

HAZARDOUS WASTE MINIMIZATION GUIDE FOR SHIPYARDS

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PROJECT OVERVIEW

The approach to this project was to identify the general waste stream common to the shipbuilding and repair industry and assign a priority based on environmental and economic impact of the various waste streams. Research was conducted on gathering of available information on on waste reduction from industry sources, regulatory agency sources, and general environmental literature. The compiled information was evaluated and organized into the various chapters identified from the priority of the various waste streams.

The development phases of the guide are summarized below:

- ° Survey shipyards to identify the types of waste generated
- Prioritize the waste and/or waste stream types
- Survey shipyards to identify existing waste minimization techniques being used in the yards by both public and private for content
- Develop a final guide and review for completeness and accuracy.

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1. INTRODUCTION

Historically, shipyards have relied on hazardous waste landfills and treatment of hazardous waste to address the environmental solution after the point of the waste generation. This approach, commonly known as “end of pipe” management, has been based on command and control regulations that rarely offered the shipyard positive incentives to reduce waste. This approach has been successful and has contributed to an overall improvement of our environment.

Recently, however, the EPA and the rest of the nation have undergone a philosophical change in which environmental protection is increasingly viewed as an opportunity to prevent the generation of pollutants at the source (source generation). The advantage of this approach is that preventing pollution at its source help shipyards avoid many costs and potential liabilities associated with treatment, storage, transportation, and disposal. The EPA and the nation have designated pollution prevention as a top priority. This approach to environmental protection became a national policy when the President signed into law the Pollution Prevention Act of 1990.

Pollution prevention encompasses any practice that reduces or eliminates the quantity and/or toxicity of pollutants through source reduction. As defined in the Pollution Prevention Act of 1990, source reduction is:

“Any practice that reduces the amount of any hazardous substance, pollutant or contaminant entering the waste stream or otherwise released into the environment (including fugitive emissions) before recycling, treatment, or disposal; and reduces the hazards to public health and the environment associated with the release of such substances, pollutants, or contaminates.”

This Hazardous Waste Minimization Guide for Shipyards is an attempt to address this transition from “end of pipe” solution to a source reduction philosophy.

2. SETTING UP A WASTE MINIMIZATION PROGRAM

2.1 Introduction

A waste minimization program is a forward looking approach to waste management that is both systematic and responsive. It is organized for future problems as it solves the current ones within a shipyard.

The problem of waste is first a problem of production efficiency. A Waste Minimization Program examines a waste stream to increase production efficiency at the yard while decreasing waste generation. The program has to be looked at as part of the shipyard's overall management strategy. This section will explain this management strategy and how it will reduce generation of hazardous waste in the future.

2.2 Elements for a Successful Minimization Program

Top Management Supports the Program

For a successful program, support must be provided at a high enough management level to influence the operation and environmental policy decision. Without this support, most minimization programs fall apart due to the lack of proper funding or key production personnel needed for many waste minimization projects.

Employees Incentive Program

Most successful minimization programs have incentive programs for submitting ideas on waste minimization. These ideas are only useful ideas if they are successfully implemented and maintained. The incentive program should reward those who originate the ideas. Reward and recognition should be given to the individual who does the hard work of implementation of the project. By publicizing the reward and recognition, other workers will be inspired to

submit their ideas on waste minimization. An example of an incentive program is to use the company's suggestion program as a vehicle to start a reward program. The company newspaper or an environmental newsletter can be used to publicize the waste minimization program and the successful ideas submitted to the suggestion program.

Shipyard Personnel Involvement in Program

As with any successful program, the shipyard personnel must be involved in the design and installation of any idea. This helps in the generation of additional ideas and inspires them to adopt the changes to the operation. Since the shipyard personnel operate and maintain the operations undergoing the change, these people should have a say in the changes so that it will meet their needs.

A Leader is Needed to Implement the Project

Many successful programs are led by a leader who strongly believes in the project and can overcome the development and start-up problems associated with a waste minimization project. If the project is led by an individual who does not believe in the project, the project is a failure from the beginning.

Increase in Productivity and Reduced Cost Through Implementation of the Program

Examine a project that can result in a reduction in production cost and increase production yield or production quality. Reducing the cost of an individual department is more likely to have upper management support than a project which is shared company-wide, as are many reductions in waste disposal cost projects. A project that can reduce personnel requirements, thus increasing productivity, will give a strong incentive for change.

Waste Disposal Cost Should be Charged to Department Within Shipyard Operation

At shipyards that have done successful waste minimization projects, shipyard operating departments were aware of the true cost of the hazardous waste disposal and considered those costs when making a decision on the implementation of the project.

Shipyard Employees Appreciate the Environmental Benefits of Waste Disposal

Most shipyard employees are motivated by the desire not to pollute the environment in which they work and possibly live. By educating the employees on the effects of pollution, most employees will be motivated to be more careful.

Training Shipyard Employees on New Environmental Product or Equipment

Many minimization projects require new equipment or products and require operators to have training on the use of such equipment or products. Successful projects require such training to guarantee that the equipment or product will be used properly and will receive the proper maintenance or support for the continuing success of such equipment or products.

Assurance of Proper Operation of Equipment at Shipyard

Care must be taken to ensure that any new modification of equipment be tested before being transferred to the yard. Be sure to solicit suggestions or advice from other users before buying any equipment to ensure that the equipment will operate to the specifications of the shipyard.

New Equipment is Reliable, Simple to Operate, and Maintain

Most modifications are successful due to the fact that the new equipment is straightforward

and simple to operate, thus requiring minimal training to key personnel and low maintenance requirements. If this does not happen, most operations resort back to the old methods of operation.

2.3 Methods for Setting Up a Successful Waste Minimization Program

Planning a Waste Minimization Program as Part of the Company Overall Goal

Many shipyard production workers are usually evaluated on meeting a production goal or product quality. If a shipyard encourages its employees to make waste reduction a part of their daily duty, the employees will realize the importance of the program. The importance of the program must be real and should be part of the job performance evaluation for the individual employee. The top management must support this concept and not be promoted solely by the Environmental Department of the shipyard.

Establishing of a Waste Minimization on Official for the Shipyard

An individual with environmental compliance expertise should be appointed to oversee the waste minimization program and to make sure that environmental effects are as important as production.

Taking an Inventory of Waste Minimization Project by Shipyard Departments

As much as possible, waste generation should be measured and listed by individual departments so the shipyard can evaluate the individual projects to determine which waste minimization effort should receive the most concentration.

Ranking Waste Minimization Efforts by Cost of Disposal

A shipyard should use waste generation data to help identify production areas which have an exceptionally high or low waste generation rate. This data allows shipyards to invest in waste minimization efforts where they can have the most potential for being cost effective.

Charge Departments for Waste Disposal costs

Charging a shipyard department for the disposal cost will force a department to budget for the waste cost and allow for the department to implement methods for waste minimization to reduce this cost within the department.

Provide a Capital Investment Budget for Waste Minimization Projects

In many cases a waste minimization project cannot be justified on waste minimization effort alone and needs the combined benefit of a production capital improvement budget for the waste minimization project to receive the needed funding.

Publicize the Successes and Learn from the Failures

By giving recognition to a successful project you will motivate other employees within the shipyard to participate in the program and to receive a reward if their idea or project is selected. You may want to publicize projects that are not successful to educate others so that the same idea is not repeated.

Encourage the Transfer of Technology

A shipyard should encourage the transfer of successful waste minimization methods within its organization so that other organizations can

share in the success and reduce their operational cost.

Conducting a Waste Minimization Audit

A waste minimization program will not be successful unless a detailed study of the various waste stream is undertaken. The first step in a waste minimization project is to obtain detailed information of the operation by doing a waste audit. A waste audit is similar to an environmental audit but the major difference is that an environmental audit is to see that the shipyard is in environmental compliance with environmental regulations. A shipyard conducts a waste audit to see how it can prevent or reduce the generation of waste.

Identify Shipyard Operations

All manufacturing processes must be identified by the function of the process and how its operation is related to the overall repair or construction process of the shipyard. After the detailed record has been completed, process flow diagrams representing the interconnections of the various operations of the shipyard should be drafted, including ship repair and new construction.

Collect Data

Collection of information about the chemicals, raw materials, inventory of hazardous materials, and waste water usage survey is necessary. This information can be obtained from the company purchasing records or through actual measurements. The data may need to be reviewed to correct for fluctuations in production.

Collect Raw Material Inventory

A detailed record should be kept of the raw materials that are purchased and the quantities being used in the various departments within

the shipyard. With this type of information, a tracking of any lost material can be calculated. The areas can be identified and steps can be taken to minimize loss during handling or storage of the materials. Purchasing practices should be examined if high inventories result in spoilage or off-spec material.

Conduct Waste water Survey

A great savings can be achieved by reducing and controlling the water usage. Using less water will result in less waste water needing treatment. The increased concentration of the contaminants will result in increased efficiency of most pollution control equipment. To begin this saving, the shipyard must do a wastewater survey that provides the following:

An understanding of the specific sources and flow within the shipyard.

An understanding of the fluctuation that occurs in both content and quantity of the shipyard wastewater.

The information provided by the survey will be invaluable when evaluating in-plant control of wastewater generation.

Track Waste

It is important to know how much of each type of waste is being taken off-site for treatment and disposal. A review of the manifest will provide this information. Information about the generator or satellite storage area should be recorded so that waste minimization effort can identify the best approach to reduce these waste streams.

Conduct Material Balance

This type of assessment is based on the principle that the total material entering a process must equal the total material that eventually

leaves the process or operation. In most cases this type of study is extremely time consuming and is required when there is a significant concern about a certain waste stream.

Evaluate Options

After data has been collected and summarized, the department or team can begin the evaluation of the waste minimization options. This involves the selection of specific waste streams which have been targeted for waste minimization. The department or team will determine which methods will be used to reduce the waste stream.

Factors that should be considered for selecting waste minimization methods include the following

- Implementation cost
- Risks involved
- Future government regulations.

It is important to pay attention to compliance and environmental regulations. Such issues are bound to become more strict as environmental issues continue to be added to legislative agendas. Due to these issues, it would make sense to aim for a degree of reduction that will keep pace with the current and future regulatory requirements.

Identify Low Cost Options

A waste minimization program should be started with projects that are easy and inexpensive to introduce. Examples are listed below.

- Improved housekeeping procedures by examining for leaks or taking other measures
- Conduct mass balance assessment of areas in which unusual losses are spotted.

- Substitute nontoxic or less toxic material when possible for raw materials that ultimately become hazardous waste.
- ∨ Separate hazardous waste streams from nonhazardous waste streams.

Select Options for Further Study

Some waste reduction options may require more detailed analysis, especially if new equipment is needed. In such cases, companies that are currently using such equipment should be contacted to learn about any problems and how to deal with them. The company using the equipment will know about the maintenance requirements and what to do if breakdown occurs.

2.4 Prepare an Evaluation Report

After a department or team has completed a waste audit and has evaluated the options available to the shipyard, the next step is to prepare an evaluation report for the upper management. After the review of the report, management can set an agenda for implementation of waste reduction measures.

The report should contain four main areas of concentration:

1. Waste audit summary
2. Technical analysis
3. Economic analysis
4. Regulatory analysis.

Waste Audit Summary

The waste audit summary should present all the collected data in a detailed and easily understandable format. The following items should be covered:

- ∨ Flow diagrams to show processes and source of specific waste streams.

- ∨ Descriptions of each waste stream generated as to its characteristics, quantity generated, method and cost of disposal, and associated health, safety, and environmental concerns.

Technical Analysis

The technical analysis should be forced on specific recommendations on waste reduction options, including advantages and guidelines for implementation.

- Include flow diagram of shipyard manufacture processes, including proposed modification.
- ∨ Describe each proposed project in detail whether capital intensive or low cost.
- List advantages of technology selected over other technologies.
- Give a detailed assessment of each technology's track record.
- Outline equipment requirements, including expected maintenance and labor costs.
- Give information on the ranges of conditions that the new equipment will effectively operate within.
- Explain how the new equipment will help bring the company into compliance with government regulations.
- Give examples on how new equipment has helped other companies.
- Give an appraisal of what is expected during installation of equipment. Give examples of an evaluation of safety and reliability factors.

Economic Analysis

The economic analysis should focus on the cost and saving associated with the implementation of the proposed waste minimization program.

- Give total capital cost and expected costs or savings related to the changes in labor, raw materials and related waste management requirements.
- Give the potential effects on the production operation and the production quality.
- Estimate the potential return on investment for the waste minimization projects.
- Give the estimated payback period for each project.
- Estimate the total costs and savings associated with the present waste management policy and the project savings with various waste minimization projects so that comparisons can be made with potential waste minimization alternatives.

Regulatory Analysis

The regulatory analysis should address the environmental concern raised by the federal, state, and local agencies in which the shipyard operates.

Outline various federal regulations with which air, water and hazardous waste discharges must comply.

Assess any community concerns that may have been expressed about the company's practices and how these concerns can be addressed through the waste reduction proposals.

Additional Information on Waste Minimization Audit

For additional information, the EPA has published a manual called the Waste Minimization Opportunity Assessment Manual which can be obtained from the Pollution Prevention Clearinghouse which is discussed in Chapter 12.2. The NSRP report #345, "Environmental Compliance Inspection Checklist" includes a checklist for waste minimization audit for shipyards which can aid shipyard personnel in conducting an audit. The report can be obtained from the NSRP Publication Coordinator, UMTRI, 2901 Baxter Road, Ann Arbor, Michigan 48109 (313-763-2465).

2.5 How to Choose and Implement Waste Minimization Projects

Once the department or team has reviewed the data obtained through the waste audit and considered the options outlined in the evaluation report, the next step is to develop a strategy for the implementation of the Waste Minimization Program. The available options for minimization are listed in the following order of priority:

1. Elimination
2. Reduction
3. Reuse
4. Recycling
5. Treatment
6. Disposal.

The higher the option is on the list the better the option is for the shipyard and the environment. In the majority of cases, it is virtually impossible to eliminate completely the production of waste, but it is possible to eliminate certain waste streams. When elimination is not possible reduction in volume or toxicity of a waste is the next best option. In many cases reduction is combined with reuse or recycling:

- Reuse when the material is reclaimed from the waste stream and put back into the shipyard process with little or no processing.
- Recycling when material is reclaimed and placed back into the production process after varying degrees of processing.

All reuse and recycling opportunities should be investigated before traditional “end of pipe” treatment and disposal technologies are considered.

Waste Reduction Techniques

There are four main techniques that are available for reducing the volume of a waste at its source. These are:

1. Good operating practices
2. Material modification/substitution
3. Production modification
4. Production changes.

When considering these options, be ready to assess all aspects of their implementation.

Good Operating Practices The most frequently used method is to improve operating and housekeeping practices. Such improvements require that existing practices be changed, but this can usually be done inexpensively. Improvements in operating practices usually require the following:

- Management/employee initiatives
- Allocation of disposal costs
- Improved material handling and storage procedures
- Waste tracking.

As explained in the section on successful

waste minimization programs, the success of a program depends on how fully the employees accept the program throughout the shipyard. Employees must be clearly informed as to why their participation and cooperation is crucial. Employees must understand that waste reduction is an important part of their job. The overall objective is to make waste reduction an everyday part of the job. To make this happen the shipyard management must remain open to observations and suggestions from production personnel. Because these employees work with the operation on a front-line basis, they can best offer important insight into the waste reduction possibilities.

One simple method of increasing awareness of the waste reduction issue is to allocate waste treatment and disposal costs to the department or operation that generates the waste rather than to a single department or overhead account. In this way, each department will acquire an appreciation of the treatment and disposal costs and will plan ways to reduce the generation of this waste within the department. If the waste is generated by more than one department, the cost should be shared between departments.

In many cases, improvements in waste reduction can be achieved by improving the methods materials are handled or stored. The following areas of operations should be examined to determine if changes should be introduced.

- Handling and storage of raw material (paint, thinners, etc.)
- Inventory control (“Just-in-Time” principles)
- Waste segregation.

The improper handling and storage of raw materials and products can result in expensive waste generation. Leaks and spills can add to significant quantities of waste material. The

volume of material stored at the warehouse can have a bearing on the waste generation, particularly when it has a limited shelf life. An example is when paint becomes off-spec due to exceeding the VOC limit as a result of regulatory agencies lowering the limit. The proper control of material inventory can mean that materials may need to be ordered under the Just-in-Time principle so that materials arrive when they are needed. This could increase material costs but in many cases the disposal rests can exceed the material cost increases.

The treatment and disposal of mixed waste is often complicated and more expensive than the cost of the separated waste and possible reuse. Methods of collecting and storing waste should be examined closely to determine the extent to which waste can be segregated.

The segregation of waste can be greatly aided by the use of waste tracking. Under this system waste can be tracked from the point the material enters the shipyard to the point it leaves as a waste or product. This type of information gives the waste reduction personnel the knowledge of how the waste is generated. It also identifies the area where a more efficient process or reduction should be used. The information for a waste tracking system is obtained by conducting an inventory of raw materials, wastes in storage, and waste streams being generated by shipyard operations.

A flow diagram prepared during an auditor a similar chart of shipyard operations should help in this tracking process. Materials should be tracked from the point they enter the shipyard. Therefore procedures should be coordinated so that all departments understand who is involved with purchasing, handling, storage, and processing of the material.

With a tracking system in place, the handling and storage of material can be made more efficient. Procedures can be put in place which

will keep waste suitable for reuse or recycling separate from those intended for treatment or disposal. With a proper system detection and prevention of problems before they become major concerns will provide the clearest insight into ways of correcting problems that already exist.

As with any waste reduction program, the proper tracking of the waste will require the full cooperation and participation of all of those involved. It is essential that all employees be informed of the importance of the tracking program and procedures and be given the opportunity to provide suggestion on ways to improve material handling or storage in an efficient manner.

Material Modification/Substitution Material modification or substitution is a waste reduction option by which certain materials are substituted for other materials to eliminate or reduce hazardous waste generation. Water-based primer, for example, may be used instead of solvent-based. If it is not possible to use materials that generate less waste, it may be possible to use materials that will result in waste that is less hazardous or more suitable for reuse or recycling. Material substitution will result in fewer treatment and disposal problems and may result in a price reduction of the raw material.

Production Process Modification It is sometimes possible to make operational changes that will result in waste reduction or in the generation of less waste. These changes can include and changes in the production procedures, equipment redesign, introduction of automation, changes in the operation conditions such as temperature, pressure, flow rates, and residence times. Many of these changes may need large capital investments; therefore, a detailed analysis should be done before any of the changes are adopted. Usually such changes result in better efficiency and increased quality.

Product Changes Product changes that result in reduced waste generation can take two different forms:

- Product substitution
- Product reformulation.

Product substitution means changing the product to eliminate the hazardous waste or to reduce the overall amount of waste associated with the product. For example, a freon product can sometimes be replaced by an aerosol product which is less harmful, or in a container which is released by a pump therefore eliminating the need for a chemical propellant.

Product reformulation is the replacement of an ingredient in a product or changing the entire composition.

Reuse/Recycling

When every effort has been made to reduce the waste, the next step is to see how the remaining waste can be reused or recycled. Recycling means processing or treating the waste material and using it in one of two ways:

- As a substitute for a virgin raw material in the same production process. An example would be recycling the lubricating base coat used on the shipbuilding sliding ways.
- As a recycled material in a different production process. An example would be the use of oil from bilge water separation used as a lubricant in a recycled motor oil product.

The waste may be recycled on-site or it may not be economically feasible to recycle on-site due to low concentration of the usable material

in the waste. If recycling on-site is not possible it is sometimes possible to send it to an off-site recycling facility. In some cases it may be possible to sell the material to another company for its reuse through a waste exchange. A waste exchange matches up waste generators with waste users.

A proper recycling program can result in lower disposal costs and increased operating efficiency. Disposal should be an option reserved only for those wastes that cannot be recycled or sold to another company for reuse.

2.6 Treatment and Disposal

Waste that remains after all reduction, reuse, and recycling possibilities have been investigated should be considered for detoxification through biological, chemical, or physical means.

Biological waste treatment can be applied only to waste that can be biologically degraded. Biological treatment procedures commonly take place in sewage treatment plants, aerated lagoons, and through the use of microorganisms. These procedures involve the removal of sludge, which is then dumped in the municipal landfill sites or used on agricultural land as fertilizer. Heavy metals or toxic organic chemicals, if not removed, can remain in the sludge and pollute the soil or ground water.

Chemical/Physical Treatment

Chemical and physical methods for treating waste uses various technologies ranging from simple separations to complex chemical reactions. A hazardous waste that has dilute concentration is usually concentrated, so that a smaller volume can be sent off for disposal. Separation and concentration technologies include ultrafiltration, reverse osmosis, ion exchange, centrifugation, flotation, distillation,

precipitation, and electrolytic filtration among others. Detoxification of waste is commonly done through such methods as chlorine stripping, neutralization of acid, and alkaline waste.

Incineration

The burning of waste is known as thermal destruction. This waste is normally incinerated at electric plants, rotary cement kilns, or hazardous waste incinerators. The process is undertaken either in the presence of oxygen (incineration) or in an oxygen-deficient environment (pyrolysis).

3. MACHINING AND OTHER METALWORKING OPERATIONS

3.1 Introduction

The machining process is the operation that involves a cutting tool or some other type of abrasive material to shape a piece of metal. The most common types of metal cutting processes are: broaching, cutting, drilling, forging, grinding, milling, planing, polishing, reaming, sawing, shaping, stamping, threading, turning, and more. In most cases, the cutting tool travels along the surface of the work piece and shaves off the metal in front of it. The high friction at the cutting edge of the blade creates heat. If allowed to become excessive, this heat can permanently deform the part that is being formed, or the cutting tool. To prevent this undesirable effect, some form of coolant is needed. Usually a liquid is supplied to the leading edge of the blade to create a medium with which the heat can be moved to a coolant sump.

3.2 Waste Streams

The various machining operations performed in shipyards yield a varying array of hazardous waste. Some of the most common of these are the waste metalworking fluids, solvents, and oils.

3.2.1 Metalworking Fluids

Metalworking fluids serve many purposes in the machining process. Their primary use is to remove heat from the cutting area, but they also serve to lubricate, inhibit corrosion, help produce a good finish, and wash away metal shavings. The coolant fluids account for the largest waste stream generated by machining operations. Waste metalworking fluids are created when the fluids are no longer usable due to contamination by oils or chemical additives. To a certain extent, this contamination is unavoidable, however; it is possible to reduce the rate at which contamination occurs.

If the contamination rate of the metalworking

fluids is reduced, the need to replace them will be less frequent. This will reduce the waste generated.

There are four major types of metalworking fluids currently used in shipyards: synthetic, semi-synthetic, soluble oil, and straight oil. Straight oil is a 100% petroleum product. Synthetic oil is an oil substitute that does not contain any actual oil and has the advantage of being less hazardous than the other types. Semi-synthetic oils are a mixture of petroleum and synthetic fluids with approximately 2-30 percent of the mixture being petroleum. Soluble oils are soluble in water and tend to contain between 60-90 percent petroleum.

The most widely used metalworking fluids are soluble oils. They are often the least expensive because they are frequently diluted to ratios of 15:1 or higher. However, the process of watering the concentrate will also lead to high fluid maintenance requirements because the fluid will not perform properly unless it is at the correct concentration.

The major contaminants found in metalworking fluids consist of: hydraulic oils, lubricating oils, phenols, creosol, alkalies, phosphorus compounds, and chlorine. These are also the constituents that require the waste fluids to be handled as hazardous waste.

A frequent problem encountered with metalworking fluids is rancidity. This is caused by bacterial breakdown of the fluid and it leads to a less effective product as well as a foul smelling work station. The odors can become strong enough that it alone will warrant changing the machine's fluid.

Maintenance of metalworking fluids is extremely important. When using water-based cutting fluids, it is crucial to maintain the proper "concentrate to water" ratio for proper performance.

Solvents

Solvents are used to clean machinery parts and can be a substantial component of the machining process waste stream. The amount of solvent waste is highly dependent on the quality of cleanliness desired. For example, if the metal is going to be plated with zinc, it is not necessary to achieve a high degree of cleanliness because the cyanide-zinc bath is known to have good cleaning properties itself. In some cases, more than one solvent must be used to properly clean the part, and a sequence of steps involving acids, abrasive, and other substances may be needed. The importance of solvent waste reduction can not be overemphasized. Methods of reducing solvent waste are discussed in more detail in Chapter 4.

Tramp Oil

The largest contaminant in cutting fluids is tramp oil. Tramp oils are lubricating or hydraulic oils that leak into the coolant through defective gaskets or other malfunctioning seals. The presence of tramp oils in a metalworking fluid will prevent the fluid from cooling as effectively as it should, decrease the lubricating properties, and increase the amount of smoke and oil mist emitted from the machine. Most significantly, a cooling fluid contaminated with tramp oil will degrade quickly due to bacterial growth. This leads to rancidity.

Hydraulic oil is the constituent that most contributes to rancidity; in part because it is often more miscible in coolant fluid than lubricating or machine oils are. Lube and machine oils will usually float to the surface of the sump where it can be skimmed off.

Metal Cuttings

Not all of the metal cuttings from machinery operations are considered hazardous. In fact,

it is usually required to classify scrap metal as hazardous only if it has been contaminated with waste fluid. This is frequently the case when the metalworking fluid is used to spray metal shavings away from the cutting edge of the blade.

3.3 Methods of Waste Reduction

Several options are available to reduce waste from the machine shop. From mechanical changes to good operating practices, some methods of waste reduction should be utilized.

Inventory and Procedures

The first thing that should be done in any waste minimization program is to take an accurate inventory of all the materials and procedures used in the process. Such records could be used to ensure that the current activity in the shop complies with local, state, and federal regulations. Good inventory practices will also make it easier to determine whether the shop is using more chemicals than it should require. If possible, the number of fluids used should be limited. It is much easier to recycle or dispose of a large quantity of one fluid than smaller quantities of several fluids.

The types of fluids, the quantities used, the cost of each, and how often they are purchased, should be recorded. The individual in charge of fluids purchasing should be notified of the project. He should be interviewed because the input of the workers who use these fluids every day is more significant than any other.

Source Reduction

After an inventory of materials and procedures is completed, the next logical step is to reduce waste by minimizing it at its source. This can be done by substituting less hazardous materials for those that are currently being used, or by modifying processes.

Preventing Fluid Contamination

Fluid can become hazardous waste if it is contaminated. Although it is not possible to eliminate contamination, it is possible to reduce the rate of contamination and thereby prolong its use.

The primary contaminant in these waste fluids is tramp oil. One way to postpone contamination is to promote better maintenance of the wipers and seals. A preventative maintenance program should be installed and enforced in the machine shop. Scheduled sump and machine cleaning as well as periodic inspections of the wipers and oil seals should be carried out. The responsibility for this should be assigned to some person or group in a position of authority to ensure its success.

Fluid Selection

The key to fluid selection is to choose the lowest number of varieties possible. This simplifies disposal and increases recycling possibilities. It may be economically worthwhile to purchase an expensive fluid that is of high quality and is versatile enough to be used in all the areas of the shop.

Fluid Quality and Testing

Fluid quality is an important concern because a low quality fluid may lead to reduced machine life and lower product quality. Therefore, it is important to have regular testing for contaminants and concentrations. Tests should also be done to determine pH level, as well as rust, tramp oil, and suspended solids concentration. The test analysis can alert the operator and preventative measures can be taken. Certain biotides can be added to decrease the rate of bacterial breakdown but concentrations of these must be closely monitored.

Synthetic Fluids

Synthetic fluids have many advantages over the non-synthetic counterparts. Usually the synthetic varieties do not lubricate as effectively, but they are less susceptible to contamination and highly resistant to biological breakdown. Most synthetic fluids have superior longevity and can operate over a large temperature range without adverse side effects. Straight oils should be replaced with synthetic ones whenever possible.

Gas Coolants

Applications for using gas as a coolant, rather than fluids, are limited. The primary advantage of using gas coolants is that the work piece remains clean. When straight air, which is the most common, is the gas used there are no toxic emissions or wastes created by the process. A gas can also be used in conjunction with a fluid to reduce the amount of liquid required.

Recycling Fluids

Once all of the source reduction options have been considered, it is time to explore the possibilities of reuse. It should be noted that in many cases, after the majority of the contaminants have been removed, further treatment with chemicals or concentrated fluid is necessary before the fluids can be recirculated through the machines.

Filtration

Filtration is a common way to recycle fluids. Many different types of filters can be used depending on the medium to be filtered and the amount of filtration desired. Two classes of filtration machines exist, one makes use of gravity to pull the fluid through the filter, the other utilizes a forced pressure differential. Both types can remove particles from the fluid

as well as tramp oils or other contaminants as required.

There are many different methods of filtering cutting fluids. They can be passed through a bag, disc, or cartridge filter or separated in a centrifuge. When using soluble or synthetic oils, the quality of the mixing water is an extremely important consideration. Water with a high mineral content will cause the oils to break down much more quickly. It is suggested that distilled or deionized water be used.

It is not uncommon to find small debris, such as gum wrappers or cigarette butts in the oil sumps of these machines. This is clearly unacceptable and can be prevented by educating the machinists on the importance of sump hygiene. Possibly the best way to prevent this problem is to install metal grating over any open sumps.

Flotation and Skimming

This is a slow process, but it is inexpensive and can be very effective. The principle is to let the fluid sit motionless in a sump or a tank, and after a predetermined amount of time, the unwanted oils are skimmed off the surface and the heavier particulate matter is collected off the bottom. Flotation refers specifically to a process in which the untreated fluid is put under high pressure and air is injected into the solution. When the pressure is released, the air comes out of solution and bubbles to the surface. As the air becomes gaseous, it attaches itself to suspended contaminants and carries them up to the surface. The resulting sludge is skimmed off the surface and the clean fluid is reused.

Centrifugation

Centrifugation uses the same settling principles as flotation, but the effects of gravity are

multiplied thousands of times due to the spinning action of the centrifuge. This will increase the volume of fluids which can be cleaned in a given amount of time.

Pasteurization

Pasteurization uses heat treatment to kill microorganisms in the fluid and reduce the rate at which rancidity (biological breakdown) will occur. Unfortunately, heat can alter the properties of the fluid and render it less effective. Properties lost in this way are usually impossible to recover.

Downgrading

Sometimes it is possible to use high quality hydraulic oils as cutting fluids. After the oils have reached their normal usable life, they no longer meet the high standards necessary for hydraulic components. At this time they are still good enough to be used for the less demanding jobs. It may be necessary to treat the fluid before it can be reused, but changing fluid's functions in this manner has proven successful in the past.

3.4 Waste Fluid Treatment

After other methods of waste minimization have been exhausted, the last option to consider is treatment of the waste before shipment. Some less problematic wastes can be sufficiently treated to be released to the sewer system. Others can be diluted to reduce hazardness or the opposite can be done by changing the waste into a more hazardous material but with reduced volume. Every case is treated individually so it is very difficult to generalize waste fluid treatment.

Ultrafiltration

Ultrafiltration is a specific method of waste fluid concentration. The fluid is separated into

a small amount of highly concentrated waste, and a large portion of minimally toxic waste water. The concentrated sludge can often be sent away to be incinerated or used as fuel, and the waste water may be discharged to a sewer.

Chemical Treatment

Chemicals can be used in a holding tank to speed up the process of oil/water separation. After this type of treatment, the oils will rise to the surface, the water will fall to the bottom, and a mixed phase solution will be found at the oil water interface. The top two layers get sent to treatment facilities, and the water may be discharged to a sewer.

3.5 Summary

Shipyards may realize that it is very cost effective to reduce the amount of machining waste. The most effective means of doing this is to implement processes that will maintain cooling/lubricating fluids to sustain their useful life for as long as possible. Through the use of less hazardous fluids and recycling programs, the cost of disposal of this wastestream can be reduced to negligible amounts.

4. SOLVENT CLEANING AND DECREASING OPERATIONS

Due to the nature of the industry, solvent cleaning and decreasing operations occur in many different areas of the shipyard. Source reduction, recycling, and treatment should be considered as cost-saving options to reduce the amount of solvent waste generated.

4.1 Solvent Source Reduction

To effectively decrease the amount of waste generated by solvent cleaning and decreasing operations, source reduction should be the primary consideration. This section addresses the various methods used to eliminate or reduce solvent usage as a means to reduce solvent waste.

Shipyards use solvents in a variety of cleaning and decreasing operations including parts cleaning, process equipment cleaning, and surface preparation for coating applications. Some of the major solvents used are petroleum distillates, oxygenated solvents (esters, ethers, ketones, and alcohols), and halogenated solvents. The type of solvent used for a process usually depends on the contamination and composition of the part being cleaned. The most common cleaning and decreasing operations include cold cleaning and vapor decreasing.

Cold Cleaning Operations

Cold cleaning operations can be divided into four methods: wipe cleaning, soak or dip tank cleaning, dipphase cleaning, and steam gun stripping.

Wipe Cleaning Wipe cleaning consists of using a rag or towel that has been dipped or soaked in solvent to wipe a part or surface clean. Wipe cleaning is usually associated with maintenance operations or processes that fabricate parts on a single item basis, such as in the machine shop. Solvent use tends to be high

because to assure cleanliness, a liberal amount of solvent is needed. Disadvantages of wipe cleaning include increased air emissions, fire hazards, the possibility of lint left on the clean surface, and the requirement to dispose of the rags as hazardous waste.

Soak cleaning consists primarily of soaking parts in a tank of cold solvent or solvent solution. Small parts are usually handled in baskets while larger objects are placed on racks. Heating units may be used to heat the solvent for a higher degree of cleaning efficiency. Additional efficiency can be obtained by means of agitation. This can be achieved by the installation of a pump and spray unit, use of air sparging, or installation of an ultrasonic unit.

Ultrasonic Cleaning Ultrasonic cleaning relies on the use of high frequency sound waves to produce cavitation in a solvent cleaning solution. Cavitation results in the formation of small vacuum bubbles that immediately collapse after formation. The rapid implosion of these bubbles creates a cleaning and scrubbing action throughout the fluid.

Diphase Cleaning Diphase cleaning combines a water rinse both before and after the solvent cleaning step into one operation. Halogenated solvents and water are relatively insoluble so that when placed together in a tank, they will separate. The water will float to the top. This causes the parts being cleaned to pass through the water bath before reaching the solvent below. After removal, the parts are rinsed by the same water. In some systems, a small pump recirculates the solvent up into a spray unit. The excess spray and runoff from the part falls back into the tank and sinks to the bottom. The part is then cleaned as mentioned before. These systems are usually fully enclosed to reduce waste due to air emissions.

Steam Gun Stripping Steam gun stripping and cleaning is most often used for removing paint or grease and oil from a metal surface. A mixture of non-halogenated solvents can be added to a storage tank and fed to the steam gun. A special valve controls the amount of solvent so that the surface can be sprayed with the steam and solvent mixture. Afterwards, it is rinsed with pure steam. This operation may require large quantities of steam, and it can also generate large amounts of contaminated rinsewater.

Vapor Phase Cleaning

Vapor phase cleaning relies on hot solvent vapor condensing directly on cold parts inserted into the vapor space of the degreaser. As solvent vapors condense on the dirty parts, the contaminants are dissolved. The dirty solvent falls to the bottom of the tank is reheated and vaporized, leaving the contaminants behind. As opposed to a soak tank with used solvent vapor phase systems maintain their cleaning efficiency because the parts are always exposed to clean solvent vapors.

The potential for air emissions is greater with vapor decreasing operations than that of cold cleaning operations. Emission control is a major concern to equipment designers for these systems.

Elimination the Use of Solvents

Eliminating the use of solvents avoids any waste generation associated with spent solvent. Elimination can be achieved by utilization of non-solvent cleaning agents or eliminating the need for cleaning altogether. Solvent elimination applications include the use of water-soluble cutting fluids, protective peel coatings, aqueous cleaners, and mechanical cleaning systems.

Water-soluble Cutting Fluids

Water-soluble cutting fluids can often be used in place of oil-based fluids. The cutting oils usually consist of an oil-in-water emulsion used to reduce friction and dissipate heat. If these fluids need to be removed after the machining process is complete, solvents may be needed.

In efforts to eliminate solvent decreasing and its subsequent waste, special water-soluble cutting fluids have been developed. Systems are available that can clean the cutting fluid and recycle the material back to the cutting operation. Obstacles to implementing this method are: cost (water-soluble fluids are generally more expensive), procurement (there are only a few suppliers available), and the inability to quickly switch between fluid types without thoroughly cleaning the equipment.

Aqueous Cleaners Aqueous cleaners, such as alkali, citric, and caustic base, are often useful substitutes for solvents. There are many formulations that are suited for a variety of cleaning requirements. Many aqueous cleaners have been found to be as effective as the halogenated solvents that are commonly employed.

The advantages of substituting aqueous cleaners include minimizing worker's exposure to solvent vapors, reducing liability and disposal problems associated with solvent use, and cost. Aqueous cleaners do not emit fumes or vapors and large losses due to evaporation do not occur. Since most aqueous cleaners are biodegradable, disposal is not a problem once the organic or inorganic contaminants are removed.

The use of aqueous cleaners can also result in cost savings. Although some aqueous cleaners may cost less than an equivalent amount of solvent the purchase price of each is about the same. The cost of disposal, loss due to evapo-

ration, and associated liabilities, however, favor aqueous cleaners.

The disadvantages of aqueous cleaners in place of solvents may include: possible inability of the aqueous cleaners to provide the degree of cleaning required, incompatibility between the parts being cleaned and the cleaning solution, need to modify or replace existing equipment, and problems associated with moisture left on parts being cleaned. Oils removed from the parts during cleaning may float on the surface of the cleaning solution and may interfere with subsequent cleaning. Oil skimming is usually required.

Mechanical Cleaning Systems Utilizing mechanical cleaning systems can also replace solvents in decreasing and cleaning operations. In many cases, a high pressure steam gun or high pressure parts washer can clean parts and surfaces quicker and to the same degree of cleanliness as that of the solvents they replace. Light detergents can be added to the water supply for improved cleaning. The waste produced by these systems is usually oily wastewater. This wastewater can be sent through an oil/water separator, the removed water discharged to the sewer, and the oil residue sent to a petroleum recycler. Some hot water wash and steam systems can be supplemented by emulsifying solutions to speed the process. Although these additives speed the cleaning process, they can make separation of the oil from the water very difficult and create problems with disposal of the waste.

Non-Solvent Based Paint Stripping Non-solvent based paint stripping methods are viable substitutes for solvent stripping. Paint stripping is normally performed by soaking, spraying, or brushing surfaces with a stripping agent such as methylene chloride, chromates, phenols, or strong acids. After the agent has remained on the parts for a period, the surface is rinsed with water and the loosened paint is

sprayed or brushed off. The alternatives to solvent stripping agents include aqueous stripping agents, use of abrasives, cryogenic stripping, and thermal stripping.

Aqueous stripping agents, such as caustic soda (NaOH), are often employed in place of methylene chloride based strippers. Caustic solutions have the advantage of eliminating solvent vapor emissions. A typical caustic bath consists of about 40% caustic solution heated to about 200 degrees Fahrenheit. Caustic stripping is generally effective on alkyl resins and oil paints.

Cryogenic stripping utilizes the use of liquid nitrogen and non-abrasive plastic beads as blasting shot. This method relies on the freezing effect of the liquid nitrogen and the impact of the plastic shot. Subjecting the surface to extremely low temperatures creates stress between the coating and the substrate causing the coating to become brittle. When the plastic shot hits the brittle coating, debonding occurs. The process is non-abrasive, and will not damage the substrate, but effects of the metal shrinkage, due to freezing, should be monitored

The most common form of non-solvent paint stripping in shipyards is the use of abrasive blasting. The use of various metallic grit propelled at high pressure against the surface is very effective to remove marine coatings. This topic is further discussed in Chapter 7.

Thermal stripping methods can be useful for objects that cannot be immersed. In this process, superheated air is directed against the surface of the object. The high temperatures cause some paints to flake off. The removal results from the drying effects of the air and the uneven expansion of the paint and the substrate. Some paints will melt at high temperatures, allowing the paint to be scraped off. Hand-held units are available that produce a

jet of hot air. Electric units and open flame or torch units are also used. While this system is easy to implement, it is limited to items that are not heat sensitive and to coatings that are affected by the heat.

Reducing the Use of Solvent

By eliminating the use or need for solvent cleaning, the problems associated with disposal of spent solvent are also eliminated. In cases where the elimination of solvent use is not possible or practical, utilization of various solvent waste reduction techniques can lead to a substantial savings in solvent waste.

Methods of reducing solvent usage can be divided into three categories: source control of air emissions, efficient use of solvent and equipment, and maintaining solvent quality. Source control of air emissions addresses ways in which more of the solvent can be kept inside a container or cleaning tank by reducing the chances for evaporation loss. Efficient use of solvent and equipment through better operating procedures can reduce the amount of solvent required for cleaning. Maintaining the quality of solvent will extend the lifecycle effectiveness of the solvent.

Source Control of Air Emissions Source control of air emissions can be achieved through equipment modification and proper operation of equipment. Some simple control measures include installation and use of lids, an increase of freeboard height of cleaning tanks, installation of freeboard chillers, and taking steps to reduce solvent drag-out.

Air cleaning units, including cold cleaning tanks and dip tanks, should have some type of lid installed. When viewed from the standpoint of reducing air emissions, the roll-type cover is preferable to the hinge type. Lids that swing down can cause a piston effect and force the escape of solvent vapor. In operations such as

vapor decreasing, use of lids can reduce solvent loss from 24 to 50%. For tanks that are continuously in use, covers have been designed that allow the work pieces to enter and leave the tank while the lid remains closed.

In an open top vapor degreaser, freeboard is defined as the distance from the top of the vapor zone to the top of the tank. Increasing the freeboard will substantially reduce the amount of solvent loss. A freeboard chiller may also be installed above the primary condenser coil. This refrigerated coil, much like the cooling jacket, chills the air above the vapor zone and creates a secondary barrier to vapor loss. Reduction in solvent usage, by use of freeboard chillers, has reached up to 60%. The major drawback with a freeboard chiller is that it introduces water (due to condensation from air) into the tank.

In addition to measures that reduce air emissions through equipment modification, it is also possible to reduce emissions through proper equipment layout, operation, and maintenance. Cleaning tanks should be located in areas where air turbulence and temperature do not promote vapor loss.

Maximize the Dedication of the Process Equipment In addition to reduction in vapor loss, reducing the amount of solvent used can be achieved through better operating practices that increase the efficiency of solvent cleaning operations. Maximizing the dedication of the process equipment reduces the need for frequent cleaning. By using a mix tank consistently for the same formulation, the need to clean equipment between batches is eliminated.

Avoid Unnecessary Cleaning Avoiding unnecessary cleaning also offers potential for waste reduction. For example, paint mixing tanks for two-part paints are often cleaned between batches of the same product. The effect of

cross-contamination between batches should be examined from a product quality control viewpoint to see if the cleaning step is always necessary.

Process pipelines are often flushed with some type of solvent to remove deposits on the pipe walls. Cleaning the pipelines can be achieved by using an inert gas propellant to remove deposits. This method can only be used if the pipelines do not have many bends or sharp turns.

Proper Production Scheduling Proper production scheduling can reduce cleaning frequency by eliminating the need for cleaning between the conclusion of one task and the start of the next. A simple example of this procedure is to have a small overlap between shifts that perform the same operation with the same equipment. This allows the equipment that would normally be cleaned and put away at the end of each shift, such as painting equipment to be taken over directly by the relief.

Clean Equipment Immediately Cleaning equipment immediately after use prevents deposits from hardening and avoids the need for consuming extra solvent. Letting dirty equipment accumulate and be cleaned later can also increase the time required for cleaning.

Better Operating Procedures Better operating procedures can minimize equipment clean-up waste. Some of the methods already discussed are examples of better operating procedures. Better operator training, education, closer supervision, improved equipment maintenance, and increasing the use of automation are very effective in waste minimization.

Reuse Solvent Waste Reuse of solvent waste can reduce or eliminate waste and result in a cost savings associated with a decrease in raw material consumption. The solvent from cleaning operations can be reused in other cleaning

processes in which the degree of cleanliness required is much less. This will be discussed in more detail in the next section.

Summary

Source reduction is the first step in minimizing solvent waste. Various methods of solvent waste reduction through source reduction can be utilized. These methods should be utilized wherever they prove to be practical.

4.2 Solvent Recycling

There are several recycling options available for solvent waste. This section will discuss the relative advantages and disadvantages of the various methods of both on-site and off-site recycling options.

The final cost of solvent used for various cleanup operations is nearly twice the original purchase price of the virgin solvent. The additional cost is primarily due to the fact that for each drum purchased, extra disposal cost, hazardous materials transportation cost, and manifesting time and expense are incurred. With the rising cost of solvents and waste disposal services, combined with continuously developing regulation, recycling waste solvents has become more sensible.

The goal of recycling is to recover from the waste solvent, a solvent of a similar purity to that of the virgin solvent for eventual reuse in the same operation, or of a sufficient purity to be used in another application. Recycling can also include the direct use of solvent waste from one waste stream in another operation.

Solvents can be recovered either on-site or off-site. The decision to recycle on-site or off-site usually depends upon the capital outlay and operating cost, volume of solvent waste generated, personnel requirements, liability cost, and other operational concerns. If volumes of

waste are small, companies are more likely to ship" waste off-site for recovery. The issue of liability, however, may discourage companies from use of an outside service. Generators can be held liable for the cost of future cleanups at disposal sites. The choice to recover solvents from a process on-site is usually based on economics for reuse of the substance. Recycling back to the generating process is favored for solvents used in large volumes or in one or more processes. Facilities that use several different solvents in low volume applications may find the economics of on-site recovery unfavorable.

Increasing the Recyclability of Solvents

Increasing the recyclability of solvents can be achieved by maintaining the quality of the solvent, standardizing the solvents used, and consolidating the use of solvent within the facility. Maintaining solvent quality can be viewed as a measure that will reduce the amount of solvent used, since solvent quality is much more critical when solvents are recycled.

Maintaining the solvent quality depends on the ability of the operator to prevent unnecessary contamination of the solvent. Contamination of solvent usually occurs from the addition of other solvents to the tank, drag-in of water or aqueous cleaning solutions, or failure to remove previous sludge from the tank. When incompatible solvent or water is entered into a tank of chlorinated solvent, the formation of hydrochloric acid can occur. Metal particles and the organic-based sludge can act as a catalyst and accelerate the process of forming acid. Once the contents of the solvent tank become acidic, the solvent cannot be recycled and extensive maintenance is required to restore the tank to usable condition. Several caustic washes and water rinses are required to neutralize any acid remaining in the tank. To help reduce the chance of solvent becoming acidic, chemical stabilizers are commonly added to

the solvent before it is sold. Unfortunately, as the solvent is used and recycled, the ability of the stabilizers to prevent acid formation is reduced. Therefore, maintaining the quality of the solvent is essential for its recyclability.

Contamination of solvents by other solvents can also occur. Proper segregation of waste must be practiced. It is much easier to recover solvent from waste than to recover two solvents from each other. Solvents with very similar names, such as 1,1,1-trichloroethane and trichloroethane, are easily mistaken and the probability of cross-contamination increases. As little as 1/10 of one percent of 1,1,1-TCA mixed with a tank of TCE can cause an acid condition.

Some chlorinated solvents can be contaminated with water and form undesirable chemical compounds. In addition to acid formation, water and solvent can form an inseparable mixture with a lower boiling point than that of the water or solvent alone. To avoid or reduce the possibility of water contamination, equipment maintenance is essential. The water separators on vapor degreasers should be checked routinely to ensure that they are clean and free of debris. The temperature of the water that excites the condenser coils and cooling jacket should be kept between 90 to 100 degrees Fahrenheit. Parts should not be allowed to enter the cleaning process while they are wet.

Parts from a cleaning operation are often rinsed with water. When solvent cleaning follows an aqueous cleaning or water rinse, drag-out from these operations can cause contamination of the solvent. The amount of drag-out should be minimized so that the need for the rinse water is lessened. Methods that reduce the degree of drag-out depend mainly on the proper design and operation of the equipment.

To ensure the proper draining of parts, it is important to follow some general guidelines.

Parts should always be racked as vertical as possible with the longest dimension horizontal. During removal from the tank, the lower edge of the part should be tilted to allow runoff. Solutions should drain from a corner rather than the entire edge of the part.

Other mechanical measures used to reduce cleaning solution drag-out and subsequent solvent bath contamination include installing air jets to blow parts dry and fog nozzles on rinse tanks. Use of air jets is limited to cases in which dry cleaning solution on the part does not interfere with the subsequent operations. Fog nozzles are specially designed high pressure spray units that provide a high degree of rinsing while using a small amount of water. They are especially useful over heated processing baths where a small amount of water introduced into the bath compensates for the losses due to evaporation.

Prompt removal of sludge from solvent tanks is important to maintain the cleaning efficiency and prevent acid formation. Stripped paint and other organic contaminants can dissolve in the solvent reducing cleaning efficiency. Contamination by organic materials should never be allowed to exceed 10% in a cold cleaning operation or 2070 in a decreasing operation. Metal fines, such as zinc and aluminum, are very reactive in chlorinated solvents and should always be removed promptly.

Standardizing the solvents used in the facility will often increase the potential for recycling. It is common to find that many different solvents are used by a facility for similar operations. Because of the variety of solvents being used, the amount of waste generated by each is small and the potential for recycling is seldom considered. Standardization of solvent may allow procurement cost to be reduced by larger order quantities, and generate enough waste to make recycling a feasible option.

On-Site Recovery

Because of the initial cost associated with the purchase of virgin solvent and the subsequent disposal of the waste, recycling is often performed as an integral part of a manufacturing process. The reduction in the amount of waste generated leads to lower disposal cost and liability associated with the disposal. The decision to procure, install, and operate an on-site recovery system must be based on a complete analysis of the technical and economical feasibility of the system. The analysis must also consider operational issues such as ease and safety of operation.

There are many advantages realized with on-site recycling. These advantages include:

- reduced solvent purchase demand
- less waste leaving the facility, and thus reduced disposal cost
- owner's control of the purity of the reclaimed solvent
- reduced liability and cost of transporting cost off-site
- reduced reporting (manifesting)
- possible lower unit cost of reclaimed solvent.

Disadvantages of on-site recycling must also be considered. These may include:

- initial capital outlay for recycling equipment
- liabilities for worker health, fires, explosions, leaks, spills, and other risk as a result of improper equipment operation
- need for operator and worker training

- additional maintenance and operating cost.

Separation Techniques for Solvent Recovery

There are a variety of methods available for solvent recovery. The feasibility of most methods depends upon many operational requirements and ways that the waste are generated. Before implementation of some of the recovery methods mentioned in the following section, careful analysis of the economics and technical aspects of each method should be researched and various options considered.

Distillation

Distillation is the oldest and most common technique utilized for solvent recovery. It relies on the principle that the solvent has a lower boiling point than the contaminants. Batch and continuous distillation are the most common procedures.

A batch process, also known as differential distillation, consists of placing a fixed amount of solvent waste into a heated chamber. Heat is applied to raise the temperature to the solvent boiling point and the resulting vapor is withdrawn and condensed. The process is terminated when the impurity level in the distillate becomes prohibitive. Batch distillation usually utilizes a single equilibrium stage. Single stage batch distillation can normally produce a purity of more than 95%. Higher purity is more probable if the process is carried out slowly and the vapor pressures of the components differ greatly.

Continuous multistage distillation, often called fractional distillation, is commonly applied when a high degree of distillate purity is required, the volatility differences of the solvent and contaminants is small, and the amount to be distilled is large. This method of distillation is carried out in a column equipped

with trays to produce maximum contact between liquid and vapor phases.

There are many different stills that are commercially available. Capacities range from 0.8 to 1,000 gallons per cycle and clean solvent output rates from 1 to 120 gallons per hour. The output rates vary depending on the heat of vaporization of the solvent, the type and concentration of the contaminant present, and power input.

In most cases, the purchase of a solvent still will result in almost immediate savings. With a usual payback period of less than a year and often less than six months, the procurement of a still can be very attractive. There are, however, some limiting factors that determine if the purchase of a solvent still is feasible. The amount of waste generated is probably the largest factor when determining the economics of investing in a solvent still. Usually, generators of large amounts of solvent waste will realize the most benefits. If the facility produces very small amounts of solvent waste, it may not be practical to purchase a still.

No special license is required by the federal government (EPA) to operate a solvent still on-site. If the still has a capacity of more than five gallons, it may be regulated by the local Air Pollution Control District (APCD) and a permit may be required.

Evaporation Evaporation is a procedure usually used for solvent sludge, still bottoms, or other solvent waste with a very high concentration of contaminants. In a turbulent film evaporator, also called a wipe-film evaporator, a set of blades spreads the waste in a thin film against the heated wall of the cylindrical vat. A high degree of heat transfer is maintained as the heavy sludge makes its way to the bottom of the vat and is collected for disposal. The solvent vapors are collected and condensed. Film evaporation is best suited for low-boiling

solvents without abrasive solids.

Another evaporation method involves the use of a dryer. In this operation, the waste is fed between two heated drums that are counter-rotated. The solvent evaporates off, leaving the non-volatile components in the form of a dry film, which is scraped off and collected for disposal. This process can handle pumpable sludge that contains up to 90% solids and can recover nearly all the solvent for reuse.

Sedimentation Sedimentation, also called gravitation, is a technique in which the particles suspended in the liquid are settled out by gravity. The contaminated solvent is put into settling tanks and after a sufficient period of time, the separated liquid is drawn off the solids that have settled to the bottom. Sedimentation is often used to remove solids from organic solvents as a preliminary purification or pre-filtration stage. This can be particularly useful to recover cleaning solvents from painting operations. Capital and maintenance costs are very low due to the simplicity of the equipment and low energy and expertise requirements. A disadvantage of this procedure is that finely dispersed colloidal particles tend to stay suspended in the solvent solution and cause the separation efficiency to be low. Settling times for small particles may be quite long, and large volumes or several tanks may be required to furnish a quantity through put. To avoid loss of solvent by evaporation into the air, steps should be taken to ensure that the settling containers have proper covers.

Recantation Recantation is a gravity separation system used to separate liquids of different densities. The mixture of immiscible liquids is fed into a decant tank where it continually separates. As the various liquids are separated into their respective layers, they are coalesced and withdrawn. Dust and dirt particles can interfere with the process of coalescence. Because the nonaqueous layer removed by recantation is

frequently saturated with water, further processing of the liquid is often needed.

Centrifugation Centrifugation is used to separate liquids and solids from the solvent through the application of centrifugal force. In sedimentation-type centrifugation, a waste stream is added into a spinning centrifuge. The slightly denser contaminates are forced against the inner wall of the unit. The solids are removed by the continuous displacement of entering fluid or by a screw conveyor. In filtration-type centrifugation, the inner wall of the unit is a filter. The solvent is forced through the filter and the solids are retained inside to be mechanically removed by blades that scrape the filter as the unit rotates.

Like gravity separation, centrifugation is used as a preliminary purification step before other recycling operations. For wastes that contain less than one percent sedimentable solids, tubular-bowl centrifuges can be used.

Filtration Filtration separates suspended particles from a liquid by using a porous filter medium. Many different types of filtration can be used. The basic operational steps of each encompasses forcing a mixture of fluid and solids through a filter using gravity or other pressure. The solids are trapped by the filter and cleaned off later or disposed of with the filter.

Some of the factors for selecting filtration equipment include particle size distribution, viscosity, production throughput, process condition, performance requirements, and materials of construction. The cost of filtration equipment may vary greatly due to the wide array of equipment available.

When using a washable filter, environmental concerns center around increasing the volume of the waste by the addition of backwash fluid, treatment and disposal of the solids, and

escape of volatile emissions into the atmosphere. Disposable bags or cartridges avoid the problem of waste increase due to backwash, at the expense of increasing the waste by their own mass.

If the solvents are contaminated by large solids, strainers may be employed to remove the coarse particles from the liquid. Equipment may include stationary or moving screens, perforated plates, or metal mesh baskets.

Membrane Separation Membrane separation, which includes ultrafiltration and reverse osmosis, is a process in which solute molecules with a molecular weight over 500, or particles with a diameter less than 0.5 microns can be separated from a waste stream using semi-permeable membranes as the filtering media. The membranes are highly efficient because the openings are submicron in size. Pore size can range from 0.0005 to 0.0025 microns for reverse osmosis and from 0.0025 to 0.01 microns for ultrafiltration. Pressure is applied to one side of the membrane to force the liquid through the pores. The larger particles are filtered out and left on the other side. Since ultrafiltration uses membranes with larger pores than those used for reverse osmosis, blockage or membrane degradation is less likely to occur, and thus it is better suited for solvent recycling.

There are three principle ultrafiltration device setups: tubular, spiral wound, and hollow fiber. The tubular device is often used for small-flow, high volume applications. Due to its construction, mechanical cleaning of the tubular setup can be done easily. The spiral wound design is better suited for high volume operations, however, it is more vulnerable to fouling. The hollow fiber method consists of a membrane wound into a hollow cylinder with the inside diameter varying from about 500 to 1,100 microns. Capital cost for ultrafiltration systems range from medium to high. The oper-

ating and maintenance costs are fair.

Solvent Extraction Solvent extraction is a process whereby the separation of components is achieved by mixing the waste stream with a liquid that acts as a solvent to one component but is immiscible with the other component. The basic operation consists of mixing the waste solvent and the addition solvent and then allowing the mixture to separate into phases in a holding tank. Separation of the added solvent from the recovered solvent usually requires distillation.

Reuse in Other Operations Probably the simplest and most economical method of recycling waste solvents and cleaners is to reuse them in a similar operation elsewhere. Contaminated solvents from one cleaning operation may be used in applications where solvent quality is not as high or in the preliminary phases of multi-stage cleaning. The energy from solvents can be recycled by using the waste as a form of fuel for other machinery, such as boilers.

Off-Site Recycling

Off-site commercial recycling services are well suited to small quantity generators. Small quantity generators usually do not create sufficient volumes of waste solvent to justify on-site recycling. Off-site recyclers are also used by generators who prefer to avoid the technical, economic, and managerial requirements of on-site recycling. The disadvantages of off-site recycling are the high transportation and liability cost. Additionally, liability associated with the disposal of the still bottoms is another concern.

Commercial recycling facilities are privately owned companies that offer a variety of services such as operating a waste treatment/recycling facility on the generator's property or accepting and recycling batches of solvent

waste at their own private facility. Although some recyclers accept both halogenated and non-halogenated solvents, used oil recyclers often accept only non-halogenated solvent waste. The recycler may have the generator by volume of the waste accepted and later credit the generator's account for the amount of the saleable solvent recovered from the batch of waste. Other recyclers charge a straight fee or may accept waste at no cost depending on the type and volume of waste received. The value of solvent waste to a recycler depends on the type, purity, quantity generated, and cost incurred to transport the waste from the generating facility to the recycling location.

Safety Kleen Inc. provides a batch tolling service for decreasing solvents, and leases the process equipment and solvents as one system. Safety Kleen's mobile units provide fully contained decreasing systems for small parts cleaning operations. Safety Kleen services these units by periodically replacing the spent solvent with fresh solvent. The waste solvent is then recycled at a central location.

The following factors should be considered before choosing a commercial recycling service:

- Permits held by the facility
- Types of solvent waste managed
- Ability to meet solvent purity specifications if the solvent is to be returned to the generator
- Any history of violations of the environmental laws.

A common arrangement between generator and recycler is batch tolling. Under this arrangement, the recycler accepts the waste from the generator, reclaims the solvent through some means, and resells the recovered

product back to the original generator. As long as the price of the recycled solvent is less than the equivalent grade of virgin solvent, this system is attractive.

Some companies may make cooperative arrangements with each other to facilitate recycling using methods other than commercial batch-tolling agreements. These usually involve arrangements between plants located near or even at some distance from each other. Under this system, two or more facilities exchange recyclable waste. This is successful as long as each facility is able to recycle the other's waste stream more efficiently than their own.

4.3 Solvent Treatment and Pretreatment

This section presents major aspects of treatment and pretreatment of solvent waste. Treatment refers to the processes that alter the waste and yield waste streams that pose little or no environmental risk.

The increasing cost for disposal and the associated liabilities can make treatment a feasible option. Waste treatment systems are often costly and the decision to rely on treatment should only have been made after considering all available source reduction and recycling options.

Aqueous waste that contain solvents are often treated on-site to reduce their toxicity and chemical or physical properties. The most common treatment systems for facilities producing large amounts of wastewater with very low concentrations of solvents involves biological degradation or stripping the wastewater with air or steam. Stripping can be followed by treatment or recovery to control air emissions. Steam stripping is more favorable than air because it produces a more concentrated solvent waste stream. Biological treatment in large open tanks can result in air emissions

and the cost for emission control can be prohibitive.

Concentrated solvent waste may be incinerated. An incinerator must be tailored to the type of waste to be treated. Chlorinated solvents form hydrochloric acid upon burning, therefore, special acid resistant construction materials and a flue gas acid scrubber may be needed.

Several arrangements for treatment of waste are available for facilities that do not have the necessary capital or technical staff to build and operate a system. Companies that market transportable incineration systems include: Ensco Environmental Services in Little Rock, Arkansas; Shirco Infrared Systems in Dallas, Texas; and Huber Corporation in Borger, Texas. G.A. Technologies (GAT), San Diego, California, and Modar Incorporated in Natick, Massachusetts, market a transportable supercritical water system.

Off-site treatment is typically justified in cases where the generation of volumes are small. Arrangements for use as a fuel for cement kilns can be made through Systech Corporation in Lebec, California. Systech also uses General Portland's facility in Fredonia, Kansas.

Treatment Technologies

Treatment technologies involve the removal of solvents from wastewater streams by physical means, the destruction of solvents in wastewater by biological or chemical means, and the destruction of solvent waste by thermal techniques. Many treatment technologies can be used in conjunction with recycling technologies, such as distillation, of solvent waste followed by the incineration of the remaining solids.

Wet Air Oxidation Wet air oxidation treats

aqueous waste streams containing organics through contact with air at 350 to 700°F and pressure up to 2,000 lbs/in². The organics are oxidized in the exothermic process by oxygen in the air. After treatment, the pressure is released and the wet air exiting the container is passed through a carbon absorption column to recover any remaining organics. Wet air oxidation is used when wastes are too dilute to incinerate and are not biologically degradable. The organic concentration typically handled ranges from 10,000 to 100,000 milligrams per liter.

Wet air oxidation is typically used for treating wastes that contain easily oxidized non-halogenated solvents. Usually, 80% of the organics present are fully oxidized. The remainder is oxidized partially and an additional bio-oxidation step may be necessary. Some halogenated solvents can be treated by employing catalysts such as bromides, nitrites, and copper. The effect of these catalysts on subsequent waste treatment processes is unclear. More information on wet air oxidation can be obtained from Zimpro, Inc. in Rothschild, Wisconsin.

Chemical Oxidation Chemical oxidation commonly uses oxidants such as potassium permanganate, ozone, or hydrogen peroxide to break down or oxidize organic materials contained in wastewater. Waste is treated in a batch reactor or a well mixed continuous reactor, followed by a separation step to remove insoluble oxidized materials that precipitate during treatment.

This treatment technique is effective on aqueous waste that contains less than one percent oxidizable material. When a waste stream contains a large amount of easily oxidizable material, all of the oxidant may be consumed before the less reactive materials are oxidized. Violent reactions can occur if the concentration of easily oxidized material is too great. Chemical oxidation may be combined with

biological treatment for more effective pollutant removal.

Supercritical Water Oxidation Supercritical water oxidation treatment is similar to the wet air oxidation process. The process begins by mixing oxygen into the wastewater and then using heat to raise the temperature and pressure above the supercritical point of the water. The water will act as a solvent for the organics and will aid in the decomposition of the waste. During the process, superheated steam and innocuous gases are produced. These by-products can be used as process steam. The Modar Company of Natick, Massachusetts has designed and built a system that achieved better than 99.99% destruction efficiency when treating highly chlorinated compounds.

Activated Sludge Activated sludge treatment is a two-step process. The process starts with bio-oxidation of organic waste by placing sludge in an aeration tank or basin for two to twenty-four hours, followed by clarification of the wastewater. Activated sludge treatment may be used to treat dilute solvent-bearing waste containing less than 1% suspended solids. Disadvantages of this system include the requirement to dispose of large amounts of sludge and the potential need for air emission control. This process may not be practical for a shipyard because of its incapacity to treat waste streams containing heavy metals, oils, and grease.

Aerated Lagoons Aerated lagoons are shallow biological treatment basins maintained in an aerobic state by mechanical agitation. Lagoons contain a wide variety of naturally occurring bacteria and algae. One of the most important disadvantages of lagoons is that significant air emissions will probably occur. Current regulations require lagoons to meet the same standards as treatment ponds. Another disadvantage is the amount of space that a lagoon occupies can be very significant and this space

might be utilized more profitably.

Trickling Filter Trickling filters are similar to activated sludge systems except that their design allows higher biological degradation rates. By filling the basin with rocks or artificial media, the surface area available for microbial growth is significantly increased. To provide for even distribution of the waste over the rocks or other media, fixed sprays or other mechanical systems are used. Up-flowing air is introduced into the system by an underdrain which also conveys effluent to the clarifier. The retention times for treatment may be as short as one hour.

The trickling filter system is acceptable for treatment or pretreatment of dilute aqueous waste that contain less than 1% suspended solids. Degradation of the organics may not be complete because of the short retention time.

Anaerobic Treatment Anaerobic treatment is conducted in a closed vessel without agitation at temperatures ranging from 31 to 60°C. Anaerobic bacteria digest simple organic compounds by a series of reactions that do not require oxygen. During digestion, large quantities of methane gas are produced, which can be used as a source of fuel. Retention times can be as long as two or more weeks.

Anaerobic treatment offers several advantages over aerobic treatment. This process requires approximately 10% as much nutrient in the waste stream, produces 1/10 the sludge requiring disposal, and produces methane gas. This operation is also more suitable for wastewater containing a higher content of suspended solids.

Boilers Boilers can destroy solvent waste by using the waste as a supplement to a fossil fuel. The process usually consists of blending the waste material with fuel and injecting the mixture onto a modified boiler burner. Care

must be taken to assure that the heating value of the resulting fuel mixture is adequate to maintain proper combustion and that the composition of the waste stream stays fairly constant. Separation of waste in storage tanks is common and can lead to a fuel mixture that is too lean or too rich. When this happens, incomplete combustion can occur.

Another concern with boilers is that the solvent/fuel mixture must be free of small particles or ash. Solids can lead to plugging of the burner nozzles or a build-up of deposits within the unit. In addition, excess solids can cause an increase in particulate emissions and require the use of air pollution control equipment. Excess chlorine in the waste can cause severe corrosion of refractory and metal parts, therefore, it is better to limit chlorine content to 3% or less.

Rotary Kilns Rotary kilns consist of a cylindrical, refractory-lined chamber tilted several degrees off the horizon. The rotation of the cylinder mixes the waste and combustion air. The tilt of the chamber causes the solids to flow towards the outlet where they are constantly removed. Gaseous combustion products pass through an afterburner and then through scrubbers. Residence times range from seconds for gases to hours for solids. Temperatures typically reach 3000°F. Waste handling capacity ranges from one to eight tons per hour for conventionally sized units.

Rotary kilns can efficiently burn viscous still bottoms, waste solvents, and solid material. The wide flexibility of the feed mechanism design allows the unit to process liquids and solids independently or in combination. Air pollution control equipment is a must because airborne particles may be carried out of the kiln before complete combustion can occur. Rotary kilns are not recommended for any waste that contains heavy metals or has a high inorganic content.

Liquid Injection Liquid injection incinerators consist of a refractory-lined combustion chamber and a series of nozzles. The nozzles atomize the waste and fuel as they are injected into the chamber. Viscous waste is blended with more free flowing waste before injection to improve the ease of pumping and combustion properties of the waste.

Liquid injection systems can incinerate a wide variety of liquid waste including phenols, PCBs, still and reactor bottoms, solvents, and polymer wastes. Usually an incinerator is geared to handle a specific waste stream to maintain a high thermal destruction efficiency. Many units are designed with electrostatic precipitators and scrubbers. This design allows chlorinated solvents to be handled. Units have been developed to handle up to ten tons of waste per hour.

Fluidized Bed Fluidized bed incinerators consist of a refractory-lined vessel containing an inert granular material. Combustion air is blown through this material and rises upward through the bed, maintaining particles in suspension. The gas in excess of the flow needed for incipient fluidization passes through the bed in the form of bubbles. Mixing occurs as the bubbles move through the liquid-like suspended particle phase. An auxiliary heater is used to supply heat to the bed to maintain operating temperatures. Solid combustible material remains in the bed until the particles become small enough to be carried out with the flue gas. These particles are removed by the air pollution control equipment. Lime or limestone is often added to the bed material to neutralize any acidic gases that may form.

Common applications for fluidized bed incinerators are in petroleum, paper, and sewer disposal industries. The circulating fluid bed has been tested for hazardous waste destruction. This design has advantages over the standard

design such as lower capital and operating cost, higher thermal efficiencies, and better responses to upsets.

Fixed Hearth Incineration Fixed hearth incineration systems usually consist of a single steel shell lined with a refractory material. The overall design of the unit is simple. Incineration of the waste takes place in stages in primary and secondary combustion chambers. The first chamber operates in a starved air mode with temperatures ranging from 600 to 1,600°F. Vortex-type burners are used to inject liquid waste into the primary chamber. Solid wastes are fed onto grates located above the chamber. Gaseous combustion products travel upward into the secondary chamber where more air is added to ensure complete combustion. Ashes fall through the grate and are discharged from below the unit. To ensure complete incineration, the secondary combustion chamber operates at a range of 1,200 to 1,800°F.

Mixed waste, such as waste solvents and combustible solids, can be handled by the fixed hearth incinerator. Based on available designs, most units are designed to process feed rates of less than one ton per hour. Fixed hearth incinerators have a limited ability to destroy the more stable compounds, such as chlorinated solvents, and they tend to be limited to non-halogenated solvents.

Multiple Hearth Incineration Multiple hearth incineration systems work on the same principle as fixed hearth incineration systems. These systems usually consist of several refractory hearths situated one above the other, a rotating central shaft, a series of arms with plows for each hearth, fuel burners mounted on the walls, an ash removal system, and a waste feeding system. The waste enters the top as a sludge and is moved across the various levels by the arms. As the waste is passed to the hearths below, it is incinerated and broken

down.

Multiple hearth incinerators have been used to dispose of industrial sludge, tars, solids, and flammable liquid waste. Highly contaminated solvents and residues from solvent reclamation can be blended and used as fuel.

4.4 Summary

Although on-site treatment may be more economical than having the waste solvents treated elsewhere, it is still more desirable to avoid treatment and implement recycling. Source reduction and recycling techniques are the most effective methods to reduce solvent waste.

5. METAL PLATING AND SURFACE FINISHING

5.1 Introduction

Metal surface treatment and plating are used by most shipyards engaged in forming and finishing metal products and involve the alteration of metal workplaces surface properties, in order to increase corrosion or abrasion resistance, improve electrical conductivity, or in some way enhance the utility of the product. Plating and surface treatment operations are typically a batch operation in which the metal objects are dipped into and then removed from baths containing various chemicals for achieving the required surface condition. The process involves moving the object to be coated (workpiece) through a series of baths designed to produce the desired end product. The workplaces can be carried on racks or in barrels. The large workplaces are mounted on racks that carry the parts from bath to bath. A set of small parts can be contained in barrels that rotate in the plating bath.

5.2 Process Description

Plating operations can be categorized as electroplating and electroless plating processes. Surface treatment includes chemical and electrochemical conversion, case hardening, metallic coating, and chemical coating. Most metal surface treatment and plating processes have three basic steps: surface cleaning or preparation, modification of the surface, and rinsing or other workpiece finishing operation.

Chemical and Electrochemical Conversion

Chemical and electrochemical conversion treatment are designed to deposit a coating on a metal surface (substrate) that performs a corrosion protection, improves electrical conductivity, or prepares a surface for painting. The processes include phosphating, chromating, anodizing, passivation, and metal coloring or lettering.

Phosphating treatments provide a coating of insoluble metal phosphate crystal that adheres strongly to the base metal. The coating provides some corrosion resistance, but the main function, due to their absorptivity, is as a base for the adhesion of paints, lacquers, and oils to a metal surface. Chromate coatings are applied to minimize rust formation and to guarantee paint adhesion. Chromating baths often contain the following ingredients: hexavalent chromium, sulfuric and/or nitric acid, and several organic and inorganic activating compounds.

Anodizing employs electrochemical means of developing a surface oxide film on the workpiece, enhancing its corrosion resistance. Passivation is a process by which protective films are formed through immersion in an acid solution. In stainless steel passivation, embedded ion particles are dissolved and a thin oxide coat is formed by immersion in nitric acid, sometimes containing sodium bichromate.

Case Hardening

Case hardening produces a hard surface over a metal core that remains relatively soft. The case is wear-resistant and durable, while the core is strong and ductile. Case hardening methodologies include carburizing, carbonitriding, nitriding, microcaseing, and hardening using localized heating and quenching operations.

Carburizing, the most widely used case hardening operation, involves diffusion of carbon into steel surfaces at a temperature of 845 to 955° Centigrade, producing a hard case in the high carbon area. Nitriding processes diffuse nascent nitrogen into a steel surface to produce case hardening. Nitriding is accomplished using either a nitrogenous gas such as ammonia or a liquid salt bath. Salt baths typically consist of 60 to 70 percent sodium salts (sodi-

urn cyanide and 30 to 40% potassium salts (potassium cyanide). Carbonitriding and cyaniding involve the diffusion of both carbon and nitrogen simultaneously into the steel surface.

Applied energy methods are those that generate a case through localized heat and quenching rather than through the use of chemicals. Very rapid heat application results in surface hardening with little heat conducted inward. Since no carbon or nitrogen is diffused into the workpiece, it is the existing carbon content of the ferrous metal that determines hardness response. Heating can be accomplished through electromagnetic induction, high temperature flame, or high velocity combustion product gases.

Metallic Coatings

Metallic coatings provide a layer that changes the surface properties of the workpiece to those of the metal being applied. The workpiece becomes a composite material with properties generally not achievable by either material singly. The coating's function is usually a durable, corrosion resistant protective layer, while the core material provides the load function. Metallic coating as defined here refers to diffusion coatings, in which the base metal is brought into contact with the coating metal at elevated temperatures allowing lattice interdiffusion of the two materials, spraying technique: (flame spraying), cladding, in which metal is applied using mechanical techniques; vapor deposition and vacuum coating.

Hot dipping is a diffusion process that involves partial or complete immersion of the workpiece in a molten metal bath. Common coating materials include aluminum, coated lead, tin, zinc, or a combination of the above. The coating metal is a cementation diffusion process applied in powdered format high temperatures (800 to 1100° Centigrade), in a mix-

ture with inert particles such as alumina or sand, and a halide activator. The main application of sprayed diffusion coatings are for workplaces difficult to coat by other means due to their size and shape, or that are damageable by high temperature heating required for other methods. Chemical vapor deposition and vacuum coatings produce a high quality, pure metallic layer and can sometimes be used in place of plating processes. A layer of metal cladding can be bonded to the workpiece under high pressure welding or casting techniques. Cladding can offer an alternative to plating in some situations.

Electroplating and Related Processes

Electroplating is achieved by passing an electric current through a solution containing dissolved metal ions as well as the metal object to be plated. The metal object acts as a cathode in an electrochemical cell, attracting metal ions from the solution. Ferrous and nonferrous metal objects are typically electroplated with aluminum, brass, bronze, cadmium, chromium, copper, iron, lead, nickel, and zinc as well as precious metals such as gold, platinum, and silver.

The sequence of unit operations in an electroplating operation is very similar when either racks or barrels are used to carry parts. A typical sequence involves various types of cleaning steps, stripping old plating or paint, the actual electroplating steps, and rinsing steps between and after each of the above operations.

Electroless plating uses similar steps, but involves the deposition of metal on a metallic or non-metallic surface without the use of external electrical energy.

The electroplating process is sometimes used to build up coating thickness on a mandrel or mold. In this process, called electroforming,

the mandrel is removed once the buildup is complete. Electroforming can produce intricate shapes whose dimensions and surface texture can be reproduced with great fidelity and detail.

In electropolishing, the metal workpiece is made the anode rather than the cathode. Instead of deposition onto the surface of the workpiece, some of the metal dissolves, leaving a bright, polished surface. High points dissolve at a faster rate than recessed areas. Electropolishing is performed to improve adhesion of subsequent electroplates, to deburr and finish parts, and for decorative purposes.

5.3 Waste Streams From Plating Operations

There are many plating and surface treatment process wastes which are generated from plating operations. Two of the waste streams, spent alkaline cleaning solutions and spent acid cleaning solutions, are generated by periodic replacement of contaminated solutions. Rinse waters are generated from overflow of rinse tanks and contaminations by drag-out from cleaning baths. Waste removed from plating tanks by the continuous filtering of the baths results in filter sludge. All of these waste streams frequently contain toxic metal concentrations.

Wastes produced at a particular facility will be similar to those listed, but their precise composition will depend on the specific process. Some or all of the waste types listed may be combined into a single waste stream before treatment or disposal. It is common to combine concentrated cyanide wastes from plating and cleaning solutions, for instance, with filter sludge. These are frequently kept separate, however, from acidic wastes and from dilute cyanide solutions.

On a volume basis, contaminated rinsewater

accounts for the majority of plating process waste as shown in the previous sections; plating processes can involve many rinsing steps. Rinse water is used to wash off the drag-out from the workpiece after it is removed from a bath. Drag-out refers to the excess solution that adheres to the workpiece surface and gets carried out of the solution bath upon withdrawal of the workpiece from the bath. In general, barrel plating involving the use of small parts barrel, carries more plating solution when withdrawn from the bath than the rack does, and because drainage of the drag-out back into the bath is more difficult with barrels. If the drag-out from one bath is carried into the next bath in the sequence due to incomplete rinsing, it is referred to as “drag-in,” and is considered a contaminant in the latter bath.

Spent cleaning and plating solutions are another source of plating wastes. Several types of cleaning solutions are used to prepare a metal surface for electroplating. Stripping wastes are a special type of cleaning waste. They result from the stripping the old plated deposit prior to deposition of a new metal plate. Cleaning solutions may be acidic or basic, and may contain organic, heavy metals, and cyanide. Spent plating solutions contain high concentrations of heavy metals. These solutions are not regularly discarded like cleaning solutions, but may require purging if impurities build up.

Waste produced from spills and leaks are usually presented to some extent in the electroplating process. Water used for rinsing is washed away into a sump collection area to be pumped to a storage area. Wastewater is also produced from wet scrubbing ventilation exhaust air.

Wastewater produced in an electroplating process may contain a variety of heavy metals and cyanide. The metals are typically removed by adding lime or other precipitating agents;

and precipitated under alkaline pH. The resulting metal hydroxide precipitate from a dilute sludge is dewatered through filter presses and sludge dryers. The sludge is then generally disposed of at a class 1 landfill site owned by a hazardous waste TSDF. Some shops, however, are sending their sludge to off-site metal recovery facilities. Technologies used by these facilities are discussed in the recycling section of this section.

5.4 Source Reduction

Process solutions for surface treating and plating contain high concentrations of heavy metal, cyanides, and other toxic constituents. Process baths are not discarded frequently, but rather are used for long period of time. The chemicals they contain, however are lost, sometimes at high rates, through drag-out on workpieces, spills, and leaks. Nevertheless, the baths do require periodic replacement due to impurity build-up or the loss of solution constituents by drag-out. A contaminated or exhausted plating solution is highly concentrated with toxic compounds and requires extensive treatment. The source control methods available for reduction of spent plating and other process waste include increasing solution life and material substitution.

Increasing Solution Life

The lifetime of plating solution is limited by the accumulation of impurities and/or by depletion of constituents due to drag-out. Drag-out reduction is examined later in this section. The impurities come from six sources : racks, dropped parts, anodes, drag-in, water make-up, and air. Corrosion and salt buildup deposits on the rack elements can contaminate the plating solutions in which they are immersed. Proper design and maintenance (mainly cleaning) minimizes this form of contamination. Parts dropped in plating baths can be removed daily using a wooden or plastic

coated rake, or a magnet for ferrous parts. Dropped parts add to heavy metal contamination. Removing them regularly can reduce the reject rate and extend bath life.

The use of purer metal for anodes also extends the plating solution life since during plating, metal from the anode is dissolved in the plating solution, and impurities contained in the original anode matrix can eventually accumulate to prohibitive levels.

Efficiently rinsing the workpiece between different plating baths reduces the carryover of plating solution into the next bath. Using demineralized or distilled water as make-up to compensate for evaporation is preferred over tap water, since tap water may have a high mineral or solid content which can lead to impurity buildup. Another method that has been successfully used to increase the longevity of plating solutions is periodic filtering to keep levels of impurities low. In many shops, continuous or daily circulation of plating baths through carbon or small-hole filters, typically 10 microns in size, has dramatically improved plating quality.

Careful control of temperature, pH, process chemical concentrations, and other process parameters is important to obtain the maximum lifetime from baths. In some applications, such as in trivalent chromium plating systems, it is essential to keep analytical solutions contained in anode boxes strictly segregated from the electrolytes in the rest of the bath. Mixing the two chemistries can ruin the effectiveness of the bath.

Material Substitution

Cyanide plating solutions can be replaced with less toxic cyanide-free solutions. Cyanide-zinc solution, for instance, can be replaced with non-cyanide, non-chelated alkaline zinc solutions eliminating the problem of handling

cyanide-containing wastes. Extensive research has been conducted to develop non-cyanide zinc plating solutions. Less effort has been spent on developing non-cyanide cadmium baths, because the volume of cadmium plating is only 5-10 percent that of zinc. Because of increased environmental concerns, however, acidic cadmium baths similar to those for zinc are now available.

A primary barrier to non-cyanide bath is that U.S. Navy contracts often specify the use of cyanide solutions, thereby preventing electroplaters from using non-cyanide replacements. Replacing cyanide solutions with non-cyanide solutions often requires upgrading the degreasing/cleaning techniques used, because the non-cyanide replacement may require a much more thoroughly cleaned surface to ensure high quality plating. Many tanks used for cyanide plating are made of bare steel, and require lining or replacement if acidic non-cyanide baths are used. Non-cyanide cadmium and zinc baths generally cost more than cyanide baths but non-cyanide can still save a plating shop considerable expense due to the reduced waste treatment cost and safety hazards. One U.S. Air Force plating shop that switched from alkaline cyanide cadmium to acidic non-cyanide cadmium found that product quality was improved, and that the elimination of the cyanide destruction step in the waste treatment plant resulted in a net cost savings. There have also been reports of reduced drag-out from non-cyanide baths.

Replacements of cadmium-based plating solutions is feasible in many applications. Cadmium is used in a wide variety of products for its excellent protective properties. Cadmium-plating products are highly resistant to corrosion in marine environments. For this reason, the U.S. Navy specifies cadmium plating for a large variety of naval equipment. It is possible in some cases to replace cadmium plating with other materials such as zinc, tita-

nium dioxide (vapor deposition), and aluminum (ion vapor deposition or spray and bake techniques). None of these coatings have exactly the same properties as cadmium, but nevertheless prove to be satisfactory substitutes.

IBM has successfully substituted zinc for cadmium in many applications, with good results. Inspection of the zinc and cadmium parts at marine sites around the world reveal that zinc-plated parts suffer less corrosion. Barriers to the replacements of cadmium parts with zinc include differences in lubricity and solderability between the two metals. Lubricity differences can be corrected with a water-emulsion post treatment after zinc plating. Solderability of zinc parts can be improved through tin or lead plating. Aluminum ion vapor deposition is a very promising process for replacing cadmium plating but it is considerably more expensive than electroplating.

Replacement of hexavalent chromium with trivalent chromium offers important environmental advantages. Trivalent chromium is considerably less toxic than hexavalent. Trivalent systems use chromium concentrations that are typically two orders of magnitude less than hexavalent systems. Thus far less chromium enters the waste stream. Trivalent systems also generate fewer toxic air emissions while hexavalent systems involve a reaction that produces hydrogen bubbles which entrain chromium compounds and carry them out of the baths. Trivalent chromium is readily precipitated from wastewater, while hexavalent chromium solutions must go through an additional step in a treatment system in which the chromium is reduced to its trivalent form before precipitation. It has been shown that a trivalent chromium system can successfully replace hexavalent systems for decorative chrome application. Trivalent systems are not suitable for hard chrome applications.

Hexavalent chromium is used in anodizing baths, and in pickling solutions that remove oxide layers from parts. The chromic acid in these solutions eventually enter the waste stream, either through drag-out or when the pickling or anodizing bath is disposed. Less hazardous alternatives exist for these chromic acid applications. At General Dynamics, chromic acid anodizing was replaced by a sulfuric acid solution. The new system required careful process control, but offered reduced environmental risk and improved worker safety.

Process Substitution

Certain processes can offer environmentally more benign alternatives to plating and chemical conversion operations. Examples of such alternatives are listed below:

Buffing Other surface treatment operations can also sometimes be replaced by other types of processes. For instance, modern buffing and polishing techniques can preclude the need for certain surface treatment operations. An example of this is provided by the experience of Boeing Aircraft. Boeing totally eliminated their copper cyanide pre-plating treatment and replaced it with a "mush buffing" process. The copper cyanide baths were used to apply a 0.6 to 0.8 mil layer that provided leveling and thus helped fill in irregularities in the steel. The waste product from this process was disposed of expensive. Cyanide destruction from pre-plating operations cost \$1,500 per week, and in addition, required the labor of three employees. Boeing also wanted to do away with the safety hazards and liabilities associated with cyanide use.

Their approach was to improve the surface finish on the steel base metal thus eliminating the need for pre-plating to smooth the surface. An automatic mush buffing system did this admirably, finishing the surface to a smooth-

ness that allows nickel plating without the need for copper undercoat. Stainless steel, brass, and bronze parts are currently buffed on the same equipment to their final surface finish.

Unexpected benefits include a 30% drop in rejects due to the uniform, consistent surfaces produced, and the elimination of a hand-polishing step that had previously been required. The per-part production cost has remained approximately the same, although the savings in the hazardous waste disposal cost has been significant.

Chemical Coatings Chemical Vapor Deposition (CVD) is the gas phase analog of electroless plating, in that it is catalytic and involves a chemical reduction of a species to a metallic material which forms the coating. CVD coatings are very pure, thus suitable for many applications which require pure metallic surfaces. The reactions require temperatures from 600-1500° Centigrade, although work is in progress to design low temperature applications that can be used on substrates unable to withstand high temperature.

In vacuum coatings, the metal coating is vaporized in a vacuum which is low enough to ensure that most of the evaporated atoms migrate to the workpiece with few collisions with background gas molecules. The atoms impinging on the workpiece condense to a solid phase. The thermal sources used to vaporize the coating include resistance heating, induction heating, electron-beam heating, and laser irradiation.

Ion vapor deposition (IVD) was developed from vacuum deposition by McDonnell Douglas Corporation. They use IVD of aluminum as a substitute for cadmium plating on steel aircraft parts. Aluminum provides corrosion protection similar to cadmium, it can withstand 925° Fahrenheit temperatures as opposed to 450° Fahrenheit for cadmium, and

it is cheaper on a volume basis than either cadmium or zinc. Aluminum is also far less toxic than cadmium and its use in an IVD system offers safer working conditions and less environmental risk.

While IVD systems are promising alternatives to plating, they are complicated to operate and are easily contaminated. Careful training of operators is essential. If the system is installed in a plating shop, ambient gases can contaminate the vacuum chamber unless it is thoroughly isolated from them. This has been a persistent problem with the IVD system at the U.S. Navy's North Island Aviation Depot plating shop in San Diego, California.

Mechanical Cladding and Coating Metals can be bonded to the workpiece using mechanical techniques in which the coating material is forced under high pressure into contact with the workpiece. The pressure at the interface between the two metals must be high enough to disrupt and disperse boundary oxide films and initiate thermal interdiffusion and mechanical attachment. Roll bonding is a type of cladding in which one strip of metal is pressed onto another with the aid of binding rollers. Metal cladding can also be melted into place using welding or casting techniques. Cladding generally produces thick coatings compared to other methods.

Metal powders can also be coated onto the workpiece. The 3M company has developed a cold welding technique in which the workpiece, the metal powder, water, glass shot, and additives are tumbled together in a barrel. Coatings are limited to ductile metals such as Cd, An, Sn, Pb, In, Ag, Cu, Brass, tin/lead Solder; the method is generally suitable only for small parts, and doesn't produce a fine surfaced, cosmetic coating. Costs are comparable to those for electroplating with afterbake.

Reduction of Rinsewater Toxicity and Volume

Waste rinsewater accounts for the largest fraction of the waste volume produced in surface treatment and plating processes. Any method of reducing the amount or toxicity of rinsewater used will significantly reduce the total waste volume from the process. Large amounts of rinsewater are used to rinse off drag-out on metal surfaces after the metal is removed from a plating cleaning bath. Rinse water usually contains dilute solutions of bath salts such as cyanides and heavy metals. There are several methods available to reduce the amount and/or toxicity of waste rinsewater produced. The methods can be grouped into two techniques: drag-out minimization and rinsewater minimization. Drag-out minimization results in a decrease of the heavy metal content of the rinsewater and of the treatment sludge. Decreasing rinsewater consumption without reduction in drag-out may thus result in a smaller, but more toxic, volume of treatment sludge.

Drag-out Minimization By minimizing the amount of drag-out carried from a plating or cleaning bath to a rinsing bath, a smaller amount of water is needed to rinse off the workpiece. Also, less of the plating solution constituents leave the process, which ultimately produces savings in raw material and treatment/disposal costs.

It must be stressed that drag-out minimization is not effective unless accompanied by a means of purging the bath of impurities that build up and that otherwise have no outlet. Impurities such as dirt, grease, and carryover from previous process baths were traditionally purged from the plating bath by being dragged out on workpieces. As drag-out is reduced, they must be removed by means such as periodic or continuous filtration, which is discussed early in this section. Otherwise, sludge will build up, plating quality will be impaired,

and the bath will have to be disposed of sooner, raising the environmental risk and defeating the purpose of reducing the drag-out.

The plating bath can also contain impurities which cannot be removed by ordinary filtration, such as solubilized metals dragged in from previous etching baths. Ion exchange treatment can often be used for removing solubilized metals, although ion exchange systems are fairly expensive compared to standard filtration technologies.

The amount of drag-out from a bath depends on the following factors:

- Speed of workpiece withdrawal and drainage time. The rate at which the workpiece is withdrawn, the time allowed for drainage over the process tank, as well as the orientation of the work being withdrawn from the bath, affect the amount of drag-out produced.
- Surface tension of the plating solution. A plating solution with a high surface tension tends to be retained in the crevices and surface imperfections of the workpiece when it is removed from the plating bath, thus increasing drag-out.
- Viscosity of the plating solution. Highly viscous solutions result in larger amounts of drag-out.
- Physical shape and surface area of the workpiece. The shape of the workpiece affects the amount of the plating solution that gets dragged out of the bath. With all other parameters remaining the same a large workpiece surface area results in more drag-out. It is noted that barrel plating operations produce more drag-out than rack plating.

Drag-out minimization techniques typically

include:

Reducing the speed of withdrawal of workpiece from the solution and allowing ample drainage time. The faster the workpiece is removed from the bath, the higher the drag-out volume will be. The workpiece should be removed as slowly and smoothly as possible. Ample time should be allowed for draining the solution back into the tank, especially for higher viscosity solutions. Usually, 30 seconds allows most of the drag-out to drain back to the tank. However, in applications where quick drying is a problem, or where production schedules do not allow a long drainage time, a 10 second draining still permits good drag-out recovery.

Lowering the concentration of the plating constituents. A decrease in the concentration of metal salts and other components in the plating solution directly reduces the amount of hazardous substances dragged out of the bath. It also leads to lower solution viscosity, which results in less drag-out volume. Many concentration reductions have been successfully implemented. Notably, it has been found that acceptable chromium plate can be obtained from bath containing only 25-50 grams per liter CrO_3 , compared to traditional concentrations of 250 grams per liter.

Use of surfactant. Wetting agents have been used to lower the surface tension of plating solutions and reduce drag-out. A solution with high surface tension is retained in the crevices and surface imperfections of the workpiece upon removal from the plating bath. Only non-ionic wetting agents, which will not be degraded by electrolysis in the plating bath, should be employed. The use of sur-

factants is sometimes limited by their adverse effect on the quality of the plate produced.

- Increasing plating solution temperature. The increased temperature lowers both the viscosity and the surface tension of the solution, thus reducing drag-out. The resulting higher evaporation rate may also inhibit the carbon dioxide absorption rate, slowing down carbonate formation in cyanide solution. Unfortunately, this benefit may be lost due to the formation of carbonate by the breakdown of cyanide at elevated temperatures. Additional disadvantages of this option include higher energy costs, higher chance for contamination due to increased make-up requirements, and increased need for air pollution control due to the higher evaporation rate.
- Proper positioning of the workpiece on the plating rack. When a workpiece is lifted out of a plating solution on a rack, some of the excess solution on its surface (drag-out) will drop back into the bath. Proper positioning of the workpiece on the rack will facilitate drainage of the drag-out back into the bath. The position of any object which will minimize the carry over of drag-out is best determined experimentally, although the following guidelines were found to be effective:
 - ° Orient the surface as close to vertical as possible.
 - Rack with the long dimension of the workpiece horizontal.
 - Rack with the lower edge tilted slightly from the horizontal so that the runoff is from a corner rather than an entire edge.
- Improve drag-out recovery. A drain

board positioned between a plating bath and rinse bath can capture the dripping solution off the workpiece and route it back to the plating bath. The drain board can be made of either plastic or metal. For acidic solutions, drain boards can be made of vinyl chloride, polypropylene, polyethylene, or Teflon-lined steel. Another option is to incorporate a drip tank between the plating bath and the rinse bath. The drip tank is an empty tank for collecting dripping solutions, which can be returned to the plating bath.

In certain situations, air knives have proven effective in blowing droplets off the workplaces and back into the baths. Care must be taken in designing the system that droplets land in the bath and not on the floor. One wire plating operation that installed air knives at first experienced problems with zinc salts drying and remaining on the substrate, but corrected the problem by humidifying the air stream.

Another alternative is the use of a still rinse drag-out tank with contents periodically transferred back into the plating bath. Installing a still rinsing tank immediately after a plating bath allows for metal recovery and lowered rinsewater requirements. In such a system, the workpiece is immersed in the still rinse tank following the plating operation. Since the still rinse has no inflow or outflow of water, the concentration of the plating bath constituents build up in it. When the concentrations become sufficiently high, the contents of the still bath are not discarded, but used to replenish the plating bath.

Rinsewater Minimization Rinsewater can be reduced through system redesign. The aim of rinsewater minimization is to use the smallest volume of water necessary to adequately clean the workplaces. While reducing rinsewater requirements does not directly reduce the

quantity of hazardous material in the plating line effluent, it does reduce the load on the treatment plant. This can result in increased hazardous substance removal or neutralization. It can also save money through reduced water requirements. Several systems were designed for lowering the rinsewater requirements, including:

- Rinse Tank Design The most important factor in the design of rinse tanks is ensuring complete mixing of rinsewater, thus eliminating short circuiting of feed water and utilizing the entire volume. In a rinse tank in which the water distribution line is located on the bottom at the far end of the tank from where the work is introduced, incoming water creates a rolling action that mixes the tank contents, and helps to scour workplaces clean. A flow control valve can also be installed in the distribution line to restrict freshwater feed to an optimum level. A conductivity control system can be used as an alternative to flow a control valve, which measures the level of dissolved solids in the rinse tank, and opens the freshwater feed valve at a predetermined maximum solid level. Air agitation removes plating solution clinging to the workpiece surface, and also mixes the tank contents. Installing the air distribution line diagonally across the bottom of the tank helps even distribution of the air.
- Multiple Rinse Tanks. The use of multiple rinsing tanks is one of the most common rinsewater reduction techniques, and can dramatically reduce rinsewater requirements. In a typical counterflow three tank rinsing system, the workpiece initially enters the first rinse tank which has the most contaminated rinsewater. It is then moved to the second tank and then the last where it contacts fresh rinsewater. Fresh rinsewater enters only the last

(third) rinsing tank. The water from the third tank flows into the second tank and then the first tank, from which it can be routed either into the plating tank as a make-up, or the treatment system.

It is preferable to route the rinse system effluent back into the plating bath, in order to prevent release of the chemicals they contain to the environment.

A second wastewater reduction method with a high implementation potential is the reuse of rinsewater. Electroplating operations use rinsewater at several stages in the process, and it is often possible to use the same stream at more than one stage. The main problem with this technique is that the quality of the product must be monitored carefully. A rinse stream can be used a second time only if the contaminants from the first rinse do not interfere with the quality of the second rinse.

- Reactive Rinsing. This technique takes advantage of the chemical makeup of the rinsewater to not only reduce water usage, but to increase rinsing efficiency as well. For example, a typical nickel plating line might consist of the following sequence processes:

Alkaline Cleaning
Rinse
Acid Dip
Rinse
Nickel Plating
Rinse.

Water from the nickel rinse tank can be fed back into the acid dip tank, allowing nickel plating solution dragged out of the process bath to be dragged back into it. This will not harm the rinse and will allow the water feed to the acid rinse tank to be turned off. Thus, both water and process chemicals are conserved, and the quality of the toxic process chemicals

in the effluent is reduced.

The acid rinse can be further recycled to the alkaline cleaner rinse tank. This conserves water by allowing the fresh water feed to the alkaline rinse to be turned off, and also improves rinsing efficiency by helping to neutralize the dragged in alkaline solution. This will prolong the life of the acid bath because the rinsewater dragged into it will already be partially neutralized. Thus the acid bath will not have to be dumped as often.

While reactive rinsing can help save water and improve rinsing efficiency, it must be used with caution, because precipitation problems can occur when acid and alkaline solutions are mixed.

- **Fog Nozzles and Sprays.** Spraying water directly onto workplaces can rinse contaminants from it using considerably less water than immersing the part in a bath. A major limitation of spraying is that it is not effective on many oddly shaped objects, since the spray cannot make direct contact with the entire surface of the object. But for simple workplaces such as sheets, it is highly effective. A variation on the spray nozzle is the fog nozzle. A fog nozzle uses water and air pressure to produce a fine mist. Less water is used than with a conventional nozzle.
- **Automatic Flow Control.** If the lowest rinsewater flow rate that can efficiently rinse a workpiece can be determined for a process line, this flow can be automatically controlled to avoid variations arising from water line pressure changes or operator errors.
- **Rinse Bath Agitation.** Agitating a rinse bath mechanically or with air increases the rinsing efficiency and cuts down on

water demand.

- **Closed Circuit Rinsing.** Routing spent rinses into the process baths is very effective in preventing the release of toxic materials into the environment.

5.5 Recycling

Recycling and resource recovery includes technologies that either directly use waste from one process as raw material for another process or recover valuable materials from a waste stream before the waste is disposed at a hazardous waste site. At the shipyard, some of the spent chemicals from process baths and much of the rinsewater can be reused for other shipyard processes. Also, process chemicals can be recovered from rinsewaters and sold or returned to the process baths. This section describes some of the recycling and resource recovery technologies available to the metal finishing shop at shipyards.

Waste Material Reuse

The more thoroughly a metal finisher understands the chemistry of the waste stream, the better able he or she is to assess the potential for reuse as raw materials, or in other applications. Successful recycling requires an attitudinal change on the part of management and plant staff, to view their waste streams as resources, rather than as something to be thrown away.

After rinse solutions become too contaminated for their original purpose they may be useful for other rinse processes. For example effluent from a rinse tank that follows an acid cleaning bath can sometimes be reused as influent water to a rinse tank following an alkaline cleaning bath. Reactive techniques must be used with caution, because it can lead to precipitation problems.

The drag-out on the workplaces coming from the alkaline bath is alkaline. Recycled water from acid bath rinse has an acid pH, and thus tends to neutralize the drag-out film. This reduces its viscosity and accelerates the rinsing process.

Other rinsewater reuse opportunities are also available. Acid cleaning rinsewater effluent can be used as rinsewater for workplaces that have gone through a mild acid etch process. Effluent from a critical or final rinse operation which is usually less contaminated than other rinse water, can be used as influent for rinse operations that do not require high rinse efficiencies. Another option is using the same rinse tank to rinse parts after both acidic and alkaline baths.

Spent process baths can also be reused for other purposes. A common example is to use spent acid or alkaline cleaners for pH adjustment during industrial waste treatment. Typically, these cleaners are dumped when contaminants exceed an acceptable level. However, these solutions remain acidic or alkaline enough to act as pH adjusters. Alkaline cleaners for example, can be used in chrome reduction treatment. Since spent cleaners often contain a high concentration of metals, they should not be used for final pH adjustments.

Metal Recovery and Water Reuse

In the past, metal recovery from metal finishing processes was not considered economical and was rarely done. Present effluent pretreatment standards, however, have dramatically increased the cost of treatment. Also, the cost of handling and disposing of spent process baths and sludge containing heavy metals has increased significantly because of the increased regulatory requirements placed on the handling and disposal of hazardous wastes. As a result, metal finishers at shipyards may

find it economical to recover metal and metal salts from spent process baths and rinsewater and to reuse rinsewater.

The waste reduction and economic saving actually achieved through metal recovery will depend on the individual metal finishing shop. Factors that will determine whether metal recovery is economically justifiable include the volume of waste that contains metal, the concentration of those metals in the waste, and the potential to recirculate some of the metal salts. Many systems may not be economically feasible for small surface treatment and plating operations because the capital cost of installing the necessary equipment might outweigh the saving from recovering process chemicals.

Metal recovery can be achieved in two ways: recovered metal salts can be recirculated back into process baths, or recovered elemental metal can be sold to a metals recycler to be reclaimed or reused in the plating process. Some of the technologies that are being successfully used to recover metals and metal salts include:

- Evaporation
- Reverse osmosis
- Ion exchange
- Electrolytic Recovery
- Electrodialysis.

While these treatment technologies are typically used to recover chemical from rinsewater effluent, they can also be employed for spent process baths. The wastewater that is produced after the metal recovery is often pure enough to be reused for rinsing.

Recovery systems can be used strictly for rinsewater recycling and not for chemical recovery. In that case, rinsewater waste streams need not be segregated since process chemicals are not being recovered. Rinsewater efflu-

ent from a variety of plating or cleaning processes can be commingled and fed to a single, centralized recycling unit, such as ion exchange. The effluent can then be returned to the rinse system and the residual disposed as a hazardous waste.

Various methods for recovering process chemicals and rinsewater from rinsewater effluent are described below:

Evaporation Evaporation has been successfully used in a number of ways to recover plating bath chemicals. In one technique, water is evaporated from rinsewater to reduce its volume sufficiently to allow the concentrate to be returned directly to the process bath. In another technique, it is water from the process bath that is evaporated, making room in the bath for spent rinsewater to be added as make-up. The water vapor can be condensed in some systems and used in the rinse system.

There are two basic types of designs that are used: atmospheric and vacuum evaporation. Atmospheric evaporation principles are similar to those of a heated open tank, with the exception that the heated liquid is sprayed over plastic packing in order to increase its surface area and accelerate evaporation. Atmospheric evaporators on plating lines have sometimes been used simultaneously as evaporators and as plating bath fume scrubbers. Atmospheric evaporators are considerably less expensive than vacuum evaporators. Typical atmospheric evaporators capital cost ranges from \$2,500 to \$4,000, while vacuum evaporator cost can be an order of magnitude higher. With atmospheric evaporator systems, vaporized water is not recovered, as it can be with vacuum systems.

Because evaporation does not remove contaminants from the concentrate, it is necessary that the system have a method of controlling buildup of metallic and organic impurities. Additional recycling techniques such as ion

exchange can be used for this purpose.

There are limitations to the use of evaporation, one of the most serious being that it is very energy intensive methodology, and is generally only economically feasible when employed in conjunction with multistage counter-current rinse systems or other methods that reduce the quantity of rinsewater required.

Reverse Osmosis Reverse osmosis is a pressure driven membrane separation process. The reverse osmosis process uses a semipermeable membrane that permits the passage of purified water while not allowing dissolved salts to pass through. These salts can be recovered and returned to the process bath. The permeate rinsewater can then be returned to the rinse system for reuse. Reverse osmosis membranes are not suitable for solutions having high oxidation potential such as chromic acid. In addition, the membrane will not completely reject many non-ionized organic compounds, and thus other methods such as activated carbon treatment must be used in conjunction with reverse osmosis.

Ion Exchange Ion exchange can be used to recover drag-out from a dilute rinse solution. The chemical solution is passed through a series of resin beds that selectively remove cation and anions. As the rinsewater is passed through a bed containing the resin, the resin exchanges ions with inorganic compounds in the rinsewater. The metals are then recovered from the resin by regenerating the resin with acid and/or alkaline solution, and by using electrolytic recovery techniques to remove the metals from the regenerated solution. The treated rinsewater is of high purity and can be returned to the rinse system. A common use of ion exchange for process bath recovery is for the treatment of rinsewater from chromic acid process baths.

Electrolytic Recovery (Electrowinning)

Electrowinning is the recovery of the metallic content from solution using the electroplating process. It is employed to recover a variety of metals including cadmium, tin, copper, silver, and gold. In a typical electrowinning process, cathodes made of thin starter sheets of the metal being recovered, or stainless steel blanks from which recovered metal can be stripped, are mounted in an open tank. As the current passes from the anode to the cathode, the metal deposits on the cathode. This type of system generates a solid metallic slab that can be reclaimed or used as an anode in an electroplating tank. Electrowinning recovery can be performed continuously in a drag-out tank, or as a bath process on spent rinse solution.

Electrodialysis Electrodialysis employs selective membranes and an electric potential as a driving force to separate positive from negative ions in the solution into two streams. To accomplish this, the rinse solution is passed through cation and anion-permeable membrane. Cation exchange membrane allows cations such as copper or nickel to pass, while anion exchange membranes pass anions such as sulfate, chloride, or cyanide. The concentrated solution can be recycled to the plating bath, while the ion-depleted water can be recycled through the rinse system. While electrowinning is most effective for recovering metals from concentrated solution such as spent plating baths, electrodialysis is very effective on dilute solutions like waste rinse-water.

5.6 Treatment

Treatment methods for wastewater and spent process baths include neutralization of acids, as well as flocculation and precipitation techniques that remove metals and other contaminants and render the effluent fit to be disposed of in the sewer. Oxidation with chemicals are used to destroy cyanides.

Metals are generally precipitated as hydroxides or carbonates, using sodium hydroxide, lime, and other chemical reagents. Hexavalent chromium is reduced to trivalent chromium prior to precipitation. Precipitation produces sludge requiring further treatment such as dewatering and disposal as hazardous wastes. Cyanides are commonly oxidized to cyanate using alkaline chlorination chemicals such as sodium hypochlorite.

Segregation of Wastewater Since the majority of the wastewater treatment system relies on removal of metal ions through formation and precipitation of insoluble metal hydroxides, it is necessary that the metal ions in the waste stream be free and that the pH be high enough to ensure optimum precipitation. This is an important matter with waste streams that contain metal complexes that must be broken down before precipitation of the metals can occur. Segregation of the various waste streams is required to ensure that new complexes do not form. Hexavalent chromium rinse also has to be segregated from cyanide rinse.

Hexavalent Chromium Treatment While hexavalent chromium is reduced to its trivalent form in treatment systems mainly so that metal can be precipitated, this also reduces the toxicity factor by a 1,000. Ferrous sulfate is used for reduction but it is not popular due to its inefficiency, high sludge generation rate, and expense. Sulfur dioxide gas is a more popular reducing agent, although it is effective only at low pH preferable below 2. There is also a problem with atmospheric emission of SO₂ in the process.

Precipitation Treatment Effluent plating and surface treatment processes requires a pH adjustment to between 8.0 and 9.5, in order to promote metal precipitation. Optimum precipitation of zinc, cadmium, nickel, lead, and copper generally require a pH over 9. Typically

chemicals used in neutralization are sulfuric acid for lowering pH, and liquid caustic (sodium hydroxide) for elevating it. Lime slurry has also been used, but it generates considerable sludge. Careful control of pH is critical in preventing soluble metal salts from being discharged in the effluent, causing environmental problems and possibly a breach of effluent standards. Good pH control requires good tank mixing for homogeneous blending of the treatment reagents with the wastewater.

Flocculation and Clarification Flocculation involves the agglomeration of small particles into larger groupings and is done because these larger groupings have improved settling characteristics. Flocculation is thus employed to ensure proper settling of precipitates and other sludge constituents, and the discharge of clean supernatant to meet the effluent standards.

Treatment of Complexed Metals When metal completing agents are present in the wastewater special methods must be employed to extract the metal from the complex. Calcium chloride, hydrogen peroxide, and sulfuric acid have been used to break metal ion from complexes. Sodium polysulfide and sodium hydrosulfide are other agents that are used. They do not produce excess sludge, but generate a highly toxic hydrogen sulfide gas. Good ventilation and pH control are needed in any system employing these chemicals.

Dewatering of the Sludge Sludge removed from the flocculation and clarification tanks typically contains about 1.5% dry solids. To reduce waste transportation and disposal costs, it is advantageous to reduce the water content as much as possible. Centrifugal dewatering devices drive the suspended solids outward, separating them to some extent from the water fraction. The sludge produced typically has a 10% to 30% solid content.

Vacuum filtration is also common in metal finishing industries. A vacuum in this method helps to draw the sludge through filter media. Nylon or polypropylene cloth filter materials are used with fairly good results, although the best filtration is achieved when the filter belts are coated with diatomaceous earth or with paper. Sludge with 20% to 30% solid content can be produced through this method. Pressure filters have recently become the most widely used dewatering devices in the industry, due to improvements in the process. Polypropylene filter material is typically used.

Waste Segregation Segregating waste and treating it separately can also reduce sludge volume generated. By isolating cyanide-containing waste stream from waste streams containing iron or completing agents, the formation of cyanide complexes is avoided, and treatment made much easier. Cyanide itself acts as a completing agent in some waste streams and should be isolated from metal wastes if possible. Segregation of wastewater streams containing different metals from each other also facilitates metal recovery or reuse. For example by treating nickel-plating wastewater separately from other waste streams, a nickel hydroxide sludge is generated which can be recycled to produce fresh nickel plating solution.

6. PAINTING AND COATING OPERATIONS

6.1 Introduction

In many shipyards, paint waste may account for more than half of the total hazardous waste generated. Paint waste at a shipyard may include leftover sludge in paint containers, overspray, paint that is no longer usable (Non-spec paint), still bottoms from recycled cleaning solvents, and rags and other materials contaminated with paint. In many cases, the amount of paint waste generated can be reduced through the use of improved equipment, alternative coatings, and good operating practices.

6.2 Application Equipment

In order to effectively reduce paint waste and produce a quality coating, proper application techniques should be supplemented with efficient application equipment. Through the use of equipment with high transfer efficiencies, the amount of paint lost to overspray is minimized.

High Volume Low Pressure (HVLP) Spray Guns

The HVLP spray gun is basically a conventional air spray gun with modifications and special nozzles that atomize the paint at very low air pressures. The atomizing pressure of HVLP systems is often below 10 psi. The HVLP system has a “soft spray” effect that provides high transfer efficiency. The design of this gun will allow better transfer efficiency and reduced overspray than that of the conventional air gun. The low application pressure decreases excessive bounceback and allows better adhesion of the coating to the substrate.

Although improvements are consistently being made to overcome its limitations, most HVLP systems have some definite drawbacks.

- Many guns have problems atomizing the more viscous coatings and those with heavy particulate.
- The guns require a fairly constant incoming pressure; a small drop in pressure can cause inadequate atomization.
- Outdoor painting can be difficult if a breeze or wind is present.
- Although the HVLP system has a high transfer efficiency, it has a much slower application rate than that of the conventional systems.

Airless Spray Guns

Instead of air passing through the spray gun, an airless system applies pressure to the paint. As the paint passes through the nozzle, the sudden drop in pressured atomizes the paint and it is carried to the substrate by its own momentum. Pressure is applied to the paint by a pump located at a remote supply. These systems have become favorable over conventional air-spray systems for three main reasons:

- Reduced overspray and rebound
- High application rates and transfer efficiency,
- Permits the use of high-build coatings with the result that fewer coats are required to achieve specific film thickness.

One major disadvantage of some airless spray systems is the difficulty applying very thin coats. If coatings with less than a mil in thickness are required, such as primers applied to objects that require weld ability, it may be difficult to use an airless system.

Electrostatic Spray

Electrostatic spray process utilizes paint droplets that are given a negative charge in the vicinity of a positively charged substrate. The droplets are attracted to the substrate and a uniform coating is formed. This system works well on cylindrical and rounded objects due to its “wrap-around” effect that nearly allows the object to be coated from one side. Very little paint is lost to overspray, and it has been noted to have a transfer efficiency of over 95%.

Although the operating costs for this system are relatively low, the initial outlay is high and the paint viscosity requires very careful control. This system has been found to work extremely well in small parts painting applications.

In order for an electrostatic system to operate properly, the correct solvent balance is very important. The evaporation rate must be slow enough for the charged droplets to reach the substrate in a fluid condition to flow out into a smooth film, but fast enough to avoid sagging. The resistivity of the paint must also be low enough to enable the paint droplets to acquire the maximum charge.

Heated Spray

If the paint is heated, its viscosity is reduced and the coating can be applied with a higher solids content, thus requiring less solvent. When the paint is heated in a special container and supplied to the gun at 140° to 160°F, coatings of 2 to 4 mils dry-film thickness can be applied in one operation and this results in considerable savings in labor cost.

Heating the coating prior to application can be used with both conventional and airless spray applications. An in-line heater is used to heat the coating before it reaches the gun. As the coating is propelled through the air, it cools

rapidly and increases viscosity after it hits the surface, allowing for better adhesion to the substrate.

Plural Component Systems

A common problem that shipyards face when working with two-part coatings is overmixing. Once the component parts of a catalyst coating are mixed, the coating must be applied. The excess unused coating will cure and require disposal. Additionally, the coating equipment must be cleaned immediately after use.

One large advantage of plural component technology is the elimination of paint waste generated by mixing an excess amount of a two part coating. This is achieved through the use of a special mixing chamber that mixes the pigment and catalyst seconds before the coating is applied. Each component is pumped through a device to control the mixing ratio and to a mixing chamber. From the mixing chamber, the mixed coating travels directly to the spray guns. The only cleaning that is required is the mixing chamber, gun, and length of supply hose connecting them.

The drag-on left in each paint container can account for a large portion of paint waste at a shipyard. By using a large tote supply bin with a plural component system, coatings can be purchased in bulk quantities in larger containers. Often, the large tote containers can be sent back to the paint supplier to be recycled.

Alternative Application Methods

Although shipyards primarily rely on spray paint operations, some alternative methods may be used in certain situations. Mainly as a means to reduce waste associated with overspray, roll coating and dip coating methods may be used.

RoII Coating Although roll coating eliminates

problems associated with overspray, its use has many limitations that make it unfavorable for many shipyard applications. Pressure-fed rollers are available that provide a continuous supply of paint to the roller. Roll application is best suited for large, flat surfaces. Because of its lack of versatility, it is not often used in shipyard applications.

Dip Coating Dip Coating is one of the simplest methods of applying paint. It provides a quick method of coating a large number of objects. Dip coating is most practical for small parts painting, in which spray painting generates large amounts of overspray. The uniformity of the coating will depend on the rate of withdrawal. It is necessary to adjust the viscosity of the paint at the rate of solvent evaporation. After removal from the tank, particles are allowed to drain and the excess paint is allowed to return to the tank.

The applications of this type of coating are very limited. Uniform finish may be difficult to achieve. Runs or trails may appear in the areas at the lower edge where the paint runs off.

6.3 Alternative Coatings

The use of solvent based coatings can lead to high costs to meet air and water quality regulations. The disposal of hazardous and flammable waste can also cause many problems. The solvent based paint systems also present potential health hazards. In efforts to reduce the quantity and toxicity of waste paint disposal, alternative coatings have been developed that do not require the use of solvents and thinners.

Powder Coatings

Metal substrates can be coated with certain resins by applying the powdered resin to the surface, followed by application of heat to

melt the resin, causing it to flow and form a uniform coating. The three main methods in use for application of the powder coating; are fluidized bed, electrostatic spray, and flame spraying.

Flame spraying is the most applicable method for shipyards. The resin powder is blown through the gun by compressed air. The particles are melted in a high temperature flame and propelled against the substrate. This process is used widely with epoxy powders for aluminum surfaces.

The electrostatic application method uses the same principles as the electrostatic spray. The resin powder is applied to the surface electrostatically. Heat is applied to the covered surface and the powder melts to form the coating. The transfer efficiency and recyclability of this method is very high.

The elimination of environmental problems associated with many liquid based systems is one of the major advantages of powder coatings. The use of powder coatings eliminates the need for solvents and thereby emits negligible volatile organic compounds (VOCs). Powder coatings also reduce the waste associated with unused two-part coatings that have already been mixed. Since powder overspray can be recycled, material utilization is high and solid waste generation is low. Recent case studies demonstrate that powder coating systems can be cleaner, more efficient, and more environmentally acceptable, while producing a higher quality finish than most solvent based, water-based, or high solid compliance coating systems.

Plastic Flamecoats

Plastic flamecoats have not been used extensively in the maritime industry, but their value has recently begun to receive more attention. Plastic flamecoat technology uses a plastic

powder that is propelled through a flame and onto the substrate. They are applied in a similar manner as flame spray powder coatings and produce a pinhole-free surface that is not effected by many corrosive agents. This property has made thermoplastics as popular as tank coatings.

Water-Based Paints

Water-based coatings are paints containing a substantial amount of water instead of volatile solvents. Alkyd, polyester, acrylic, and epoxy polymers can be dissolved and dispersed by water. In addition to reduction in environmental hazards due to substantially lower air emissions, a decrease in the amount of hazardous paint sludge generated can reduce disposal cost.

The application for water-based coatings in the shipyard are limited. Some of the areas of use may include the inside of the superstructure of a vessel, and other surfaces that are protected from extreme conditions.

Some of the disadvantages of water-based paint applications include:

- The coating may be of inferior quality.
- Since water is not as volatile as solvents, the drying time is longer, and could slow production. It may be necessary to provide additional drying units.
- The quality of water-based coatings varies with the ambient conditions, such as temperature and humidity.
- The substrate may require additional surface preparation for proper adherence.

Thermal Spray Coatings

Thermal spray coating application is similar to

that of thermoplastics and powder coatings. Thermal spray coatings differ in that they usually consist of zinc or aluminum, rather than epoxy or plastic powder. The material used may be in either a powder or wire form. As the material is heated, it will change into molten form and can be propelled onto the substrate by compressed gas. After the object has been coated by the thermal spray coating, it is often sealed with an organic paint.

Surface preparation for this type of coating application requires that the substrate be clean and free of debris. An additional step is required to roughen the surface for proper adherence of the coating.

Two Part Catalyst Coatings

Two part catalyst coatings, such as two component epoxies, consist of separately packaged reactive resin and hardener formulations that react when mixed together to produce a coating. Care must be taken to mix the minimum required amount when using this type of coating. If the two components have been mixed, the coating must be used or be disposed. Paint waste from this type of coating can generally go to a landfill, as long as the constituents of the components are not hazardous.

6.4 Good Operating Practices

In many cases, simply altering a process can reduce waste by better management of paint waste generation.

Coating Application

A good manual coating application technique is very important in reducing waste. Most shipyards rely primarily on spraying methods for coating application. If not properly executed, spraying techniques have a high potential for creating waste, therefore; proper application techniques are very important.

Overlap An overlap of 50% can reduce the amount of waste by increasing the production rate and overall application efficiency. Overlap of 50% means that for every pass that the operator makes with the spray gun, 50% of the area covered by the previous pass is also sprayed. If less than a 50% overlap is used, the coated surface may appear streaked. If more than a 50% overlap is used, the coating is wasted and more passes are required to coat the surface.

Uniform Finish Application of a good uniform finish provides the surface with quality coating with a higher performance than an uneven finish. An uneven coating does not dry evenly and commonly results in using excess paint.

To obtain a uniform finish, gun distance should be kept constant from the surface. If the gun is too far from the surface being coated, very small amounts of the coating dry before reaching the surface, thus reducing its adhesion to the substrate. If the gun is placed too close to the surface, the coating splashes onto the surface and will result in an uneven coating.

The gun should be moved at a constant speed over the surface being coated. High speed passes result in inadequate film build and requires more passes to finish the coating. This may fatigue the gun operator and result in an uneven coating. A very low gun speed usually results in a film that is too thick. Optimal gun speed is about 250ft/min.

The spray coating should be kept perpendicular to the surface being coated. Tilting the gun results in excessive buildup in some areas.

Reducing Overspray One of the most common means of producing paint waste at shipyards is overspray. Overspray not only wastes some of the coating, it also presents environ-

mental and health hazards. It is important that shipyards try to reduce the amount of over-spray as much as possible.

At the beginning and end of each pass, the gun should be triggered. If the gun is not triggered at the end of each stroke, a build-up of the coating will occur in the area where the gun reverses direction. Many operators avoid this by carrying the gun past the edge of a surface before reversing direction. This practice generates overspray and material is lost into the atmosphere. The preferable procedure is to trigger the gun to stop at the end of a stroke and triggering the start of the spray after reversing the gun.

When the spray coat method is used, the amount of air pressure used to atomize and propel the paint should not be excessive. Excessive air pressure will result in increased overspray and emissions. In many cases, 70% of overspray can be reduced to 40% by proper air pressure adjustment.

Keeping the gun perpendicular to the surface being coated will also reduce overspray. When the gun is tilted about 45° from the surface, overspray can be as high as 65% in addition to producing an uneven coat.

Inventory Control

A major effort must be made to keep inventories at a minimum. Large inventories of paint can lead to the large disposal cost of paint that has aged and no longer meets specifications. Regulatory changes to the allowable VOC emissions limits may make a coating obsolete and cause it to be disposed.

Control over the issue of paint for a particular task can reduce wasteful usage. The quantities of paint distributed should be limited to the approximate amount required to complete a task. The issuance of large quantities can

result in wasteful practices by the operators of the painting equipment.

General Housekeeping

Small quantities are often lost daily due to poor housekeeping techniques. There is a variety of ways that can be implemented to control and minimize spills and leaks. Specific approaches to product transfer methods and container handling can effectively reduce product loss.

The potential for accidents and spills is at the highest point when thinners and paints are being transferred from bulk drum storage to the process equipment. Spigots, pumps, and funnels should be used whenever possible.

Evaporation can be controlled by using tight fitting lids, spigots, and other equipment. The reduction in evaporation will increase the amount of available material and result in lower solvent purchase cost.

Scheduling

By improving the scheduling of the products to be coated, the amount of mixing and cleanup time can be reduced. This will inherently reduce the amount of cleanup waste. If practical, products that are to be coated with the same color and type of coating should be scheduled together. If a group of objects are to be coated with the same type of coatings, but of different colors, those to be coated with the lighter color should be scheduled ahead of those of a darker color to minimize the equipment cleaning requirements.

If more than one shift of painters are used, the second shift personnel should be scheduled to start work at least 15 minutes before the first shift ends. This practice eliminates the need to clean equipment between shifts and allows the second shift to start immediately rather than

spend time setting up the coating equipment.

Paint Containers

A large amount of paint waste is generated by the paint that remains inside a can after the can is emptied and by paint that is placed in storage, not used, and becomes outdated or non-spec. Shipyards should try to consolidate paint use to facilitate the purchase of paint in bulk. Since a large bulk container has less surface area than an equivalent volume of small cans, the amount of drag-on paint waste is reduced. Large bulk containers can sometimes be returned to the paint supplier to be cleaned for reuse.

If the purchase of paint in bulk containers is not practical, the paint should be purchased in the smallest amount required to minimize residual. Workers should not have to open a gallon can when only a quart is required. Usually, any paint that is left in the can will require disposal as hazardous waste.

Spray Booth Operations

There are some fairly inexpensive technologies available for the minimization of solid and liquid waste that result from the use of water wash spray booths. In the past, the waste water from spray booths was disposed in the sewer. Regulatory changes now require these wastes to be disposed at a proper treatment facility.

The water used to capture overspray should not be disposed as hazardous waste except in extreme cases. The paint particles can usually be extracted and the water reused. By using a centrifuge separator, the paint sludge can be removed and disposed.

Dry filter booths are increasingly replacing the the conventional water wash booth. Dry filter panels are used only once before requiring dis-

posal. When laden with paint, they must be disposed, unfortunately; the filters themselves will often constitute more of the volume of a drum of waste than the paint.

6.5 Recycling

The recycling options available for paint waste are very limited. The most common recyclable waste associated with painting operations is waste solvent from cleaning operations. Methods of solvent recycling are discussed in Chapter 4.

6.6 Treatment

Resource recovery and recycling techniques are generally considered the most appropriate technologies for the disposal and waste minimization of thinners and paint sludge. If none of these methods are feasible, there are various means available for the disposal of paint associated waste.

Since the thinners and solvents in paint waste are more adapted to recycling techniques, steps should be taken to remove the thinners from the coatings. These methods of separation, as well as treatment for solvents and thinners, are discussed in detail in Chapter 4.

Treatment options for paint sludge is usually limited. In some areas, water-based paint sludge can be air dried and disposed of as solid waste. Other water-base paints can be treated through flocculation and settling to remove suspended solids. Paint sludge that is not amenable to other treatments is usually incinerated and sometimes used as a secondary fuel.

6.7 Summary

Paint waste can account for a large amount of the hazardous waste generated at shipyards. In order to get maximum usage of coatings that

are purchased, active measures should be taken to efficiently apply coatings and prevent excess waste.

7. SURFACE PREPARATION

Very few surfaces are ready to be coated without some previous surface preparation. Surface preparation can be the most important factor in coating performance. In order for the coating to be able to properly adhere to the substrate, it is important that the surface is dry and clean.

7.1 Abrasive Blasting

In order to repaint the hull of a vessel, any marine growths and the existing coatings must first be removed. The most common method of surface preparation used in shipyards is abrasive blasting. It serves as an effective and relatively inexpensive means of surface abrasion. The most common materials used are sand, steel shot, garnet, lead shot, and copper slag.

In the past, abrasive blasting was often done without much concern of how much waste was made. The expansion in regulations regarding hazardous waste disposal has changed this routine. Since many blast wastes are found to be hazardous, reducing the quantity of waste can be an economic necessity. Most blasting mediums are not hazardous themselves, but may become contaminated with paint chips containing hazardous materials. Although these paint chips are generally hazardous, they may or may not make the spent blasting material hazardous. Depending upon the local regulations, the determination of whether the media is considered hazardous will vary. If the waste is determined to be non-hazardous, it can be handled as solid waste. Spent blast waste that is not hazardous can be recycled by using it as construction fill or in cement kilns. If it is hazardous, it must go through the proper disposal means such as to a landfill

The volume of waste generated can be reduced by using blast media that is relatively easy to recycle. Not all abrasives, such as mineral

abrasives, are easy to recycle. Copper slag has a very low reuse factor and will probably be useable no more than twice before breaking down. One of the most widely used recyclable abrasives is steel grit; this is a crushed form of steel shot. While slags and sands can only be used a couple of times, steel abrasives can be recycled 50 times over. With recycled steel abrasive, care must be taken to watch that the abrasive does not become rounded. The abrasive works best if it has a sharp angular shape.

Copper Slag

Copper slag blasting media is commonly used in repair yards. This blasting abrasive is very cost effective and performs well. Due to its high copper content, it is often deemed as hazardous in its virgin state. Some local regulatory requirements may require the spent blast media to be containerized and handled as a hazardous waste. It can be recycled through use in a cement kiln.

Steel Shot and Grit

Steel shot and steel grit require a high initial outlay of capital, but they can repeatedly be reused to the point that they are more cost effective than copper slag. This media is only deemed hazardous when it is contaminated with a sufficient amount of paint chips. Some softer surfaces are suitable to be blasted by steel shot.

Improving Recyclability of Abrasive Blasting Media

In order to realize the maximum usage of reusable grit, measures must be taken to ensure its recyclability. Some media, such as steel shot, can be reused hundreds of times. It is important that the used grit is recovered as much as possible. With wheelabrator type equipment, this is done automatically. The

used abrasive may be vacuumed up or mechanically fed the abrasive to the blasting equipment. Containment of the area will allow the grit to be recovered, where otherwise it could suffer from loss to overspray. Protection from the weather, such as rain, will also prolong the life of the grit. It is very important that wastestreams, especially hazardous waste, are not mixed with used blasting media. Outside debris and other waste could render the grit unfit for use.

Often, air powered cleaning equipment is used to screen abrasive to remove large paint particles. These systems may also remove lighter dust from the heavy abrasive. This media separation can be especially important when the paint being taken off contains heavy metals. An alternative to on-site reclamation is to send it for bulk processing off-site. The U.S. Navy has examined this approach with copper slag and realized a 40% reuse rate.

Plastic Media Blasting

As a substitute for other blast media, the military has experimented extensively with plastic media stripping. This process is particularly good for stripping coatings from parts with fragile substrates such as zinc, aluminum, and fiberglass. It can be a lengthy process because it strips paint layer-by-layer. The same types and quantities of waste are generated as with grit blasting, but the plastic media is more recyclable with the use of pneumatic media classifiers that are part of the stripping equipment. The only waste requiring disposal is the paint waste itself. Plastic blasting media does not work well on epoxy paints. The blasting equipment is expensive and requires trained operators. The use of plastic media is fairly limited in shipyards.

Water Jet Stripping (Hydroblasting)

A cavitating high pressure water jet stripping

system has been developed to remove most paints. These systems may use pressures as high as 50,000 psig. The water removes hard coatings from metal substrates. The harder the coating is, the easier hydroblasting will remove it. This process can be used for stripping hulls, removing scales and deposits from heat exchangers, and removing rubber liners. Some systems are designed to remove the paint from the water and reuse the water for further blasting. By recirculating the water in this manner, the amount of waste is greatly reduced. Wastewater from this process is usually suitable for sewer disposal after the paint particles are removed. Although this process produces very little waste, it is not as efficient as abrasive grit blasting and requires high capital and maintenance cost.

Dry Ice Pellets

The use of CO₂ dry ice pellets as a blast media is still in its developmental stages. After use, the dry ice would evaporate and the paint chips could be collected for disposal. The cost of the dry ice, storage, and handling are substantial. One major disadvantage of CO₂ blasting is that there is no bounceback effect to aid in removing coatings from the sides and back of objects.

Thermal Stripping

Thermal stripping is limited in its applications. A flame or stream of superheated air is used to soften the paint and allow it to be easily removed. Although the paint waste is the only waste generated, this method is not applicable to heat sensitive areas and is very labor intensive.

7.2 Chemical Stripping

Although grit blasting is probably the most effective method of removing marine growth and hull coatings, some surfaces, such as

fiberglass, aluminum, or delicate steel parts, may require an alternative method. Chemical strippers, such as methylene chloride based or caustic solutions, may be the most applicable. Many times the surface preparation process begins with solvent cleaning to remove oil, grease, dirt, and other organic compounds. Inorganic compounds such as chlorides, sulfates, weld, flux, and mill scale are not removed by cleaning with organic solvents.

Small parts may be immersed in dip tanks containing a stripping solution. The parts must then be rinsed to remove the stripping agent. This process can often produce a large amount of contaminated rinse water. Some reduction in drag-out of the stripping agent can be reduced by allowing the parts to drain above the dip tank for a longer period of time. Waste minimization of solvent waste is discussed in more detail in Chapter 4.

Inorganic strippers, usually caustic soda solutions, can be used as a substitute for organic strippers. It is very important that residues from alkaline solutions do not remain on the surface after cleaning. Although the waste stripper is hazardous, it is much easier to treat on site by neutralization and filtration, and may then be suited for sewer disposal. The local regulatory authorities may require a permit for this type of disposal.

Special attention needs to be given to chemical stripping agents used on non-ferrous surfaces. Many solvent or chemical cleaners will react with metals like aluminum, bronze, and galvanized metals. Caustic solutions and chlorinated solvents usually cannot be used on these surfaces.

7.3 Mechanical Stripping

Mechanical stripping is one of the more primitive methods of removing coatings. This method of paint stripping involves chipping or

grinding the coating off through the *use* of needle guns, three-fingers, chipping hammers, sanders, grinders, etc. This process primarily generates paint waste, but it is extremely labor intensive and not an efficient means of paint removal. In cases in which a very small area aboard a vessel requires paint removal and setup of blasting equipment will be timely, mechanical removal may be the best alternative.

7.4 Summary

Abrasive grit blasting is the most commonly used method of paint removal in shipyards. Although many alternatives exist which may produce less waste, they are not as efficient or cost effective (the exception to this may be hydroblasting technology). Steps should be taken to implement processes that will improve the recyclability of blasting media to get maximum usage before requiring disposal as hazardous waste.

8. VESSEL CLEANING

8.1 Introduction

The term vessel cleaning covers many different areas during the repair or new construction of a ship or vessel. In many cases this work entails tank cleaning or bilge/ballast cleaning which in many cases generates a large quantity of waste which must be disposed of in an environmentally safe method. This chapter will discuss waste minimization in this area to help reduce or eliminate hazardous waste produced during this operation at a shipyard.

Vessel Cleaning Requirements

Vessel cleaning is required on all types of vessel. The cleaning operations may be for maintenance cleaning, tank inspection or minor repairs, overhaul or major repair, cleaning for a change in cargo, cleaning after a contaminated cargo, cleaning in preparation for ballasting, cleaning prior to inactivation and activation of vessel, and engine room cleaning operations such as boiler line descaling and various decreasing operations. A discussion of each of these operations follows.

Maintenance Cleaning

As a result of extended service in carrying certain types of cargo, it is necessary to clean the cargo tanks in order to maintain them in good condition. The frequency and the thoroughness required for this type of cleaning will depend on the nature of the service, the use and non-use as a ballast tank, and the type of tank coating system, if any. Vessels in crude service which alternatively run empty or in ballast will have a frequent need for maintenance cleaning since the crude products will result in heavy sludge accumulation. This is further compounded by the corrosive action of the sea water ballast. In contrast are vessels which carry clean products in coated tanks and only need flushing and seldom require cleaning for maintenance.

Tank Inspection and Minor Repairs

occasionally vessels must be inspected for leaks or to make minor repairs to pipes, valves, or bulkheads. The degree of cleaning will depend upon if cold or hot work is required during the minor repair operation. The cleaning may necessitate a rinsing, spot washing, or a complete tank washing. It is understood that gas-freeing of the area will be required during these types of operations.

Overhaul or Major Repair at a Shipyard

A vessel entering a shipyard for a major overhaul is subject to stricter regulations regarding cleanliness and gas-free condition, since these conditions must be maintained over an extended period of time. During this type of operation at a shipyard and prior to commencement of overhaul the vessel must have "safe for men - safe for hot work certification. This certification includes all enclosed spaces on a vessel.

Cleaning for a Cargo Change

The extent of cleaning required for change in cargo will depend on the preceeding cargo and the next cargo to be carried. If the cargo is a similar product, then a routine water washing may be sufficient. But if a upgrading such as a black to a refined oil is required, a more thorough cleaning and gas-freeing may be required.

Cleaning After a Contaminated Cargo

After a cargo is contaminated, the first requirement for cleaning is to determine the nature and cause of the contamination. It is then necessary to remove the contaminant from the vessel. In some cases the contamination may have resulted from improper cleaning.

Cleaning in Preparation for Ballasting

Tanks should be machine washed using butterworth equipment prior to ballasting a vessel. The dirty machine washing wastewater (slop) is treated at the shipyard or port treatment facility.

Cleaning Prior to Inactivation or Activation

When a vessel is being inactivated, tanks, cofferdams, and void should be stripped clean. The engine room cleaning will depend upon the type of power system (steam versus diesel) If the vessel is being activated, the extent of cleaning will depend upon the cargo and engine room condition.

Various Types of Vessel Cleaning Operations and Waste Reduction Methods

8.2 Tank Washing Operations

Generally tankers and oilers have tank washing machines which are usually a hydraulically rotated nozzle device attached to a hose and inserted in the tank. The nozzle is a small and self-contained and constructed of non-ferrous metals to eliminated the possibility of spark generation. Pressurized water is supplied to the machine through the hose. The nozzle automatically rotates causing the stream to strike the surfaces either directly or indirectly. This method of tank cleaning is superior over hand cleaning since higher pressure and higher temperatures can be used. The cleaning processes with machines is reduced in time and surface cleanness is improved. The stripping pump removes the accumulated wash water. The stripping operation also drains the bottom of oil, water, and washing which drain down from the upper sections of the tank. The slop is normally accumulated in the centerline tank from the stripping operation and discharged ashore by a main cargo pump.

Pipeline Cleaning Operations

During the machine washing operation the lines are normally cleaned by stripping each tank separately through both the main cargo and stripping suction lines. On completion of the routine machine washing, hot water is circulated through all main cargo and stripping lines to remove any oil.

Mucking Operations

This operation consists of removing scale sediment and sludge which has accumulated on the tank bottom during the machine washing or hand washing operation. It is accomplished by scraping, sweeping, and shoveling the scale, sediment, and sludge into containers for disposal. This material, in the majority of cases, is hazardous waste. In some cases educators and large capacity vacuum pumps are used to remove the waste material more rapidly. Hand hosing is usually used in the final operation in tank bottom cleaning processes.

8.3 Chemical Cleaning

Various chemical agents are used to assist in the tank cleaning process. The chemicals are usually detergents used with hot water to break down the oil on the tank surface. Solvents should not be used due to the increased disposal cost of these contaminants in the waste stream especially halogen solvents. In some cases, the chemical cleaning solution can be reused in another tank due to the extended life of the solution. This helps reduce the waste water generated. In addition, the final rinse water can sometimes be reused on another tank to extend the rinse water usage and reduce wastewater generation.

Chemical Spot Washing with Printable Units

Chemical spot washing can be effectively accomplished by using steam cleaning units.

These units deliver a high-velocity jet stream which can penetrate difficult and remote cleaning areas. A hand lance is used to direct the spray application.

Brush Application of Chemical Cleaners

When the spot washing is not extensive, the chemical mixture can be applied by brush with proper protection. This eliminates waste by overuse of chemical cleaner and reduces the waste generated.

Chemical Cleaning Using Ballast and Soak Method

The ballast and soak method consists of ballasting, adding chemicals, and soaking. This method is restricted to small tanks and bilges and large tank bottoms. Normally the solution is heated prior to application to increase the cleaning action and penetration of the chemical.

8.4 Engine Room Cleaning Methods

Carbon Removal

The cleaning of carbon deposits from engine and power systems is an essential part of maintenance on vessels. The cleaning process usually involves soaking the part or equipment in a bath of heated cleaning solution. The time required for cleaning depends upon the hardness of the deposit and the type of base metal. Care should be used with caustic cleaning and aluminum based metal.

Decreasing Operations

This cleaning operation involves the removal of grease and oil from various metal operations. Alkaline detergents are better cleaning agents than solvents due to the disposal and air emission problems associated with these types of cleaning methods. Steam cleaning increases

the cleaning process and reduces the wastewater generated in certain cases. Heated alkaline baths are currently the most common type of cleaning systems for parts. In many cases, new biodegradable cleaning agents are becoming common on the market and are being reused or treated by recycling companies such as Safety Kleen.

Descaling Operation

Descaling operation refers to the removal of oxide layers that form on metal surfaces. The removal is usually done by pickling the surface with a dilute acid solution. In many cases an abrasive blasting or sanding method can be used in place of the pickling process to prevent the generation of waste acid. Many vessel power systems such as boiler and heat exchanger and cooler systems require acid cleaning to remove deposits. Waste reduction can be achieved by using the correct amount of solution to treat the boiler system thus minimize the quantity of waste acid generated during the cleaning operation.

Preservative Compound Removal

Preservative compounds are normally removed by wiping or rinsing the surface with standard solvents or by boiling or recirculating a hot solution consisting of about 2 percent sodium metasilicate solution. Removal using a hot solution is best to reduce the exposure to solvent fumes and reduce the disposal cost of solvent over a water solution.

8.5 Tank Cleaning Waste Water Treatment

The most common type of treatment of tank cleaning waste water is with chemical precipitation to remove metals other than hexavalent chromium. Chemical precipitation refers to both the primary steps of forming the insoluble metal precipitates from dissolved metal ions by the precipitant(s), and follow-up oper-

ation that separates the solid precipitates from the tank cleaning waste water.

There are two treatability groups of dissolved metals for chemical precipitation, complexed and non-complexed metals. Non-complexed metals can be removed by direct precipitation with a chemical such as lime ($\text{Ca}(\text{OH})_2$), Caustic (NaOH), sodium sulfide (Na_2S), ferrous sulfate (FeS), or sodium carbonate (Na_2CO_3). Complexed metals required co-precipitation with ferrous sulfate (FeSO_4), ferrous chloride, or sodium dimethyl dithiocarbamate (DTC) in addition to regular precipitant such as caustic or lime.

Lime or Caustic Precipitation

Lime or caustic precipitation is the most commonly used method of treatment of aqueous tank cleaning waste water with non-complexed metals. Alkaline reagents such as lime, or caustic rises the pH of the waste water and causes the metals to precipitate out of the solution as metal hydroxides. For metal there is a specific pH at which the metal hydroxide is least soluble. Since metals such as copper, zinc, nickel, and lead co-exist in the waste water, it is not always possible to operate a waste water treatment system at a single pH value that is optimum for all metal removal. As a compromise, a pH between 9.0 and 12.0 is selected on a treatment system to remove a metal from waste water generated from a tank cleaning operation.

In typical waste water treatment system, lime or caustic is added to a reaction vessel and converts the dissolved metal ions to insoluble metal hydroxides. The metal hydroxides are subsequently separated in a clarifier or settling tank or are filtered using ultrafiltration filters, followed by sludge dewatering using a filter press. Because metal hydroxide tends to be colloidal in nature, coagulating agents, such as polyelectrolyte, are added for effective solid removal.

If the treated waste water has a high pH, neutralization will be required before discharge to the POTW or receiving water if permitted within the shipyards NPDES permit.

Completing Agents:

Many compound soaps or other cleaning agents used in tank cleaning operations may contain strong completing agent such as EDTA. Tank cleaning waste water containing completing agents requires a two step precipitation for metal removal.

Step 1: Acidification of the water is needed to break up the complexes and transform the metals to a "free" form. This can be accomplished by lowering the pH to 2-3. To prevent recomplexation of completing agents, a reducing agent such as ferrous sulfate or ferrous chloride is added at the low pH waste water.

Step 2: The pH is then raised with caustic or lime. As the pH is increased, the free metal in the water precipitate as metal hydroxides.

Other waste characteristics affecting precipitation performance are the presence of oil and grease or surfactant. The presence of these materials affects the settling characteristics of the sludge by creating emulsion requiring a long settling time. Removal of these constituents (by adding a demulsifiers and skimming oil) from the waste water before treatment as mentioned above.

9. PHOTOGRAPHIC PROCESSES

9.1 Introduction

Photography is the process of rendering optical images on photosensitive surfaces. Wastes from photographic processes are low in volume and toxicity, but, as with all wastes from industrial sources, they are under scrutiny and minimization is desired.

There are two major operations in photographic processes: developing negatives, and printing the negatives onto paper. (See Figure 9.1.) To develop negatives you must utilize film developer, bleach, a film processor or fixer, and a stabilizer. To print these on to paper, only bleach-fix and developer is used.

Black and white photographs are produced in a different way from their full-color counterparts. Both processes, however, use similar chemicals and have similar methods of waste disposal. The color negative and print-making process works in the following manner: the film goes into the developer, then a bleach, then it is washed. Next it goes to a fix, and it is washed once more before it enters the stabilizer. The color negative is then complete. The photographic paper is put in the developer and then into a bleach-fix. Next it is washed and the finished print results. Most photographic laboratories make use of wash water in their processes. This will have a net effect of increased volume but decreased toxicity of the effluent from these labs.

9.2 Sources of Waste

In almost all photographic processes, the only hazardous chemical used is the fixer. The fixer contains traces of heavy metals which may exceed the limits of the local sewer authority. Usually all of the other chemicals used can be legally disposed of in the sewer unless they have become toxic through contact contamination.

Non-Hazardous Waste

In most areas, "chemicals such as bleach, wash water, developer, and stabilizer, can be legally disposed of in the sewer. The toxicity of these fluids is low, and the few toxic constituents that they do have will not disrupt the treatment process in sewage treatment facilities.

Hazardous Waste

The primary light-sensitive constituent in a photographic process is silver. Silver is a hazardous material and its disposal is regulated. Other hazardous materials that can be found in the effluent from photographic shops include: chromium, zinc, cadmium, phenol, cyano complexes, hydroquinine, ammonium, phosphates, nitrates, and detergents. Although these materials can be regarded as hazardous, the amounts that are found in a photographic shop effluent are so small that they are considered negligible.

Because silver is a precious metal, it is often worth the effort to recover the silver that remains in the fixer. Usually, the fixer itself can be disposed of in the sewer after the silver has been removed. The negatives and photographs also contain small quantities of silver, and it should be extracted prior to disposal.

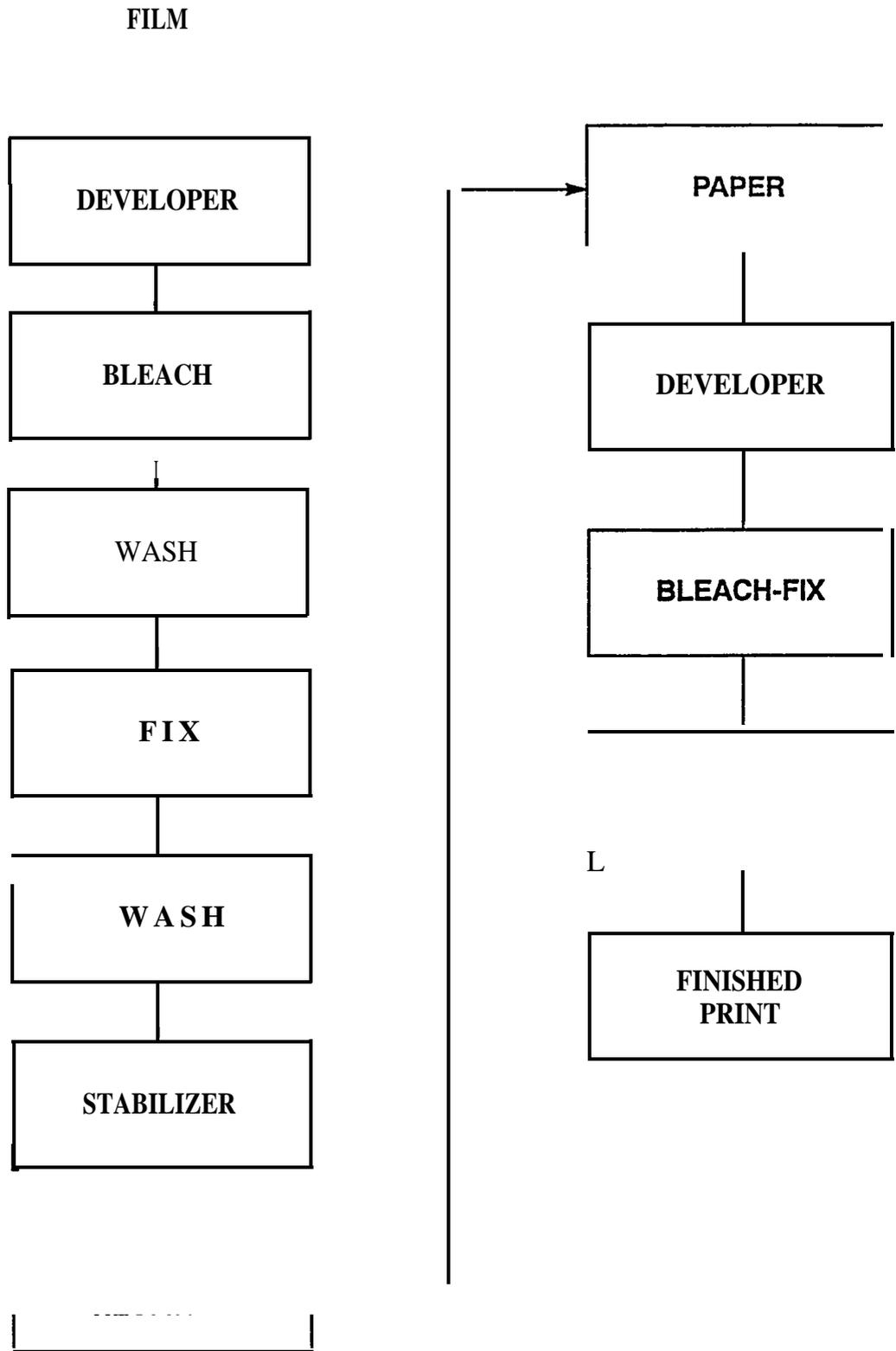


Figure 9.1 Typical Stages in a Photographic Process

9.3 Waste Management

New regulations and tight restrictions make it increasingly important to have good waste management practices. Hazardous wastes need to be stored in designated collection zones and these zones need to be closely monitored to prevent contamination of surrounding land or nearby waters.

Disposal

Disposal of photographic waste is not difficult. Usually, once the silver has been removed, the remaining chemicals can be disposed of in the sewer. Depending on the method of silver removal employed, either metallic silver or a silver chloride sludge will be the final waste stream.

If the silver is not removed, the waste fixer must be disposed of as hazardous waste. The rinsewater and the prints are contaminated as well as the fixer and any other fluid that comes in contact with these chemicals. The effluent from the shop in this case will be minimally hazardous, but the volume could be large and it may be costly to have this material shipped out regardless of its low toxicity.

costs

It is not uncommon to see costs upwards of one thousand dollars for disposal of a fifty-five gallon drum of hazardous waste. It usually does not come as one fee, rather it is hidden among many small fees such as waste determination, transportation, disposal site profile, acceptance into the disposal site, incineration, etc. This should be considered when the raw materials are being purchased, and it should help determine whether a waste minimization program would be profitable.

9.4 Waste Reduction

The way to reduce hazardous waste from the photography lab is to have a silver-removal method on-site. Once the silver has been removed from the effluent, most or all of it can be disposed in the sewer.

Incentives

A significant incentive for waste reduction in the photographic lab is the money that can be saved by removing silver from the effluent. It is not so much the value of the silver itself, but the reduced quantity of hazardous waste that will result from silver removal. The recovered silver may also contribute to the cost benefits of the program, although the quantity and the quality of the silver recovered is usually low.

Methods

There are many different proven methods for waste minimization in the photofinishing industry. The main thrust of the program should be toward silver recovery but there are also other methods that should be employed in conjunction with that process.

A simple thing that should be done is to use a squeegee between photographic baths. This will squeeze off the excess liquid to reduce drag-out to the next bath and contamination. Non-absorbent "twin-checks" can be used to identify negatives. This will also reduce the amount of chemicals carried over to the next bath.

Changes can be made in the initial purchasing for the lab that can result in a reduced waste stream. To accomplish this, chemicals that are less hazardous should be used. For example, in the photographic lab, chemicals that contain heavy metals or trichloroethylene should be avoided.

It is also a good practice to utilize floating lids on the developer and bleach containers. This will protect the chemicals from airborne particles and from direct prolonged contact with the air which can produce undesirable oxidation.

There is a waste reduction method called counter-current washing that effectively recycles the wash water. Clean water must be used in the final rinse but the wash water in earlier stages is not required to be as pure. When the water in the final rinse is no longer clean enough to be used in that stage, it is still possible to use it in the first film rinse. This can usually be done by changing a procedure and will not require a capital expenditure.

Most developers and fixers can be recycled. This should be done and the proven process of bleach regeneration should be used. The bleach-fix can also be recycled on-site through the addition of specific chemicals.

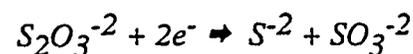
Silver Recovery

Silver recovery is achieved primarily through two methods: metallic replacement and electroplating. Other methods exist but they are much less popular due to high capital investment and because they require constant attention from workers with high technical expertise.

Electroplating works in the following way: The fluid is passed through a channel with two charged electrodes. A controlled DC current flows between the electrodes and the silver plates-out on the negative or cathode side. The silver is then periodically chipped off the cathode and can be sold to create extra revenue. This method is popular because the silver produced is in an almost pure form.

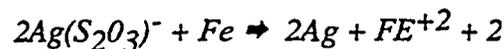
Disadvantages are the relatively high capital investment, the difficulty of producing an

effluent with very low silver content, and the constant need to adjust the current. Current must be closely monitored because an improper amperage will cause the formation of silver sulfide according to the following equation:



This sulfide can coat the electrodes and make the plating less effective or lower the quality of the silver produced. Despite these minor grievances, electroplating remains one of the most popular methods of silver removal.

The other predominant method of silver recovery is metallic replacement. In this technique, the silver solution is passed through a cartridge which is filled with steel wool. The more active metal (iron) reacts with the silver thiosulfate and goes into solution. The less active metal (silver) settles out as a solid. The reaction proceeds according to the following equation:



This method is popular because of the low capital investment and because the silver content in the effluent is reduced to very low levels.⁶

The disadvantage is the fact that spent cartridges cannot be reused, rather they must be constantly replaced at thirty to sixty dollars each. Also, the recovered silver is in the form of a sludge and requires further processing. Furthermore, the effluent from the cartridges is usually high in iron and may be unacceptable to some sewer codes.

9.5 Summary

Waste minimization is a goal set by all industries for ecological and other reasons. Waste minimization in the photographic lab is especially desirable because it is relatively easy to do and substantial amounts of money can be

saved. The following is a summary of the steps that should be taken in a waste minimization program for a photographic laboratory:

1. Take accurate measurements of the quantities of products coming into the lab and of the effluent going out.
2. Examine the possibility of utilizing methods of waste reduction that do not require large capital investment such as using squeegees, counter-current washes, in-process recycling, floating lids, or less hazardous chemicals.
3. Decide on the method of silver recovery that best suits your needs depending on the amount of effluent produced and local sewer code requirements.
4. Do an economic analysis to determine the cost of the recovery unit as well as the upkeep. Then determine the amount of money that will be saved by putting this unit on line. Calculate the payback period, if there is one, and if cost effective, implement the system.

10. LUBRICANTS AND USED OIL AT SHIPYARDS

10.1 Introduction

Used oil and lubricants present a complicated problem from a regulatory standpoint. Oil products represent a valuable non-renewable resource and should be recycled when possible. Used oil frequently contains contaminants that can pose substantial environmental and health risks if managed improperly. Regulating used oil presents some special problems. Simply defining all used oil as the same material is difficult because oil is used for so many different applications and varies widely in chemical composition. Each application demands a different additive ingredient, and introduces different contaminants through its use. Approximately 1.2 billion gallons of used oil are generated each year by hundreds of thousands of generators. Approximately two-thirds is recycled, primarily for use as fuel. The abuse of the used oil management system as a dumping ground for hazardous waste is another factor that has highlighted the need for regulations of used oil and lubricants.

Statutes

Congress recognized the need to address this problem, and in 1930 and 1984 enacted legislation amending the Resource Conservation and Recovery Act (RCRA) that establishes specific goals and provisions for regulating used oil. The Used Oil Recycling Act (UORA) of 1980 mandated the EPA to promulgate regulations establishing standards to protect the public health and environment from the risks posed by improper management of used oil.

The Hazardous and Solid Waste Amendment of 1984 (HSWA) established additional mandates and provided additional constraints on the regulations of recycled used oil consistent with Congress earlier stated goals. These amendments established a special provision within Subtitle C (Hazardous Waste

Management) of RCRA that authorizes EPA to develop a separate regulatory framework for recycled used oil, regardless of whether it is listed or identified as a hazardous waste.

Regulations

In response to these mandates and constraints, the EPA has conducted a number of studies, has promulgated regulations to restrict burning used oil, and is developing other regulations to bring used oil under broader regulation control.

The existing regulation (40 CFR part 266, Subpart E) was promulgated on November 29, 1985 (50 FR 49164), and contains administrative requirements and restrictions on used oil that is burned for energy recovery. Used oil that is not used for energy recovery is currently not regulated unless it has been mixed with a listed hazardous waste.

The rule establishes a used oil fuel specification consisting of six parameters including four toxic metals, flashpoint, and total halogens. Used oil fuel that meets the specification is conditionally exempt from regulations, while off-spec used oil is subject to certain restrictions and requirements. The requirements include recordkeeping and use of invoice, notification, and require notices. Under the rule, "off-spec" used oil can only be burned in devices such as industrial boilers and industrial furnaces. A new regulation passed concerning the burning of hazardous waste in industrial boilers and industrial furnaces (EPA's BIF Regulations).

Mixtures of used oil and listed hazardous wastes are subject to more stringent hazardous waste management regulations. The used oil fuel rules (40 CFR part 266 Subpart E) establish a rebuttable presumption as a means for determining when mixing used oil and haz-

ardous waste has occurred. Under this provision, used oil containing greater than 1000 ppm of total halogens is presumed to have been mixed with hazardous waste. The presumption can be rebutted by showing that the source of the halogens is not a listed halogenated solvent.

In November 1985 EPA published two proposals that would bring used oil under broader regulatory control. Both of these proposals generated a great deal of concern within the regulated community. The major concern was that the listing would increase cost and create a stigma associated with the listing such that it would disrupt the used oil management system and be environmentally counterproductive to current recycling efforts.

On November 19, 1986 (51 FR 41900) the EPA published a final determination not to list used oil bound for recycling as a hazardous waste under RCRA, and set out a strategy to decide how to control used oil bound for disposal. The proposed management standard and certain other initiatives were deferred pending the outcome of the decisions on disposal controls.

On October 7, 1988, the Court of Appeals of the District of Columbia found that the EPA acted contrary to law in its determination not to list used oil under RCRA section 3001 based on the stigmatic effects. The court ruled that the EPA must determine whether to list any used oil based on the technical criteria specified in the statute.

Currently the EPA is reviewing new data due to the "unrepresentativeness" of the 1985 data and the age of the data. Finally, the promulgation of the toxicity characteristic (TCLP) (55 FR 117978, March 29, 1990), is known to identify certain used oils as hazardous and these findings will be reviewed with current collection of data. On September 23, 1991, a

notice of proposed rule making was issued on the identification and listing of used oil as a hazardous waste. EPA will use the comments and data collected to make a final decision to list some or all used oil as hazardous waste, as proposed in November 1985.

10.2 Description of Process Operations That Use Lubricants

There are hundreds of different types of oil used for a wide variety of purposes in the shipyard and on ships. Some, such as engine lube oils, are formulated to satisfy a wide range of engine types and uses. Other oils may be formulated for special applications where each operating department requires a special additive or specific properties to suit their needs.

A brief description of some of the major types of oils follows.

Fuels Fuels can become used oils if they are contaminated and cannot be used for their original purpose. Fuels are also the most common means for disposal of used oils. Two major types of fuel are used at a shipyard, distillates and residuals. As implied, distillates are products which are distilled to produce specific boiling ranges for various engines such as gasoline, diesel and clean burning fuels (boilers). Residual fuels (# 4, 5, 6 bunker, etc.) may be mixtures of distilled and undistilled petroleum fractions blended to meet specific flash points, viscosity, sulfur, BTU, and other properties.

Erwine Lubricants Gasoline engine lubes may contain from 10% to 30% additives and may be made from paraffinic and/or naphthenic petroleum oils. Synthetic oils are also used. Truck lubes require somewhat higher detergency than passenger cars and a high viscosity index (VI) to ensure good cold-starting characteristics.

Diesel engine lubes require a relatively high level of detergency to minimize the effects of soot formation in the combustion chamber. In addition, high compression ratio of diesel engines creates very high piston ring zone temperatures. This requires lubricants with good oxidation stability (paraffinic-base stock). Diesel lubes use high alkaline detergent additives to neutralize some of the effects of high sulfur diesel fuels.

Hydraulic Fluids Petroleum-based materials are used for many applications. These materials are similar to lube oils but generally contain a lower percentage of additives.

Synthetic Fluids These fluids are employed where fire resistance is required. These fluids consist of phosphate esters, polyglycols, polyolifins, silicones, silicate esters, and halogenated hydrocarbons such as chlorofluorocarbon polymers, fluoroesters, and blends of these compounds.

Transmission Oils Petroleum based oils are generally used for these applications with special additives to provide shear resistance. Some synthetic oils are also used.

Cutting and Cooling Oils These oils may be petroleum or synthetic oil formulations. The latter are used where fire resistance and high stability are required. Additives are used to impart special properties such as shear or high pressure resistance. Emulsifiers may also be included to enable use as a 1% to 2% water emulsion or to provide the ability to wash off the oil after a cutting operation.

Bilge and Ballast Oils Ships generate large volumes of oil/water mixtures either from bilge or ballast tanks. These oils vary considerably depending upon the fuels used and the oil transported. While the concentration of the oil in water may be only a few ppm to 2% by volume, the quantities generated are often so

large that the separated oils can amount to significant volumes.

Building-Ways Lubricants Building-ways generate large volumes of launching greases (basecoat and slipcoat) that are used for launching or moving ships on sliding ways. The base coat is a paraffin wax and the slipcoat is usually a calcium base petroleum grease.

10.3 Source Reduction or Minimization

One of the first objectives of any oil management program is the minimization of the volumes of used oil generated. Also included in this category of management is the minimization of contaminants, which reduce the value of oil for recycling purposes. Listed below are ways to accomplish minimization.

Extending the Useful Life of the Oil

Following is a list of ways to accomplish this objective, along with some related concerns.

Increase the Period Between Oil Changes In effect, this would allow the oil to get dirtier between changes. This may be acceptable under certain instances, but could jeopardize engine warranties, wear, or performance characteristics. Some automotive engines have run over 50,000 miles between oil changes, but this is not recommended for the average user. Large shipyard users can justify oil quality testing to maximize use times.

Use a Better Oil A higher quality oil may prove cost-effective. Synthetic lube oils have better wear properties but many engine warranties may be voided if the lubricant is not changed on a specific schedule, thus negating the advances of synthetic lubes in some cases.

Check Seals and Gaskets Reduce contamination by checking seals and gaskets frequently

to minimize contamination.

Control Operating Conditions Control is required to avoid excessive temperatures that tend to degrade oil. Operating at extreme loads can have the same deleterious effect.

Segregation

Segregation is the key to a successful reclamation and cost reduction program. The most common types of contaminants that are often easy to eliminate are noted below.

Low Flash Point Gasoline, carburetor cleaner, paint thinner, and other volatile materials, when mixed with used oils, create several problems in reclamation and/or disposal.

Chlorinated or Freon Solvent Mixing these materials with unused oils should be avoided since they severely reduce the potential for reclamation.

Synthetic Oil and Fluids It is often profitable to segregate these materials from used oil since the synthetic materials can be reclaimed separately. Currently, synthetics can be used as plasticizers if contamination does not exceed about 2% to 5%.

Waste Exchange

Waste exchange or downgrading are the same activities. Generally, waste exchange is downgrading to an off-site facility, whereas downgrading is an on-site activity. Some states, areas, and industries have extensive waste exchange operations. This can be very beneficial. An example is the use of a high purity oil after drainage for another less critical application. A common use is to emulsify and use the oil as a cutting or cooling oil. Some used lubes could also be used as quench oils.

On-Site Contracted Services

There are a number of companies that provide mobile units for all treatments. For example, certain lube oils are commonly reclaimed by treatment to remove volatile hydrocarbons, water, and accumulated solids. Equipment to accomplish this can be provided by outside contractors who service on-site units.

Cutting and cooling oils can also be reclaimed by similar services. These emulsified oils can degrade biologically and emit objectionable odors. Also, oils may accumulate or separate out (tramp oils) which need to be removed or reemulsified. Contracted services can provide equipment and manpower to reclaim such oils.

10.4 On-Site Recycling and Resource Recovery

On-site treatment for reclamation of oil should be limited to physical processing such as centrifugation, coalescence, distillation-evaporation, stream stripping, and graving settling. A description of the most common unit operations and their application to on-site reclamation is briefly discussed below. A complete system for oil reclamation may contain one or more of the following unit operations.

The Control Technology for Removal of Oil and Grease

The control technology for oil and grease removal varies in complexity and the basic processes are involved in the collection and recovery of the oil and removal of the desired pollutants before discharge to the receiving system (receiving waters or POTW). The treatment of the waste water to remove pollutants other than oil and grease will not be covered in this section.

Oil and grease contained in the waste water from shipyard operations or in bilge and ballast systems on ships can be removed by the use of widely accepted techniques. Since the removal of the oil and grease depends on the condition of the oil-water mixture, the type of equipment must be carefully selected. The type of oil-water mixture may be classified as oil and grease present as free oil, dispersed oil, emulsified oil, or dissolved oil. Free oil is usually characterized by an oil-water mixture with droplets greater than or equal to 150 microns in size while a dispersed oil mixture has a droplet size range between 20 and 150 microns, and an emulsified oil mixture will have a droplet size smaller than 20 microns. A wastewater with an oil-water mixture where the oil is said to be soluble is a liquid where oil is not present in the form of droplets (oil particle size would be less than 5 microns). Soluble oils can be selectively extracted by varying degrees by solvents if extraction is needed.

Centrifugal Separators Centrifugal separators can be used to separate solids from used oils when settling rates need to be enhanced and gravity separation requires a long residence time or when space limitations require small volume equipment. Disadvantages of this type of separation are large power requirements and in effectiveness when solids are trapped in emulsions.

The most common type is the mechanical centrifuge. The simplest mechanical centrifuge is the tubular design which is a high speed small diameter bowl. Normally it is fed at one end with separated liquid removed at the other end through effluent take-offs at different radii. The machine capacity is limited to about 20 gallons per minute.

The most common type today is a disk-type centrifuge which is often operated to generate forces up to 9,000 times that of gravity. Figure

3 gives an example of a vertical bowl with feed entering from the top axis. The inclined disks aid in the separation by a mechanism similar to plate settlers. The oil or light liquid moves to the top of the disks and travels to the center of the bowl. The water or heavy liquid and any solids moves to the outer wall of the bowl. Capacities of disk machines range from 5 to 500 gallons per minute. The specific gravity differences should be greater than 0.01 and droplet sizes greater than 1 micron.

Coalescers This treatment provides a large surface area media that attract one phase of an emulsion (e.g., water) and repel the oil phase. For media and water removal, emulsion of used oil is pumped through the media and water droplets attracted to the surface coalesce and are separated and removed. Often, filtration and coalescence are accomplished together in a combined unit called a filter-coalescer. Such units are commonly used to remove solids and water from fuel oils and other distillate fuels. Coalescers can remove water from oil down to levels of 5-10 ppm oil depending on the quality of input and system design.

The most common coalescers pass the phases through some type of solid bed, fiber mesh, metal screen, or membrane. The actual mechanism for coalescing using a solid surface is not well understood. A mesh or cartridge of fiber is the most common type. Polypropylene, nylon or polytetrafluorocarbon fibers are common for oil and water separation. Glass and glass treated fibers can be used. The fiber size or media pore size decreases with the need to handle smaller droplet sizes. Various single material coalescers are available. A big use for coalescers application is the removal of low concentration of droplets less than 20 microns in diameter as a polishing unit after other separation techniques are being used. Coalescers have their problems. The pore size in the elements are small and the stream needs to be free of solids. Most vendors recommend a pre-

filter to remove solids. Even then, especially with emulsions, finely divided solids are removed in the coalescing elements and require a periodic backflushing or replacement of elements. For situations where solids are a problem, a packed bed similar to a deep bed filter can be used with a periodic backflush.

Filters A wide range of filters are available to separate solids from used oil streams. The nature of the filter media and design of the unit will depend on the particle size and concentration of the solids to be removed. Typical filter media include sand, clay, and fibrous material which can be also selected to coalesce and remove water.

Gravity Separators The primary function of an oil and water separator is to separate free oil from wastewater. Such gravity separators will not separate oil droplets smaller than the size of the free oil nor will it break down the emulsion. The three main forces which act on a discrete oil droplet are buoyancy, drag, and gravity. The buoyancy of the oil droplet is proportional to its volume and the drag is proportional to the area of the droplet. As the diameter of the oil droplet decreases, the ratio of its volume to the surface area also decreases. Because of the droplet size relationship, larger droplets tend to rise while smaller droplets tend to remain suspended. With particle diameters greater than 150 microns, the rate of rise (ft/min) of oil droplets in waste water may be expressed as:

$$V_t = 0.0241 (S_w - S_o/u)$$

where

V_t = rate of rise of oil droplet in wastewater (ft/min)

S_w = specific gravity of wastewater at design temperature of flow

S_o = specific gravity of oil in wastewater at design temperature flow

u = absolute viscosity of the oil in waste water at design temperature, in poises

An API Separator is based upon the concept of the rising oil droplet as expressed above and is based on the following four relationships.

$$A_h = F(Q_m/V_t)$$

$$A_c = Q_m/V_h$$

$$d/B = 0.3$$

$$L = F (V_h/V_t)d$$

where

A_h = minimum horizontal area, in sq ft

F = design factor for turbulence and short-circuiting factor

Q_m = wastewater flow, in cubic feet per min

A_c = minimum vertical cross-sectional area in sq ft

V_h = horizontal flow velocity, in ft/min, not to exceed $15 V_t$ or 3 ft/min

d = depth of wastewater

B = width of separator chamber, in ft

L = length of separator chamber, in ft

When a free oil or dispersed oily water mixture is brought to a quiet state within a sufficient amount of time, the oil droplets will coalesce and separate from the waste water forming a floating oil layer which can be separated from the wastewater by skimming off. Figure

10.1 shows the effect of the retention time on the oil separation by gravity separation. This figure shows that a drastic reduction in oil removal (approximately 70 percent) can be achieved within 40 minutes and little improvement of oil removal can be seen after two hours of retention time.

The use of dissolved air flotation devices in a gravity separator is a technique used in the removal of oil and grease from wastewater. This techniques tends to be more effective than just API separators because of the buoyancy differential by inducing small air bubbles. Coagulant aids such as polyelectrolyte are commonly used to promote agglomeration of the oily wastewater into large flocs which are more easily removed. Dissolved air flotation devices have been reported effective in producing effluents with 1-20 ppm of oil and grease.

The use of chemical coagulant, such as alum and iron salts, has been an aid in the dissolved air flotation process by emulsion breaking when needed. These chemicals function by modifying the liquid/liquid and liquid/air surface properties. For instance, the coagulant serves to decrease the interracial tension between the dispersed oil phase and the waste water and increase the interracial tension between the air bubble and oil phase. As a result, the chemical and physical phenomena

tend to increase air bubble-oil droplet adhesion. With proper operation a dissolved air flotation unit can remove oil and grease globules greater than 40 microns.

10.5 Off-Site Recycling and Treatment

Recycling Programs at Refineries

Recycling processes treat used oil so that it meets the standards defined by EPA and industry. Recycling includes reprocessing and re-refining. Reprocessing removes some of the solids, organic contaminants, and water contained in the oils. Reprocessed oils are generally used as fuels. Some reprocessing techniques are simple and inexpensive, such as gravity settling and blending. Others are more complex, such as distillation and solvent extraction. There are currently about 300 reprocessors in the United States. The most commonly used reprocessing steps are:

- 1 Blending to meet standards
- 1 Gravity settling to remove heavy particulate, tramp oils, and water
- 1 Heating to facilitate physical separation
- 1 Coalescing/skimming to separate oil from water

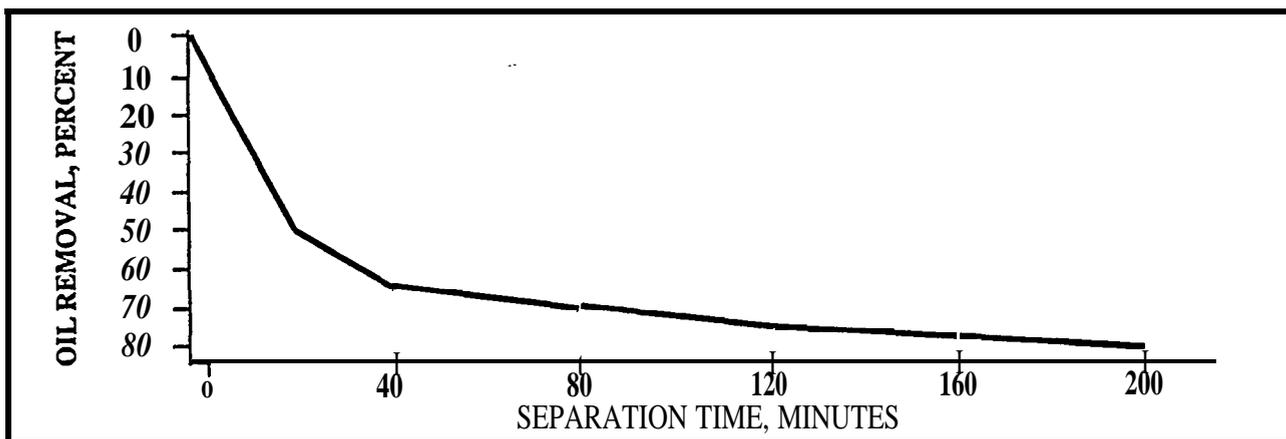


Figure 10.1: Effect of Detention Time on Oil Removal by Gravity Separation

- Solvent extraction to remove ketones, alcohols, and hydrocarbons
- Distillation to remove water and light fuel.

A number of other types of unit operations are used to a lesser extent, including magnetic separation, centrifugation, hydrocyclone separation, ultrafiltration, and carbon adsorption. Techniques are chosen based on their cost, efficiency, capacity, and residue production. Reprocessing often produces residues that require disposal. Reprocessing is generally applicable to streams that are not highly contaminated by metals or hazardous organic compounds. Reprocessing techniques are relatively simple and inexpensive to operate. However they have difficulty in removing metals and additives.

Redefining involves a full scale treatment of used oil to produce lube oils of equivalent quality to virgin oils. In the 1960s there were about 150 rerefineries in the United States. Today there are only about 15 rerefineries due to stricter regulations and low oil prices. The general approach is to:

- Remove water by atmospheric distillation
- Remove volatile organic and solvent by atmospheric distillation
- Remove additives and sludge by chemical treatment, extraction, vacuum distillation, or membrane processes
- Remove metals and chlorides by chemical treatment, clay treatment, or extraction
- Fractionate by vacuum distillation
- Perform final finishing by hydrotreatment clay treatment, or vacuum distillation.

Processes that generate by-products such as

the acid-clay process, are declining in popularity due to by-product disposal problems. Rerefineries can handle almost all oil wastes, although processing is easier for relatively uncontaminated streams. Products include light ends, which are burned as fuels, lube oil, and asphalt flux. The asphalt flux contains the heavy bottoms, which include the metals and sludge. Redefining reutilizes used oils for its original purpose and produces little or no waste by-products. However it requires a significant capital investment and has high operating cost.

Fuels Programs and Thermal Treatment

The second type of treatment category consists of a process designed to reduce the volume of oil waste and the hazards it presents. Thermal techniques are used for waste disposal and energy recovery. Used oils are similar in quality to No. 6 fuel oil and have a relative high BTU content. This makes them well suited to burning in furnaces and boilers. Before burning, the oil must be processed to meet environmental regulation specifications. Air emissions are also regulated. Since used oil has a high heat content and usually requires minimal processing to meet standards, combustion for energy recovery is often the most cost effective way to manage used oil. Most reprocessors use recycled oil as a fuel source on ships, cement kilns, furnaces, and external combustion boilers.

Oxidation and Biological Treatment

Oxidation techniques can also be used for destruction of used oil waste. These techniques use high temperature and pressure to decompose organic compounds and convert metals into easily managed salts. This technique has been gaining in popularity in recent years.

Biological processes breakdown hydrocarbons in oil waste. They are commonly used for pretreatment of oily wastewater, and for waste in which excessive contamination and low oil content makes recovery infeasible. Microorganisms that decompose oil waste are ubiquitous. The two types of biological systems are:

- Solid based system, including landfarming and attached/entrained growth systems
- Liquid based system, including biological reactors and lagoons.

A number of innovative biological processes have emerged in recent years. Biological activated carbon treatment (BACT) is one such process. Bioaugmentation is another process in which microorganisms specifically suited to decompose a particular waste are added to the system. Virtually all oil wastes are suitable for biological treatment, although high levels of metals or other toxic substances can inhibit efficiency. The efficiency depends on the treatment system, oil content, and contaminant concentration. Biological process effectively reduces the volume and hazards of oil waste, and has low capital and operating costs. However they are slow, require a lot of space, and do not reutilize oil. In addition, they produce a sludge requiring disposal and some processes such as landfarming, have a high risk of environmental contamination.

10.6 Factors in Selecting a Treatment Option

The main factors to consider in selecting a treatment option are regulatory compliance, economics, environmental acceptability, and technological capabilities. Each of these factors should be considered before a treatment option is selected.

Treatment must comply with all regulations. Unless used oil is shown to meet specific standards, it must be managed as a hazardous waste in some states. Thus proper manifests and permits must be obtained for all transportation and treatment. Generators maintain liability for oil waste until it is destroyed or recycled. Thus by destroying or recycling the waste, proper treatment can ensure that generators manage oil waste legally and can relieve them of liability.

The treatment system must be cost effective. A treatment system should be selected that maximizes oil waste recycling values and minimizes disposal costs of waste and waste treatment by-products. Economic factors include current market oil prices, capital and operating cost permitting, insurance costs, transportation costs, and treatment product values.

The treatment system must be environmentally acceptable. The treatment system should minimize exposure of employees to hazardous waste, generate little or no waste by-products, and not emit air, land, or water contaminants. Oil waste often contains heavy metals and hazardous organic compounds. Shipyards have both the legal and ethical responsibility to ensure that these compounds do not contaminate the environment.

The treatment system must be technologically feasible. The system must produce oil of required purity and composition. It must also have enough capacity to handle the flow of waste to be processed. In addition, the treatment system should be within the technical capabilities of the company operating it. Employees must have training and experience needed to operate, maintain, and repair the physical and chemical processing equipment.

11. FIBERGLASS REINFORCED CONSTRUCTION OPERATIONS

11.1 Introduction

Many shipyards and boatyards are involved in the use of fiberglass-reinforced composite plastic for production of hulls and other shipbuilding material. This process involves the combination of resin and reinforcing material. The combination is a product which has an excellent strength to weight ratio. The resin is a polymer and the reinforcing material is fiberglass. The resin and fiberglass is sprayed onto a mold which is shaped in the definition of a hull or other type of structure. The structure is usually lighter than metal or wood structures and may be stronger. The waste is generated from the fiberglass construction and includes solidified resin, contaminated solvent from clean-up, scrap fiber, and resin waste stream.

11.2 Recreational and Commercial Shipbuilding Manufacturing

Thermoplastic and thermoset reinforced plastic are used in many products used in the development of Commercial and naval vessels.

Raw Materials

The material used in the construction of fiberglass reinforced plastic include fiberglass, solvents, catalysts, and other chemical additives.

Resins

The resin is usually supplied dissolved in an organic solvent. The solvent acts as a carrier to help processing and to dissipate heat generated in the exothermic crosslinking reaction which occurs with the catalyst. The classes of resins used include polyesters, epoxies, polyamides, and phenolics compounds. The classes refer to the functional group which is attached to the monomer and are normally not a hazardous material but the solvent in which the resin is dissolved may be hazardous.

Waste resin used in shipbuilding construction is determined to be hazardous if the resin contains any residual solvent. If the waste contains a residual solvent and the solvent is listed as an F series solvent it is a hazardous waste. If the solvent is not listed additional testing may be required before a solvent is determined to be non-hazardous.

Fiberglass Substrate

Fiberglass is manufactured in several different forms. This gives several variables in strength, cost, and compatibilities with resin systems. The fiberglass content ranges from 10 to 50 percent. The forms include continuous-strand fiber, chipped fiber, and milled fiber.

catalysts

With epoxy resins, curing is done by using a catalyst to develop desired properties. Agents include amines, anhydrides, aldehyde condensation products, and Lewis acid catalysts. Amines such as diethylenetriamine and triethylenetetramine are often used for room temperature curings. Some of these chemicals may be classified as non-hazardous and the generator is responsible for the determination. The generator must keep up-to-date information on all hazardous waste classification.

Additives

Chemical additives may be added to obtain certain property characteristics. These product characteristics include resistance to heat aging and processibility. The additives include mold release agents, foilers, low-shrink, low profile additives, tougheners, thickening agents, colorants, forming agents, lubricants, plasticizers, and free radical initiators. There are four classes of additives which are used in plastics and include fillers, plasticizers, reinforcements, and colorants. These additives account for

90% of additives used in plastics. Compared to resins, these materials are generally chemically inert. The hazardous waste classification for additives should be reviewed to determine if these materials are hazardous.

Solvents

Solvents are used in large quantities for diluting the resin mix and for equipment clean-up. Acetone, MEK (methyl ethyl ketone) and methanol are most often used. These are listed **hazardous materials**.

Process Description

The manufacture of fiberglass ships and boats involve a number of process steps which are described below:

- 1 Mold Preparation
- 1 Resin Preparation
- 1 Gelcoat Application
- 1 Fiberglass Application.

Mold Preparation

Molds are used to give structure and support to the shape of the structure being built such as the hull of a ship or boat. Most molds are made of wood with a plastic finish.

Resin Preparation

Most resins are pre-promoted resin. The resin is in 55 gallon drums and is pumped from a storage into a spray gun. The solvent and catalyst are added through a separate feed line.

Gelcoat Application

The gelcoat is a pigment resin or a polyester resin based paint with a styrene content of

approximately 30 percent. The application is with either an air atomizer or airless spray gun. This application is usually conducted in a spray booth. The catalyst can be added by hand mixing or by a plural component system which is injected through a separate line into the gun where it mixes with the resin. Once reacted the polyester resin begins to thermoset. Once cured, the resin cannot be softened or reshaped by heat. The polyester resin lay-up operation results in the use of solvent. Acetone and methylene chlorine are often used in this operation. These solvents are used to prevent clogging and to clean the operator's hands during clean up.

Fiberglass Application

For fiberglass operations, the resin is either mixed, sprayed or brushed onto the surface of the fiberglass material. The fiberglass material comes in a woven mat or cord-like roving which is applied with the resin during fabrication.

Waste Generation

The generation of hazardous waste in the manufacture of fiberglass and composite plastic material is very common. These hazardous waste by-products are in the form of chemical-contaminated reagent, additives, solvents, wastewater, and hydraulic fluids. The quantities vary from a few gallons to several tons depending upon the size of the operation.

Liquid Waste Generation

Liquid hazardous waste includes:

- 1 Cleaning solvent from equipment cleanup
- 1 Resin leftover in tanks and other sources.

The solvent waste is contaminated with resin from the cleaning operation. The scrap resin is

from the waste which is leftover and cannot be used later.

Solid Waste Generation

The solid waste includes:

- b Gelcoat and resin overspray material which does not land on the fiberglass mold surface.
- l Unused raw material resin that has exceeded the shelf life of the material.
- l Raw material containers which include fiberglass boxes, drums of gelcoat, and other containers.
- l Empty resin and solvent drums
- l Clean-up rags.

Volatile Waste Generation

An open container or drum which contains solvent and generates fugitive emissions is a volatile waste generation. The fugitive air emissions are often generated during mixing and treatment during which the solvent from the coated fiberglass is driven off during the curing operation. The use of ventilation and thermal oxidation is used to incinerate the solvent emissions. Some recovery systems use activated carbon to recover the solvent emissions. The various techniques used must undergo economical analysis to determine the best technique to be used.

11.3 Source Reduction

Source reduction is used to reduce the amount of hazardous waste generated during the manufacturing operations. Many source reduction approaches have low capital cost requirements. Some source reduction techniques require only housekeeping changes to reduce

hazardous waste and yield significant cost savings. Areas which have been identified as source reduction are the following:

- l Material Application
- l Thermal Plastic Resin
- l Operation and Waste Management
- l Inventory Control.

Waste reduction opportunities are discussed below.

Material Application

Major waste reduction is available by optimizing material application processes. These processes include spray delivery systems and non-spray resin application methods. The non-spray application includes close mold system, vacuum bag mold system, resin roller dispenser prespray fiber reinforcing and in-house resin impregnation. These non-spray techniques reduce material waste and energy cost during application. The lower application pressures reduce the cost and maintenance of pressure lines, pumps, controls, and fittings. Routine cleanup of work area is also reduced.

Spray Delivery Systems

Most shipbuilding mold fabrication of fiberglass materials utilize resin spray application for the transferring and application of coatings and resin to the mold. Conventional gun-type resin application systems use compressed air, high fluid pressures, or combinations of fluid pressure and compressed air to atomize resin material. Catalyst for the resin systems are normally introduced inside the spray apparatus or as the resin is atomized from the spray nozzle.

The fabrication process for fiberglass con-

struction and the waste which is produced is highly dependent on the equipment and procedures used. The current system of resin and gelcoat delivery systems include high-pressure air, medium-pressure airless, and low-pressure air-assisted airless spray guns.

- 1 The high-pressure air system is used less due to the large amount of expensive high-pressure compressed air required and the high air emission produced.
- 1 The airless method produces a pressurized resin stream electrostatically atomized through a nozzle. The nozzle orifice and spray angle can be varied by using different tips. The size of the orifice affects the delivery efficiency, with larger orifices resulting in greater raw material loss. Airless spray guns are considered to be very efficient in the delivery of resin to the work surface.
- 1 The air-assisted airless technology modifies the airless gun by introducing pressurized air on the outer edge of the resin stream as it exits the pressure nozzle. The air stream forms an envelope which focuses the resin to follow a controllable spray pattern. Since more resin ends up on the mold with this technology, the amount of spraying is reduced leading to a reduction in air emissions. It is estimated that a savings of 5 to 20 percent in net loss of resin spray waste for the air-assisted airless gun is achieved compared to the airless gun.

Non-Spray Resin Application Methods

The standard practice for most open mold application of fiberglass has been the use of spray delivery of resins. The conventional gun-type resin application systems are very efficient in delivery of large quantities of resin to the work surface. The spray delivery sys-

tems are also advantageous when the product mold has many different surface shapes. Many non-spray application techniques have been developed but are normally messy to handle during application. However, these techniques should be considered because they may be applied at the shipyard in certain cases. The non-spray applications are as follows.

Prepreg Fiber Reinforcing

The use of prepregs which is reinforced fiber that is presaturated with resin, offers a number of advantages over conventional spray techniques. The prepregs are normally formulated with epoxy-based resins which require placing the mold in an oven or autoclave to complete the curing cycle. The disadvantages of this technique are that the material requires refrigeration for storage and material costs are higher. These techniques are best suited for application requiring high strength to weight ratio.

Resin Roller Application

This application uses pumped resin and catalyst from drums or bulk containers. The resin and catalyst are precisely metered in a gun-type line much like the paint plural component systems. A resin roller dispenser transfer the catalyzed resin to the mold surface while reducing material lost due to overspray and bounceback of the resin. Air emissions are greatly reduced with this type of delivery system.

Thermoplastic Resins

Thermoplastic resin can be easily rescued by the application of heat which returns the resin to a liquid state. The resin can then be reused in the manufacture of fiberglass components in shipbuilding. The used of thermoplastics offer faster curing cycles, lower emission during processing, lower costs per pound of raw material used, ease of recycling material, and in some cases, lower labor costs. With the

recent advances in the processing technologies and thermoplastic resin systems the shipbuilding industries are reexamine in the application of thermoplastics versus therosets material systems.

Operation and Wrote Management

By improving operating efficiency and waste management practices, significant source reduction opportunities can be achieved. Listed below are operating practices and waste reduction methods.

1. Change spray orientation in the spray mold to reduce overspray and bounce-back wastes.
2. Reduce and recycle solvent usage for clean up application.
3. Segregate waste to improve recyclability and reduce treatment of various waste streams.

11.4 Recycling and Resource Recovery

Recycling and resource recovery includes direct use of waste as a raw material for another process or product. It requires recovery of the valuable material from the waste stream. This helps reduce the hazardous waste generation in many instances.

Solvent Used and Waste Management

Solvents play a major role in the application of fiberglass operations. Solvents such as acetone, methylene chloride, methanol, methylethylketone, toluene, and xylene are commonly used in this type of operation. The solvents are used to clean-up equipment and adjust the specific gravity of the resin before use.

Acetone and other solvents are used for general cleanup applications. The solvents are used

to remove uncured resins from spray equipment, rollers, brushes, tools, and furnished surfaces.

Disposal of contaminated solvent has become a major cost in the operational expense area. In addition RCRA imposes long term liability for these wastes which must be addressed in the disposal consideration. Currently major research and engineering studies are occurring to find alternative solvents and techniques to reduce air emissions due to reportion required under the EPRCA regulations.

Considerable effort should be placed on the recovery of solvents to reduce the disposal costs and save on material cost due to recycling. Due to the current air emission regulation and pollution prevention requirement, alternative solvent management systems such as solvent substitution, onsite recycling, off-site recycling, and alternative fuels incineration should be considered.

On-Site Solvent Recovery

Distillation can provide a cost efficient solvent waste management. The solvents produced are reused for cleanup application. This reuse reduces the purchase of new solvents. The application of solvent reuse is discussed in the chapter on solvent recycling.

11.5 Treatment

Incineration

Incineration is a waste management option for contaminated solvents, resins, contaminated cleanup rags and off-spec materials produced during production. Incineration of these wastes provide an economical heat recovery due to high BTU content and low halogen content. Transportation is a negative in the off-site facilities because they must be hauled by a licensed waste hauler. Again the RCRA regu-

lation places the liability issue on the generator as well as the transporter.

Due to the land disposal phaseout and restrictive use of landfill sites, the demand of incineration services has grown rapidly in the United States and Canada. At the same time, new incineration capacity is slow due to NIMBY opposition and regulatory requirements from federal, state, and local regulatory agencies. Restrictive use of landfills will increase the costs for these services and the competition among generators for access will be great. Thus generators should avoid this developing trend by seeking alternative methods versus incineration.

12. WASTE MINIMIZATION AND EDUCATION

12.1 Introduction

Waste minimization is a constantly changing field with many innovations in the waste minimization field. To keep abreast of these new changes, shipyards must use the various resources that are available to them to stay abreast of these changes. The following sections give options to shipyard personnel to keep abreast of this field to make the needed changes to reduce the hazardous waste generated at the shipyard.

12.2 Pollution Prevention Information Sources

The Pollution Prevention Information Clearinghouse (PPIC)

EPA established the PPIC in 1988 to promote source reduction and recycling through information exchange and technology transfer. The PPIC is a free clearing house service containing technical, policy, programmatic, and legislative information relating to pollution prevention and recycling. The clearinghouse is available to the public at no charge.

The PPIC is comprised of the following exchange systems.

RePosito ry. A hard copy reference library containing the most current pollution prevention and recycling literature. The repository includes case studies, fact sheets, training materials videotapes, and general references.

Pollution Prevention Information Exchange System (PIES) A free, 24 hour electronic network accessible by personal computer equipped with a modem. The PIES consist of message center, bulletins, down-loading files, technical data bases, and conference listings.

Hotline. Telephone services to answer or refer questions and to provide links to the PIES for users without access to a personal computer.

Outreach Effort. Workshops, training, and industry-specific pollution prevention materials are developed for designed user groups.

To obtain additional information on the PPIC and PIES write to:

U.S. Environmental Protection Agency
Office of Environmental Engineering and
Technology Demonstration
Pollution Prevention Information
Clearinghouse
401 M Street, S.W. (RD-681)
Washington, D.C. 20460
Tel: 202-260-3161
Fax: 202-260-4524

12.3 State Waste Minimization Programs

Alaska:

Alaska Health Project Waste Reduction
Assistance Program
431 West Seventh Avenue
Anchorage, AK 99501
(907) 276-2864

California:

California Department of Toxic Substances and
Control
Office of Pollution Prevention and
Technology
714/744 P Street
Sacramento, CA 94234-7320
(916) 322-3670

Connecticut:

Connecticut Hazardous Waste Management
Service
Suite 360
900 Asylum Avenue
Hartford CT 06105
(203) 244-2007

Oregon:

Oregon Hazardous Waste Reduction Program
Department of Environmental Quality
811 Southwest Sixth Avenue
Portland, OR 97204
(503) 229-5913

Virginia:

Office of Policy and Planning
Virginia Department of Waste Management
11th Floor, Monroe Building
101 North 14th Street
Richmond, VA 23219
(804) 225-2667

Washington:

Hazardous Waste Section
Mail Stop PV-11
Washington Department of Ecology
Olympia, WA 98504-8711

Wisconsin:

Bureau of Solid Waste Management
Wisconsin Department of Natural
Resources
P.O. Box 7921
101 South Webster Street
Madison, WI 53707

12.4 Educational Material and Classes

The following organizations offer material and education classes that cover waste minimization:

Environmental Resource Center
3679 Rosehill Road
Fayetteville, NC 28311-6634

Government Institute, Inc.
966 Hungerford Drive #24
Rockville, MD 20850

Executive Enterprises Publications Co., Inc.
22 West 21st Street
New York, NY 10010-6904

Federal Publication, Inc.
1120 20th Street, N.W.
Washington, D.C. 20036

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14. DEFINITION OF TERMS AND ACRONYMS

APCD	Air Pollution Control District	NIMBY	Not In My Back Yard
API	American Petroleum Industry	PCBs	Polychlorinated Biphenyls
BACT	Biological Activated Carbon Treatment	PIES	Pollution Information Exchange System
BIF	Boiler Industrial Furnace	POTW	Public Owned Treatment Works
BTU	British Thermal Unit	PPIC	Pollution Prevention
CFR	Code of Federal Regulations	Information	
CVD	Chemical Vapor Deposition		Center
EPA	Environmental Protection Agency	RCRA	Resource Conservation and Recovery Act
EPRCA	Emergency Planning and Community Right to Know	SNAME	Society of Naval Architects and Marine Engineers
FR	Federal Register	TCE	Tri-Chloroethylene
HSWA	Hazardous and Solid Waste Amendment	TCLP	Toxic Characteristic Leaching Procedure
HVLP	High Volume Low Pressure	TSDF	Treatment Storage Disposal Facility
IVD	Ion Vapor Deposition	VOC	Volitical Organic Compound
MEK	Methyl Ethyl Ketone		
NSRP	National Shipbuilding Research Program		

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