p>
Primer, preparation for deep drawing	<b>baths -for pure Al</b> : ammonium hydrogenfluoride, nitric acid
Brightening (chemical or electrolytic)	<p><b>-for Al-alloys, Al with impurities</b> : <math>H_3PO_4</math>, <math>H_2SO_4</math>, <math>HNO_3</math>, <math>H_3BO_3</math>, <math>Cu(NO_3)_2</math>, stabiliser, wetting agents,</p> <p><b>-for pure and alloyed Al</b> : <math>H_3PO_4</math>, <math>H_2SO_4</math>, <math>HNO_3</math>, <math>H_3BO_3</math>, <math>Cu(NO_3)_2</math>, stabilisers, wetting agents; chromic acid</p> <p><b>bath wall and instrumentation coating</b> : Pb</p>

Eloxation (electro-chemical oxidation, anodic oxidation)

**agents** : boric acid, alkaline borates, K-permanganate solution, sulphuric, phosphoric, oxalic, chromic acid, glycerine, salts of inorganic acids, organic acids, foaming agents (volatilisation inhibitors), volatile baths, Pb (cathodes, bath coating)

#### AFTERTREATMENT

Colouring

**agents** : Ti, Mo, V, Cr, Mn, Cu, Ni, Si, Co, Fe, Ag, Au, Pb, Sb, U, organic colours, alcohols, acetone, methylethylketone

Photographic colouring

**agents** : Ag-halides,  $K_2Cr_2O_7$

Sealing

**agents** : acetic, formic acid, Ni-, Co-acetate, boric acid, dichromates, Pb-acetate

Dewatering  
(displacement of water)

**agent** : petroleum hydrocarbon

Absorbents

**agents** : sawdust, proprietary absorbents

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ANNEX D

INTERNATIONAL ORGANIZATIONS ABLE TO ADVISE  
ON HAZARDOUS CHEMICALS

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**International Register of Potentially Toxic Chemicals (IRPTC)**

Palais des Nations, CH 1211 Geneva 10, Switzerland

Telephone : (41) (22) 98 84 00/98 58 50

Telex : 28877 Geneva

Telefax : (41) (22) 33 26 73

Contact for : information on chemicals, on waste disposal, on discharge regulations

**International Programme for Chemical Safety (IPCS)**

c/o World Health Organization,  
CH 1211 Geneva 27, Switzerland

Telephone : (41) (22) 91 21 11

Telex : 27821 OMS

Telefax : (41) (22) 91 07 46

Contact for : toxicological information on chemicals

**International Labour Organization (ILO)**

4 route des Morillons,

CH 1211 Geneva 22, Switzerland

Telephone : (41) (22) 99 61 11

Telex : 22 271 BIT CH

Telefax : (41) (22) 98 86 85

Contact for : occupational health and safety information

**International Safety and Health Information Centre (CIS)**

c/o International Labour Office

4 route des Morillons

CH 1211 Geneva 22, Switzerland

Telephone : (41) (22) 99 67 40

Telex : 22 271 BIT CH

Telefax : (41) (22) 98 86 85

Contact for : information on hazardous materials and workplace safety

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## ANNEX E

### CHEMICAL SAFETY DATA

The following pages show examples of information sheets available for some hazardous chemicals.

Such sheets should always be sought in the first instance from the manufacturer of the

chemical through his agents.

For some common chemicals independent publishing houses may also produce such sheets. The sheets shown here are reproduced with the kind permission of Genium Publications.

# Material Safety Data Sheet

from Genium's Reference Collection  
Genium Publishing Corporation  
1145 Catalyn Street  
Schenectady, NY 12303-1836 USA  
(518) 377-8855



No. 5

CHROMIC ACID, SOLID  
(Revision B)  
Issued: September 1977  
Revised: August 1985

## SECTION 1. MATERIAL IDENTIFICATION

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**Material Name:** CHROMIC ACID, SOLID

**Other Designations:** Chromium Trioxide; Chromic Anhydride; Chromium (VI) Oxide;  
CrO<sub>3</sub>; CAS No. 1333-82-0



**Manufacturer:** Contact your supplier or distributor. Consult the latest edition of the Chemicalweek  
*Buyers' Guide* (Genium ref. 73) for a list of suppliers.

## SECTION 2. INGREDIENTS AND HAZARDS/EXPOSURE LIMITS

Chromium Trioxide, ca 100 %

**OSHA PEL**  
Ceiling: 0.1 mg/m<sup>3</sup>\*

**ACGIH TLVs, 1985-86**  
TLV-TWA: 0.05 mgm<sup>3</sup>\*\* (as Cr)

**Toxicity Data\***  
Dog, Subcutaneous, LD<sub>50</sub>: 330 mg/kg

\*Current OSHA PEL (ceiling limit) from chromic acid and chromates.

\*\*Current ACGIH TLV for water-soluble chromium VI compounds.

Note: The NIOSH-recommended exposure limit for chromium VI oxide is 0.025 mg Cr (VI)/m<sup>3</sup> average over a work shift of up to 10 hours, with ceiling level of 0.05 mg Cr (VI)/m<sup>3</sup> (15-minute period).

## SECTION 3. PHYSICAL DATA

**Boiling Point:** Decomposes at 250°C to Cr<sub>2</sub>O<sub>3</sub> + O<sub>2</sub>

**Solubility in Water (%):** 63 gm/100 cc at 20°C

**Melting Point:** 197°C

**Specific Gravity (H<sub>2</sub>O = 1):** 2.7

**Molecular Weight:** 99.99

**Appearance and Odor:** Dark red deliquescent flakes or crystals; odorless.

## SECTION 4. FIRE AND EXPLOSION DATA

**Flash Point:** Not Combustible

**Autoignition Temperature:** Not Applicable

**LEL:** Not Applicable

**UEL:** Not Applicable

Chromic anhydride is not flammable but is a strong oxidizing agent and can ignite many hydrocarbons such as acetic acid and alcohol when brought into direct contact with them. Certain inorganic chemicals will produce incandescence when mixed with chromic anhydride; e.g., arsenic, ammonia gas, hydrogen sulfide, phosphorus, potassium, sodium, and selenium. Flammable materials placed in the vicinity of such reactions could be easily ignited.

Fire fighters should wear self-contained breathing apparatus and full protective gear to prevent contact when fighting fires involving this material.

## SECTION 5. REACTIVITY DATA

This material is stable when properly stored and handled. It is a strong oxidizing agent and will react with many oxidizable substances such as oils, grease, paper, and plastics. The reactions can be rapid enough to ignite these materials. Chromic anhydride will ignite many hydrocarbons from direct contact. Incandescence is also produced from contact with the inorganic materials mentioned in section 4.

**SECTION 6. HEALTH HAZARD INFORMATION**

Inhalation of dust or mist can cause irritation of the respiratory tract due to high acidity and tissue oxidation. Ulceration of mucous membranes of the nose and mouth can result from inhalation. Skin contact with acid solutions or the solid may cause irritation. However, the major damage occurs up to 48 hours after contact. The chromates slowly dissolve the skin, forming ulcers. Secondary infections can then occur on the broken skin. Chromic acid is also a sensitizer and may cause allergic skin rash. Eye contact may result in severe burns with loss of vision. Ingestion may cause severe burns of the intestinal tract with internal damage. Ingestion of 5 grams or less may be lethal for an adult. Long-term absorption may cause liver damage. Increased instances of respiratory cancers have been reported in the chromate-producing industry. In its 1975 criteria document, NIOSH identified chromium trioxide as a "noncarcinogenic chromium IV." The IARC has classified "chromium and certain chromium compounds" as being carcinogenic to humans. The specific chromium compounds responsible for the carcinogenic effects are not identified.

**First Aid**

**Inhalation:** Remove person to fresh air. If necessary, aid breathing and seek medical attention.\*

**Eyes:** Immediately flush eyes, including under the eyelids, with running water for at least 15 minutes. Obtain medical assistance promptly.\*

**Skin:** Promptly remove contaminated clothing and wash infected area with soap and water. Seek medical attention\* if irritation persists or other symptoms develop.

**Ingestion:** Give person large quantities of milk or water to drink, then induce vomiting. Get prompt medical attention.\* (Never induce vomiting or give anything by mouth to an unconscious person.)

\*Get medical assistance: in plant, paramedic, community.

**SECTION 7. SPILL, LEAK, AND DISPOSAL PROCEDURES**

Notify safety/environmental personnel of spills. Cleanup personnel should wear respirators and protective gloves and clothing to prevent inhalation and skin contact. Provide adequate ventilation. Spread a reducing agent such as sodium sulfite or ferrous sulfate on liquid acid spills. Scoop up the resulting slurry into a container of water and neutralize with soda ash. Solid spills may be carefully scooped into containers, taking care to minimize dust generation.

**Disposal:** Solutions containing this material should be chemically treated with reducing agents and pH adjusted to precipitate chromium. The precipitate and other solids containing this material should be disposed of in an approved chemical-waste landfill. Follow applicable local, state, and Federal regulations.

EPA Hazardous Waste Number: D007 (EP Toxicity, 40 CFR 261)

Reportable Spill Quantity: 1000 lbs. (454 kg)

**SECTION 8. SPECIAL PROTECTION INFORMATION**

Provide general and local exhaust ventilation to meet TLV requirements. NIOSH-approved high-efficiency dust/mist respirators with full facepieces should be used during nonroutine/emergency operations and whenever the TLV may be exceeded. Self-contained breathing apparatus or supplied-air respirators (both in positive-pressure mode) should be worn under severe exposure conditions (75 mg/m<sup>3</sup>). Tanks of chromic acid must be adequately exhausted, with chemical-resistant duct work and fans. Employees should wear chemical safety goggles to prevent eye contact. Face shields should also be worn where splashing can occur. Neoprene or other synthetic rubber gloves and apron or protective clothing should be worn. Caution: Chromic acid can attack some of these materials. If clothing becomes contaminated; fresh clothing should be obtained immediately. Launder contaminated clothing before reuse. Eyewash stations and safety showers should be readily accessible in areas of use. Contact lenses pose a special hazard: soft lenses may absorb irritants, and all lenses concentrate them

**SECTION 9. SPECIAL PRECAUTIONS AND COMMENTS**

Store in closed containers away from oxidizable materials and other incompatible materials. Protect containers from physical damage. Maintain good housekeeping procedures. Avoid breathing dust and mist. Avoid skin contact. Practice good personal hygiene. Wash hands thoroughly before eating and smoking. Wash all areas of the body that may have come in contact with this material at the end of each work day. Eating and smoking should not be permitted in areas where this material is handled.

DOT Hazard Class: Oxidizer

DOT ID No. NA 1463

DOT Label: Oxidizer, Solid

References: 2, 4, 9, 12, 19, 20, 27, 58, 60, 61.

Prepared by C Venezia, CIH; Industrial Hygiene Review: DJ Wilson, CIH; Medical Review: ER Plunkett, MD

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# Material Safety Data Sheet

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No. 312  
TRICHLOROETHYLENE  
(Revision E)

Issued: July 1979  
Revised: August 1987

SECTION 1. MATERIAL IDENTIFICATION			23	
<p><b>MATERIAL NAME:</b> TRICHLOROETHYLENE</p> <p><b>DESCRIPTION (Origin/Uses):</b> Prepared from <i>sym</i>-tetrachloroethane by way of eliminating HCl by boiling with lime. Used to manufacture organic chemicals, pharmaceuticals; in degreasing and dry cleaning; and as a solvent for fats, waxes, rubbers, oils, paints, varnishes, ethers, and cellulose esters.</p> <p><b>OTHER DESIGNATIONS:</b> Ethylene Trichloride; TCE; Trichloroethene; 1,1,2-Trichloroethylene; C<sub>2</sub>HCl<sub>3</sub>; NIOSH RTECS #KX4550000; CAS #0079-01-6</p> <p><b>MANUFACTURER/SUPPLIER:</b> Available from several suppliers, including: Dow Chemical USA, 2020 Dow Center, Midland, MI 48640; Telephone: (517) 636-1000; (800) 258-CHEM</p> <p><b>COMMENTS:</b> Trichloroethylene is a toxic solvent and a suspected occupational carcinogen.</p>				
<p style="text-align: right;">HMIS H 2 F 1 R 1 R 1 I 3 PPE* S 1 * See sect. 8 K 0</p>				
SECTION 2. INGREDIENTS AND HAZARDS		%	HAZARD DATA	
<p>Trichloroethylene, CAS #0079-01-6; NIOSH RTECS #KX4550000</p> <div style="text-align: center;"> <math display="block">\begin{array}{c} \text{Cl} &amp; &amp; \text{Cl} \\ &amp; \diagdown &amp; / \\ &amp; \text{C} = &amp; \text{C} \\ &amp; / &amp; \diagdown \\ \text{H} &amp; &amp; \text{Cl} \end{array}</math> </div> <p>* The TLV-TWA is set to control subjective complaints such as headache, fatigue, and irritability. ** The TLV-STEL is set to prevent incoordination and other beginning anesthetic effects from TCE. These levels should provide a wide margin of safety in preventing liver injury. *** The OSHA PEL is 300 ppm for 5 minutes in any 2 hours.</p>		100	<p>ACGIH Values 1987-88 TLV-TWA*: 50 ppm, 270 mg/m<sup>3</sup> TLV-STEL**: 200 ppm, 1080 mg/m<sup>3</sup> OSHA PEL 1986*** 8-Hr TWA: 100 ppm Ceiling: 200 ppm NIOSH REL 1986 10-Hr TWA: 25 ppm TOXICITY DATA Human, Oral, LD<sub>50</sub>: 7 g/kg Human, Inhalation, TC<sub>Lo</sub>: 6900 mg/m<sup>3</sup> (10 Min) Human, Inhalation, TC<sub>Lo</sub>: 160 ppm/ 83 Min Human, Inhalation, TD<sub>Lo</sub>: 812 mg/kg</p>	
SECTION 3. PHYSICAL DATA				
<p>Boiling Point ... 188.6°F (87°C) Vapor Pressure ... 58 Torr at 68°F (20°C) Water Solubility ... Insoluble Vapor Density (Air = 1) ... 4.53</p>		<p>Evaporation Rate ... Not Listed Specific Gravity ... 1.4649 at 68°F (20°C) Melting Point ... -120.64°F (-84.8°C) Molecular Weight ... 131.40 Grams/Mole</p>		
<p>Appearance and odor: Colorless, nonflammable mobile liquid; sweetish odor like chloroform.</p> <p>COMMENTS: TCE is highly soluble in lipids. A high vapor pressure at room temperature provides the potential for TCE vapors to contaminate use areas.</p>				
SECTION 4. FIRE AND EXPLOSION DATA			LOWER	UPPER
Flash Point and Method	Autoignition Temperature	Flammability Limits in Air	8%	10.5%
Not Listed	770°F (410°C)	% by Volume		
<p><b>EXTINGUISHING MEDIA:</b> TCE has no flash point in a conventional closed tester at room temperature, but it is moderately flammable at higher temperatures. Use dry chemical, carbon dioxide, alcohol foam, or other extinguishing agents suitable for the surrounding fire.</p> <p>OSHA Flammability Class (29 CFR 1910.106): Not Regulated</p> <p><b>UNUSUAL FIRE/EXPLOSION HAZARDS:</b> During fire conditions TCE emits highly toxic and irritating fumes, including hydrochloric acid and phosgene. <b>SPECIAL FIRE-FIGHTING PROCEDURES:</b> Wear a self-contained breathing apparatus with a full facepiece operated in a pressure-demand or another positive-pressure mode. At TCE vapor levels of 300-1000 ppm, fire fighters who lack the proper respiratory equipment may experience incoordination and impaired judgment.</p> <p>DOT Flammability Class (49 CFR 173.115): Not Regulated</p>				
SECTION 5. REACTIVITY DATA				
<p>Trichloroethylene is stable. Hazardous polymerization can occur under certain circumstances (see Conditions to Avoid and Comments, below).</p> <p><b>CHEMICAL INCOMPATIBILITIES</b> include magnesium or aluminum powder, NaOH, KOH, or other strong alkaline materials. Reactions with alkaline materials may lead to the formation of dangerous explosive mixtures of chloroacetylenes.</p> <p><b>CONDITIONS TO AVOID:</b> When TCE is heated (as in the case with vapor degreasers) or exposed to sunlight, it requires extra stabilization against oxidation, degradation, and polymerization. It is slowly decomposed by light when moist.</p> <p><b>PRODUCTS OF HAZARDOUS DECOMPOSITION</b> include hydrochloric acid and phosgene under certain conditions at elevated temperatures.</p> <p><b>COMMENTS:</b> TCE is stable under normal handling and storage conditions, and hazardous polymerization is not expected to occur. However, failure of the stabilizer at elevated temperatures or other extreme conditions may allow polymerization to take place.</p>				

**SECTION 6. HEALTH HAZARD INFORMATION**

Trichloroethylene is listed as a carcinogen by the NTP, IARC, and OSHA. NIOSH recommends that trichloroethylene be treated as an occupational carcinogen. IARC carcinogenic results are animal suspect, animal positive, and human indefinite. **SUMMARY OF RISKS:** Moderate exposures to TCE cause symptoms similar to those of alcohol inebriation. Higher concentrations cause narcotic effects. Ventricular fibrillation has been cited as the cause of death following heavy exposures. TCE-induced hepato cellular carcinomas have been detected in mice during tests conducted by the National Cancer Institute (*Chem & Eng News* 54 [April 5, 1976]:4). Organ systems affected by overexposure to TCE are the central nervous system (euphoria, analgesia, anesthesia), degeneration of the liver and kidneys, the lungs (tachypnea), heart (arrhythmia) and skin (irritation, vesication, and paralysis of fingers when immersed in liquid TCE). Contact with the liquid defats the skin, causing topical dermatitis. Certain people appear to experience synergistic effects from TCE exposure concomitant with exposure to caffeine, alcohol, and other drugs. When combined with alcohol intake, toxic effects are increased and may cause a red, blotchy facial and upper body rash commonly called "degreaser's flush." Other reported symptoms of TCE exposure include abnormal fatigue, headache, irritability, gastric disturbances, and intolerance to alcohol. Toxic effects from testing of TCE on humans include hallucination, distorted perception, somnolence (general depressed activity), and jaundice. **TARGET ORGANS:** Respiratory system, central nervous system, heart, liver, kidneys, and skin. **PRIMARY ENTRY:** Ingestion, inhalation, skin contact. **ACUTE EFFECTS:** Headache, vertigo, visual disturbance, tremors, nausea, vomiting, dermatitis, dizziness, drowsiness, and irritation to the eyes, nose, and throat. **CHRONIC EFFECTS:** None Reported. **MEDICAL CONDITIONS AGGRAVATED BY LONG-TERM EXPOSURE:** Diseases of the liver, kidneys, lungs, and central nervous system. **FIRST AID: EYE CONTACT:** Immediately flush eyes, including under the eyelids, gently but thoroughly with plenty of running water for at least 15 minutes. Get medical help.\* **SKIN CONTACT:** Wash thoroughly with soap and water. Remove and launder contaminated clothing before wearing it again; clean material from shoes and equipment. Get medical help.\* **INHALATION:** Remove victim to fresh air; restore and/or support his breathing as needed. Do not give adrenalin to the victim. Get medical help.\* **INGESTION:** Call a poison control center. Never give anything by mouth to someone who is unconscious or convulsing. A professional decision regarding whether or not to induce vomiting is required. Do not give adrenalin to the victim. Get medical help.\* **\*GET MEDICAL ASSISTANCE = IN PLANT, PARAMEDIC, COMMUNITY.** Get prompt medical assistance for further treatment, observation, and support after first aid.

**COMMENTS:** Workers' responses to TCE vary significantly because of many factors, including age, health status, nutrition, and intake of alcohol, caffeine, and medicines. Do not use these substances before, during, or after exposure to TCE. If a worker displays any of the symptoms of exposure to TCE, thoroughly investigate all the possible contributing factors to determine, if possible, how much the work environment levels of TCE are responsible.

**SECTION 7. SPILL, LEAK, AND DISPOSAL PROCEDURES**

**SPILL/LEAK:** Inform safety personnel of any trichloroethylene spill or leak and evacuate the area for large spills. Cleanup personnel must use respiratory and liquid contact protection. Adequate ventilation must be provided. Confine the spilled TCE to as small an area as possible. Do not allow it to run off to sewers or open waterways. Pick up spilled TCE with a vacuum cleaner or an absorbent such as vermiculite.

**DISPOSAL:** Consider reclamation, recycling, or destruction rather than disposal in a landfill.

Trichloroethylene is designated as a hazardous substance by the EPA (40 CFR 116.4).

Trichloroethylene is reported in the 1983 EPA TSCA Inventory.

EPA Hazardous Waste Number (40 CFR 261.33): U228

EPA Reportable Quantity (40 CFR 117.3): 1000 lbs (454 kgs)

Aquatic Toxicity Rating, TLM 96: Not Listed

**SECTION 8. SPECIAL PROTECTION INFORMATION**

**GOGGLES:** Always wear protective eyeglasses or chemical safety goggles. Follow the eye and face protection guidelines of 29 CFR 1910.133. **GLOVES:** Wear impervious gloves. **RESPIRATOR:** Use a NIOSH-approved respirator per the *NIOSH Guide to Chemical Hazards* (Genium ref. 88) for the maximum-use concentrations and/or the exposure limits cited in section 2. Follow the respirator guidelines in 29 CFR 1910.134. Any detectable concentration of TCE requires an SCBA, full facepiece, and pressure-demand/positive-pressure modes. **WARNING:** Air-purifying respirators will not protect workers from oxygen-deficient atmospheres. **OTHER EQUIPMENT:** Wear rubber boots, aprons, and other suitable body protection appropriate to the existing work environment. **VENTILATION:** Install and operate general and local exhaust ventilation systems of sufficient power to maintain airborne concentrations of TCE below the OSHA PEL standards cited in section 2. **SAFETY STATIONS:** Make eyewash stations, washing facilities, and safety showers available in areas of use and handling. Contact lenses pose a special hazard; soft lenses may absorb irritants, and all lenses concentrate them. **OTHER SPECIAL MODIFICATIONS IN THE WORKPLACE:** Because of the unresolved controversy about the carcinogenic status of TCE, all existing personal protective equipment and engineering technology should be used to prevent any possibility of worker contact with this material.

**COMMENTS:** Practice good personal hygiene. Keep material off of your clothes and equipment. Avoid transfer of material from hands to mouth while eating, drinking, or smoking. Adhere to the sanitation requirements of 29 CFR 1910.141 and 29 CFR 1910.142.

**SECTION 9. SPECIAL PRECAUTIONS AND COMMENTS**

**STORAGE SEGREGATION:** Prevent TCE from coming into contact with strong caustics such as NaOH; KOH; chemically active metal like Ba, Li, Na, Mg, Ti; and powdered aluminum or magnesium in acidic solutions. **SPECIAL HANDLING/STORAGE:** Store this material in a cool, dry, well-ventilated area. Avoid elevated temperatures because products of toxic and corrosive decomposition from TCE may form. Monitor the level of any stabilizer component that may be added to the TCE. (Consult the technical data from the supplier to determine the specifics of any added stabilizer.) If applicable, follow the supplier's recommendation concerning proper rotation of stock, shelf-life requirements, and levels of particles.

**ENGINEERING CONTROLS IN THE WORKPLACE:** Avoid collecting aluminum fines (very small particles) or chips in a TCE vapor degreaser. Monitor TCE stabilizer levels regularly. Only trained personnel should operate vapor degreasers.

**TRANSPORTATION DATA** (per 49 CFR 172.101-2):

DOT Hazard Class: ORM-A	DOT ID No. UN1710	IMO Class: 6.1
IMO Label: St. Andrew's Cross (X)*	DOT Shipping Name: Trichloroethylene	DOT Label: None

\* Harmful - Stow away from foodstuffs (IMO Label, Materials of Class 6.1 Packaging Group III).

References: 1-9, 12, 14, 21, 73, 87-94. PI

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