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An analytical approach to toxic substance replacement in support of pollution prevention

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ABSTRACT

AN ANALYTICAL APPROACH TO TOXIC SUBSTANCE REPLACEMENT IN SUPPORT OF POLLUTION PREVENTION

by
Ithan B. Zimmer

In support of pollution prevention and in accordance with Executive Order 12856 concerning pollution prevention, all federal agencies must comply with the Toxic Release Inventory (TRI) chemical release reduction and pollution prevention planning. The inventory lists hundreds of chemicals and choosing those to replace and finding actual replacement chemicals or procedures is not always clear. This study focuses on an analytical approach to this problem by understanding the application of two substances. The representative chemicals are two volatile organic compounds (VOC), ethyl ether and ethanol, used as solvents in ammunition manufacturing.

Thirteen military specifications provide the cases involving ether. Ethanol's use as the solvent for shellac in a primer lacquer is characterized in the laboratory. Due to interest in substituting acetone for ethanol, an acetone based primer lacquer is fabricated and tested in comparison to its ethanol counterpart. The results form the basis for broader application and chemical change.

AN ANALYTICAL APPROACH TO TOXIC SUBSTANCE REPLACEMENT IN SUPPORT OF POLLUTION PREVENTION

by
Ithan B. Zimmer

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CAS	Chemical Abstracts Service
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
DOD	Department of Defense
EO	Executive Order (EO 12856)
EPA	Environmental Protection Agency
EPCRA	Emergency Planning and Community Right-to-Know Act
FAR	Federal Acquisition Regulation
LEPC	Local Emergency Planning Committee
MILSPEC	military specification
MSDS	Material Safety Data Sheet
MTBE	methyl-tert-butyl ether
NAS	National Academy of Sciences
NFPA	National Fire Protection Association
ODC	ozone depleting compound
OSHA	Occupational Safety and Health Act
PPA	Pollution Prevention Act of 1990
SARA	Superfund Amendments and Reauthorization Act
SERC	State Emergency Response Commission
Temp	temperature
TNT	trinitrotoluene
TRI	Toxic Release Inventory
VOC	volatile organic compound

LIST OF SYMBOLS

C	viscometer constant
c	capillary scale calibration (mm/drop)
cm	centimeter
cp	centipoise (dynamic viscosity unit)
cs	centistoke (kinematic viscosity unit)
°C	degrees Celsius
F	force dimension
g	grams
h	height
L	length dimension
l	length
lb/gal	pounds per gallon
M	molar concentration
mg/L	milligrams per liter
ml	milliliter
mm	millimeter
mPa·s	milli-Pascal second (dynamic viscosity unit)
μ	dynamic (absolute) viscosity
N	number of drops
N_o	whole number of drops counted
N_w	water drop number engraved on stalagmometer
ν	kinematic viscosity
ρ	density
ρ_w	density of water
S	surface tension
s	seconds
S_w	surface tension of reference liquid (water)
T	time dimension
τ	shear stress
V	volume
x	top capillary scale reading (mm)
y	bottom capillary scale reading (mm)

CHAPTER 1

INTRODUCTION

1.1 Project Definition and Objectives

In support of pollution prevention and under Executive Order 12856 concerning pollution prevention, all federal agencies (e.g., the U.S. Army and all of the DOD) must comply with the Toxic Release Inventory (TRI) chemical release reduction and pollution prevention planning requirements. To achieve compliance with these requirements, the Army has taken several actions. They have started procedures that facilitated the gathering of data necessary to report on TRI emissions. Moreover, they have traced to the source significant portions of the TRI reportable emissions and transfers. Knowing the source of the materials facilitates changes in operations that lead to reduced levels of use. The Army has instituted significant changes in some operations that include improved management of potential leaks, reduction in spills, improved material handling, and use extension of some materials. These changes have already been responsible for reductions in the TRI reported emissions.

A larger challenge is further reductions in use and emission of hazardous materials in manufacture and maintenance of military-related products such as armament and weapon systems. Much of the challenge lies in the necessity of assuring performance and long shelf life of the military articles that include bullets, guns, tanks, aircraft, and other critical items. The military has evolved a system of military specifications and related requirements that carefully specify materials to be used and practices to be employed in the manufacture and maintenance of performance critical items. The specifications assure appropriate performance levels through the military specifications. An effort is underway to make changes in the approach to military specifications with a greater effort to require levels of performance to be assured by a manufacturer without requiring adherence to the current material and process specifications. The impact of that change cannot be evaluated for a few more years. In the meantime, changes in processes and materials that appear to have potential to lead to pollution prevention opportunities are hampered because of the seemingly rigid military specifications that currently apply.

The major focus of this research is to identify common themes in military specifications and related requirements that lead to TRI emissions of volatile organic compounds, to analyze the reasons for the specific requirements, and to develop a sound approach to identify and evaluate options that lead to the expected level of performance while allowing reduction of emissions at the source.

In the course of this research program, opportunities were identified to reduce or eliminate the use of two TRI chemicals in Army operations. These two chemicals, ethyl ether and ethanol, have several uses in both military and civilian applications. These two chemicals emerged from the evaluation of military requirements not necessarily because they represent the largest volume or the greatest potential risk. Rather they and the processes that currently require their use are illustrative of the requirements and of systematic approaches that can be used to identify and qualify changes that result in reduction of use and emissions.

Ethyl ether and ethanol are hazardous materials used in Army production processes that should be substituted for, if at all possible, with materials that are environmentally benign. The substance names ethyl ether, diethyl ether, and ether are synonymous for common ether. "Ether" denotes any of the aforementioned names throughout this document, although the other names are used to avoid confusion with other ethers. Ethyl alcohol, alcohol, and grain alcohol are synonymous with ethanol, the name used in this work.

The methodology for elimination or reduction of ether and ethanol in manufacturing is the principal interest of this thesis. The methodology is an analytical approach to define the substances based on performance criteria in their respective processes. A review of the processes requiring these hazardous substances is essential so that opportunities for substitutions can be identified. The performance requirements of DOD must still be met when the new procedures are in place.

1.2 Ether and Ethanol as Toxic Chemicals

Commercially, ether is used in chemical manufacturing and as a solvent, extractant, or reaction medium. It formally was used as an anesthetic in medical procedures. Use of ethers involves risks of fire, explosion, and toxic effects. A review of the properties of ether clarifies its designation as a potential health, safety, and environmental problem.

Ethanol's primary industrial uses are as a solvent and as a fuel additive. Its foremost hazard to the environment is as a volatile organic compound (VOC) with accompanying impact on air quality. Flammability, reactivity, and toxicity are the safety issues. Liquid ethanol can react vigorously with oxidizing materials. Ethanol poisoning and intoxication are almost always limited to ingestion as opposed to vapor inhalation as would be encountered in a typical industrial environment.

CHAPTER 2

BACKGROUND

2.1 Legal Aspects - Executive Order 12856

2.1.1 Statutory Authority

Executive Order 12856 (EO), "Federal Compliance with Right-to-Know Laws and Pollution Prevention Requirements," subjects federal agencies to compliance with the Emergency Planning and Community Right-to-Know Act (EPCRA). EPCRA is Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA).

The EO, issued on 9 August 1993, has two principal objectives. First, federal agencies and facilities must be "good neighbors" to local communities. Second, it directs the federal government to exhibit pollution prevention leadership. These objectives are met through requirements in the following four areas:

1. Compliance with the Toxic Release Inventory reporting requirements of EPCRA.
2. Compliance with other planning and reporting requirements of EPCRA.
3. Toxic chemical release reduction and pollution prevention planning.
4. Modification of acquisition and procurement practices to support pollution prevention.

The EO applies to any federal agency that owns or operates a facility within the customs territory of the United States that is subject to any reporting requirement under EPCRA. The customs territory includes all territories and possessions of the U.S. except the Virgin Islands, American Samoa, Wake Island, Midway Island, Kingman Reef, Johnston Island, and Guam.

The presence of listed substances in excess of specified threshold quantities at a facility triggers EPCRA.

2.1.2 Technical Requirements

Each federal agency must develop voluntary goals to reduce total releases and off-site transfers of toxic chemicals at least 50 percent from 1994 levels by 31 December 1999. Toxic chemicals for the EO are those described in EPCRA section 313 (i.e., the TRI or SARA 313).

Federal facilities must develop written pollution prevention plans setting forth their contributions to their agency's overall release reduction goal by 31 December 1995. Pollution prevention means source reduction as defined in the Pollution Prevention Act of 1990 (PPA). Source reduction includes equipment, technology, process, or procedure modifications, product redesign or reformulation, substitution of raw materials, and improvements in housekeeping, maintenance, training, or inventory control. It does not include any practice which alters the physical, chemical, or biological characteristics, or the volume of a hazardous substance, pollutant, or contaminant through a process or activity which is not integral to the production of a product or the providing of a service.

Each federal agency must establish a plan to eliminate or reduce the unnecessary acquisition of products containing toxic chemicals or extremely hazardous substances. Each agency must produce a plan to reduce its own manufacturing, processing, and use of these materials.

The head of each federal agency must develop a written pollution prevention strategy to achieve the required EO actions. The strategy must include:

1. A statement of commitment to use pollution prevention as the primary method of achieving and maintaining environmental compliance.
2. A pollution prevention policy statement reflecting the agency's commitment to pollution prevention and the designation of principal responsibilities for development, implementation, and evaluation of the strategy.

The EO required submission of the strategies to the EPA by 3 August 1994. Federal agencies were encouraged to seek public involvement for strategy development.

The EO encourages agencies to develop and test innovative pollution prevention technologies at their facilities. Agencies may enter partnerships with industry, academia, government laboratories, and others to assess and deploy innovative technologies domestically and abroad.

2.1.3 Administrative Requirements

EPCRA provides a method to increase public awareness of toxic substances released from industrial facilities in their communities. Facilities must report annual releases of over six-hundred toxic chemicals to the Environmental Protection Agency (EPA) as well as the state where the facility is located.

EPCRA reporting requirements apply to all facilities meeting the following criteria: (1) employ ten or more full time employees and (2) use more than 10,000 pounds total of any listed toxic chemicals per year, or manufacture or process more than 25,000 pounds total of listed toxic chemicals in a calendar year.

Facilities covered under EPCRA must annually submit a Toxic Chemical Release Inventory Reporting Form (Form R). Form R includes releases of toxic chemicals to any environmental media, including chemicals in wastes sent off-site for treatment or disposal.

Subtitle A of EPCRA establishes State Emergency Response Commissions (SERCs). SERCs are required to establish emergency planning districts and appoint Local Emergency Planning Committees (LEPCs).

LEPCs must develop and implement emergency response plans for any potential chemical accidents or releases in their jurisdictions. Facilities under LEPC jurisdiction must notify the appropriate SERC of their existence.

All facilities that have material safety data sheets (MSDS) as required by the Occupational Safety and Health Act (OSHA) must submit the MSDSs to their SERC, LEPC, and local fire department if they have these substances on-site in excess of the minimum threshold quantities. Facilities that must submit MSDSs must also submit an Emergency and Hazardous Chemical Release Inventory Form to the same offices.

2.1.4 Enforcement

EPCRA contains a complex set of administrative, civil, and criminal penalties for violations of its various provisions. Non-compliance with the EO can include some or all of these penalties. Enforcement authorities vary for each requirement in EPCRA. The EPA, SERCs, LEPCs, and citizens may take legal action against owners or operators of facilities who fail to comply with the law.

In the past, EPCRA has been interpreted as exempting federal facilities. In response, the EO specifically requires federal facilities to comply with EPCRA reporting requirements as modified by PPA. The first applicable year for federal facilities is 1994. Form R reports were due from covered facilities by 1 July 1995.

By 3 August 1995, federal agencies were to complete a review of their standardized documents, including specifications and standards. This review identifies opportunities to eliminate or reduce extremely hazardous substances and toxic chemicals. The EO directs the EPA to assist other federal agencies in prioritizing reviews and identifying substitute materials.

By 1999, the federal agencies must complete appropriate revisions to their specifications and standards to eliminate or reduce the use of extremely hazardous substances and toxic chemicals wherever possible. Revisions to the Federal Acquisition Regulation (FAR) necessary to implement changes to standardized documents were to be made by 3 August 1996.

2.1.5 Pollution Prevention Potential

A major objective of Executive Order 12856 is pollution prevention. Source reduction is a key aspect. Expanding on the previous description of source reduction, it includes any practice which reduces the amount of any hazardous substance, pollutant, or contaminant entering the waste stream before waste treatment or recovery and recycle. Source reduction reduces the hazards to public health and the environment associated with such releases.

The elimination or reduction of hazardous substances in various aspects of federal operations is in progress. The 50 percent reduction goal is ambitious. Some chemicals will be eliminated entirely, some will be kept for lack of a better procedure or substitute.

However, there will be a significant waste reduction from federal agencies because of EPCRA compliance.

The Department of Defense, as a major buyer, consumer, and maintainer of manufactured materials, faces a particular challenge in progressing to the emission reduction goal. In addition to the volume of goods acquired, the existing system of military specifications and other detailed process specific requirements makes difficult any changes or replacements in the use of hazardous substances. A major objective of this research is to examine, in a systematic way, two illustrative examples of opportunities for change in military specifications. The goal is to explore how two different types of specifications impact on the use of hazardous materials, specifically volatile organic compounds in this case, and to develop technical approaches that can be used to change the requirements while maintaining appropriate levels of quality and cost of manufacture.

The two categories of specifications chosen included a set of laboratory analytical procedures that are repeatedly specified as part of quality control/quality assurance practices for many ordnance-related products. One of the solvents frequently required in these procedures is ether. In this research program, the uses of ether and approaches to its elimination have been explored.

The other type of specification examined is one where a specific product is designated for use in a manufacturing step. The product selected for examination is the lacquer used in manufacture of primer cups for small caliber ammunition. The lacquer has an ethanol solvent base. Because ethanol is on the TRI list, the DOD has an objective of reducing or eliminating its use. The other important component of the lacquer is shellac. One of the possible alternatives for the use of ethanol is acetone. Although acetone is also a volatile organic compound, it is not currently on the TRI list. Therefore, one of the approaches to change in specifications could be to consider the use of acetone as a total or partial replacement for ethanol.

2.2 Ether Properties Review

Ethers are weakly basic compounds with a distinct odor. They have little or no solubility in water, but are soluble in organic compounds.

Most ethers are relatively unreactive compounds because the carbon-oxygen bond is not readily broken. This makes them effective solvents in organic synthesis. However, different families of ethers react differently. Some are potentially hazardous chemicals because in the presence of atmospheric oxygen a radical-chain process can occur. This results in the formation of peroxides that are unstable and frequently volatile compounds. Ethyl ether can form explosive peroxides on extended storage and exposure to air and light.

Ethyl ether can be prepared directly by the vapor-phase dehydration of ethanol with a strong acid catalyst and a high reaction temperature:

$$2\ CH_3CH_2OH \underset{H_2SO_4}{\overset{140^{\circ}C}{\leftrightarrow}} CH_3CH_2OCH_2CH_3 + H_2O$$

Most ethers burn in air. They have low flash points and low autoignition temperatures. Ethyl ether is particularly dangerous. For example, the 34.5°C boiling point is close to room temperature in a lab with failed air-conditioning. Table 1 lists some key properties.

Table 1 Typical Properties of Selected Substances (Kirk-Othmer)

Property	Acetone	Ethanol	Ether	MTBE	n-Hexane
Chemical Formula	C_3H_6O	C_2H_5OH	$C_4H_{10}O$	$C_5H_{12}O$	C_6H_{14}
Boiling Point, °C	56.3	78.3	34.5	55.0	68.7
Autoignition Temp, °C	538	423	160	426	225
Flash Point, °C	-19	14	-40	-30	-22
Density, g/ml	0.790	0.789			
Dynamic Viscosity, cp	0.32	1.17			
Surface Tension, dynes/cm	23.7 (20°C)	23.1 (25°C)			
Molecular Weight	58	46	74	88	86

Table 2 CAS Registry Numbers

Acetone	[67-64-1]
Ethanol	[64-17-5]
Ether	[60-29-7]
MTBE	[1634-04-4]
n-Hexane	[110-54-3]

Upon ingestion, skin contact, or inhalation, ethers can cause drowsiness, lack of coordination, or death. They have low toxicity when ingested. Prolonged skin contact can cause defatting and dehydration leading to dermatitis. Some compounds can penetrate the skin in harmful amounts and are carcinogenic. Inhalation is the most common way for ethers to enter the body. Effects may include narcosis, irritation of the nose, throat, and mucous membranes, and chronic or acute poisoning. Ethers are central nervous system depressants and ethyl ether is still used as a general anesthetic in some areas of the world.

Most ethers absorb and react with atmospheric oxygen to form unstable peroxides. These peroxides can detonate when concentrated by evaporation or distillation, when combined with other compounds that give an explosive mixture, or when disturbed by heat, shock, or friction.

Ethyl ether is a principal member of the ether family. It is colorless, extremely volatile, highly flammable with a sweet odor and a burning taste. The flammability and volatility make it dangerous to handle and ship. Its low autoignition temperature and low conductivity property enable it to generate static electrical charges that can result in explosion. Ether's presence requires special work and storage areas as well as explosion-proof tools.

Prevention of health hazards depend on prevention of exposure to toxic atmospheric concentrations and conscientious precautions to prevent fires and explosions.

Ether has a wide range of industrial uses, especially as an organic solvent and as an extractant. It is also a denaturant for several alcohol formulations, a starting fuel for diesel engines, and an entrainer for ethanol dehydration. It is used abundantly for the military production of smokeless powder.

2.3 Shellac Properties Review

Shellac is the purified product of the hardened resinous secretion of a parasitic insect on certain trees and bushes of India, Myanmar, and Thailand. The insect secretes it as a protective coating for its larva. The shellac resin is hard, tough, and non-toxic and produces water resistant films. It can be handmade and machine-made.

Since shellac is a natural product of animal origin, it differs somewhat from one source to another. Average property values are questionable since early studies neglected temperature and humidity effects. The best solvents for shellac are the lower alcohols, methyl and ethyl, followed by amyl alcohols, glycols, and glycol ethers. Shellac is insoluble in esters, ethers (except glycol ethers), hydrocarbons, chlorinated solvents, and water. It can be dispersed in water with soda ash, borax, ammonia, morpholine, or triethanolamine.

Shellac contains approximately 67.9 percent carbon, 9.1 percent hydrogen, and 23.0 percent oxygen for an empirical formula of C_4H_6O. Based on a molecular weight of about 1000, the average molecule has the formula $C_{60}H_{90}O_{15}$. It contains one free acid group, three ester linkages, five hydroxyl groups, and possibly a free or potential aldehyde group. This is indicated by the acid value, hydroxyl value, saponification value, and carbonyl value. Its ionization constant is $1.8X10^{-5}$.

Shellac can be modified with urea-formaldehyde resins and catalyzed with acid to produce a protective coating. This coating is extremely tough, has excellent water and solvent resistance, and is fast-drying.

2.4 Ethanol Properties Review

Ethanol is a versatile oxygen containing organic chemical. Its unique combination of properties make it useful as a solvent, a germicide, a beverage, an antifreeze, a fuel, and a depressant. It is also a chemical intermediate for other organic chemicals such as glycol ethers, ethyl acetate, and vinegar. Under normal conditions it is a volatile, flammable, clear, colorless liquid. As discussed in section 1.2, its toxicity and reactivity are the prime safety issues. Liquid ethanol can react vigorously with oxidizing materials. Ethanol intoxication is usually limited to ingestion as opposed to vapor inhalation as would be encountered in a typical industrial environment.

Ethanol's physical and chemical properties are primarily dependent on the hydroxyl group. The group gives polarity to the molecule and gives rise to intermolecular hydrogen bonding. These properties account for the differences between the physical behavior of lower molecular weight alcohols and hydrocarbons of equivalent weight. The hydroxyl group provides the majority of the chemical properties including dehydration (e.g., ether formation), oxidation, dehydrogenation, and esterification.

Industrial ethanol is produced most commonly from ethylene in a synthetic process. It is also a by-product of some industrial operations and can be fermented from sugar, starch, or cellulose. Two of the primary synthetic processes from ethylene are the indirect hydration process using sulfuric acid, and the direct hydration process using no sulfuric acid. The latter is the method of choice in the United States.

For the purposes of ammunition manufacturing, denatured ethanol is used. The costs are less due to its tax-free status. The denaturants make it unfit for human consumption, and therefore the tax-free ethanol will not be used for beverages.

2.5 Acetone Properties Review

Acetone, also called 2-propanone or dimethyl ketone, is the simplest and most important ketone. It is a colorless, flammable liquid that is miscible with water and most organic solvents. Its primary uses are as a solvent and as a reaction intermediate for the production of other compounds which themselves are solvents or reaction intermediates.

Most manufactured acetone is from a coproduct in the process for phenol from cumene and from the dehydrogenation of isopropyl alcohol. It occurs naturally in the environment and is biodegradable.

Acetone has comparatively low acute and chronic toxicity as compared to other organic solvents. High vapor concentrations produce anesthesia and may irritate the eyes, nose, and throat. Generally, there are no injurious effects other than skin irritation or headaches from prolonged exposure.

Acetone is of interest mainly because it was removed from the TRI and may be substituted for ethanol as a solvent in some circumstances. The testing of acetone in place of ethanol as the solvent for cut shellac is of principal importance for this thesis.

CHAPTER 3

THE ETHER CHEMICAL PROCESS

3.1 DOD System Ether Application

Upon review of laboratory military specifications (MILSPEC) provided by Picatinny Arsenal, New Jersey, various system uses of ether are apparent. All specifications for ether that appear in this kind of requirement deal with extracting a substance and determining its quantity. Ether acts as a solvent. In one case, ether is also an extractant. Table 3 lists these applications. Only the last part of the MILSPEC is listed. For the complete number, see REFERENCES. SUBSTANCE is the chemical extracted. ETHER USE is "Extractant" or "Solvent".

Table 3 MILSPEC Applications of Ether

MILSPEC	Substance	Ether Use
11233J	Aluminum	Solvent
46432B	Lead Azide	Solvent
71090	Potassium Perchlorate	Solvent
46462B	Antimony Sulfide	Solvent
50998	Antimony Sulfide	Solvent
382C	Oil & Grease	1) Extractant 2) Solvent
13392B	Antimony Sulfide	Solvent
20449C	Antimony Sulfide	Solvent
12951F	TNT	Solvent

Table 3 MILSPEC Applications of Ether (continued)

MILSPEC	Substance	Ether Use
20517H	Black Powder/ Aluminum Powder	Solvent
45474B	Aluminum	Solvent
46647B	Lead Azide	Solvent
48239	Aluminum	Solvent

The solvent and extraction procedures must be reviewed for each MILSPEC to determine specific performance characteristics, if any, for a given application.

3.2 Organic Solvent Procedure Using Ether

Ether is a solvent for ethanol in virtually the same procedure for all cases. The essential process follows:

1. Rinse the sample with ethanol (few ml). (Ethanol used as a solvent).
2. Rinse the sample with ether (few ml).
3. Aspirate the sample until there is no odor of ether.
4. Dry the sample in an oven at 80-100°C for 15-60 minutes. (100°C is most common).
5. Cool the sample in a desiccator.
6. Weigh the sample.

This denotes a gravimetric approach for identifying the amount of a substance in a sample. Gravimetry, although a valuable analytical approach, is time consuming and labor intensive. It can often be replaced with newer methods. A more updated method may exist for a given substance determination which does not employ ether.

Another detail about the procedure is interesting. The ether washes away the ethanol and then the sample is placed in an oven at about 100°C. Frequently this type of ether rinse is done to facilitate drying. A look at the boiling points for ethanol and ether may provide some insight into the approach. Generally, if drying overnight at elevated temperatures is required, complete removal of ethanol itself should be expected. Transition to a non-gravimetric approach would generally eliminate the need for this type of drying altogether.

3.3 Extractant Procedure Using Ether

Ether is an extractant for oil and grease. A typical procedure follows:

1. Extract 50.0 g sample with 250 ml of chemically pure ethyl ether (redistilled over sodium) for one hour in a Soxhlet extractor.
2. Evaporate on steam bath to volume of approximately 50 ml.
3. Filter the extract into a tared 150 ml beaker.
4. Rinse the filter using 10 ml portions of ether.

Once again, a modified method for the gravimetric approach appears appropriate.

Alternative techniques for the solvent and extraction procedures have been identified through a literature search based on the particular substances extracted. These are discussed in Chapter 5.

CHAPTER 4

PRIMER LACQUER SOLVENTS - ETHANOL AND ACETONE

4.1 Problem Definition and Background

In response to EPCRA, Picatinny Arsenal, the military weapons research and development facility in Rockaway Township, NJ, is developing new ammunition that is manufactured in an environmentally appropriate way. This "Green Bullet" program aims to find substitutes for the hazardous substances used to make, clean, and paint bullets. These new bullets could reduce the environmental problems at an estimated 16,000 shooting ranges nation-wide as well as at the manufacturing plants.

The military produces 400 million to 500 million rounds of small caliber ammunition annually, requiring between 1000 and 1500 tons of hazardous materials in the process.

Ethanol, a VOC in ammunition manufacturing, is used as a solvent with shellac. A mixture of ethanol, shellac, and purple dye is used to seal primer into the primer cup at the rear of the bullet. This mixture, called the "primer lacquer" or "purple primer lacquer" is the subject of this work.

The ammunition product drawings require the primer lacquer to prevent primer dusting, pellet cracking, and water entry. Primer dusting is evaluated via a "rotap" test. Additional requirements are to: be visibly present (quality control), be easily processed, not diminish barrel life (non-corrosive), not degrade ballistic performance, no ozone depleting compounds (ODC), and low VOC. A VOC level of less than 5 lb/gal is desirable.

Drying time is another aspect. The primer lacquer must dry to the touch in fifteen minutes and be completely dry within one hour. The aim is to form a crust over the primer. These conditions must be met when searching for a substitute.

The equipment and machinery used in applying the primer lacquer are considered a constant in this problem due to high capital costs for replacement. It is undesirable to purchase new equipment and massively change assembly-line procedures in this particular case. Therefore, any substitute should be applied with existing machinery.

The current equipment uses brass pins, or punches, to apply the primer lacquer. The punches are lowered mechanically into a reservoir and then placed over the primer cups where a drop is placed into the cup. The cup already contains the primer and a paper covering, also called a foil covering. The primer lacquer must spread over the paper, penetrate the paper somewhat to grip the primer, and seal to the brass primer cup. Clean operations are essential for safety and bullet integrity.

Once the primer lacquer is in place, an anvil is inserted into the cup. The anvil keeps the entire cup intact and plays a role in the actual firing process. A satisfactory cup must have the anvil properly seated. The primer lacquer can adversely affect this seating by making the anvil cocked, loose, high, or deep.

Based on these requirements, testing of the primer lacquer may characterize what approaches to chemical or procedural change could fulfill the requirements. What are the significant properties for foil penetration and crust formation? Ammunition manufacturing guidelines use solids content as the method of measuring the primer lacquer's ability to perform. However, performance may or may not depend on solids content depending on the make-up of the primer lacquer or any replacement. With the current application technique, it is suggested that primer lacquer viscosity and surface tension are key indicators of performance.

Because of the method of transfer of the lacquer or any replacement from the process tank to the primer cup, the characteristics of the fluid are important, in addition to whatever product performance characteristics are required. An assembly of pins is dipped into the tank and it is expected that each pin will take from the tank one drop of lacquer of sufficient size and viscosity to withstand the trip to the primer cup without falling off. Moreover, the quantity must be sufficient to provide the needed coverage of the top of the primer cup.

As a result of this research program, it is clear that a search for modification or replacement of the presently used lacquer will require careful consideration of the requirements for the transfer operation as well as any performance characteristics.

Viscosity and surface tension are measured directly in laboratory testing and are recommended as benchmarks in the search for substitutes.

It is this analytical approach that is central to finding replacement candidates for hazardous substances. Measuring the appropriate performance characteristics of what works and using those results as a search aid will greatly reduce the field of choices, quicken the search, and increase the probability of success.

4.2 Primer Lacquer Composition

The standard formula for the primer lacquer is thirteen gallons of four-pound cut shellac, thirty-nine gallons of denatured ethyl alcohol (ethanol), and one gallon of purple dye. The base formula provides 9.4 percent solids. These components are mixed into a 55 gallon mixing drum until thoroughly blended (about thirty minutes). The color is checked and more dye mix is added as necessary to achieve the "appropriate" color intensity while maintaining transparency. Production experts define the "appropriate" color.

Four-pound cut shellac is made using four pounds of dry shellac mixed with one gallon of ethanol. Therefore, the VOC component comes from the already-mixed shellac and the additional ethanol. This mixture (plus or minus one gallon of ethanol) has been used at least as far back as the 1940s without appreciable change. The reasoning behind using the aforementioned requirements (e.g., solids content as a performance characteristic) have been lost. The system works as is, so there was little if any reason for change, until EPCRA.

An Army ammunition manufacturing facility is testing an acetone primer lacquer as a substitute. Its formulation is exactly as above with thirty-nine gallons of acetone substituted for the thirty-nine gallons of ethanol. This maintains the solids content of the lacquer - the property believed important by the facility.

4.3 Laboratory Experimentation

The aim of the laboratory work is to characterize the primer lacquer's viscosity and surface tension. The acetone lacquer's viscosity is measured and compared to that of the primer lacquer. Finally, a solubility experiment determines the ability of the shellac to stay in solution in the acetone primer lacquer. Sustaining a solution is integral to the manufacturing line performance.

Both dynamic (or absolute) viscosity (μ) and kinematic viscosity (ν) are measured as they differ by only the factor of density (ρ):

$$\mu = \nu \cdot \rho \tag{1}$$

The Cannon-Fenske viscometer gauges kinematic viscosity as a function of time. Density is measured by weighing (or massing) a known volume.

The drop-weight method employs the stalagmometer to gauge surface tension. It is the best general method when considering accuracy and speed compared to the capillary rise or ring methods. Additionally, it only requires a small quantity of liquid.

To ensure the proper amount of shellac is placed in the primer cup, it is important for the lacquer to stay in solution. The solubility test is approached by two routes. The first is to add acetone to four-pound cut shellac until shellac precipitates out or the solution is not maintained. The second is to add ethanol to the acetone primer lacquer until the mixture becomes a solution.

4.3.1 Viscosity Theory and Determination

The viscosity of a fluid is a measure of that fluid's resistance to flow when acted upon by an external force such as a pressure differential or gravity. Most viscous fluids flow more easily at higher temperatures. Fluid behavior when temperature, pressure, or stress are varied will depend on the type of fluid. For a Newtonian fluid, shear stress (τ) is proportional to the velocity gradient, or rate of strain, (dv/dy) by the factor of dynamic viscosity (μ):

$$\tau = \mu \cdot dv/dy \tag{2}$$

which is known as Newton's law of viscosity.

Dynamic viscosity has units of centipoise (cp) which have dimensions $F \bullet T/L^2$. Kinematic viscosity units are centistokes (cs) which have dimensions L^2/T.

The Cannon-Fenske viscometer is a capillary-flow method for determining the kinematic viscosity. The volume rate of flow is measured through a tube of known circular cross section and length. Manipulating equation (2), the dynamic viscosity equation becomes:

$$\mu = [(\pi \bullet r^4 \bullet g \bullet h \bullet \rho)/8V \bullet l] \bullet t \qquad (3)$$

where r is the tube radius, g is gravity, h is the difference in height of the two reservoirs, V is the fluid volume, and l is the tube length. By using equations (1) and (3), this number divided by the density will yield the kinematic viscosity. The quantity in square brackets represents a constant for a given viscometer, call it C. Therefore, kinematic viscosity can be obtained by:

$$\nu = C \bullet t \qquad (4)$$

which is the equation used by Cannon-Fenske.

Assumptions for viscosity measurements are:

1. The fluid is assumed to be a Newtonian, incompressible fluid.
2. The flow is assumed laminar, with flow lines parallel to the walls. Therefore, the laminae consist of concentric cylinders coaxial with the tube.
3. The layer next to the wall is assumed to stick to the wall, so that its velocity is zero.
4. The flow is assumed to be steady, in the sense that the velocity of the fluid at any fixed point in the tube is constant in time.

The procedure for performing viscometry tests uses the instructions from the Cannon Instrument Company of State College, PA which are based on ASTM D 445. Two sizes are used for verification purposes. Size 100 has C=0.015 centistokes/second (cs/s) and is recommended for viscosity ranges of 3 to 12 cs. This viscometer provides the primary data since the viscosity of the primer lacquer is assumed to be in that range based on the lacquer constituents (assumption verified by actual test). Size 200 has C=0.1 cs/s and is recommended for a 20 to 80 cs range. Essentially, the viscometer is charged, the fluid flows due to gravity, and the time to flow between two points is clocked. The viscometer constants were verified by timing a known substance, water, and comparing those values to the water viscosity of 1 cs. Viscosity results are accurate to two significant figures.

Table 4 Purple Primer Lacquer Viscosity,
Size 100 Viscometer, C=0.015 cs/s, Temp=21.2°C

Trial	**t (s)**	**$v=C\bullet t$ (cs)**
1	209.0	3.1
2	208.7	3.1
3	205.4	3.1
4	201.5	3.0
5	200.2	3.0
		average = 3.1

Table 5 Purple Primer Lacquer Viscosity,
Size 200 Viscometer, C=0.1 cs/s, Temp=19.0°C

Trial	**t (s)**	**ν=C•t (cs)**
1	28.16	2.8
2	29.13	2.9
3	29.53	3.0
4	29.44	2.9
5	29.59	3.0
		average = 2.9

A 50 ml volume of primer lacquer weighs 42.0 g. Therefore, ρ = 42.0 g/50ml = 0.84 g/ml.

Using ν = 3.1 cs, μ = 3.1 cs • 0.84g/ml = 2.6 cp.

Table 6 Acetone Primer Lacquer Viscosity,
Size 100 Viscometer, C=0.015 cs/s, Temp=19.8°C

Trial	**t (s)**	**ν=C•t (cs)**
1	66.4	1.0
2	64.0	0.96
3	62.0	0.93
4	58.9	0.88
5	57.0	0.86
		average = 0.93

Table 7 Acetone Primer Lacquer Viscosity,
Size 200 Viscometer, C=0.1 cs/s, Temp=19.5°C

Trial	**t (s)**	**ν=C•t (cs)**
1	9.40	0.94
2	9.43	0.94
3	9.28	0.93
4	9.31	0.93
5	9.50	0.95
		average = 0.94

A 50 ml volume of acetone primer lacquer weighs 40.9 g. Therefore, $\rho = 40.9$ g/50 ml = 0.82 g/ml.

Using $\nu = 0.93$ cs, $\mu = 0.93$ cs • 0.82 g/ml = 0.75 cp.

Difficulties were encountered in keeping the acetone primer lacquer in solution.

Although the densities of the two primer lacquers are similar, dynamic and kinematic viscosities differ considerably.

4.3.2 Surface Tension Theory and Determination

The molecules at the surface of a liquid are subject to the attractive forces of the interior molecules. A resultant force, whose direction is in a plane tangent to the surface at a particular point, acts to make the liquid surface as small as possible. The magnitude of this force acting perpendicular to a unit length of line in the surface is called the surface tension. Surface tension is a property of interface. It has units of dynes/cm, dimensions F/L.

In the drop-weight method, a drop forms at the end of the stalagmometer and the boundary line is the outside perimeter. When the drop just detaches itself, the downward force on the drop is equal to the force acting upward. Surface tension decreases as the temperature rises and is virtually unaffected by changes in area, pressure, or volume.

The procedure for performing the surface tension tests uses the Traube Stalagmometer directions from SGA Catalog No. S-9725. This stalagmometer is a pipette with a broad, flattened tip which permits large drops of reproducible size to form slowly and finally drop. The surface tension calculation is base on the number of drops which fall, the density of the sample, and the surface tension water which is used as a reference liquid for factory standardization of the stalagmometer.

The water drop number engraved on the stem of the pipette indicates the number of drops of distilled water at 25°C which fall from the tip during passage of a particular volume included between corresponding marks on the two engraved scales. Drop weights are proportional to surface tension. The relationship for calculating surface tension in terms of drop numbers is:

$$S = [\ (S_w)\bullet(N_w)\bullet(\rho)\ ]/[\ (N)\bullet(\rho_w)\ ] \tag{5}$$

$$= [\ (72.0)\bullet(N_w)\bullet(\rho)\ ]/(N) \tag{6}$$

where S is the surface tension of the sample (dynes/cm), S_w is the surface tension of the reference liquid (water), N is the number of drops of the sample, N_w is the water drop number engraved on the stalagmometer, ρ is the density of the sample (g/ml), and ρ_w is the density of water.

The factory determination of the water drop number for each stalagmometer is made at 25°C. This is the ideal temperature at which to conduct the trials. However, little error is involved when measurements are made at another temperature. In this case, $(72.0)\cdot(N_w)$ in the numerator of equation (6) is not changed. Since the water drop number is inversely proportional to the surface tension of the water, the product of $(S_w)\cdot(N_w)$ remains essentially independent of any changes in the surface tension caused by temperature alterations. Therefore, without involving much error, the sample drop number and density for any temperature may be substituted into equation (6) along with the water drop number and water surface tension for 25°C.

The basic steps of the procedure are drawing the fluid, counting the drops (N_o) between the upper and lower graduations (x and y in mm), and calibrating the capillary scale calibration (c in mm/drop). Reading the graduations accurately and maintaining a slow drop flow (less than twenty per minute) are the key aspects of this test. The actual drop number, N, is calculated as follows:

$$N = N_o + (x-y)/c \tag{7}$$

The fractional part of a drop, given by the second part of equation (7) may be either positive or negative.

The stalagmometer technique was verified by measuring a known substance, ethanol, and comparing that value to the known value of 23.1 dynes/cm at 25°C. Surface tension results are accurate to one decimal place. A total of four trials are performed, two each on two different stalagmometers, for consistency of results.

Table 8 Purple Primer Lacquer Surface Tension Test,
Temp=20.5°C, ρ=0.84 g/ml

Trial	**N_o drops**	**x mm**	**y mm**	**c mm**	**N drops**	**N_w drops**	**S dynes/ cm**
1	73	21.0	7.5	9.5	74.4	28	22.8
2	72	23.0	11.0	9.0	73.3	28	23.1
3	53	6.0	7.5	8.5	52.8	20	22.9
4	54	8.0	1.0	8.0	54.9	20	22.0
						average = 23.1	

The surface tension for the acetone primer lacquer could not be measured due to its incapacity to stay in solution.

4.3.3 Solubility Test

The primer lacquer must be able to stay in solution over a reasonable period of time, at least a few hours. This is important so that an accurate amount of shellac can be delivered to the primer cup. If a lacquer cannot stay in solution, an unknown amount is delivered to the cup and performance will be at issue.

The solids contained in the acetone primer lacquer precipitate out over a short period of time. This time is observed to be from less than one hour down to a few minutes making this lacquer inappropriate for an assembly line process that requires a lacquer to stay in solution for at least a few hours.

The question arises as to how much (or how little) acetone will take the shellac out of solution. As previously noted, this solubility test is approached by two routes. The first is to add acetone to four-pound cut shellac until shellac precipitates out or the solution is not maintained. The second is to add ethanol to the acetone primer lacquer until the mixture becomes a solution.

In the first case, acetone is added 1 ml at a time to 5 ml of four-pound cut shellac. After only 3 ml are added, the mixture is no longer a solution. Compare this 3 ml addition to 15 ml that would normally be added to 5 ml of the cut shellac for the acetone primer lacquer. Based on this trial, the acetone primer lacquer not only comes out of solution, but it likely is never in solution.

In the second case ethanol is added 1 ml at a time to 5 ml of the acetone primer lacquer. Since solids are already precipitated in the lacquer, the question is how much ethanol is required place the mixture back into a solution. The results are that no addition of ethanol could take the precipitate out. The mixture could not be brought to a solution.

Both tests demonstrate that shellac simply is not sufficiently soluble in acetone to allow the mixture to be used in this manufacturing step.

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 Organic Solvent Procedure Using Ether

From an examination of Table 1 and section 3.2, two improvements come to mind. The first is an observation of the boiling points of ethanol and ether; the second, an investigation into possible alternative methods for the gravimetric approach.

The boiling point of ethanol is 78.3°C and of ether is 34.5°C. Based on the 100°C oven temperature, both solvents will boil away. Actually, the ethanol would boil away without the ether present because the boiling point of ethanol is less than the oven temperature. The ether is extraneous if the drying time is long enough and may be left out entirely. Oven temperatures and times may need adjustment, but most likely will remain the same. These statements may be verified in the laboratory. This laboratory work is not performed for this thesis.

If results indicate that a rinsing solvent is required for the ethanol, Eaton et al. prescribes an alternative solvent of 80% n-hexane and 20% methyl-tert-butyl ether (MTBE) for gravimetric methods. These substances are not on the TRI.

Hexane is flammable and requires appropriate handling precautions. It is a central nervous system depressant. The vapors are mildly irritating to mucous membranes. High level exposure may cause dizziness, unconsciousness, prostration and death. Main uses include fuel applications and oil extraction.

MTBE, although an ether, has a uniquely stable structure that contains no secondary or tertiary hydrogen atoms. Therefore, it is resistant to oxidation and peroxide formation (less prone to explode). Its higher autoignition temperature and narrower flammability range make it comparably safer to use than ethyl ether. MTBE's chief uses are as a fuel additive and a solvent. It also has medical applications. There have been some recent questions about its human toxicity.

A literature search for determination methods for the chemicals in Table 3 reveals that analytical methods such as spectroscopy and voltammetry are available. Spectroscopy uses instrumental analysis to identify elements by measurement of the radiant energy absorbed or emitted by a substance. Specialized and sophisticated techniques include, but are not limited to: Raman spectroscopy, nuclear magnetic resonance, nuclear quadropole resonance, dynamic reflectance spectroscopy, microwave and gamma-ray spectroscopy, and electron paramagnetic resonance. Capital costs, required training, and operational difficulties can be high for some of these methods.

Voltammetry, an electrochemical method, is common for lead azide determination and is highly accurate. It also has applications for other propellants and high explosives. Asplund (1984) describes the determination of azide based on the oxidation of azide at a carbon paste electrode and that of lead on reduction of lead at a dropping mercury electrode in a 0.1 M acetate solution at pH 4.6. The solubility of lead azide in pure water is very low, but in an acetate solution adequate amounts of lead azide dissolve.

Other methods are specified in REFERENCES. Their discussion is beyond the scope of this research. However, the relevant citations are included because of their importance in establishing precedence for alternative methods to gravimetry (and therefore ether). Additionally, they provide a beginning for follow-on research.

5.2 Extraction Procedure Using Ether

on et al., section 5520 "Oil and Grease," contains information pertinent to replacing ɜr as an extractant. Five methods are described in detail. Although none of the hods uses ether, the listed reagents should be checked against the current TRI before . Most of the methods use the n-Hexane/MTBE mixture.

The partition-gravimetric method, the partition-infrared method, and the Soxhlet hod are designed for oil and grease extraction in liquid samples. The partition-infrared hod is recommended for low levels of oil and grease (<10 mg/L) because gravimetric hods do not provide the required precision. A modified Soxhlet method is provided the extraction of sludge samples. Lastly, a hydrocarbon method is given for use with of the above methods to obtain a hydrocarbon measurement in addition to or instead he oil and grease measurement.

5.3 Laboratory Experimentation Discussion

kinematic viscosity of the acetone primer lacquer is 0.93 cs as compared to 3.1 cs for purple primer lacquer. This represents about a 70 percent decrease in viscosity. The lacquers have similar densities, hence, the dynamic viscosities are considerably erent as well. This viscosity difference is not surprising since acetone and ethanol have y different viscosities themselves as noted in Table 1. Surface tension for the acetone ner lacquer is virtually meaningless because it is a suspension, not a true solution. wever, it is worth noting that acetone and ethanol have similar surface tensions.

Based on these results, it is unlikely that the acetone primer lacquer will deposit

In fact, the amount of shellac delivered by the acetone primer lacquer will change depending on how long the mixture has been sitting in the reservoir without thorough stirring.

Since the solubility tests confirm that shellac is not soluble in acetone, it is highly unlikely that acetone would be an appropriate substitute for ethanol in the primer lacquer. This is true independent of viscosity or surface tension.

Among the many factors that may not be reflected in the price of a solvent are its removal and disposal costs. The solids precipitating out of the acetone primer lacquer yield an additional waste stream, the costs for which must be accounted.

It should be noted that a test of the acetone primer lacquer was conducted by an Army ammunition manufacturing facility. The rounds were manufactured under "ideal" conditions. The mixture was shaken, the pins dipped, and the acetone primer lacquer delivered. In other words, because of the short time of the test, actual assembly line manufacture may not be adequately represented. Expert inspectors stated, from visual inspection, that the correct amount of shellac was delivered to the primer cup and it spread appropriately. This visual inspection is based upon criteria that include, but are not limited to: color intensity, cup shape, and coating integrity. The subject ammunition rounds were fired successfully.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Recommended Actions for Ether

The objective of reducing or eliminating ether from use within the military specifications evaluated is complete. Upon laboratory confirmation, the following recommendations are provided:

1. Eliminate the use of ether as a solvent for removal of ethanol from precipitates to aid drying. The cost of the ether is saved. If lab results indicate ether's necessity as an extraction or solubilization agent, substitute an 80% n-hexane, 20% MTBE mixture for the ether.
2. Explore the implementation of analytical techniques more advanced than gravimetry. Possible methods include spectroscopy and voltammetry. Results will often be obtained more quickly. The newer methods typically require smaller samples and reduced amounts of chemicals. Availability of equipment and funds is a factor.
3. Use the methods described in Eaton et al. for oil and grease extraction.

6.2 Recommended Actions for Primer Lacquer

The results of this thesis extend those obtained at the facility. This brings up many considerations. Does the visual inspection accurately depict the solids content of the primer lacquer delivered, or simply the amount of the dye that is delivered? If the actual shellac delivered to the cup is unknown, what is the relationship between the amount of shellac and the firing of the round. Will there be long-term storage effects? Perhaps most importantly, is the quality control criteria currently employed sufficient to monitor quality if there are changes in manufacturing procedures? What was the purpose of these criteria fifty years ago and is it equally applicable today?

A critical review of military specifications and drawings, their purpose, and their basis for continuance is necessary. Pollution prevention requires environmentally conscious decisions early in the design stage. If the eventual replacement for the primer lacquer requires considerable equipment and process change, significant cost may be accompanied. Whatever future action is followed, the removal of hazardous substances from the environment should be approached in a systematic, analytical manner.

6.3 Suggestions for Further Study

Additional laboratory work is needed to qualify all the above recommendations. Without experimental confirmation, theories remain as theories. The intent of the MILSPEC must be satisfied.

6.3.1 Alternative Coatings

The paint and coatings industry is constantly looking for improvements in film (coating) development. Improvements include reducing hazards to the environment and complying with EPCRA.

Thermoplastic systems, including lacquers and latex-based systems, may provide some avenues for improved coatings. A useful definition of a solid film used in thermoplastic systems is that it does not flow significantly under the pressures to which it is subjected during testing or use. Therefore, a film can be defined as a solid under a set of conditions by stating the minimum viscosity at which flow is not observable in a specified time interval.

Viscosity can be used to measure dry to the touch. If the viscosity is greater than about 10^6 cp, it is dry to the touch. The viscometers used in this thesis would be inappropriate for such high viscosities. However, the falling-ball viscometer would be useful in this case. It is one of the simplest methods for determining viscosity.

Studies using aqueous based solvents may be explored. Some experimental studies performed by an Army ammunition manufacturing plant to replace the primer lacquer did not identify an appropriate substitute. The problems encountered were excessive dry time, reduced primer sensitivity, and poor absorption into the foil. Wetting ability is a major limitation of aqueous based solvents since the surface tension of water is much greater than that of organic solvents. This wetting ability is important for a primer lacquer since the solvent must wet the shellac, the foil, and the brass.

Ample literature exists concerning alternative substance determination techniques. Applicable techniques must be explored and feasibility studies performed as necessary.

6.3.2 Toxic Chemical Ranking

The development of methodologies to initially screen and rank toxic chemicals is of interest. This section mentions some of the other work done in this general area. These methodologies may be of use in future research.

Bosch proposes a quantitative hazard analysis methodology to screen and prioritize plants as opposed to actual processes. The procedure defines an organization based on the hazard potential inherent in each plant's use of toxic, flammable, and explosive chemicals. The hazard potential is a function of the type and severity of chemical hazards present and of the quantity manufactured, consumed, or stored on-site. Information necessary to determine the hazard potential is available with either direct or indirect knowledge of plant operation. The methodology may also be modified to account for specific organizational needs.

OSHA uses the concept of threshold quantity for highly hazardous chemicals to determine the application of their rules to a specific site. Bosch's methodology conducts a more comprehensive review of chemical use than one based on OSHA rules. Chemical threshold quantities may be based on either the maximum quantity stored on-site or the total quantity processed in one year provided a consistent basis is used for all evaluated plants and chemicals. Chemicals with multiple hazards are categorized according to flammability, reactivity, and toxicity.

Horvath et al., of Carnegie Mellon University contrast the one-to-one ranking of the TRI with a ranking based on relative toxicity, using threshold limit value indices. The weighting scheme is a first step in correcting the "equality" of toxic chemicals in the TRI. This methodology addresses basic problems with the TRI. These problems are TRI inaccuracy, discharge focus as opposed to environmental fate, and simplistic interpretation of TRI data. Toxic weighting systems are generally limited by lack of data and subjective input requirements. However, this toxicity-based measure can be a useful first step in modifying the TRI.

Generally, engineers have three strategies for complying with environmental discharge permits: (1) apply end-of-pipe approach, treating the discharge just upstream of the compliance point; (2) treat the pollutant source streams throughout the plant individually; or (3) change the overall process to avoid generating the pollutants at all.

Ammann et al. list seven steps to find the best compliance strategy which can be used as a starting point for toxic substance identification. The engineer should consider not only the present permit limitations, but also any future regulatory requirements that could arise. The steps are (1) analyze pollutant sources; (2) make a pollutant balance; (3) develop control schemes; (4) consider process changes; (5) make a rough cost estimate; (6) check on compliance; and (7) analyze the economics.

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