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34p

IN-DEPTH TRAINING COURSE

ON

CLEANER PRODUCTION TECHNOLOGY: SURFACE FINISHING

prepared and presented for the

Environmental Co-ordination Unit,

UNIDO

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July, 1991

Acknowledgements

This seminar was designed as an introduction to pollution control in the Client Member Countries (`CMCs') of UNIDO. The decision to use the surface treatment group of industries as an example was made on the grounds that experience in the Donor Member Countries (`DMCs') was more nearly similar; the difficulty of introducing new technologies more nearly equivalent; and the benefits of low technology, internally instigated approaches to process control, whether for environmental or for cost-saving reasons are more immediately felt.

The technical parts of this report draw extensively on an excellent publication issued by Environment Canada:

> Chemical Industries Division, Environment Protection: Overview of the Canadian Surface Finishing Industry, Report EPS 2/SF/1, Environment Canada, Ottawa, December 1987

and some of the more process descriptions are simply summaries of those to be found in this report. Anyone wishing more technical detail is directed to this, and full acknowledgement of this source is gratefully made.

`Skip' Luken of UNIDO's ECU was instrumental in developing this seminar in UNIDO, and also more than tolerant of the report's prolonged gestation. My personal thanks are due to him, and to the staff of UNIDO who made the all-too-brief stay so enjoyable.

I MITIGATING THE IMPACT OF INDUSTRY ON THE ENVIRONMENT IN DEVELOPING COUNTRIES: ALTERNATIVE APPROACHES

The philosophy of environmental management currently being propounded by the international agencies responsible for promoting environmental quality in a development context is broadly as follows:

i. adopt cleaner, waste minimising technologies;
ii. recycle where this is not possible;
iii. treat residues/effluent/gaseous emissions where recycling is not possible;
iv. if all else fails, dispose (in as environmentally sound a manner as possible).

Unfortunately, this view is one which is `first world' centred. It assumes:

- access to technology (in terms of the financial and human resources to acquire, operate, maintain and repair the technology);
- the presence of a regulatory system which is resourced to enforce comprehensive laws and regulations designed to control effectively the environmental impact of industrial production;
- an industrial culture which places great importance on regulatory compliance.

The reality in many developing countries is quite different. A legal and regulatory structure may be in place but it is rarely adequately resourced. (An example will help reinforce this point. At a seminar on hazardous waste management in which the author recently participated, a representative from the Environmental Protection Agency of an African country explained that there were no vehicles allocated to the Agency, nor was there any means by which an allocation for the expenses of using their own vehicle could be given to Agency officials. As a result, all enforcement was done from the offices of the Agency, without site visits).

Apart from the question of an operating regulatory system, the question of access to technology also can present severe problems. Most of the developing countries are experiencing severe foreign exchange problems, and can only access advanced technology through the medium of bilateral or multilateral aid. This aid, if given, will be given for the acquisition of the capital goods in which the technology is physically embodied, but more rarely for the essential spares required for repair and maintenance, or for the often radical upgrading of the knowledge and skills of the plant operators.

It must also be said that the industrial culture (as opposed to the traditional or popular culture) of the developing countries is much less influenced by environmental concerns than it is in the developing countries, where environmental considerations weigh ever more heavily on the shoulders of company managers and directors. This is probably results from a combination of expedience and perception: direct costs are lower without pollution control equipment, and industrial output is seen as having a greater foreign exchange earning potential than clean river water or city air.

Although this is a brief and necessarily simplified statement of the position of many of the CMCs of bilateral and multilateral aid agencies, it is nevertheless a sufficiently accurate description of the circumstances to be found in these countries to suggest that the pre-eminence of adopting technologies which are still considered advanced in the DMCs must remain a very long term goal. In the meanwhile, there remains the problem of how to achieve improvements in environmental management in the individual countries concerned. The 'alternative' approach to improved environmental management proposed here is good housekeeping supported by training, with alternative technologies (encapsulating waste minimisation and maximisation of recycling) being an integral but long term target rather than the first priority.

The Term 'good housekeeping' when applied to an industrial process refers to a wide variety of individual steps such as:

- ensuring that individual inputs are as required in the process specification;
- assuring regular and proper maintenance;
- ensuring that the physical parameters of the process (temperature, pressure, levels of moisture or oxygen, for example) are as required in the process description;
- ensuring that a simple monitoring system is in place to ensure that these requirements are met continually.

The training element is essential to the process of good housekeeping. A well trained work force will operate a plant according to the design specifications, regardless of the vintage of the technology. It is also in the interests of the managers and owners of the plant to ensure that a plant is so operated, as an efficient plant is more profitable.

A quality control system to ensure that 'good housekeeping' practice is followed at the plant is important, and is part of an environmental audit. The short, two-day seminar which this report represents was meant as an introduction to certain aspects of `good housekeeping' practice in the metal treatment and surface finishing industry, in effect using this as an allegory for a more comprehensive discussion of these matters.

From the perspective of the , the `good housekeeping' approach to environmental improvement has many advantages to commend it:

i. it can be implemented within the existing resource base of the company, without any delay (except for any training that may be required);
ii. the benefits to the company, in terms of lower costs, less rejection of off-specification product and reduced waste disposal costs (where these are levied) are immediate and visible;
iii. the environmental benefits, in terms of lower levels of waste, effluent and gaseous emissions, arise without the need for an extensive and efficiently implemented and enforced legal and regulatory infrastructure;
iv. a national campaign to encourage better housekeeping can be achieved with a very small input of resources.

II INTRODUCTION

The term 'Surface finishing' is an imprecise term to cover many operations, including:

- cleaning of surfaces;
- preparation of surfaces;
- coating of surfaces.

Surface finishing also encompasses intermediate operations.

Surface finishing activities may have significant effects on human health and safety and the environment because:

- the chemicals used may be toxic;
- the toxicity of some of the metals which are treated;
- it is usually carried on in a confined atmosphere;
- the extensive use of water in many of the surface treatment, finishing and related processes.

The surface finishing industry is quite diverse, varying from large plants to small companies, with most of the output in the former and most companies in the latter. In many instances, for example in the metal smelting and forming industry, the surface treatment step is simply one or more stages in a more complex process. In other instances, for example the plating industry, the plating of metal or plastic articles is the sole activity of the firms involved.

Firm size distribution being heavily skewed to small companies means that cash flow is typically a limiting factor in any expenditure decision, and profitability is low. Investment decisions, whether in new plant or pollution/health and safety control measures, are difficult to justify.

Approaches to control pollution and regulate health and safety exposure include:

- improved housekeeping in the plant;
- retrofitting processes;
- replacing chemicals of concern;
- the use of different processes;
- post-process resource recovery and recycling.

The seminar looks at:

- industrial processes;
- the emissions, effluent and wastes produced;
- the health and safety and environmental problems that the wastes present;

- alternative approaches to managing the environmental and health and safety problems within existing technology;
- waste minimisation;
- new technologies;
- resource recovery;
- economic and other non-regulatory incentives to improve environmental and health and safety management in the surface finishing industry.

The choice of the surface finishing industry for this seminar is particularly appropriate from the view point of industry in developing countries for a number of reasons:

1. the environmental impact of emissions/residues/effluent from the industry is potentially highly significant if not mitigated.
2. It demonstrates the benefits that can be achieved with good housekeeping and minor process modifications arguably better than any other industry.
3. The high proportion of small companies in the industry in both DMCs and means that the difficulties of introducing advanced waste minimisation technologies is the greater, and that the benefits of an alternative, in-house approach to improved cost efficiency and waste reduction is more readily adopted.

III SURFACE FINISHING

" Surface finishing consists of various chemical and physical processes which change the surface (decorative), increase its corrosion resistance, or produce surface characteristics essential for subsequent operations (functional)"[1].

The focus of the seminar is on metal finishing. The approach used in the seminar is, however, applicable to other industries, although the process detail will obviously differ from industry to industry. The seminar will be of most use to UNIDO personnel if the use of the surface finishing industry is regarded as a case study, rather than the approach used being regarded as applicable only to surface finishing.

The types of processes we consider are:

Mechanical processes	sandblasting grinding barrel finishing polishing and buffing
Chemical processes	solvent cleaning alkaline cleaning acid pickling/etching/bright dipping salt bath cleaning quenching/`cyaniding' chemical conversion coating `electroless' and immersion plating
Physical processes	plastic and paint coatings hot dip coating
Electrolytic processes	electrocleaning electropolishing anodising electroplating.

We outline these processes below, giving more emphasis to those which present more severe environmental or health and safety problems.

III.1 Mechanical Processes

III.1.1 Sandblasting This is used to give a cleaner, smoother finish to metal parts, using either a dry or a wet process. Aluminium oxide or silicon carbide rather than sand is used as an abrasive for the dry process. In wet blasting a slurry of abrasive, wetting agent, rust inhibitors and anti-settling agents is used.

Sandblasting can present both environmental and health and safety problems, the most serious of which is work place exposure. The abrasive is disposed as a solid waste in DMCs, and the rinse waters may contain abrasive, metal scale and oils. However, it is the dry process that yields the potential for the more serious problems. If there is not sufficient exhaust control in the sandblasting bay, inhalation both of the abrasive and of the metal or metal finish which is being treated is a potential cause of health problems resulting from inhalation of process dust.

III.1.2 Grinding This process requires the use of lubricating oils, wetting agents, rust inhibitors and other additives applied to an abrasive wheel or belt. This produces an oily sludge containing metal which must be disposed. In addition, oil, grit, and metals may produce further solid or liquid waste streams.

III.1.3 Barrel finishing (`tumbling'). This can be used to clean, remove the burns from and polish metal, ceramic or plastic. The pieces to be treated are loaded into a rotating barrel together with whatever treatments are required, including: abrasives and additives such as alkaline cleaners, anti-rust agents, acids and oils. Following tumbling the parts are rinsed, which may put oils, chemical additives, grit, metals and cyanide compounds into the effluent stream.

III.1.4 Polishing and buffing. In this treatment abrasive material is applied to a rotating wheel which is in contact with the piece to be treated. Greases, oils soaps are among the compounds used. They are eventually to be found either in the waste or the effluent from the process, together with metal. Fine metal and abrasive dust can also be found in the work place atmosphere.

III.2 Chemical Processes

III.2.1 Solvent cleaning Solvent is used, both in the liquid phase and also in the gaseous phase in a vaporisation chamber, to remove surface oil and grease. The volatilised solvent is usually recovered in DMCs by passing the vapour through condensing coils and returning it to the solvent reservoir.

The most commonly used solvents are chlorinated solvents such as:

- 1,1,1-trichloroethane
- trichloroethylene
- perchloroethylene
- methyl chloride

There is also limited use of:

- toluene
- kerosene
- alcohol.

There is little waste from this process, but considerable effluent is generated which contains oil, grease and solvent. The solvent can be recovered from the process effluent by redistillation if the solvent content of the effluent is sufficiently high. In DMCs the effluent is disposed to a specialist facility, as it is classified as a `hazardous'/`special'/`difficult' waste. Stringent limits on the discharge of chlorinated solvents are imposed in most DMCs. In addition, there is a risk of work place exposure to solvent fumes, or of these being released to the external environment.

III.2.2 Alkaline cleaning Water soluble mixtures of alkalis and chemical additives are used frequently in surface treatment, either in baths or by spraying the solution on to the pieces. An alkali cleaning stage is often introduced before or after the stage itself.

The particular combination of cleaning agents used varies with the nature of the surface and the nature of the contaminant to be removed.

The alkalinity of the solutions varies. Contaminants include saponified and emulsified greases, metals and miscellaneous solids. They generate significant quantities of sludge. Vapours from the tanks may be classified as hazardous under national health and safety regulations and by criteria developed by WHO.

III.2.3 Acid Pickling/etching/bright dipping Up to 50% concentration of hydrochloric, sulphuric, nitric, chromic and phosphoric acids are most commonly used in the `pickling' process to remove any scale, rust or any alkaline residue which may remain after cleaning. In some instances the acid solution is heated.

Chemical inhibitors are used to prevent metal either from the equipment or from the items themselves being dissolved and contaminating the solution, but these are of limited effectiveness. Rinse waters are contaminated with `dragout' from the baths, which contains metals, acids, oils, wetting agents, detergent and additives. Open acid tanks can release acid fumes into the work place atmosphere and the surrounding environment. Concentrated acid solutions from spent baths also are considered to be hazardous in many European countries.
Etching baths of mixed acid solutions are used to dissolve the surface of a metal or plastic item in a controlled way, usually

to produce a design on the surface. Etching baths can also be used to prepare surfaces for the `electroless' plating of printed circuit boards with nickel or copper, as well as for achieving improved coating adhesion on plastic surfaces. The spent acids themselves contribute to the effluent/waste disposal problems. Other contaminants in process effluent include plastics and metals in solution. Unwanted deposits can be removed by immersing the item in an acid bath in a similar way.

`Bright dipping' is used when the need is to remove oxides from the surface of copper and copper alloys, aluminium and stainless steel for different finishes. The wastes and effluent produced are similar to the other effluent and wastes identified in this subsection.

III.2.4 Salt bath pot cleaning. Baths of molten sodium hydroxide or sodium cyanide, together with other additives, are used to remove rust and scale from metal. A sludge is produced from this process, and the baths themselves have a relatively short life. In addition, the rinse waters from the process may contain metal, cyanide and other residues.

III.2.5 Quenching. Quench baths consist of one of the following:

- pure oil;
- oil with chemical additives;
- water-oil emulsions;
- brine solutions;
- water-based solutions;
- molten cyanide.

The choice of medium in the bath depends upon the material to be cooled and the cooling profile required.

Quench baths may have the following constituents:

(i) brine quenches: sodium chloride, calcium chloride, sodium hydroxide, sodium carbonate, hydrochloric or sulphuric acid;
(ii) water-based quenches and rinses: dissolved salts, soaps, alcohols, oils, and emulsifiers;
(iii) cyanide baths (for heat treatment): sodium cyanide and inert salts.

Liquid effluent from quenching include the baths themselves and rinse waters. As well as the quench solutions themselves, they may also contain other chemicals, metal scale and oil. These may form a sludge which is likely to be classified as `hazardous'/`special'/`difficult' in many DMCs, presenting particular disposal problems.

III.2.6 Chemical coating There are two principal types of coating: `chromating' and `phosphating'. Chromating is a means of producing a thin chromate coat on zinc, cadmium, aluminium, copper and brass. This also provides corrosion protection.

`Chromating' baths usually contain chromic acid, dichromate, and active organic or inorganic compounds. Both trivalent and hexavalent chromium compounds are used in `chromating' baths, the hexavalent form being of particular concern from a health and safety and environmental perspective. They may enter the effluent stream either through rinse water or through the discharge of spent baths.

`Phosphating' is a similar process which is used to give iron or steel an improved surface for bonding paints, waxes, oils and lubricants. It also improves the metal's forming potential. Baths are made up of phosphates of calcium, iron, manganese and zinc in phosphoric acid. The coating may be completed with a rinse in dilute chromic acid.

In addition, colouring baths may be used to blacken a phosphate coating to leave an oxide layer of various shades depending on the solution used. The baths consist of solutions of salts of arsenic, copper, iron, lead, nickel or zinc. Effluent and wastes come from rinse waters or spent baths.

III.2.7 Autocatalytic (`electroless') and immersion plating. Autocatalytic plating is used to apply nickel, cobalt, palladium, platinum, copper, gold, silver (and sometimes their alloys) onto metal or plastic. Common applications of this plating method include:

- plating copper or nickel on plastics (printed circuit boards);
- providing a metal base on plastic to prepare for electroplating. (Plastics need to be pretreated eg. by etching, before autocatalytic plating because plastic is nonconducting).

Immersion plating applies a metal coating without an outside source of electricity. Metal in solution is deposited on the items to be plated by displacing the base material.

The effluent produced are either rinse water or effluent bath discharges. Among the chemicals encountered after immersion coating are metal salts, dissolved metals, chromates, alkalis and cyanide or ammonia complexing agents. Effluent from autocatalytic coating include the coating metal, sodium hypophosphite, formaldehyde or other reducing agents and complex chelating agents.

III.3 Physical Processes

III.3.1 Plastic and paint coatings Plastic powder coatings are applied by spraying electrostatically charged plastic onto the item which carries an opposite charge, and then fusing the coating thermally. Excess powder can be recycled. The items are initially prepared by surface cleaning and preparation processes, and, often, phosphating.

Industrial paints are applied either by spraying in booths or by dipping. The surface to be treated is prepared by conventional mechanical and/or chemical surface treatment processes prior to coating.

Effluent from these coating operations includes rinse waters, solvents, pigments, resins, metals and additives. The waste plastic or paint forms a sludge which requires care in disposal, as it may be defined as a hazardous waste in DMCs. Solvent fumes are an important health hazard in the work place and also in the environment surrounding the plant.

III.3.2 Hot dip coating. Dipping an item in molten metal in order to coat it is an approach which is sometimes used. The process forms an alloy of the two metals at the contacting surface which binds the coating metal to the surface. The surface must be cleaned and fluxed prior to coating, and subsequently quenched. The most common form of hot dip coating is galvanising with zinc, although the method is also used for decorative coating with aluminium, lead or tin.

No wastes are generated directly in hot dip coating other than spills. However, rinse waters from quenching and precleaning may contain similar contaminants to those from electroplating.

III.4 Electroplating

III.4.1 Electrocleaning

This method removes the final traces of contamination on the surfaces to be treated and chemically activates the metal surface for plating by passing an electric current between the item (the cathode) and an anode. An alkaline bath is used which contains caustic solution, wetting agents, buffering agents, dispersant and other chemicals. The item repels negatively charged colloidal contaminant particles and hydrogen is generated. This creates a scouring action. The current can be reversed, the item then representing the anode with oxygen being generated. The positively charged item repels metal ions.

Wastes from the process include spent baths and the contaminants that they contain, together with the rinse waters generated when the items are rinsed following the electrocleaning stage.

III.4.2 Electropolishing. This can produce a highly finished surface, on stainless steels in particular. The item to be polished represents the anode, and the electrolyte is phosphoric and/or sulphuric acid. The polishing step is followed by a rinse stage, and rinse waters may contain acids, bases, metals soil and oil. The rinse waters generate a significant volume of sludge.

III.4.3 Anodising. In this process, the item to be treated acts as the anode and a thin oxide coating forms on the surface. This is usually used for aluminium, but it can also be used for items made of magnesium. Anodic coatings can protect against corrosion and abrasion, and also can produce a base for coloring and decoration. The conventional electrolyte is sulphuric acid, although chromic acid is also used for specific applications.

III.4.4 Electroplating. This is the deposition of a thin metallic coating on the surface of an object to give corrosion protection, to decorate, or to affect the finish or appearance of an item in some other way. Metal ions are donated by the metal anodes dissolving or by the addition of metal salts to the electrolytic solution. The item to be plated acts as the cathode, and metal ions migrate towards it and are deposited on it by reduction. The items are usually suspended on plating racks or loaded into perforated 'barrels'.

A wide variety of electroplating solutions are used, and this is not the time or place to list them. However, they are the cause of significant environmental and health and safety concern. Among the most common electroplating applications are:

- nickel plating (eg. automobile industry, household appliances and articles, furniture): nickel sulphate, nickel chloride and boric acid;
- chromium plating (either hard plating for to resist wear or thin top plating for decoration): dissolved chromium salts in hexavalent form, although being gradually substituted by less toxic trivalent form;
- copper plating, either as end in itself or as intermediate stage: either copper cyanide or copper sulphate;
- cadmium plating offers superior corrosion resistance to zinc: usually cyanide bath, but presents severe toxicity problems, also acid baths are used;

- zinc plating is used for corrosion resistance or decoration: zinc cyanide is conventionally used, but are being replaced by acid or alkaline solutions;
- tin plating is used in the food and electronics industries: a variety of solutions are available, depending on the application.

IV POTENTIAL ENVIRONMENTAL EFFECTS OF SURFACE TREATMENT

It has traditionally been the case that the potential environmental effects of metal plating and surface treatment have been thought to arise from the effluent stream. However, it has been noted above that the industry generates wastes and gaseous emissions, as well as effluent. Each is discussed briefly below.

IV.1 Effluent

Effluent from metal plating and surface treatment are produced from many of the processes identified above. These are shown in Table 1.

For proper plating to occur, the parts must be clean and free of contamination from previous processes. Therefore, considerable quantities of water are used to rinse the parts. Depending on the process for which the rinsing takes place, the waste water produced may be acidic or alkaline and may contain metals, solvents or cleansing solution, and particulates (dirt).

Another source of water pollution from surface finishing is effluent from drains. Often, because of poor housekeeping, plating solution is allowed to drip as the rack or barrel is passed from tank to tank, and this solution is subsequently found in the plant's sewer system.

Table 1 (2)

	Effluent						
Process	Metal	Cr	Cn	Oils	Solvents	Wastes	Emissions
Burr Removal	X	X	X	X		X	X
Polishing	X			X		X	X
Solvent Cleaning	X			X	X	X	X
Alkaline Cleaning	X		X	X	X	X	X
Pickling	X	X					X
Etching	X	X					X
Bright dipping	X	X					X
Salt bath descaling	X		X	X		X	
Quenching	X		X	X		X	
Chromating	X	X					
Phosphating	X	X					X
Passivating	X	X					X
Plastic coating					X	X	X
Paint coating	X				X	X	X
Hot dip coating	X						X
Electroless plating	X	X	X				X
Anodizing	X	X					X
Electropolishing	X						X
Electroplating	X	X			X	X	X
Electrocleaning	X		X	X	X	X	X

2. Source: Environment Canada, op.cit.

Spent process solutions include:

a) acidic waste from pickling, etching, bright dipping and electropolishing;
b) alkaline cleaning baths and electrocleaning baths;
c) solvent degreasing waste;
d) salt bath descaling solution;
e) spent baths when they can no longer be rehabilitated.

The acidic waste contains a high level of dissolved metals, oils and suspended particles. Acid contained in the spent liquors or waste water, if discharged to sewer, can corrode the sewer line and damage municipal treatment facilities. Alkaline discharges have similar undesirable effects in cleaning solutions often making recovery of metals or chemicals from the spent solutions impractical.

IV.2 Hazardous Wastes, including Sludge. Several waste streams, including spent process solutions and sludge, are considered 'hazardous'/'special' in DMCs. 'Hazardous' wastes are those wastes which, due to their nature and quantity, are potentially hazardous to human health and/or the environment and which require 'special' disposal techniques to eliminate or reduce the hazard. Any substance or mixture being discarded is considered hazardous if it is flammable, carcinogenic, toxic, corrosive, explosive or meets other criteria developed by a federal-provincial working group. Table 2 summarizes the types of wastes generated by surface finishers.

Solvent waste contains soil and oil. This waste can interfere with sewage pumps, pH sensors and other effluent treatment equipment. Many solvents themselves are toxic and classified as hazardous. Oily waste is composed of free oil, emulsified oil, and grease. Many process additives and organic pollutants are soluble in hydrocarbons and are found in the oily layer of cleaning waste. Oils affect the odour and taste of water and are harmful to aquatic life. A moderately sized surface finishing operation will generate about 5 m^3 of solvent and oily waste annually. Solvents and oils should be separated from aqueous waste and recovered by distillation (if feasible) or suitably disposed.

Spent plating and coating solutions are generated during electroplating, autocatalytic plating, hot dip coating, anodising and chemical conversion coating operations. These wastes, and the accompanying rinse water, may be acidic or alkaline and may contain hexavalent and trivalent chrome, cyanide and other toxic compounds.

A number of metal finishing operations leave sludge on the bottom of the plating bath. Large amounts of sludge are also formed during cleaning, painting and effluent treatment. Sludge from effluent treatment only contains 1% - 5% solids and can be filtered to reduce its volume. Sludge usually contain hazardous materials which could upset the municipal treatment plant if discharged to sewer.

IV.3 Air Emissions. Air emissions from surface finishing operations include volatile organic air compounds (VOC), acid mists, metal and abrasive dust, and grit generated during polishing and buffing. VOC, from all solvent related operations, particularly degreasing and printing, may irritate the nasal passages and the lungs; they may also contribute to photochemical oxidant problems. Acid mists, from open acid baths and particularly those that are heated, as well as metal and abrasive dust and grit generated during polishing and buffing, may present health hazards in the work area.

V PREVENTIVE MEASURES FOR POLLUTION AVOIDANCE

Previous sections 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.

V.1 Operating Practice

Occasional mention has been made above of the need always to operate plant according to the supplier's design specifications. It is true in many instances that current operating practice owes more to history than the original design. This can be particularly true for equipment which is particularly dated, or which has been acquired second-hand rather than new. Concentrations of plating solutions or treatment solutions, plating/treatment time, minimum plating thickness are all areas where best practice may have been overtaken by current practice.

In all events, it is advisable to attempt to determine the operating specifications for which the plant was originally designed. Even for old or second-hand equipment this may be possible, if the original supplier of the equipment can be identified. Alternatively, it may be possible to obtain at least some of the information from alternative sources, such as patent offices in the country of origin. An experienced consultant may also be able to advise on at least some aspects from personal experience.

V.2 Good Housekeeping and Work Place Safety

Untidy and crowded working conditions are a safety hazard to personnel, and can also increase the waste of consumable inputs as well as to a greater number of unplanned discharges to the environment. Good housekeeping is a matter of attitude; essentially the attitude of management, and the degree to which this is transmitted to the shop floor.

Material losses can often be identified by undertaking simple mass balance calculations. Spills can be reduced through careful handling and transfer of materials, and the strategic location of drip and spill trays where these events are most likely to occur. An energy balance calculation can also be used to determine savings that can be made in energy consumption. Adherence to the suppliers requirements for optimal maintenance cycles can prolongs service life and minimise downtime and off specification rejects. Proper receptacles for wastes ensures that contamination of the surroundings of the plant is reduced.

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 work place hazards often have an impact on the environment and people surrounding the industry as well.

In DMCs specialist bodies concerned with work place hazard reduction should also pay attention to the external issues so as to support the initiatives of the environmental agencies. In CMCs it is essential that management familiarises itself with WHO/ILO guidelines on work place safety and ensures that workers are made familiar with these, as well as providing for such equipment and measures as to enable them to be met.

V.3 Management of Spills and Leaks

In addition to the running rinses that carry many of the pollutants to the effluent stream, large quantities of process effluent are often lost to the environment through accidents and deliberately dumping such material. In some instances, these two sources may account for as much as 80% of the heavy metal load to the environment from a surface treatment plant. The shock effect of introducing high concentrations of pollutants in a short time period 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 the focus of regular inspection, control and prevention measures:

- tanks (for leaks);
- filters and process tanks (for solutions remaining);
- equipment such as filters, pumps, heat exchangers, and their hoses and connections (for leaks);
- overflows (to check for blockage and safe containment);
- valves (for seizure, accidental opening or rupture);
- materials storage and handling (for spillage).

Deliberate, unauthorized release of solutions should never be permitted. Whilst easy to ensure in DMCs, particular effort needs to be paid to this in CMCs, where disposal alternatives may be fewer.

V.3.1 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.

V.3.2 Residual Solutions. These should generally be re-used, or if this is not possible, processed in the effluent treatment plant.

V.3.3 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 m^3 per day of solution from process tanks through any of these routes may be blamed on evaporation or dragout and go on for long periods.

Filters can be a major source of problems, providing containment around the area of the filter will act as an aid to inspection, allow leakage to be identified, and provide an opportunity for remedying the problem.

Heat exchangers and heating coils deteriorate slowly, developing 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 a boiler to save water and energy, there is the likelihood of corrosion damage to the boiler as well as solution loss. In addition, an alarm system can be installed on the boiler condensate return line as an aid to periodic examination.

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.

V.3.4 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.

VI REPLACEMENT OF HAZARDOUS CHEMICALS BY LESS TOXIC SUBSTANCES

There are a number of compounds used in surface treatment which are potential dangerous to both the work force and the environment. Opportunities for reducing or replacing process chemicals which have been introduced in DMCs are shown below, accepting that the introduction of some of the substitutions involves the introduction of new, more technologically advanced equipment with all of the associated problems in CMCs identified above.

VI.1 Cyanide. The greatest success so far in the reduction of cyanide in DMCs has been in zinc plating. Cyanide-free processes for other metals include:

- pyrophosphate copper as a substitute for cyanide copper.

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.

VI.2 Cadmium. The high toxicity of cadmium in the work place, and the contribution to its environmental dispersion from plated products, makes cadmium substitution a high priority with many authorities. Some DMCs have banned cadmium from non-essential uses, and discharge limits are often stringent.

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.

VI.3 Chromium As a substitute for hexavalent chromium, the less toxic trivalent chromium should preferably be used in making up baths. Trivalent chromium also rinses more freely and permits simpler waste treatment facilities.

VI RECOVERY OF CHEMICALS

Recovery of process solutions provides a simple and economical way of avoiding the discharge of contaminants to the environment. Recovery of process solution has been standard practice for a long time in the metal finishing industry.

To enhance the possibility of recovering the various solutions used in surface treatment, it is advisable to keep the bath solutions as uncontaminated as possible. To this end it is useful either to prevent the baths becoming contaminated with impurities, or to purify the bath solutions more frequently. Regular analysis of the process solution, and making it up regularly is essential.

Profitable recovery of solutions 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. In addition, hydroxide sludge containing significant quantities of recoverable metal may still be discarded, even in DMCs. These sludge are potentially saleable for the heavy metal content, particularly if the effluent stream from which they are precipitated is single rather than mixed.

Recovery of chemicals can offer both savings and environmental benefits. Items for treatment 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 the tanks are used to make up for evaporative losses. Some recovery is possible on cold tanks if drag-in can be reduced sufficiently. In extreme cases of drag-out, 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 mist spraying of parts while they are suspended over the plating bath. This is a very effective way of carrying drag-out directly back to the bath. The quantity of water used in the spray can be controlled to approximate the evaporation rate.

VII ENVIRONMENTAL CONTROL TECHNOLOGIES

VII.1 Waste Water Treatment Technology

Waste Water treatment technologies employed by surface finishers include in-plant water conservation measures to minimise effluent discharges, as well as end-of-pipe treatment. The focus in this section is on the water conservation aspects, as they are `good housekeeping' alternatives which are of particular benefit in the CMCs where there is a significant shortage of potable water.

VII.1.1 Water Conservation. Water conservation results in lower water use and less effluent to treat. Savings can be realised in the capital cost of lower capacity treatment equipment, chemical costs, and conserved floor space.

Rinse tanks follow almost all surface finishing operations and are the largest source of waste water. The amount of rinse water used can be reduced by at least 50% by:

a) counterflow rinsing (at least two stages are required but usually no more than four);
b) spray rinsing, which consumes less water than the conventional bath;
c) conductivity meters in rinse tanks so that slightly contaminated water can be re-used to the maximum extent;
d) flow control valves set at minimum fresh water flow requirement;
e) delay over plating baths and rinse tanks to reduce dragout to the following tank;
f) drag-in/drag-out tanks before and after plating tanks.

Unnecessary wastage of process solutions can be prevented by:

a) the use of holding tanks or dams to retain splashes, spills and leaks;
b) segregation of acids, alkalis, cyanide and chrome wastes by trenching and piping.

VII.2 Effluent Treatment. Effluent treatment options used by surface finishers are summarized below.

VII.2.1 Cyanide Chlorination. Cyanide-containing effluent from plating, conversion coating and cleaning are oxidized to break down the cyanide to carbon dioxide and nitrogen. The most common treatment method is alkaline chlorination because the operating costs are low, the process can be automated and efficiencies of 99% reduce the cyanide to very low concentrations.

Alternatives to alkaline chlorination have been developed and are commercially available. These include ozonation, ultraviolet radiation, the use of hydrogen peroxide and electrolytic oxidation. However, these methods may be more expensive and require specially trained operators.

VII.2.2 Electrolytic Destruction of Cyanide. The electrolytic destruction of cyanide is used for heat treatment waste and concentrated cyanide dumps, although it may also be used to treat high-concentration cyanide plating baths.

The use of electrolytic destruction is limited to waste waters with cyanide concentrations over 100 mg/L. Below this level, conductivity is reduced and the reaction normally cannot proceed. Sulphates in the waste inhibit process performance.

VII.2.3 High-Pressure and High-Temperature Hydrolysis. A hydrolysis process to destroy cyanide in dilute rinse waters and spent plating solutions has been developed recently and may provide surface finishers with an economical alternative to chlorination.

VII.2.4 Chromium Reduction. Chromium effluent are generated during electroplating, chromate conversion coatings, etching, and any cleaning operation applied to chrome metal. Chromium can be precipitated and removed as a hydroxide after being reduced to its less toxic trivalent form.

Alternatives to reduction of chromium compounds by chemical means are electrochemical chromium reduction, electrochemical chromium regeneration, evaporation and ion exchange.

VII.2.5 Neutralization and Hydroxide Precipitation. Neutralization is required for the large volume of acidic effluent generated during acid cleaning, acid cleaning rinses and plating rinses. A smaller amount of alkaline effluent results from detergent and alkaline cleaning and is usually combined with the acid stream.

Hydroxide precipitation of metals is the most common treatment process. It has a long history of use, is usually very effective and can be automated. The use of expensive chemicals and electrical power is avoided. Cyanide and complexed metals must be broken down prior to hydroxide precipitation because they inhibit this process.

VII.2.6 Sedimentation. After neutralisation and hydroxide precipitation, the suspended solid particles formed can be removed by gravity settling in a sedimentation basin or clarifier. Coagulants or flocculents may be added to shorten the retention time of several hours and increase removal efficiency. Clarifiers are the preferred equipment because they offer a shorter retention time, higher efficiency, and are more compact than sedimentation basins.

Large volumes of metal hydroxide sludge are removed from the effluent but this sludge has no commercially viable recovery potential at present. It may, however, be hazardous and must be disposed of at an accepted landfill site. To reduce transportation and disposal costs the sludge should be dewatered to increase the solids content from about 2% to 40%. Plate and frame filters offer the lowest operating cost but large plants often use vacuum filters for dewatering.

VII.2.7 Electrodialysis. Electrodialysis is a method separating the ions from solutions by means of an ion-selective membrane under the influence of an electric field, and is a means of recovering and concentrating the metal ions in plating rinse waters for recycle to the plating bath.

Electrodialysis is relatively new and, although there are a wide number of uses for this recovery process, it has not yet gained popularity, perhaps because of its high capital cost. It should considered as one of the technologies whose general application in CMCs will be limited to particular, large-scale circumstances.

VII.2.8 Reverse Osmosis. Reverse osmosis is a means of separating solutions by means of a suitable semi-permeable membrane and the application of pressure to the solution. This forces metal ions to permeate through a semipermeable membrane into a dilute solution. Many applications have been found including reclaiming of plating salts. Other applications are the recovery of zinc chloride, copper cyanide, zinc cyanide and cadmium cyanide. An important and valuable by-product of reverse osmosis is pure water which can be recycled back to the rinse tanks.

Reverse osmosis has been particularly successful at recovering nickel salts from spent nickel plating and rinse baths. In the context of the commercial environment of DMCs, payback periods of about three years have been realised.

VII.2.9 Ion Exchange. Ion exchange is another recovery process which removes and concentrates metals in plating rinse water. In some cases the metals recovered by the ion exchange unit can be returned to the plating bath. Nickel, for example, can be recovered as nickel chloride or as nickel sulphate. The rinse water is usually recirculated after this treatment. Another important use of ion exchange is the purification of hexavalent chromium baths. Rather than discard the bath when contaminants have built-up, unwanted metals, calcium, trivalent chrome and sodium impurities can be removed in the cation exchanger. Ion exchange units are used in many surface finishing plants.

When the resin surface is spent, it can be regenerated. The cation resin is regenerated by hydrochloric or sulphuric acid to remove the metal deposits and leave hydrogen ions in their place on the resin surface. The anion resin is regenerated with sodium hydroxide, leaving hydroxyl ions on the resin surface. The concentrated metal solution produced by resin regeneration may be used in the plating bath, as in the case of nickel or chrome plating but in many cases it is a waste stream. In many DMCs the regeneration of the ion exchange columns is undertaken by waste disposal companies. The absence of such an infrastructure in CMCs may limit the applicability of this effluent treatment technology there, although it may still be of relevance in larger entreprises able to regenerate their own resins.

VII.2.10 Evaporation. Evaporation water from rinses yields a concentrated solution of process chemicals and a purified condensate. The condensate does contain some metal carry over but still can be reused as a final rinse. The concentrate recovered can be returned to the plating bath.

An evaporator and ion exchange unit together may continuously recover and purify solution and rinse water in a closed-loop system. Open-loop systems allow the use of additional rinse water in excess of the evaporator capacity.

Evaporators have a higher capital cost than other recovery systems, and high power costs are also associated with steam generation. At a large plant, chromium, nickel or cyanide recovery from rinse waters may contribute to a favorable payback period and savings will also be realised if conventional treatment of rinse waters can be avoided (9).

VII.3 Control of Air Emissions

The pollutants present in air emissions from surface finishing operations include particulates, volatile organic compounds (VOC) and acid mists. These pollutants may be toxic and harmful to plant workers as well as to the surrounding environment. Some are transported long distances and may contribute to more general atmospheric pollution problems.

The control of air contaminants may be achieved in three ways:

a) quality control on the use of VOCs where these emanate from a vapour chamber, as well as good repair and maintenance of chamber seals (and ensuring that doors are closed during operation!);
b) substitution of less hazardous materials or processes;
c) dispersion of the pollutant to acceptable concentrations;
d) treatment or removal of the pollutant from the emissions.

A simple quality control system ensuring that vapour chamber is properly maintained and operated can achieve significant reductions in work place concentrations of VOCs. The substitution of less toxic solvents for hazardous solvents is the most desirable practice. Conventional solvent-based paints may often be replaced with water-based or high-solids paints, which have a low solvent content.
Concentrations of air pollutants in the work place can be minimised by ventilation. Exhaust hoods partially enclosing open tanks can remove contaminated air from the plating area to outside as long as any required air quality emission regulations are met. However, controls on the concentrations of emissions of VOCs to atmosphere exist in many DMCs, and a scrubbing system may need to be attached to the emission system for this reason.

Open-tank operations from which mist, spray and volatile components may escape are pickling, cleaning, plating, degreasing, coating and some rinses. In addition to local ventilation, air emissions may be reduced by surface foam inhibitors or plastic chips or balls. Condensation coils above tanks containing volatile solvents and heated baths can prevent the escape of vapour.

Air-borne particulates in surface-finishing units are produced during mechanical surface preparation and consist of abrasives, dirt and metal dust. Cyclones and dust collectors can remove these coarse particles from wet or dry air flows. The entrained particles lose their velocity when they impact the sides and the force of gravity causes them to fall out of the air stream. Cyclones have low capital and operating costs.

Fabric filters, or bag filters, allow the air to pass through while particles collect on the filter. Periodically the filter is cleaned by reverse flow, shaking or other methods. Fabric filters are applied when a low volume, low humidity stream must be cleared of particulates efficiently. The capital cost is high for such an air filtration system due to the cost of the filter medium.

Mist eliminators capture droplets formed by spraying and should be used over acid cleaning baths and electroplating baths with an integrated ventilation system (if a fume scrubber is not being used). Most operate by slowing down the air flow by changing its direction. Liquid particles condense on the sides and are drained out.

Wet scrubbers remove liquid, solid and gaseous pollutants from air emissions by the action of a fluid, usually water. Pollutants are dissolved in the fluid which is sprayed over a packed bed. This fluid can be recirculated with a make-up stream to economise its use. The spent fluid waste should be treated. In some cases, such as for chrome-plating emissions, the scrubber fluid can be returned to the plating tank when spent to make up for evaporative losses and dragout.

Wet scrubbers are used on pickling, etching, bright dipping, plating, electroless plating, anodizing and phosphating lines. Units can be designed to handle high temperature and corrosive streams. Efficiency of removal of water soluble pollutants is high (up to 99%). Capital costs range from moderate to high and operating costs, because of the large volume of water and power required, are also high.

Table 2
HAZARDOUS WASTES GENERATED BY SURFACE FINISHING

Source	Waste Component(s)
solvent degreasing	The following spent halogenated solvents used in degreasing: tetrachloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, carbon tetrachloride, and chlorinated fluorocarbons; and sludge from the recovery of these solvents in degreasing operations.
solvent degreasing drying painting coating machining miscellaneous	The following spent halogenated solvents: tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, chlorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, ortho-dichlorobenzene, and trichlorofluoromethane; and the still bottoms from the recovery of these solvents.
solvent degreasing drying acetate, painting methyl coating machining miscellaneous	The following spent halogenated solvents: xylene, acetone, ethyl ethyl benzene, ethyl ether, isobutyl ketone, n-butyl alcohol, cyclohexanone; and methanol; and the still bottoms from the recovery of these solvents.
solvent degreasing	The following spent non-halogenated solvents: cresols and cresylic acid, nitrobenzene; still bottoms from the recovery of these solvents.
solvent degreasing	The following spent non-halogenated solvents: toluene, methyl ethyl ketone, carbon disulphide, isobutanol, and pyridine; and the still bottoms from the recovery of these solvents.
effluent treatment	Waste water treatment sludge from electroplating operations except for the following: (1) sulphuric acid anodizing of aluminium; (2) tin plating on carbon steel; (3) zinc plating (segregated basis) on carbon steel; (4) aluminium or aluminium-zinc plating on carbon steel; (5) cleaning/stripping associated with tin, zinc, and aluminium plating on carbon steel; (6) chemical etching and milling of aluminium.

Table 2 (cont'd)
HAZARDOUS WASTES GENERATED BY SURFACE FINISHING

Source	Waste Components
effluent treatment	Wastewater treatment sludge from the chemical conversion coating of aluminium.
electroplating	Spent cyanide plating bath solutions electroplating operations except for precious metals electroplating spent cyanide plating bath solutions.
electroplating	Plating bath sludge from the bottom of plating baths from electroplating operations where cyanide are used in the process (except for precious metals electroplating plating bath sludge).
cleaning	Spent stripping and cleaning bath solutions from electroplating operations where cyanide are used in the process (except for precious metals electroplating spent stripping and cleaning bath solutions).
quenching	Quenching bath sludge from oil baths from metal heat treating operations where cyanide are used in the process (except for precious metals heat treating quenching bath sludge).
salt bath pot cleaning	Spent cyanide solutions from salt bath pot cleaning from metal heat treating operations (except for precious metals heat treating spent cyanide solutions).
effluent treatment	Quenching wastewater treatment sludge from metal heat treating operations where cyanide are used in the process (except for precious metals heat and treating quenching wastewater treatment sludge).
pickling	Spent pickle liquor from steel finishing operations.
effluent treatment	Sludge from lime treatment of spent pickle liquor from steel finishing operations.

VIII UNIDO AND POLLUTION CONTROL

The emphasis throughout this report has been on the direct advantage at the level of the individual plant in CMCs of measures which could be implemented at any plant without recourse to a programme of bilateral or multilateral capital aid. The question of improved pollution control technologies has also been addressed, but assistance in the provision of these is closer to UNIDO's traditional role. It is to those measures which do not fall within this traditional role to which this brief prologue to the report is addressed.

The problem of mitigating the rate of environmental degradation in developing countries is receiving increasing attention from the aid agencies, but the programmes in place rarely address the fundamental question of `good housekeeping' in the work place. UNIDO can support such activities by introducing programmes of training on plant repair and maintenance and quality control and quality assurance of this, but, in addition, much more can be achieved by relatively simple and cost effective measures which CMC governments could instigate themselves (perhaps with a little pump priming support from UNIDO or some other bilateral or multilateral aid network.

The measures which could be introduced fall without the main remit of the seminar, and are, therefore, not discussed extensively here. Nevertheless, a list is given below of possible measures which could be taken. They are not mutually exclusive, and the benefits would increase more than proportionately if the schemes were to be introduced together rather than serially.

VIII.1 Awareness Campaigns

A government sponsored awareness campaign has the possibility of raising the profile of good housekeeping, and the benefits that it can bring. This would need to be carefully planned, and implemented in such a way that the message was reinforced rather than presented once and then forgotten. It might be that sucn a campaign could be sponsored by some of the multinationals present in the country, focussing on those with a strong commitment to a corporate environmental policy in their home country.

VIII.2 Good Practice Awards

Those companies who can be shown to have reduced waste, effluent or gaseous emissions could be given an award, which may simply be a question of publicity or could be a combination of this and money (or a government contract).

VIII.3 Economic Incentives

Economic incentives are becoming of increasing importance in some DMCs as a way in which market signals can be adjusted to reflect more accurately the environmental benefits and costs of economic activity. Their application in CMCs is less advanced, but some of those listed below may have applicability in certain CMCs:

- the provision of tax relief on the costs of training the work force in the quality control and quality assurance of repair and maintenance programmes (`good housekeeping');
- reserving a certain proportion of government contracts for companies with an effective `good housekeeping' programme;
- tax credits for measurable reductions in waste/effluent/gaseous emissions resulting from effective `good housekeeping' programmes.

VIII.4 Education and Continuing Education

The importance of bringing young people fully trained in all aspects of `good housekeeping' into the work force cannot be emphasised. It is for this reason that the technical education facilities in CMCs be encouraged to introduce comprehensive training in this field into the syllabus of technical schools. In addition, provisions for continuing technical education should also incorporate this into the courses they offer.

IX CONCLUSION

The purpose of the in-depth course reported here was to give UNIDO personnel an introduction to the various facets of environmental control in industry, using the surface finishing industry as a generalised case study, or allegory.

The emphasis of the course was on measures that could be taken within the context of CMCs as they currently exist, without the need for major capital aid to implement the measures needed, although the question of more advanced pollution control or waste minimising technologies was addressed in various parts of the course. Nevertheless, the importance and value of quality control/quality assurance repair and maintenance programmes (usually referred to in the seminar as `good housekeeping') to reducing the impact that industry has on the environment in CMCs was self-evident.

The fact that a properly implemented `good housekeeping' programme could also provide significant gains in profitability, and that both the environmental and profit-related gains could be realised immediately further commends this approach, and the report ends with a cursory examination of ways in which CMCs might encourage the establishment of effective `good housekeeping' programmes, perhaps with some modest pump-priming aid from UNIDO or other bilateral and multilateral agencies.

It is recommended that UNIDO's ECU give further thought to ways in which it can instigate demonstration programmes in `good housekeeping' in CMCs to reduce the impact of industry on the environment, either through its own good offices, in association with other divisions of UNIDO, or other elements of the United Nations system.