

NIOSH

TECHNICAL REPORT

CONTROL OF EMISSIONS FROM SEALS AND FITTINGS IN CHEMICAL PROCESS INDUSTRIES

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health

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IN CHEMICAL PROCESS INDUSTRIES

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ABSTRACT

Seals and fittings are the closures and seal points on chemical processing equipment in the various major chemical processing industries: petroleum refining, petrochemical, synthetic organic chemical, and commercial chemical products manufacturing. Seals and fittings are the source of both liquid and gaseous "fugitive" emissions, those frequently unexpected (unpredictable as to timing, emission rates, and individual source identification) emissions from chemical processing equipment. The National Institute for Occupational Safety and Health (NIOSH) has done an inhouse study of chemical processing equipment seals and fittings and emissions therefrom, because these fugitive emissions are a major source of occupational exposure of production and maintenance workers to hazardous, toxic, or carcinogenic volatile organic compounds (VOC). Exposure can be by inhalation, skin contact, and ingestion, or a combination of these modes.

The U.S. Environmental Protection Agency (EPA) has been conducting a systematic program over the past few years to characterize and determine means of detecting, measuring, sampling, monitoring, and controlling these fugitive emissions. Information from these studies, summarized in this report, will be valuable to both occupational health and engineering professionals in carrying out their responsibilities to eliminate and/or minimize occupational exposure of production and maintenance workers to hazardous chemicals in industrial manufacturing facilities, particularly the various chemical processing industries. In using this report, the reader must remember the differences in approaches to safeguarding the environment, and preventing occupational hazards. Evaluation of occupational hazards involves as a major consideration the location and activities of individual workers (i.e., dermal contact by maintenance workers) as well as permissible exposure limits (PEL's) and fugitive emission rates.

The EPA studies have culminated in the initiation of proposed standards by the Commission Standards and Engineering Division of the EPA Office of Air Quality Planning and Standards for specific controls for reducing fugitive emissions from the seals and fittings components of chemical processing equipment. Two types of control techniques are included in the proposed standards: 1) implementation of systematic monitoring, maintenance, and record keeping programs; and 2) compliance with equipment, design, and operational requirements.

Compliance with these future standards by the various chemical processing industries should provide major improvement over current environmental pollution and worker exposure conditions. However, these standards should be considered minimum requirements for normal working areas where worker exposure to highly toxic or carcinogenic VOC fugitive emissions (PEL's less than 10 ppmv) is possible. Here, the additional seals and fittings improvements which EPA lists as technically feasible, but not sufficiently cost effective from the environmental pollution standpoint, should be incorporated based on worker exposure considerations. Even complete retrofitting or new facility installation of optimum seals and fittings selections does not eliminate the need for periodic hazard evaluation via personal sampling conducted by occupational health professionals.

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LIST OF ABBREVIATIONS

API	American Petroleum Institute
CCPI	Commercial chemical product industries
CTG	Control techniques guidelines (EPA)
CMA	Chemical Manufacturers Association
cm.	Centimeter
EPA	Environmental Protection Agency--a separate agency of the Federal Government
FID	Flame ionization detector
GC	Gas chromatography
gpm	Gallons per minute
LDRP	Leak detection and repair plan
lb/hr	Pounds per hour
M.wt.	Molecular weight
NAPETAC	National Air Pollution Control Techniques Advisory Committee (EPA)
NIOSH	National Institute for Occupational Safety and Health--a component of DHEW--Federal Government
NO _x	Nitrogen oxides
OAQPS	Office of Air Quality Planning and Standards (EPA)
OSHA	Occupational Safety and Health Administration--a component of the Dept. of Labor--Federal Government
OVA	Organic vapor analyzer
PEL	Permissible exposure limit (OSHA)
PVC	Polyvinyl chloride
psig	Pounds per square inch gauge

ppmv	Parts per million - by volume
SOCMI	Synthetic organic chemical manufacturing industry
SO _x	Sulfur oxides
STEL	Short-term exposure limit (normally 15 minutes)
TOC	Total organic carbon
TLV	Threshold limit values (identical in concept to OSHA's PEL values but are the recommendations of the ACGIH--American Conference of Governmental Industrial Hygienists)
TWA	Time-weighted average (normally for 8-hour worker exposure period)
VCM	Vinyl chloride monomer
VOC	Volatile organic compounds

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INTRODUCTION

SOURCE OF STUDY DATA

Seals and fittings components of chemical processing and other industrial manufacturing equipment and the leaks and emissions arising from their use are the concerns of this National Institute for Occupational Safety and Health (NIOSH) report. The information is primarily based on recently completed and ongoing U. S. Environmental Protection Agency (EPA) contract assessments of all types of environmental emissions occurring in the petroleum refining, petrochemical, and organic chemical manufacturing industries. Two NIOSH reports^{1,2} contribute a discussion of successful control technology and other measures adopted to control carcinogenic emissions (vinyl chloride monomer) in the plastics and resins polymerization industry to meet both strict EPA environmental regulations and low permissible exposure limits (PEL) issued by the Occupational Safety and Health Administration (OSHA).

The intent of this inhouse NIOSH project is to: 1) correlate the results and measurement method information pertinent to volatile organic compound (VOC) emissions from seals and fittings (as developed by the EPA studies) with the engineering design of these items, and 2) provide recommendations on the most suitable choices in each category of seals and fittings application for minimizing leaks and emissions therefrom. NIOSH did not undertake any emission measurements or chemical identification in this study primarily because of the extensive experimental testing studies conducted by the EPA contractors, including the Radian Corporation, Monsanto Research Corporation, Hydroscience, Inc. and numerous others. EPA's large-scale testing program was essential to obtain sufficient sampling to provide emission results having statistical significance over the range of experimental items tested.

PAST PRACTICES

Industrial experience indicates that, until the past few years, industrial process engineering design groups did not view leakage as an important factor in selecting seals and fittings for use in the manufacture of relatively low cost materials. Good engineering practice taught the designer to select the most economical equipment that fit the process requirements of providing the maximum yield of acceptable quality products. Loss of undetermined quantities of raw materials, intermediates, by-products, and products to the workplace and the environment was accepted, particularly because optimum containment frequently cannot be justified on the basis of economics. The leaks from seals and fittings, termed "fugitive" emissions, are unpredictable as to timing, leakage rate, and individual source identification. The fugitive emissions that were normally corrected were generally large ones that could be readily detected through being seen, heard, or smelled. Other less obvious but important fugitive emissions were largely ignored. In petroleum refining,

for example, loss of up to 0.3 percent of total thruput was generally considered acceptable.

There has been and still is a relatively low awareness on the part of many mechanical and chemical engineers about the occupational exposure hazards of toxic or carcinogenic chemicals. This is in contrast to a distinctly higher level of awareness about safety (i.e., fire and explosion). Only very recently has the American Institute of Chemical Engineers formed a Division of Occupational Safety and Health.

Current chemical processing technology involves wide variations in application of processing equipment, by-product disposal techniques, and levels of equipment maintenance. Hence, a wide range of emission levels occur in different chemical processing installations, both in the work area and to the environment. Frequently, when new rigorous exposure limits for toxic carcinogenic chemicals are issued by regulatory agencies, the initial reaction has been that adequate control technology is unavailable. Faced with the consequent need for improved controls, industrial groups have demonstrated great ingenuity and resourcefulness in developing satisfactory control means.

SOURCES OF WORKER EXPOSURE

Although EPA is mandated by Federal law to eliminate and/or minimize environmental pollution, their findings concerning VOC emissions from the seals and fittings of chemical processing equipment are useful in protecting the health of the industrial worker. The extent of worker occupational exposure to various VOC emissions, as differentiated from environmental pollution, is influenced by the specific type of emission, the type of industry, and the general manufacturing setups in the industry.

Continuous Operation

The petroleum refining, petrochemical, and a major share of the organic chemical manufacturing industry predominantly operate high thruput installations on a continuous basis using equipment designed to function while exposed to all weather conditions in outside locations, and without the building enclosures normally envisioned as constituting a manufacturing plant. Centralized control instrumentation, situated in small control buildings, permits operators to remotely control process conditions, bulk receipt, bulk transfer, and bulk shipment of relatively volatile liquid phase feed materials, intermediates, and products. These installations operate with a minimum of production workers and, wherever possible, normally use computer controls and on-stream automatic analyzers. In such a high-thruput, continuously operating, automated manufacturing setup, worker exposure to toxic or carcinogenic chemicals is minimized. Worker exposure primarily occurs when:

1. The process operator is taking samples for laboratory analysis.
2. The pumper has to couple and uncouple transfer lines from bulk shipment (rail car or truck) containers to or from raw material or finished product storage tanks.

3. The maintenance worker has to repair, by-pass, or replace defective equipment.

Batch Operation

Chemical production employing batch type unit operations is conducted for a variety of reasons-technical, economic, and output requirements. Generally a continuous processing installation can't be justified economically for a low-output situation. Limited output by batch operation occurs in several situations:

1. A small company with limited capital produces and sells limited quantities (regardless of the unit value of the product).
2. Companies and/or plants produce high value chemicals (i.e., dyes, optical brighteners, etc.) having a limited market.
3. Companies and/or plants produce a series of similar products successively in the same batch processing installation.

These cases are frequently accompanied by nonautomated handling of raw materials, intermediates, and finished products. The greatest potential for worker occupational exposure (both skin contact and respiratory) occurs during batch operation where bag and drum quantities of raw materials are opened and manually emptied into a reactor by a production operator. Large-scale batch operation to provide high total output occurs in situations where the kinetics of reaction, the composition requirements of product, or the physical forms of material prevents continuous processing operation. Polyvinyl chloride (PVC) polymerization plants and the manufacturing operations for a number of the major organic chemicals are examples. Hence, control technology to prevent worker exposure to toxic or carcinogenic chemicals in batch production installations will vary from the simple to the highly sophisticated. In some cases, controls will follow the ideal of being designed into the initial installations. In most, the existing controls will have been retrofitted. Generally these batch chemical processing setups are located within building enclosures. Here conditions of the air surrounding the production workers can vary substantially from that of the outside environment. These variations in chemical manufacturing operations are mentioned to emphasize the occupational health exposure variations for production workers in different chemical manufacturing setups in most cases with the processing equipment fitted with substantially similar types of seals and fittings.

INDUSTRIAL SOURCES OF VOC EMISSIONS

Review of the important sources of all volatile organic compounds (VOC) emissions in relationship to the fugitive emissions emanating from seals and fittings is useful. EPA³ estimates total U. S. hydrocarbon emissions (1975) were approximately 16 percent from petroleum refineries, 32 percent from the petrochemical and synthetic organic chemical manufacturing (SOCMI) industries combined, and 38 percent from motor vehicle engines (all types). Crude petroleum is the natural resource on which a whole series of American chemical processing industries are primarily based. A description and sequential

listing of this chain of chemical processing industries is summarized from Patrick's reports^{4,5}.

- o About 10 major chemical feed stocks are primarily produced by petroleum refineries.
- o These refinery-produced feed stocks are transferred to generally adjacent installations for chemical processing to petrochemicals (intermediates).
- o In turn, the petrochemicals are the feed stocks to the SOCOMI. About 400 major chemicals are produced by this industry group, with about 60 percent of the total volume output coming from installations in Texas and Louisiana. Patrick estimates that 140 of these 400 chemicals provide approximately 90 percent of the total VOC emissions for the SOCOMI industry—approximately 1.5 billion pounds yearly.
- o The next chemical processing tier in the sequence contains the commercial chemical product industries (CCPI). Typical products are plastics and resins, pesticides, and pharmaceuticals.
- o In this sequential chemical processing chain:
 - Each stage contains more individual chemicals than the proceeding.
 - The plants generally become successively smaller.
 - The volatility of the successive tier products become generally lower.
 - VOC's are basically nonmethane hydrocarbons falling in the C₂-C₆ range. They are generally photochemically reactive (oxidize to form the familiar U.S. urban phenomena-smog).

TYPES OF VOC EMISSIONS

For the preceding series of chemical process industries, Patrick^{4,5} defines four major types of VOC emissions:

Emissions from Process Vents and Stacks (Point Sources)

Emissions from stacks and vents predominantly involve venting of inerts, NO_x and SO_x compounds, and release of VOC that have been considered in past years to be uneconomic to capture. These vents and stacks are termed point sources. A vital component of the EPA environmental mandate is to characterize these point emissions, define their hazards to the environment and the general population, and develop both regulations and disposal techniques other than general area air dilution via tall stack discharge. Point source emissions can be measured quantitatively since both concentration and volumetric flow rate are readily monitored in a confined system. In general, these point emissions do not occupationally expose industrial production or maintenance workers.

Fugitive Emissions

Fugitive emissions are the leaks and spills from the seals and fittings components of chemical process equipment including those at loading and unloading facilities. The term "fugitive" is employed for these diffuse emissions into the work enclosure or directly to the environment because they occur unexpectedly and are unpredictable as to timing, emission rate, and individual source identification. The real world of imperfect and variable performance of various types of chemical process equipment seals and fittings makes it difficult to detect and quantify fugitive emissions and identify resultant occupational health exposures.

Waste Disposal Emissions

VOC waste disposal emissions are these from (1) solid and liquid wastes during and after transfer from plants to disposal sites, and (2) wastewater drainage and treatment facilities. These emissions are also classed as secondary emissions. Contaminated water in cooling towers provide secondary emissions since the original contamination is caused by fugitive emissions from imperfect seal operation on some equipment (primarily heat exchangers). Location may make the category more of an environmental problem than an occupational health hazard. Nevertheless, rapid detection and quantification of low level emissions by sensitive VOC detectors is needed to protect personnel likely to be exposed to the emissions.

Emissions from Storage Tanks and Transportation Units

Emissions from storage tanks and transportation units are predominantly breathing losses through vents on fixed tanks. The vents are designed to accommodate pressure and temperature changes and tank filling. Modification of fixed tanks to floating roof tanks can eliminate vent emissions, but there can still be fugitive emissions past these specialized seals. Worker exposure tends to be limited simply because of infrequent presence. However, if toxic or carcinogenic VOC emissions are indicated by detection instruments, exposed workers need protection.

Based on these four category sources of VOC emissions, Patrick^{4,5} provides the following estimated percent ranges of the total amount of VOC emissions for each type within the SOCFI.

<u>Sources of VOC Emissions</u>	<u>Percentage Range</u>
Process (vents and stacks)	65 - 70
Fugitive (seals and fittings)	15 - 20
Waste disposal	2 - 5
Storage tank and transportation units (vents)	8 - 10

When the storage tank and waste disposal categories of the petroleum refining industry are compared with those of the SOCFI, the percentages in both are undoubtedly somewhat higher. This is based on the known greater volatility of

the materials handled and refinery use of oil-water separators (API separators) as the primary step in wastewater disposal. The above figures relate to a situation of uncontrolled point sources, i.e., before EPA issued standards for point sources emissions in both processing and storage areas of chemical process industries. When and if point source VOC emissions are completely controlled, the processing equipment seals and fittings fugitive emissions category might become as much as 60 to 70 percent of total VOC emissions from the chemical processing industries. In recent years, both because of improvement in point source controls and EPA's earlier attention to VOC emissions from point sources, fugitive emissions are becoming an increasing portion of total VOC emissions. This does not imply that fugitive emissions are increasing, simply that they are not decreasing as rapidly as point source emissions.

DESIGNING TO MEET STANDARDS

Before industry personnel can design, operate, and maintain chemical processing and manufacturing equipment that will meet both OSHA individual chemical permissible exposure limits (PEL) and EPA environmental standards, they must have thorough knowledge of the following factors in their own manufacturing situation:

- o The identity and characterization of all chemicals present in feed materials, intermediates, by-products, and finished products that are or can be inadvertently released as liquid or gaseous emissions.
- o The acceptable occupational exposure limits for each identified chemical. Toxicological support may be needed to ensure that exposure hazards, including biological effects and seriousness of both short term and long term overexposure of the industrial worker, are properly assessed.
- o The probability of worker exposure—with frequency and duration of exposure directly affecting decisions as to possible modifications of engineering or work practices or both.

SEALS AND FITTINGS

Seals are defined⁶ as "tight perfect closures as against gas or water," and "a device to prevent the passage or return of gas, air or liquid into or out of a pipe or container." Fittings are defined as small, often standardized, accessory parts, i.e., in plumbing. So defined, seals and fittings include: 1) means of joining equipment items together, and 2) providing the means for liquid and gas movement, transfer, and measurement. Indispensible industrial applications of seals and fittings are:

<u>Processing Equipment Items</u>	<u>Emission Sources</u>
Pumps	Drive shaft seal
Valves	
In-line	Stem, bonnet

Open-ended	Stem, bonnet, flow-seal
Valves-pressure relief	Seat, flange face
Agitators	Drive shaft seal
Compressors	Drive shaft seal
Flanges	
Pipe line	Face seal
Reactor manheads	Face seal
Measurement devices (pressure, vacuum, temperature, level)	Face seal or thread seal
Process sampling assemblies	Flange, valve
Heat exchangers and process heaters	Process side closures

All the above seals and fittings emission sources are termed primary sources. Additionally there are a group of secondary emission sources which provide worker occupational exposure. These are:

Cooling towers and drains
Wastewater handling and treatment
Waste material disposal

The secondary emissions from these operations are normally a consequence of prior primary emissions from processing equipment seals and fittings.

The remainder of this report will discuss fugitive emissions from chemical processing equipment seals and fittings under the following major headings:

- o Seals and fittings-description and discussion of effectiveness
- o VOC leak detection instruments, sampling techniques, and analytical characterization
- o Emission factors
- o Monitoring
- o Maintenance
- o EPA and chemical industry--potential standards and operating codes
- o General control principles and examples of industrial advances

SEALS AND FITTINGS DESCRIPTION AND DISCUSSION OF EFFECTIVENESS

For purposes of this discussion, the various chemical processing equipment components (all potential sources of fugitive emissions) are grouped into seven major equipment categories: 1) pumps, 2) valves, 3) compressors, 4) flanges, 5) pressure relief valves, 6) cooling towers and drains, and 7) process sampling assemblies. A major factor influencing the extent of fugitive emissions from any seal or fitting is whether the chemical being handled is a gas or a liquid, and if a liquid, its volatility (vapor pressure) at the handling temperature. Compressor seals for gas streams present unique size, design, and operational problems, so they are treated separately from pump seals. On the other hand, agitator shaft seals are considered sufficiently similar to pump seals that they are not discussed individually. The inclusion of cooling tower fugitive emissions does not mean seals and fittings are a major part of the cooling tower design. Rather, recirculating water used as a means of heat transfer becomes contaminated via leaky seals in condensers, heat exchangers, and process heaters. The volatile contaminants in the warm water are released during evaporative cooling. Pressure relief valves are different in function and design from other valves and are discussed separately.

PUMPS

The predominant type of pump employed in the chemical industries is the centrifugal pump. Positive displacement pumps, mostly rotary but some reciprocating, are also employed. The cylindrical shaft linking the drive motor to the rotating pump necessitates some form of shaft seal to retain the moving stream within the pump casting and thus prevent leakage along the shaft to the outside atmosphere. The three common types of shaft seals, listed in order of increasing effectiveness in minimizing leakage are packed, single mechanical, and double mechanical.

Packed Seal

With a simple packed seal (Figure 1) specialized packing material is compressed along the shaft within a stuffing box by means of a packing gland. The basic weakness of this seal is the need to constantly lubricate the interface of shaft and packing to minimize frictional heat buildup that causes deterioration of the packing and loss of seal effectiveness. The lubricant, generally the fluid being pumped or another injected fluid, must therefore be allowed to flow between the shaft and packing at a controlled rate. As explained by Hoyle⁷, a minimum controlled leakage rate of a drop per second provides 15 cups per day for a 300 gallon per minute (gpm) pump. Success in maintaining low controlled leakage depends on proper initial installation of the appropriate packing plus frequent maintenance adjustment. For pumping

toxic or carcinogenic fluids, industry associations recommend pumps be equipped with mechanical seals.

Single Mechanical Seal

With a basic single mechanical seal (Figure 2), shaft leakage is prevented by two sealing surfaces, facing perpendicular to the shaft, one stationary and the other rotating. Usually the primary ring rotates, and the mating ring remains stationary with a close fitting face clearance in millionths of an inch. The single mechanical seal is not a zero leakage device. The face surfaces must be lubricated but the leakage rate is low at about one drop per minute (1/60th that of a packed seal). Ramsden⁸, who identified many design variations, stated that single mechanical seals are inadequate for handling toxic or carcinogenic materials. Single mechanical seals operate effectively for extended periods only if the material being pumped is clean (completely free of grit or solids).

Double Mechanical Seal

The most common multiple seal arrangement is the double mechanical seal (Figure 3). Two single mechanical seals, oriented back-to-back, are mounted to provide a void space between them. Seal fluid is independently circulated through this void space (at a somewhat higher pressure than the product stream and at controlled temperature). Because this design provides limited flow of seal fluid into the product stream, the seal fluid must not be a contaminant in the product stream.

To avoid environmental safety related problems, Ramsden⁸ advocates a tandem seal design wherein two single seals face in the same direction and the seal fluid circulating in the void space is kept at a slightly lower pressure than the product stream. This provides limited flow of the product stream into the seal fluid. In turn, the seal oil reservoir should be connected to a degassing control device to eliminate possible emissions. Seal fluid pressure monitoring can warn of possible seal failure.

Because double mechanical seals perform well, especially at high pressures (150 psig and above), Ramsey and Zolker¹⁰ strongly recommend their use with agitators. Although the initial cost of double mechanical seals is greater than that of other seals on initial installation, the frequency of maintenance is only one-half to one-fourth that of packed seals. Unitary double mechanical seal assemblies, termed cartridge seals, can be replaced without need to remove the drive shaft or enter the vessel. Compared to pumps, agitators require a larger diameter shaft and a more ruggedly constructed double seal to compensate for the lack of a bottom bearing. Also, because the seal is above the liquid level, there is no problem with dust or grit getting into the seal.

General Conclusions and Recommendations

Mechanical seals, both single and double, have some practical limitations:

1. They can only be installed on rotating shafts.

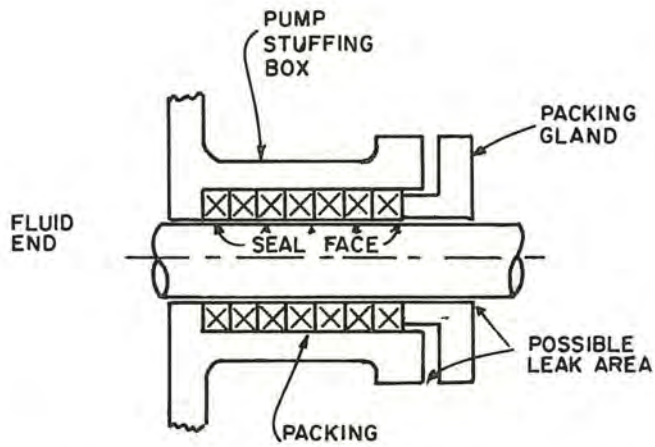


Figure 1. Diagram of a Simple Packed Seal

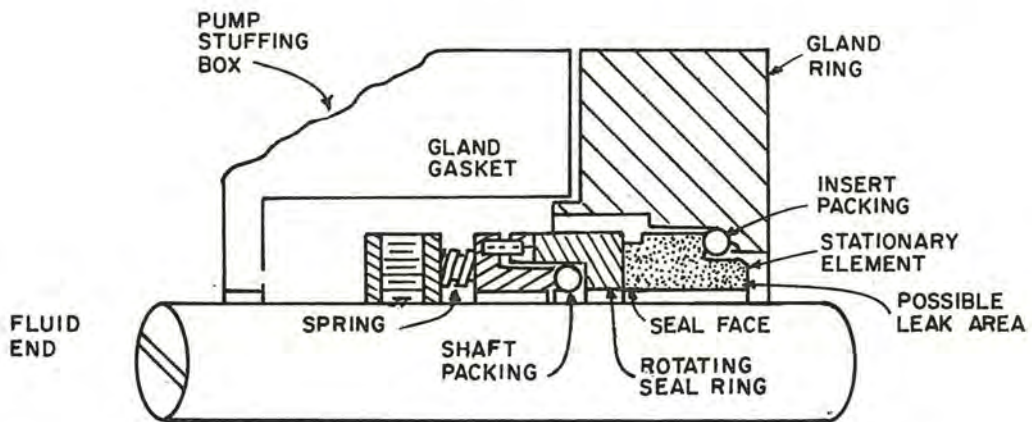


Figure 2. Diagram of a Basic Single Mechanical Seal

Figures 1, 2, 3, reprinted, with permission, from EPA, Reference 9, Page II-3.

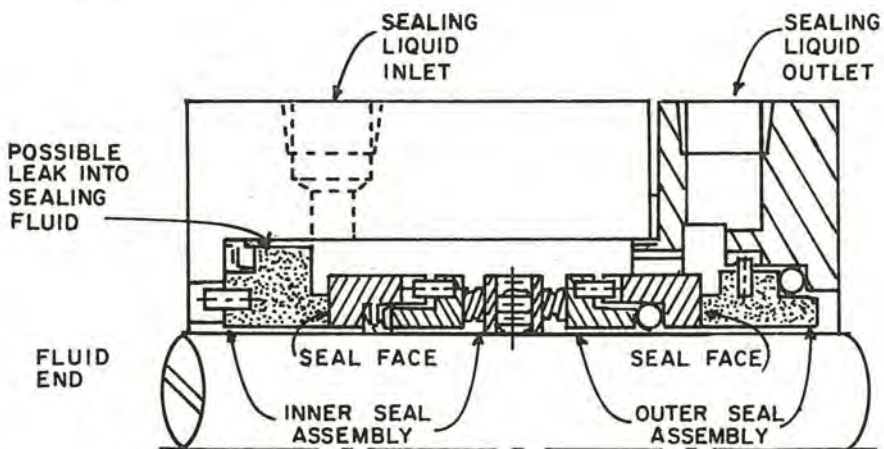


Figure 3. Diagram of a Double Mechanical Seal (back to back)

2. Maximum normal service temperature is approximately 750°F (400°C).
3. Means for filtration of seal fluid must be provided and serviced.
4. Construction materials must be carefully selected to meet the operating situation.

Ramsden⁸ concludes:

1. The initial higher capital cost of mechanical seals (vs. packed) is offset by lower maintenance costs.
2. Installation and initial startup are critical. If properly selected and installed (a skilled maintenance operation), an operating life of up to 2 years can be expected with mechanical seals.
3. A single mechanical seal is not adequate where emission control requires essentially zero leakage of toxic or carcinogenic VOC; either a double mechanical seal or preferably a sealless pump should be selected.

Recent conclusions⁹ for the SOCFI are that:

1. With properly operating double mechanical seals, VOC leakage occurrence is negligible.
2. In the SOCFI, approximately 10 percent of the seals used with the current pumps are packed seals; 72 percent, single mechanical seals; 17 percent, double mechanical seals; and 1 percent, sealless.
3. Double mechanical seals can be used in most new pump applications and probably can be retrofitted to replace many current single mechanical seals and some packed seals.

Sealless Pumps

A limited number of canned and diaphragm type sealless pumps (hermetically sealed) are now used in the chemical process industries. Although they have the advantage of being leak proof, they have not been widely adopted, probably because of somewhat higher initial cost and lack of long-term performance history. The canned pump, a centrifugal type, has the motor rotor and pump casing interconnected and the motor bearing running in the process fluid. The diaphragm pump, the other type of sealless pump, is piston activated; a flexible diaphragm of suitable material provides the necessary pulsations. Sealless pumps are being employed in the chemical process industries for pumping highly volatile organic solvents and toxic or carcinogenic liquids whose emissions are likely to exceed OSHA exposure limits. To date, the petroleum refining industry has not used these pumps, possibly because the American Petroleum Institute (API) pump standard does not recommend them.

Slurries (liquid streams suspending solid particles) containing VOC components present a difficult pump selection problem. Rapid pump seal abrasion or failure result in major fugitive emission rates. Neerkin¹¹ states sealless pumps, canned or diaphragm, are almost mandatory. Some successful experimental trials with special mechanical seal pumps have been conducted recently, however.

VALVES

Valves provide the second largest number of fugitive emission sources in the petroleum refining and chemical processing industries, and also the largest percentage of fugitive emissions. They can be classified by:

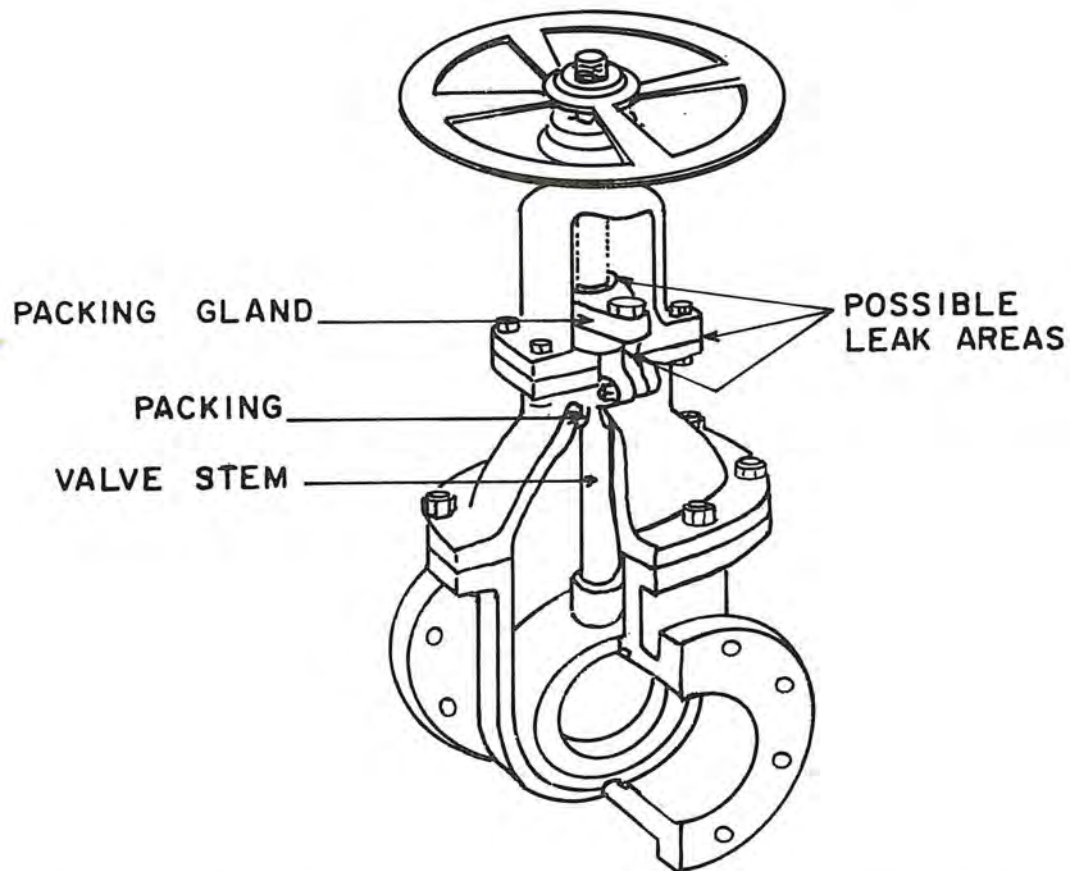
1. Where placed--in-line or open-ended
2. How operated--manual or remote control
3. Type--globe, gate, plug, ball, etc.

Pickulik¹² states that about 50 percent of all industrial valves are on/off; 40 percent, flow throttling; and 10 percent, back flow preventing. Back-flow prevention is usually by totally enclosed check valves. With proper installation, their only emissions would be from flange facings. Most remote control valves are flow-throttling according to Carey and Hammitt¹³ with four basic valve design styles employed--cage style globe, ball, eccentric disk, and butterfly.

Three types of leakage occur with valves:

- o Flow seal leakage occurs when process material leaks past the closed flow control element. This type of leakage is a process problem for inline valves and a major source of occupational exposure with open-end valves. Open-end valves, estimated at approximately 30 percent of all valves employed in the SOCFI⁹, are largely employed for sampling, venting, and draining. Flow seal leakage from open-end valves can be prevented by closing the open end with blind flanges, caps, or plugs. A short length of pipe, with a small diameter bleed line and bleed valve attached, should be inserted between the valve and cap or plug for worker protection.
- o Process material escapes from the valve via two paths. Figure 4 identifies these two points of leakage for a gate valve: 1) from the stem; and 2) from the joining ring to the valve body (the bonnet). Both types of leakage can occur simultaneously, but stem leakage is both more common and normally greater.
- o Air leaks into the valve and joins the process material under vacuum operation. This leakage presents a difficult processing problem, but not an occupational worker exposure hazard.

Except for relief and check valves, most valves are opened or closed by a



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Figure 4. Diagram of Gate Valve

rotating valve stem. This stem needs a seal to isolate the interior flowing material from the outside atmosphere. The majority of valves use a stem seal in the manner of a packed pump. Flexible packing material in a stuffing box around the stem is compressed by a gland. Unlike most pumps, valves are operated intermittently. A valve that has not been used (set either in an open or closed position) will frequently leak through the stem packing when reset. Frequent maintenance is necessary to minimize leakage. The bonnet seals of valves come in a number of designs, but the basic closure consists of a suitable gasket between the faces of a flange. Hence the leakage problems for bonnet seals are similar to those of flanges in general.

Most manual stem valves are operated by a hand wheel or lever, which places the production operator in close contact with VOC emissions. Partly for this reason and also ease of operation, a number of manual accessories are employed to open or close manual valves. From the occupational exposure standpoint, they help place the production worker at some distance from the valve during its opening or closing.

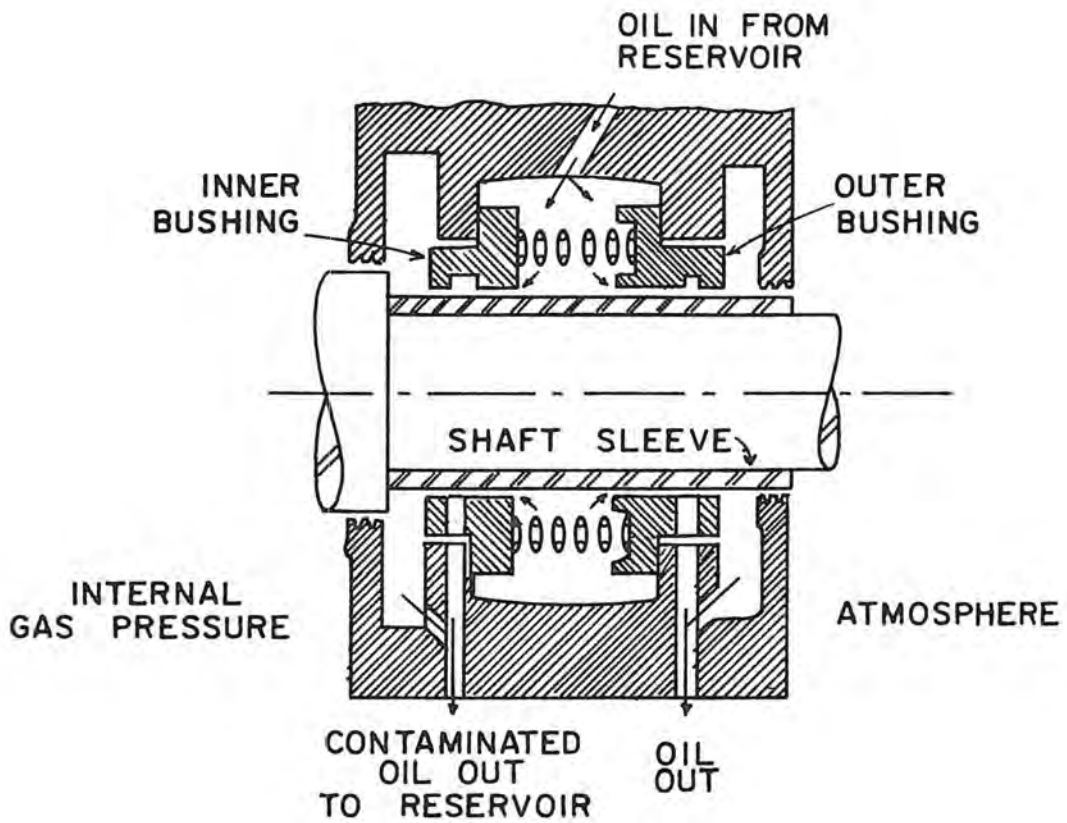
Packless type valves are commercially available for handling toxic or carcinogenic fluids and gases. There are two main types, differing chiefly in the means of isolating the valve stem from the process stream. In the diaphragm type, closure of a flexible diaphragm to vary flow rate is accomplished by means of a plunger attached to the stem. Service life and allowable operating conditions are dependent on the choice of flexible diaphragm material. Temperature extremes and high pressures have to be avoided. For high temperature and pressure service, a sealed metal bellows type of packless valve is a more suitable choice. The sealed metal bellows type has major disadvantages of capital cost and service life restriction.

COMPRESSORS

Like pumps, both centrifugal and positive displacement type compressors require a seal around the shaft to isolate the internal high pressure compressed gas from the atmosphere. Sealing this shaft is considerably more difficult than sealing a pump shaft. Also, the high-speed centrifugal compressor is itself a complex unit that must be very carefully balanced at its operating speed before use. Boyce¹⁴ describes and details a complex mechanical seal in which the special seal oil entering the seal cavity is maintained at about 25 to 30 psig above the gas pressure within the compressor. A liquid film seal (Figure 5) can also be successfully employed. The seal is the film of oil that flows between the stationary gland and the rotating shaft. Oil leaving the compressor seal under the system's internal gas pressure is admixed with some pressurized gas. On return to the independent oil reservoir, the contaminating gas is released through pressure drop. This released gas should be vented to a central disposal unit.

FLANGES

Flanges are a means of joining two pieces of pipe or equipment together by inserting a suitable gasket between two adjacent flange faces. Generally, the flanges are compressed against the gasket material by means of bolts. Additionally, flanges or modified flanges are used to attach reactor manheads,



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Figure 5. Liquid-Film Compressor Shaft Seal

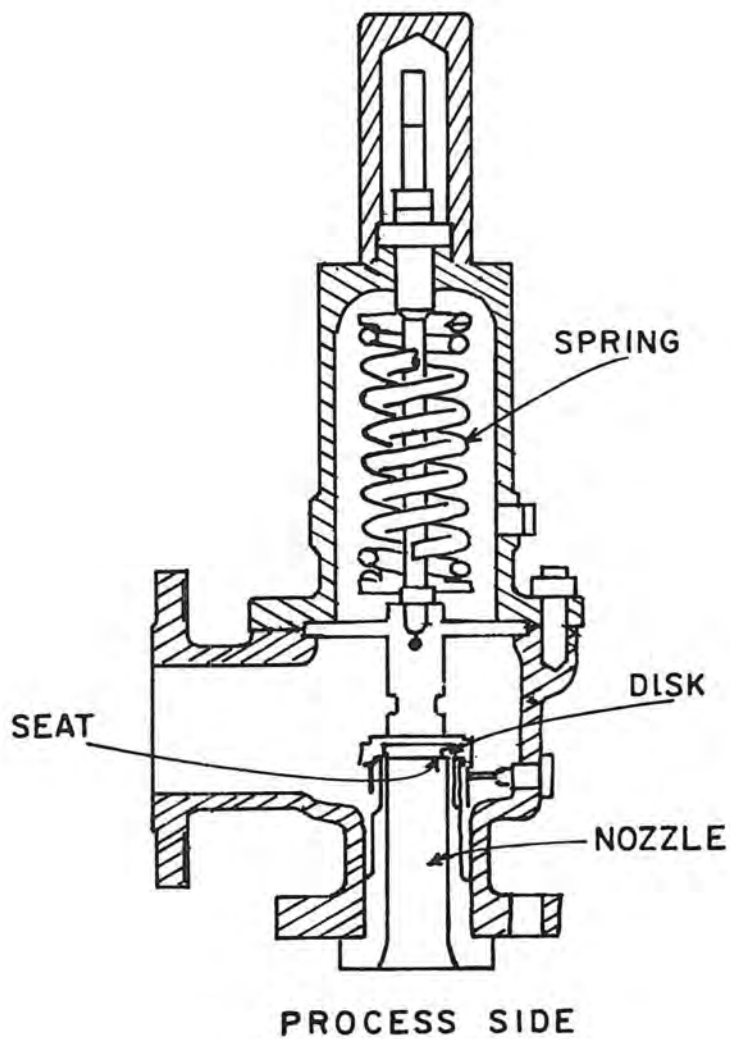
agitators, and a variety of measurement devices to chemical processing equipment such as reactors, pressure vessels, etc. The primary causes for VOC emissions from flanges are: 1) improper fit due to nonaligned flange faces; 2) seal deformation due to stresses from adjacent piping or equipment; and 3) repeated openings without changing the gasket. The last presents problems in getting a tight seal on reactor manheads. Joining of equipment and pipe sections by welding is preferable from the standpoint of emissions control and is probably less expensive; however, because equipment frequently requires replacement, removal, isolation, or individual cleaning and repair, flanges are needed.

PRESSURE RELIEF VALVES

On any closed chemical processing system where pressure conditions may unexpectedly exceed the maximum the equipment design allows, a means "to relieve excess pressure" must be included. Figure 6 details a common spring-loaded relief valve, which has a seal surface held in place by means of a vertically mounted spring. The spring is designed to withstand the maximum safe operating pressure; if the maximum is exceeded, the spring opens to release gas or fluid or both. In manufacturing practice, there are two causes for fugitive emissions. The first is imperfect reseating following a relieving operation. Here material fouls the seat surface, frequently materials which solidify at ambient air temperatures. Second, simmering can occur when the system pressure fluctuates closely about the relief valve set pressure. A practical and relatively inexpensive means of minimizing relief valve fugitive emissions is installation of a rupture disk upstream from the relief valve (Figure 7). The rupture disc, like the relief valve, is designed to break at the maximum allowable system pressure. The odd configuration of Figure 7 is deliberately designed to prevent shattered rupture disc particles from entering the relief valve and preventing its later reseating. Installing a pressure gauge provides a visual means to readily detect a ruptured disc. Estimates that pressure relief valves provide 10 percent of SOCOMI total fugitive emissions emphasize the importance of this source of fugitive emissions, and the inadequacy of many current relief valves installations. The normally gaseous fugitive emissions from relief valves should be vented to a disposal unit.

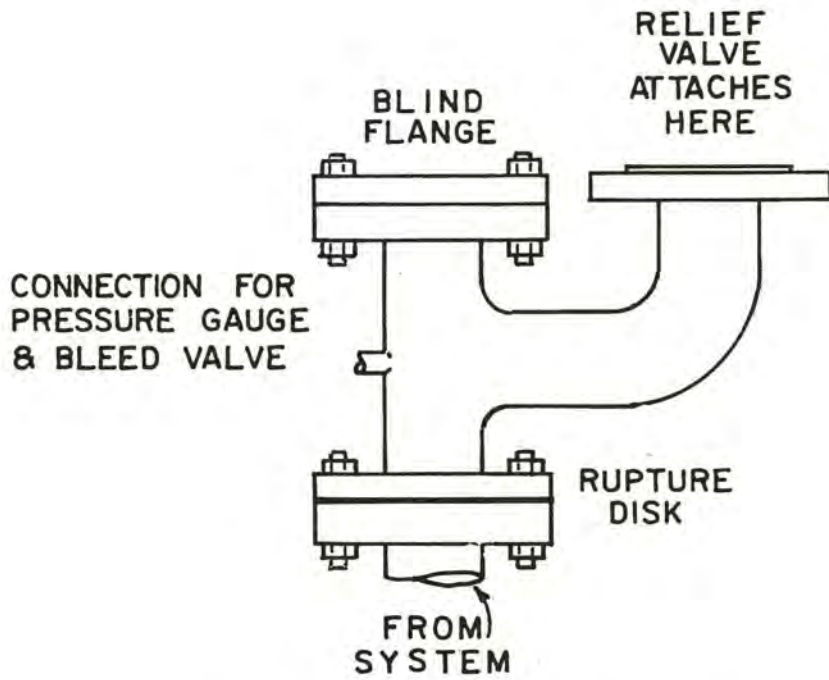
COOLING TOWERS AND DRAINS

Both cooling towers and process drains, while considered secondary fugitive emission sources, are important from the standpoint of the occupational exposure of production workers. The recirculating water coming to the cooling tower for evaporative cooling picks up VOC emissions from seal leaks on the process side of a number of types of heat transfer equipment. Getting a reliable reading of VOC content of the air near the cooling tower is difficult because of wind currents. Another way to detect VOC emissions is to monitor the recirculating water flowing to the cooling tower using a total organic carbon (TOC) analyzer. Above normal organic carbon results are an indication that one or more of the heat transfer seals leak. These must be tracked down by water analysis of effluent from the different units making up the entire cooling water equipment chain. Portable VOC detection units can be used to locate VOC fugitive emissions coming from open flow channels and drain openings on waste water systems. Installation of drain outlets incorporating



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Figure 6. Diagram of a Spring-Loaded Relief Valve



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Figure 7. Diagram of a Rupture Disk Installation Upstream of a Relief Valve

check valve type traps and elimination of any open drain channels is important. Again, systematic checking of individual process equipment items will be needed to locate the specific sources of VOC emission contamination of the waste water stream.

PROCESS SAMPLING ASSEMBLIES

Sampling of chemical process flows at various points in the processing sequence presents an important occupational health exposure problem. Too little attention has been given to VOC emissions from the seals and fittings of process sampling assemblies. The production worker is in close proximity to any emissions while taking samples. A prime requisite for valid sampling is that sufficient flow be purged through the line to ensure a representative sample. The POOR sampling technique (Figure 8) represents the unfortunately too common situation where the flushing liquid contaminates the floor or ground before running down a surface drain to also contaminate the wastewater stream.

Ideally, a sampling plan and program should be planned in the process design stage and be part of the initial equipment installation. Automated sampling coupled directly to a process analyzer may be justifiable on the basis of occupational health exposure. The sampling plan must provide the means of safely obtaining all the samples needed to adequately: 1) evaluate process operation; 2) establish material balances; and 3) ensure finished product quality. Additionally, short term sampling may be required to trouble shoot equipment operating problems and during startup.

The following devices may be employed where only small samples are needed for analysis:

- o A sampling plug cock, as an indirect sampler, modified by adding sample and vent parts to the valve body.
- o A piston-ram type valve.
- o A hypodermic type syringe to withdraw materials through a septum attached to a by-pass loop of the process line.

For larger samples, the BEST solution (Figure 8) is the closed loop with flow directly through a sample bomb. Following adequate flushing to provide a representative sample, this special sample container is removed and transferred to the laboratory. The laboratory, in turn, needs ventilated hoods within which the laboratory analyst can handle the sample container and analytical equipment without exposing himself.

OTHER SOURCES AND FUGITIVE EMISSIONS CAPTURE SYSTEMS

Another VOC fugitive emission source, considered of minor importance from the standpoint of total fugitive emissions, is threaded pipe connections. Now obsolete in the chemical processing industries as a means of joining piping, threaded connections attach a number of measurement devices (pressure, vacuum, temperature, etc.) to chemical process equipment units. The production workers' close proximity to these measurement devices while noting process

SAMPLING SYSTEMS

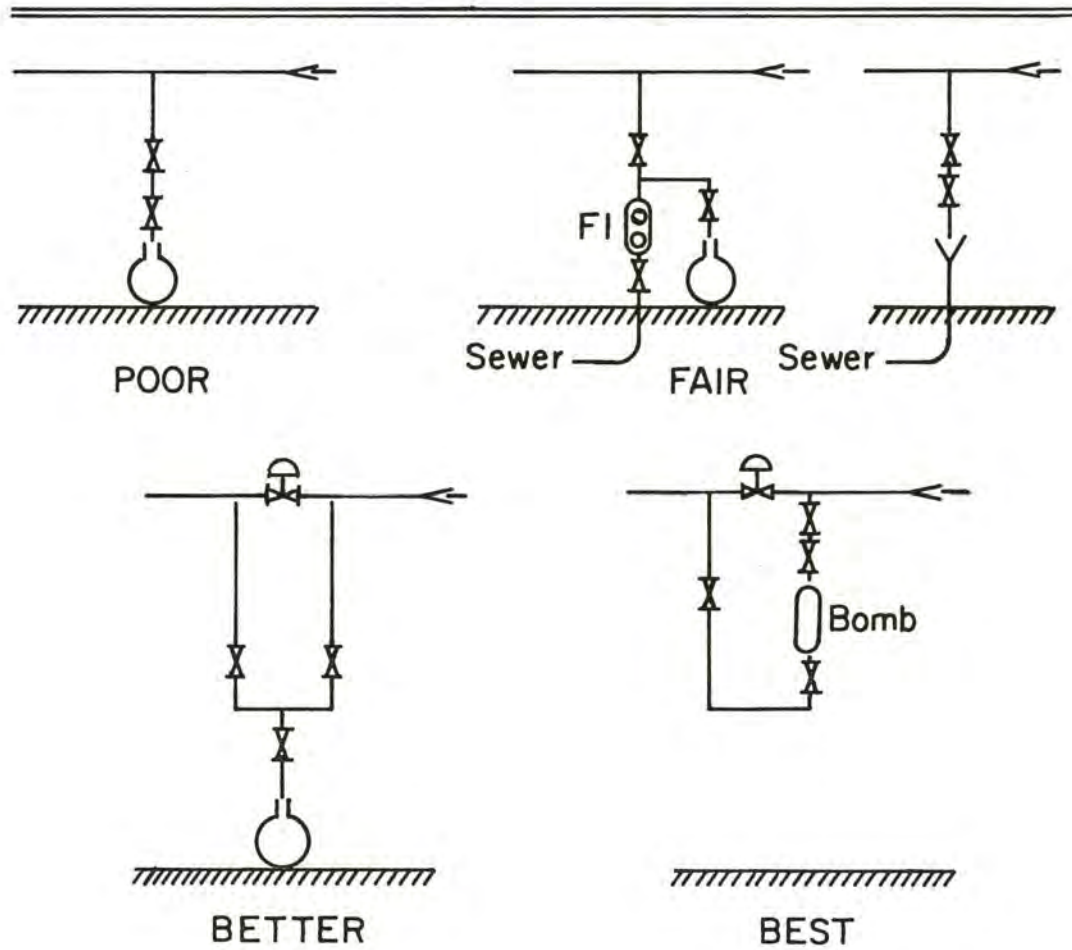


Figure 8. Sampling Systems

conditions provides exposure to any emissions from leaking threaded connections.

Fugitive emission capture systems are needed for handling toxic or carcinogenic chemicals. As part of the strict regulation of vinyl chloride monomer (VCM) in polyvinyl chloride (PVC) polymerization plants, EPA emission standards set a 10 ppm VCM concentration limit for any stream leaving the plant enclosure. As detailed by Knox^{2a}, current PVC plant design includes multiple-source vent collection of VCM emissions (both point and fugitive) and storage within a large gas holder. The gas holder provides a steady feed flow to a VCM recovery system. Nonrecovered VOC emissions leaving the recovery unit are burned (thermal oxidation in a flare-type incinerator). Such flare-type incinerators can be useful in other chemical processing installations to dispose of both point and fugitive emissions, and thereby help meet EPA environmental standards. Local ventilation (vent lines collecting fugitive emissions from selected processing equipment seals and fittings) followed by flare disposal is preferable to general ventilation discharge of large volumes of warm, contaminant-laden air directly outside plant buildings. This combination minimizes worker occupational exposure by maintaining low PEL values near the emission sources and also reduces environmental pollution. Local ventilation with flare disposal is not economically practical for the extended outdoor installations of the petroleum refining, petrochemical, and synthetic organic chemical manufacturing industries. However, in specific areas of an extended petroleum refinery installation (i.e. catalytic cracking, coking, asphalt processing, aromatics extraction, and API separators), this approach should be considered for minimizing emissions of toxic or carcinogenic chemicals such as benzene, anthracene, biphenyl, and other polynuclear aromatics (PNA's).

Important segments of both the petroleum refining and chemical processing industries are the loading and unloading facilities for raw materials and finished products, respectively. For high thruput industries, these operations are generally conducted in the open via bulk handling (trucks, rail cars, barges and ships). For small specialized chemical processing operations within building enclosures, material containers normally range in size up to 55 gallon drums. In either situation, open vapor sources as well as fugitive emissions require emission collection via local ventilation capture vents to maintain low levels of toxic or carcinogenic chemical in the air around the workers. Disposal of the captured VOC will depend on EPA environmental standards, feasible disposal techniques, and economic considerations.

VOC LEAK DETECTION INSTRUMENTS, SAMPLING TECHNIQUES, AND ANALYTICAL CHARACTERIZATION

The information in this section on the means to detect, sample, and characterize fugitive emissions occurring from seals and fitting components of processing equipment in the petroleum refining and chemical processing industries is also of use to other manufacturing industries where toxic or carcinogenic chemicals may similarly leak.

The EPA contractors employed portable detecting instruments to locate leaks from the various types of seals and fittings. After experimental trials with instrument probes held at different short distances from the surface of a leaking seal, it was concluded that the most consistent set of readings would be obtained with the probe placed directly on the seal face (zero centimeters or 0 cm). A leak was deemed sufficiently large to warrant sampling, followed by testing to establish an emission rate (pounds per hour), when the instrument reading was at least 200 parts per million by volume (ppmv) at 0 cm distance. While EPA was investigating instrument detection levels from 200 ppmv upward, sizable seal and fitting leaks actually provided detector readings above 10,000 ppmv (at 0 cm).

Production supervisors, industrial hygienists, and production workers while normally not concerned with instrument readings taken directly at the seal surface, are concerned with the contaminant level in the air within a few feet or further from the origin of the fugitive emission. Radian¹⁶ demonstrated a 10,000 ppmv instrument reading taken directly at the leak source (0 cm) is roughly equivalent to a 1,000 ppmv level measured 5 cm from the leak source. For EPA emission factor determination, instrument sensitivity, care in instrument calibration and emission compound identification are not critical factors. However, for worker occupational exposure determination, all three factors are vitally important; since for toxic or carcinogenic VOC's, maximum 8-hour TWA permissible exposure limits (OSHA PEL limits) fall within a zero to 200 ppmv range. Hence for leak detection, a readily portable instrument is required that will quickly detect and roughly quantify suspected fugitive emissions; whereas for worker occupational exposure measurements, instrument requirements are the ability to accurately quantify low contaminant levels and identify chemical components of the fugitive emissions.

VOC LEAK DETECTION INSTRUMENTS

The various EPA contractors employed the following detection instruments manufactured by two separate suppliers: Organic Vapor Analyzer, OVA models 108 and 128, Century Systems Corporation, Kansas City, Kansas and TLV Sniffer, Bacharach Instrument Company, Mountain City, California.

All three instruments provide direct readings of hydrocarbon concentrations in

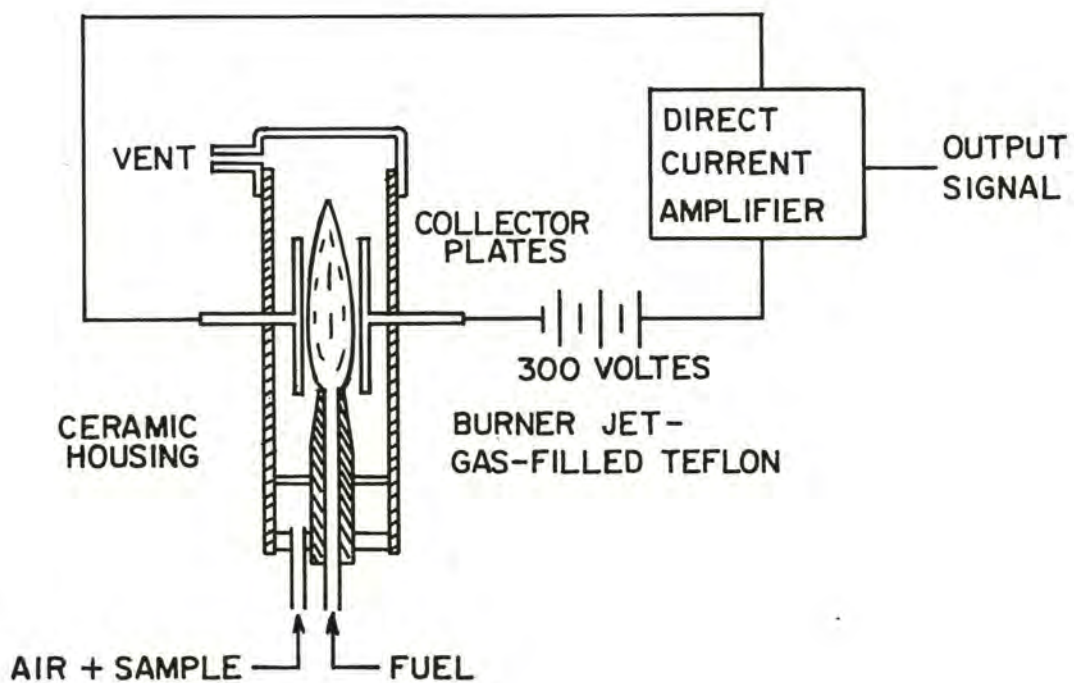
ppmv. The OVA models 108 and 128 utilize a hydrogen flame ionization detector (FID) and are standardized by the manufacturer against methane (CH_4 -M.wt. 16). The TLV Sniffer operates on a heat of combustion principle (catalytic oxidation) and is standardized against hexane (C_6H_{12} -M.wt. 84). The manufacturer's list the instrument sensitivities as 0.5 and 0.2 ppmv methane for the OVA 108 and 128 models, respectively, and 2 ppmv hexane for the TLV Sniffer. Scale readout for the OVA 108 model is 1 to 10,000 ppmv methane; the OVA 128 scales cover three ranges: 0 to 10, 0 to 100, and 0 to 1,000 ppmv methane. By employing a calibrated dilution probe, the OVA 128 model scale can be read in ranges of 0 to 10,000 ppmv and 0 to 100,000 ppmv methane. The TLV Sniffer can be set to scales of 0 to 100, 0 to 1,000, and 0 to 10,000 ppmv hexane, and with the use of a calibrated dilution probe, the sniffer can read 0 to 100,000 ppmv hexane. Although the manufacturers standardize against methane and hexane, respectively, the customer can restandardize any of the three instruments again either standard, or indeed against a completely different chemical or mixture of chemicals, if desired.

For most individual hydrocarbons, the OVA response falls within 50 to 250 percent of the response of methane. Unfortunately, VOC's having either chlorine or sulfur bonding are relatively unresponsive to both OVA and TLV Sniffer instruments. With OVA models factory-calibrated with methane to give a 100 ppmv response, other common hydrocarbons respond as follows: propane - 85; ethylene - 65; acetylene - 225; benzene - 235; and toluene - 150. In the unlikely case that a specific area in an oil refinery contains only benzene as an air pollutant, the OVA reading would simply be multiplied by a 2.35 factor to provide a true ppmv benzene occupational exposure figure.

Figure 9 presents a schematic diagram of the flame ionization detector (FID) employed in the OVA models 108 and 128. The laboratory FID units mix pure hydrogen (which on burning is both free of ions and nonconducting) with the sample (hydrocarbon material) before burning. On burning, ions are formed, the flame becomes conductive, and the conductivity is measured. Unlike the laboratory FID units, the OVA models introduce a sample-air mixture and the pure hydrogen fuel separately. The sample-air stream enters through a porous bronze filter which disperses the mixture around the hydrogen flame. By altering the ion formation process, the OVA instrument response to various hydrocarbons varies significantly from that of the laboratory FID instruments (see responses listed above for individual hydrocarbon compounds).

To obtain consistent reading when using any of these three fugitive emission detection instruments, the EPA contractors prepared and followed detailed measurement operation instructions for each category of seals and fittings. These detailed instructions are included in an EPA Guideline.¹⁵

A common situation in the various chemical processing industries and particularly in petroleum refining is that of mixed pollutants in a chemical processing area. Identifying and quantifying of the individual chemicals in such a mixture is necessary to evaluate worker occupational exposure to specific individual toxic or carcinogenic compounds having low exposure limits. Fortunately, the OVA model 128 has a portable gas chromatograph (GC) option. By using the combination instrument with a strip chart readout, the concentration of specific compounds in a known mixture can be obtained directly



Reprinted, NIOSH Symposium, Reference 2b, Page 53.

Figure 9. Flame Ionization Detector Hydrocarbon Analyzer Burner-Detector - OVA Type

in the field within a half-hour. Adding the GC option and strip chart printout does add to instrument weight and size, and somewhat reduces its portability. Preconsultation with plant personnel about stream flow composition at any particular processing point is helpful.

A complication, which must be anticipated, is that composition of a fugitive emission at a leaking seal or fitting may differ from a flow stream analysis because of differences in volatilities of the mixture components. A calibration curve for the mixture needs to be developed in a field laboratory by recording and plotting the OVA model 128 responses to a range of known concentrations of an equivalent or laboratory blended mixture.

For occupational exposure investigations, the Wilkes series of infrared analyzers (Moran tradename) can also be used. Of these, the most sophisticated and useful in handling mixed component fugitive emissions is the Moran model 80. This unit is an accurate single-beam infrared spectrometer coupled to a micro-computer. Analytical results are obtained within minutes. However, the unit is expensive, only semi-portable for field investigations, and sensitive to any mistreatment or rough field handling. Unlike the OVA models 108 and 128 and TLV Sniffer, the Wilks infrared analyzers readily detect and quantify hydrocarbon compounds having chlorine and sulfur bonds.

SAMPLING TECHNIQUES

When a seal or fitting is determined to be leaking sufficiently to warrant sampling, a procedure for enclosing the unit, termed "bagging," is applicable. Bagging is the construction of an enclosure around the leaking item using duct tape and flexible Mylar or Teflon plastic films. It is difficult, particularly with bulky, hot, and hard to reach seals and fittings. Although the samples are generally gaseous, they can be liquid or two-phase gas/liquid combinations (techniques for sampling both liquid and two-phase liquid/gas streams were developed by the EPA contractors.) This discussion concerns gaseous emissions since they occur more often. Bagging a seal or fitting provides the means to: 1) get a representative sample; 2) measure the emission flow volumetrically; and 3) provide the basis for calculation of the emission flow in pounds per hour.

With an enclosure in place, a sampling train is connected. Two basically similar sampling trains are used: one (Figure 10) is a suction operation with a vacuum pump at the exhaust end; the other (Figure 11) is a pressurized sample train that uses an installation instrument air source. With the suction train, the background VOC concentration in the area around the tented unit must be carefully determined as this background concentration must be subtracted from the fugitive emission concentration. The gaseous fugitive emission is pulled through a cold trap where heavier hydrocarbons and water condense (to prevent fouling of the train). From there, the fugitive emission is drawn by the vacuum pump past a sampling outlet and through an orifice meter for flow rate measurement. An analytical sample is obtained by syringe withdrawal of a portion of the main flow. The syringe gas sample is later pushed into an evacuated Teflon sample bag via the three-way valve. A water manometer provides the pressure reading needed to correct sample volume to standard conditions. After analytical determination of the VOC content of the

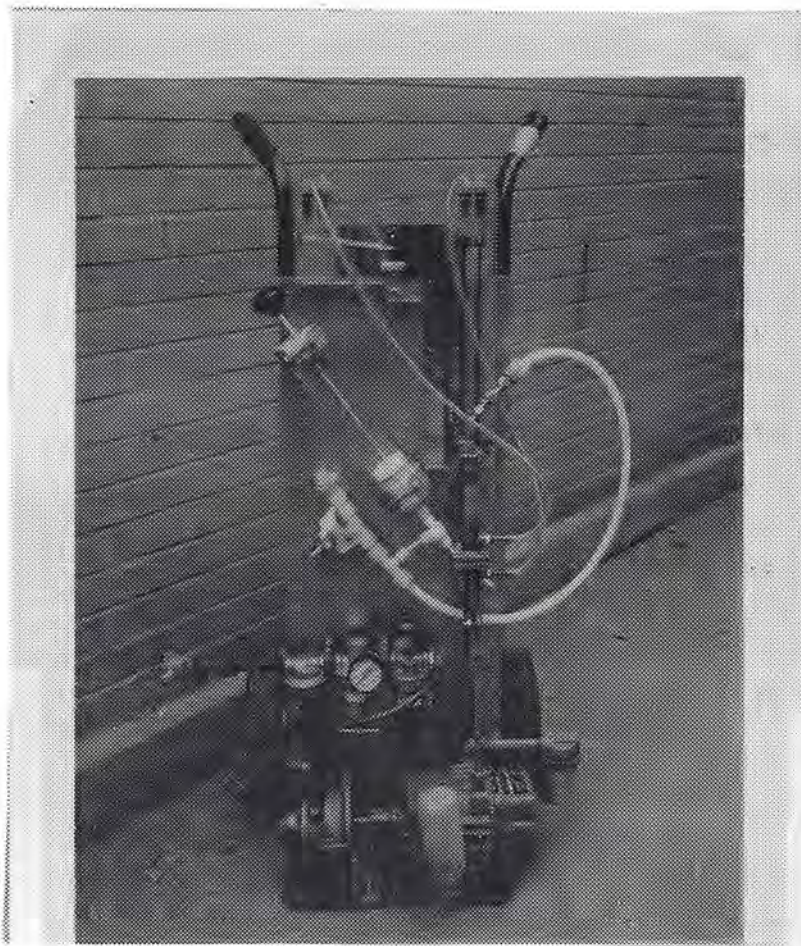


Figure 10. Vacuum flow-through sampling train used for fugitive hydrocarbon emissions testing. (Photo and diagram supplied by Monsanto Research Corporation)

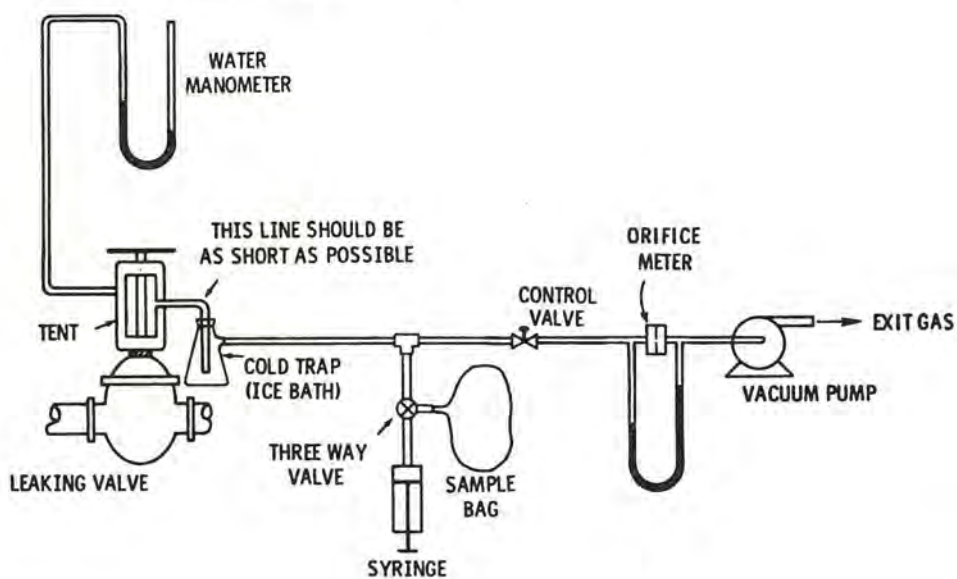
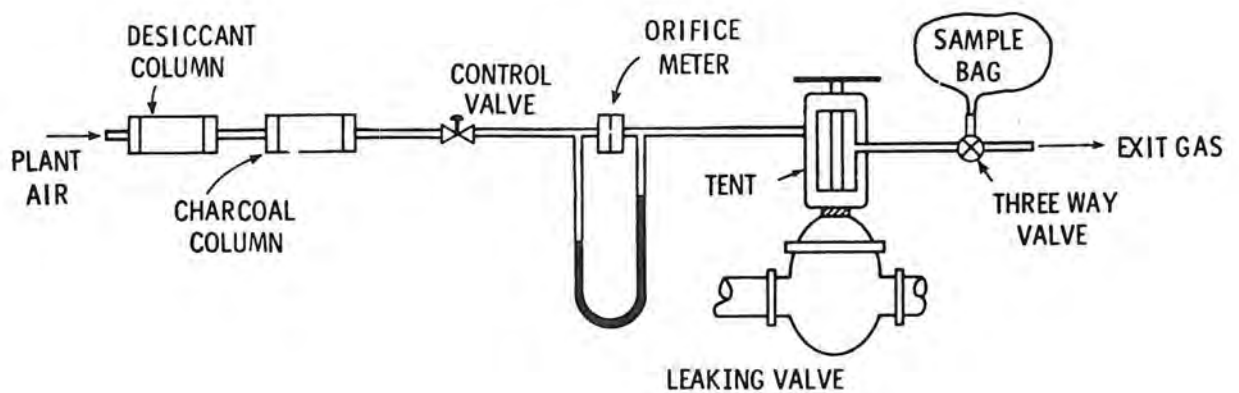




Figure 11. Pressurized flow-through sampling train used for fugitive hydrocarbon emissions testing. (Photo and diagram supplied by Monsanto Research Corporation)



Teflon bag sample, the emission rate (pounds per hour) is calculated from the VOC content and the measured gas flow rate (corrected to standard conditions). The pressurized sample train system is recommended since its use obviates the need for determining the ambient air contaminant concentration. Within plant enclosures with ambient background concentrations above 10 ppmv, it is especially valuable. Also the desiccant and charcoal columns do a better job of removing water and heavier hydrocarbons than does the cold trap in the suction system. The photos in Figures 10 and 11 demonstrate compact, portable designs of the two types of sampling trains.

ANALYSIS

In an organized study of fugitive emissions in a large outdoors installation, such as a petroleum refinery, the bagged samples are taken to a field laboratory. Here the fugitive emission samples are analyzed, normally by gas chromatography. Before the actual analyses, the analyst does a considerable amount of preparatory work:

- o Preidentifies the specific peaks at which all the chemicals in the fugitive emission samples may show up in the GC strip chart.
- o Develops response curves for each chemical present so that the concentrations can be calculated in ppmv from the peak heights shown on the chart.

For large-scale sampling programs, fugitive emission detection, sampling, and analysis should be organized so that the entire cycle is performed in a minimum time, certainly within the same day. Only with this capability can sample re-checking and recalibration be meaningful.

EMISSION FACTORS

The specific provisions of the Federal Clean Air Act of 1970, with 1977 amendments (sections 110, 111, and 112) authorize EPA to oversee industrial air pollution in the United States. Of particular importance to industry is the EPA requirement for a new source review for any added manufacturing activity that would cause emission of 100 tons or more per year of total pollutants to the environment. This applies both to proposed construction of an entirely new installation or a sizeable expansion of an existing installation. Over a full year's continuous operation, the 100-ton-per-year requirement equates to 23 pounds per hour of pollutants from all sources. Total pollutant generation covers not only fugitive and point source emissions of VOC but also particulates, nitrogen oxides (NO_x), and sulfur oxides (SO_x) gases. To estimate total fugitive emissions from a complete installation, accurate fugitive emission factors are needed for all types of processing equipment operated under normal manufacturing conditions (including maintenance). Additionally, equipment layout drawings, process flow sheets, piping drawings, and process material balance information are useful for valid estimation of fugitive emissions in pounds per hour. Similar detailed information on stack and vent emissions is necessary for valid estimation of these point source pollutants in pounds per hour.

For the past few years, issuance and enforcement of EPA regulations for point source emissions has been underway; more recently, investigation has been directed toward fugitive emissions from the seals and fittings of chemical process equipment. At this stage of their fugitive emission investigation, information on the petroleum refining industry is sufficient to provide satisfactory statistical analysis. Therefore, this discussion covers the results from Radian contract studies of this industry.¹⁶

Accurate emission factors must be based on statistically valid data. Most previously published fugitive emission factors were based on (1) somewhat faulty statistical programming and (2) the assumption that fugitive emission leak rates were normally distributed; hence, the arithmetic mean was employed. In this petroleum refinery study, the distribution of potential leak sources among the process units was determined from piping and instrumentation drawings and process flow diagrams before contractor entry to the refineries. From these, a random sample set was selected for screening. This preselection procedure was adopted to eliminate the human bias inherent in on-the-spot choice of items going into the sample set for testing as individual sources of fugitive emissions. In each of the refineries studied, the approximate number of each of the following categories were preselected for screening:^{16a} valves 250 to 300; flanges 100 to 750; pump seals 100 to 125; compressor seals 10 to 20; drains 20 to 40; relief valves 20 to 40. All refinery process streams were classified into three groups:^{16b}

- o Gas/vapor--completely vaporized at process conditions
- o Light liquid/2-phase systems--light hydrocarbon liquids
- o Heavy liquids--primarily kerosene and heavier hydrocarbon liquids

Compressor seal service was defined as being either for hydrocarbon or hydrogen gases.

In Table 1, the statistics and emission factors for nonmethane hydrocarbons from baggable sources are summarized. Listed along with emission factors (pounds per hour), are percentages of leaking units in each seal and fitting category. The percentages are based on emission rates from leaking units providing detection readings of at least 200 ppmv (as hexane) or more than 0.00001 lb/hr. The results generally support a conclusions that the more volatile a process stream, the higher the emission factor and the larger the percentage of leaking units in any seal and fittings category. Percent leakers in different categories range from 3 percent for flanges to 81 percent for compressor seals in hydrogen service.

Three series of nomographs (26 total) were developed:¹⁶

1. correlation of screening value (ppmv hexane) and leak rate (lb/hr),
2. correlation of log normal screening value (ppmv) and percent of total mass emissions, and
3. correlation of log normal screening value (ppmv) and percent of sources.

Because the number of both nonleakers and low level leakers far exceeds the number of moderate and high leakers, a log normal distribution represents the results far better than the arithmetic mean.

Table 2 is of major interest in respect to worker occupational exposure to toxic or carcinogenic VOC. The total population of leakers in any category is broken down into percentages in each of the following leak ranges (pounds per hour): 1) 0.00001 to 0.001; 2) 0.001 to 0.01; 3) 0.01 to 0.1; 4) 0.1 to 1.0; and 5) > 1.0. These percentages are presented in column A. For each category, the A column percentages should add up to the total percent leakers listed in Table 1. Column B presents the percent of total mass emissions attributable to each of the above leak ranges for each category of seals and fittings.

Table 3 (data extracted from Table 2) demonstrates that a relatively small percentage of the leaking units in each category provides the major share of the total emissions from that category.

Table 1. Summary Statistics and Estimated Vapor Emission Factors for Nonmethane Hydrocarbons from Baggage Sources (Petroleum Refineries)*

SOURCE TYPE	TOTAL SCREENED†	NUMBER LEAKING‡	PERCENT LEAKING	95% CONFIDENCE INTERVAL FOR PERCENT LEAKING	PERCENTILE FOR INDIVIDUAL LEAKS (lb/hr)		EMISSION FACTOR ESTIMATE (lb/hr-source)	95% CONFIDENCE INTERVAL FOR EMISSION FACTOR (lb/hr-source)	EMISSION FACTOR PERCENTILE
					1st	99th			
Valves									
Gas/Vapor Streams	683	200	29.3	(25.9, 32.7)	0	0.61	0.047	(0.027, 0.084)	94.4
Light Liquid/Two-Phase Streams	1019	372	36.5	(33.6, 39.5)	0	0.31	0.023	(0.016, 0.034)	89.7
Heavy Liquid Streams	522	35	6.7	(4.6, 8.9)	0	0.08	0.0007	(0.0002, 0.002)	95.8
Pump Seals									
Light Liquid Streams	470	300	63.8	(58.9, 68.8)	0	4.0	0.26	(0.17, 0.39)	89.8
Heavy Liquid Streams	292	66	22.6	(17.1, 28.1)	0	0.87	0.045	(0.02, 0.11)	88.4
Flanges (All)									
Gas/Vapor	2030	62	3.1	(2.2, 3.9)	0	0.008	0.00058	(0.0002, 0.001)	97.4
Light Liquid/Two-Phase Streams	369	10	2.7	(0.8, 4.6)	0	0.008	0.0005	(10 ⁻⁵ , 0.005)	
Heavy Liquid Streams	616	33	5.4	(3.3, 7.4)	0	0.011	0.0005	(0.0002, 0.001)	
	325	6	1.9	(0.2, 3.5)	0	0.009	0.0007	(10 ⁻⁵ , 0.02)	
Compressor Seals									
Hydrocarbon Service	145	102	70.3	(62.9, 77.7)	0	17.0	0.98	(0.46, 2.0)	83.4
Hydrogen Service	85	69	81.2	(71.2, 88.8)	0	2.0	0.10	(0.04, 0.24)	86.5
Drains (All)									
Light Liquid/Two-Phase Streams	255	49	19.2	(14.4, 24.0)	0	1.3	0.070	(0.02, 0.20)	93.3
Heavy Liquid Streams	100	26	26.0	(14.6, 37.4)	0	1.9	0.085	(0.02, 0.32)	
	107	19	17.8	(9.5, 26.1)	0	0.63	0.029	(0.003, 0.21)	
Relief Valves (All)									
Gas/Vapor Streams	148	58	39.2	(25.1, 40.6)	0	4.9	0.19	(0.06, 0.52)	91.9
Light Liquid/Two-Phase Streams	92	42	45.6	(35.2, 56.4)	0	4.0	0.36	(0.10, 1.30)	
Heavy Liquid Streams	28	7	25.0	(10.7, 44.9)	0	0.38	0.013	(0.001, 0.23)	
	23	8	34.8	(16.4, 57.3)	0	0.42	0.019	(0.001, 0.20)	

*Reprinted, with permission, from EPA, Reference 16, Table 4-2, page 22.

†Some streams could not be accurately classified into stream category, so totals are not the sum of the stream groups.

‡Leaking sources in this report are defined as sources with screening values greater than or equal to 200 ppmv or sources with measured leaks greater than 0.00001 lb/hr.

Table 2. Distribution of Measured Leak Rates*†‡
(Petroleum Refineries)

Leak Range (lb/hr)	VALVES						PUMP SEALS			
	Gas/Vapor Streams		Light Liquid/ Two-Phase Streams		Heavy Liquid Streams		Light Liquid Streams		Heavy Liquid Streams	
	A	B	A	B	A	B	A	B	A	B
>1.0	1.0	68.4	0.0	13.8	0.0	0.0	4.0	70.5	0.0	0.0
0.1-1.0	2.6	22.7	3.3	58.8	0.2	33.6	15.7	24.8	5.5	73.2
0.01-0.1	8.6	7.9	11.5	23.7	0.9	48.0	22.5	4.3	9.6	25.6
0.0001-0.01	8.9	0.9	13.4	3.5	2.7	16.9	16.4	0.4	5.8	1.2
0.00001-0.001	8.1	0.1	8.1	0.2	2.9	1.5	4.9	0.0	1.7	0.0
>0.00001	29.2%	100%	36.3%	100%	6.7%	100%	63.5%	100%	22.6%	100%
	COMPRESSOR SEALS				FLANGES		DRAINS		RELIEF VALVES	
Leak Range (lb/hr)	Hydrocarbon Service		Hydrogen Service		All Stream Groups		All Stream Groups		All Stream Groups	
	A	B	A	B	A	B	A	B	A	B
>1.0	15.9	74.2	0.0	0.0	0.0	0.0	1.5	61.6	3.4	76.0
0.1-1.0	33.1	24.3	16.5	75.6	0.2	63.2	4.7	33.0	10.1	19.2
0.01-0.1	16.6	1.4	25.9	22.5	0.6	30.1	6.7	4.9	14.9	4.5
0.001-0.01	4.8	0.1	24.7	1.8	1.4	6.0	5.1	0.5	7.4	0.3
0.00001-0.001	2.1	0.0	14.1	0.1	0.9	0.7	1.2	0.0	2.7	0.0
>0,00001	72.5%	100%	81.2%	100%	3.1%	100%	19.2%	100%	38.5%	100%

*Reprinted, with permission, from EPA, Reference 16, Table 4-4, page 26.

†Most sources were bagged and sampled to obtain leak rates; some were estimated using procedures described in Section 1 of Appendix A, Reference 16.

‡Column A = Percent of total sources screened with sampled leak rates within leak range.
Column B = Percent of total mass emissions attributable to sources within leak range.

Table 3. Correlation of Percentage of High Leakers with their Percentage of Total Mass Emissions (Petroleum Refineries).

<u>SEALS AND FITTINGS</u> <u>CATEGORY</u>	<u>HIGH LEAKERS*</u> (% of each category)	<u>% OF TOTAL MASS EMISSION</u> (% of total for each category)
<u>Valves</u>		
Gas/Vapor	3.6	91.1
Light Liquid	3.3	92.6
Heavy Liquid	0.2	33.6
<u>Pump Seals</u>		
Light Liquid	19.7	95.3
Heavy Liquid	5.5	73.2
<u>Compressor Seals</u>		
Hydrocarbon	49.0	98.5
Hydrogen	16.5	98.1
<u>Flanges</u>	0.2	63.2
<u>Drains</u>	5.2	94.6
<u>Relief Valves</u>	13.5	95.2

*High leakers are defined as the sum of the leaks from the top two leak ranges: 0.1 to 1.0 and 1.0 lb/hr.

As previously mentioned, a random sample set of each category of seals and fittings were preselected, and then inspected for potential leaks by means of the OVA or TLV Sniffer emission detectors. The seals and fittings showing over 200 ppmv readings were bagged and sampled and their emission rates (lb/hr) determined. To relate the random sample set to an entire refinery, Table 4 was prepared for a theoretical refinery having a capacity of 330,000 barrels of crude oil daily. Conclusions drawn from Table 4 are:

- o In this model refinery, the number of flanges and valves is very large (in the thousands). This contrasts to the category totals for pumps, compressors, drains, and relief valves. The refinery size and complexity emphasizes the major scale of monitoring and maintenance requirements for petroleum refinery installations.
- o Proportions of fugitive emissions from each category of seals and fittings in relationship to the model refinery total fugitive emissions* are (in weight percent):

Table 4. Hypothetical Refinery - Based on ADL Texas
Gulf Cluster Model (330,000 BPCD) *

SOURCE TYPE	NUMBER OF SOURCES (PERCENT)		PERCENT OF TOTAL NONMETHANE HYDROCARBON EMISSIONS			
	CASE I †	CASE II ¶	CASE I		CASE II	
			ESTIMATE	(95% CI) §	ESTIMATE	(95% CI) §
Valves	14300	14300	61.6	(46.5, 86.4)	67.3	(48.3, 100)
Gas/Vapor	1430 (10%)	4290 (30%)	17.6	(10.1, 31.4)	40.4	(23.2, 72.1)
Light Liquid/2-Phase	7150 (50%)	5720 (40%)	43.0	(29.9, 63.3)	26.3	(18.3, 38.9)
Heavy Liquid	5720 (40%)	4290 (30%)	1.0	(0.3, 3.0)	0.6	(0.2, 1.7)
Pump Seals	264	264	9.1	(6.3, 13.6)	9.2	(6.3, 13.5)
Light Liquid	106 (40%)	158 (60%)	7.2	(4.7, 10.8)	8.2	(5.4, 12.3)
Heavy Liquid	158 (60%)	106 (40%)	1.9	(0.8, 4.5)	1.0	(0.4, 2.3)
Compressor Seals	27	27	3.9	(2.0, 7.7)	4.1	(1.9, 8.1)
Hydrocarbon Service	14 (52%)	20 (74%)	3.6	(1.7, 7.3)	3.9	(1.8, 8.0)
Hydrogen Service	13 (48%)	7 (26%)	0.3	(0.1, 0.8)	0.2	(0.01, 0.15)
Flanges	51200	51200	7.7	(2.9, 13.4)	5.9	(2.2, 10.2)
Drains	793	793	14.5	(4.1, 41.4)	11.1	(3.2, 31.7)
Relief Valves (Venting to atmosphere)	64	64	3.2	(1.0, 3.9)	2.4	(0.8, 6.7)
			100%		100%	

*Reprinted, with permission, from EPA, Reference 16, Table 4-3, page 25.

†Case I - distribution of stream types for valves and pump seals is weighted toward heavier streams.

¶Case II - distribution of stream types for valves and pump seals is weighted toward lighter streams.

§95% CI - 95% confidence interval for percent of emissions from process fittings attributable to a particular source type. The width of the interval is due only to the uncertainty in emission factors; the percentage of each source type is assumed fixed or known.

δTotal is the sum of nonmethane hydrocarbon emissions from the six sources discussed in this table.

Valves -	62-67
Pump seals -	9
Compressor seals -	4
Flanges -	6-8
Drains -	11-14
Relief valves -	2-3

*Note: Includes the listed categories only; excludes emissions from storage tanks, cooling towers, and waste and wastewater disposal.

There is still a question whether the petroleum refinery emission factors are directly applicable to the other chemical processing industries. Elements favoring lower emission factors for these other industries are: 1) the generally lower volatilities of the chemicals handled; and 2) possibly more rigorous levels of maintenance. A possible adverse factor is the more general handling of slurries, corrosive materials, and multiphase systems in the other chemical processing industries. Regardless of the specific emission factors, the general conclusions derived from the Radian petroleum refinery study are applicable to the other chemical process industries.

MONITORING

As already noted, a small percentage of the total seals and fittings components of petroleum refinery processing equipment in any installation account for the major share of the total fugitive emissions therefrom. The key to effective fugitive emission control is monitoring to locate the high emission rate leakers and quick repair to eliminate the leaks. This is much easier stated than effectively carried out. There are many practical problems and also an overriding economic question of cost effectiveness. Four techniques of monitoring to provide systematic emission detection were studied by EPA¹⁷:

- o source monitoring--complete individual component survey
- o area monitoring,
- o unit boundry survey, and
- o fixed point monitoring

The first three techniques basically apply variations of the use of portable VOC leak detectors: the fourth is based on placement of automatic sensors.

SOURCE MONITORING

For a complete individual component survey, each potential leak source is screened with a portable leak detector. By this approach, all significant fugitive emission sources can be located. However, it is very labor intensive as the monitoring must be conducted carefully and completely. A two-man team is recommended--one to operate the detector and the other to record results. For the model refinery (Table 4) with its thousands of seals and fittings components, an effective complete component survey was estimated to require approximately 1,000 hours (two-man teams) and cost approximately \$14,000.^{15,17} A still unresolved question is how frequently such surveys would need to be scheduled.

AREA MONITORING

Area monitoring means measuring the ambient VOC concentrations as the detection team walks along prearranged paths (via a grid diagram) in any specific processing area. Using a portable VOC detector equipped with strip chart recorder, any high reading points in the planned path are noted on the recorder. After this area walk-through is completed, individual equipment units located near the high reading points would need to be closely and individually checked. For this type of monitoring in petroleum refineries,

current estimates are a two man team can tour the entire model refinery (Table 4) in 60 hours compared with 1,000 hours for a complete source monitoring. If unit area surveys were performed monthly, the annual monitoring cost for the model refinery are estimated at approximately \$10,000. There are obvious disadvantages. From the standpoint of reducing fugitive emissions to the environment, unit monitoring may be effective; for prevention of worker exposure to toxic or carcinogenic chemicals, it is deemed inadequate.

UNIT BOUNDARY SURVEY

This is a variation of area monitoring, where the monitoring team walks around the perimeter of each entire installation or possibly around each processing area module. It is the least expensive method of monitoring and also the least effective.

FIXED-POINT MONITORING

Fixed point monitoring means placing automatic sensors within process areas having the potential for toxic or carcinogenic VOC emissions. Placement can either be near specific pieces of equipment or located in a grid pattern throughout a process area. The monitoring equipment can be chosen to analyze onsite or at a central location. Location of the samplers and choice of the type of analyzer should be carefully planned in the initial engineering stage. Currently, there are three types of automatic fixed-point monitoring systems for specific chemicals: 1) gas chromatography (GC); 2) Fourier transform infrared; and 3) Wilks infrared. These fixed-point systems have high capital installation costs but relatively low manpower requirements. With a grid pattern installation, any alert must be followed up by portable VOC detector testing to pinpoint the leak or leaks. A tremendous plus for this monitoring approach is that it provides an alarm system that alerts production workers to evacuate the trouble area or don protective breathing apparatus and clothes. Knox^{2a} discloses that for the high containment PVC batch polymerization plant, previously mentioned, four individual GC analyzers were installed to continuously monitor 35 sample points for VCM. Provision was made for local strip chart recording as well as computer storage for daily printout. Additionally, alarms for the control room and flashing lights near each sample point alert production workers. This fixed point monitoring approach works excellently when leaks develop gradually. However, in the event of a sudden major seal failure, the sequential nature of the sampling and GC identification may allow a sizeable emission to go undetected for a short but variable period of time before the alarm system is triggered.

Industry sources indicate the future trend is to greater employment of such computerized automated analyzers not only for toxic or carcinogenic chemical monitoring but also for process control purposes. Such process control include detecting of leaks in equipment seals on vital units. An example is pressure monitoring of the seal fluid in a double mechanical seal unit, i.e., for agitators, pumps, and compressors.

MAINTENANCE

Preventing fugitive emissions from seals and fitting components of chemical processing equipment requires systematic maintenance operations applied at regular intervals. Systematic maintenance reduces fugitive emissions and also minimizes the need for emergency maintenance with its attendant dislocation of production. The petroleum refinery investigation was conducted accepting on-going maintenance operations at each of the refineries investigated.¹⁶ In a recent study, variations in fugitive emission levels were correlated with different degrees of programmed maintenance in a petrochemical installation. Delaney describes the maintenance levels as: 1) routine, 2) improved, and 3) special.^{2b} The special maintenance program had previously been developed to reduce unacceptable losses of a costly chlorinated hydrocarbon. No specifics on the three maintenance programs were reported and no attempt was made to define the manpower requirements and operating costs for the three levels of maintenance operation.

Table 5 shows the fugitive emission factors determined for three levels of valve maintenance covering production of three different petrochemicals. (The investigation was conducted in a very similar manner to that employed by Radian.) The procedure was to:

- o determine total number of valves concerned,
- o randomly select approximately 10 percent of the total valves,
- o screen valves with OVA 108 and 128 instruments (leak level identification as ppmv of VOC at 0 cm not listed),
- o bag leaking valves, and
- o sample emissions and measure emission rate (pressure train unit similar to Monsanto, Figure 11)

In analyzing the fugitive emission data, the log normal distribution principle was used. Results from this small scale but statistically valid study (Table 5) indicate:

- o A dramatic drop in the valve emission factors (lb/hr/valve) from routine, to improved, to special maintenance (0.032 to 0.019 to 0.008)
- o An approximate halving of the percent of leaking valves (17%-16%-8%).
- o Probable elimination of the high leakers by the shift from routine to special maintenance.

Table 5. Fugitive Emission Factors for Three Levels of Maintenance (Petrochemicals)*

SOURCE (Sample Size)	LEAKING SOURCE EMISSION FACTOR (lb/hr/valve)		PERCENTAGE OF LEAKING COMPONENTS	PLANT PRODUCT LINE EMISSION FACTOR (lb/day/valve)†
	Mean Value	30 Confidence Limits		
Total Plant Valves (197)	0.031	0.017 - 0.057	15	.11
Product Lines:				
A-Routine Maintenance (100)	0.032	0.014 - 0.076	17	.13
B-Improved Maintenance (49)	0.019	0.008 - 0.047	16	.07
C-Special Maintenance Program (48)	0.008	0.002 - 0.026	8	.014

*Reprinted, NIOSH Symposium, Reference 2b, Table IV, page 65.

†Plant product line emission factor (lbs/day/valve) = mean value (lbs/hr/valve) x 24 x percent of leaking components.

A direct quote from Delaney^{2b} illustrates the potential of improved maintenance in reducing possible worker exposure to toxic or carcinogenic compounds. He discusses benzene, a carcinogenic compound, for which OSHA has proposed an 8-hour TWA exposure level of 1 ppm with a short-term exposure limit (STEL--15 minutes) of 5 ppm.

"The magnitude of the reduction can be illustrated by assuming that a plant has 1,000 valves. If the plant had a routine maintenance program, the amount of hydrocarbon lost per day would be approximately 130 pounds. If this same installation has a well executed maintenance program, this loss could be reduced to 14 pounds. Assuming that all 1,000 valves are located within a building having a volume of 10,000 cubic feet, and that the leaking compound is benzene, the 1,000 valves would contribute approximately 600 cubic feet of benzene per day to the plant atmosphere. If the air were changed 10 times per hour this would result in a daily concentration level of 25 ppm for a routine maintenance program and about 2.5 ppm for a well executed maintenance program. Thus, the initiation of a valve maintenance program could be expected to reduce fugitive emissions by up to a factor of 10. Reduction by this magnitude could be sufficient to reduce the need for additional, more costly controls which may be required to meet some of the newer standards being proposed and instituted."

The results of Delaney's study are encouraging relative to two fundamental assumptions:

- o Increased maintenance effectiveness will significantly decrease fugitive emissions from chemical processing equipment seals and fittings.
- o Production of high value chemicals is a major economic incentive to improved maintenance. OSHA PEL values and EPA environmental standards should be equally effective incentives to improved maintenance during manufacture of low value chemicals.

Radian has recently commenced an EPA contract study of maintenance factors in the SOCOMI to: 1) cover a large screening base (both numbers and seals and fittings categories), 2) ascertain manpower requirements and added maintenance costs for different levels of maintenance programming, 3) ascertain frequency of scheduled maintenance for optimum fugitive emission control (this may vary substantially for different categories of chemical processing equipment seals and fittings), and 4) determine economic feasibility of various maintenance intensity levels.

To ensure the quality of maintenance operation, maintenance needs to be directly coupled with emission detection; that is, VOC detection readings need to be taken after as well as before maintenance work on each specific seal or fitting. This combination, termed "directed" maintenance, will prevent the cases where inadequate maintenance work can result in actual increase or no improvement in fugitive emission rates. The EPA Guidelines¹⁵ recommend fugitive emission leaks over 10,000 ppmv at the source (0 cm.) be repaired

within 15 days. If directed maintenance does not control a leak, equipment failure has probably occurred. In this case, the faulty unit requires isolation followed by either major repair or replacement. An important factor in reducing occupational exposure of maintenance workers is to reduce the need for emergency repairs during on-stream operation. Occurrence of emergency repair situations can be minimized by complete repair or replacement during scheduled down-time periods.^{2c}

EPA AND CHEMICAL INDUSTRY -
POTENTIAL STANDARDS AND OPERATING CODES

The 1977 amendments to be the 1970 Federal Clean Air Act will influence American industry handling of fugitive emissions from chemical processing installations. Sections 110, 111, and 112 are detailed and complex in their requirements. Section 110 includes state regulation to meet ambient air standards. To help the state EPA organizations, the Federal EPA Office of Air Quality Planning and Standards (OAQPS) has issued Control Techniques Guidelines (CTG) for specific industries such as petroleum refining.¹⁵ These are advisory in nature and not regulatory (they are not published in the Federal Register). Section 111 is concerned with New Source Performance Standards and Section 112 covers National Emission Standards for Hazardous Air Pollutants. This section requires the EPA administrator to formally list (in the Federal Register) specific hazardous chemical compounds. So far this has been done on an individual case basis. For vinyl chloride monomer, EPA set a 10 ppm maximum emission stream concentration standard. Benzene is the only other chemical the EPA administrator has formally designated as hazardous. Standards for benzene fugitive emissions are in the process of being issued.

Late in 1978, EPA informally discussed with industry groups a CTG draft document "Control of Organic Chemical Compound Emissions from Chemical Plant Equipment." In response to the draft copy CTG proposals, the Chemical Manufacturers Association (CMA) has recently proposed its own version.¹⁸ The draft EPA guidelines covered the following subjects in considerable detail:

- o A program of fugitive emissions detection
- o Good housekeeping practices
- o Administrative operation--recordkeeping and reporting
- o Maintenance plans--with scheduled inspection intervals

A key EPA hazardous pollutant proposal is for a cut-off point that excludes process streams (liquid or gaseous) containing small proportions of hazardous pollutants. This proposed minimum stream concentration of hazardous pollutants is 10 percent by weight with a 10,000 ppmv fugitive VOC emission limit as measured by a hydrocarbon emission detector at the seals and fittings leak source (0 cm).

The CMA version¹⁸ accepted the EPA listing of fugitive emission sources. However, it proposed the following variations from the EPA draft guidelines:

- o Application of regulations should be limited to process streams containing 10 percent or more of hazardous air pollutants; but regulations should not apply to any fugitive emission source that

does not emit hazardous air pollutants into the ambient air, nor to research and development installations that process less than 5,000 pounds per day of a hazardous chemical.

- o Each manufacturing installation should develop its own individual leak detection and repair plan (LDRP) based upon EPA criteria. A minimum LDRP shall detail:
 - A schedule and recordkeeping program for routine surveillance and/or monitoring of fugitive emissions
 - Detection means and schedules for maintenance repairs
 - Sampling procedures, housekeeping, and on-site waste handling
 - A recordkeeping program with records to be kept for 1 year
 - Manpower and organizational structure requirements for efficient operation of the leak detection and repair plan
 - Personnel training program and written manuals

In addition to these CMA specific proposals, chemical industry technical personnel have outlined the general requirements for long-term successful operation of an emissions control program by industry. A program of good manufacturing practice should be soundly based on process technology, on the personal commitment of all involved personnel, and on an optimum blend of engineering controls, work practices, and administrative controls.^{2d,2e} To ensure long-term success, top management of any chemical company must be truly involved and supportive as follows:

- o Provide necessary technical and financial resources on a long-term basis.
- o Expect both supervisory and production workers to be constantly involved during all their work activities.
- o Cooperate with and aid various governmental regulatory agencies.
- o Provide programs covering:
 - education, training, motivation, and auditing for knowledge retention of both veteran employees and new hires;
 - scheduled updating and audits of written procedures covering both normal operations and emergency situations;
 - periodic, regularly scheduled reviews of process (engineering and design) and equipment changes for compliance with current standards and regulations;
 - scheduled preventive maintenance to ensure reliability of (1)

process equipment and the seals and fittings with which it is equipped; (2) control systems; (3) electrical systems; and (4) fire and explosion protection systems;

- testing and inspection including scheduling, recordkeeping, and equipment evaluation; and
- audit programs, internal and external, with mandatory followup action reported.

Regulations issued and enforced by OSHA (with technical advice from NIOSH) limit the ambient pollutant levels to which workers may be exposed. Most of the OSHA PEL limits for toxic or carcinogenic VOC's (i.e., vinyl chloride monomer, acrylonitrile, and benzene) fall in a 1-10 ppmv range. The OSHA regulations do not stipulate how such levels shall be achieved nor require reduction in VOC fugitive emissions to meet these limits. However, the EPA regulatory approach limits total emissions from a proposed installation to a maximum amount and proposes specific controls for reducing fugitive emissions in both existing and new facilities. The Emission Standards and Engineering Division in the Office of Air Quality Planning and Standards has started the official procedure for promulgation of Federal regulations for:

1. VOC fugitive emissions in the Synthetic Organic Chemical Manufacturing Industry, and
2. Benzene fugitive emissions, National Emission Standard for Hazardous Air Pollutants.

The first stages of the EPA regulatory process have recently been completed. These cover (a) issuance and dissemination to interested parties of draft copies of Proposed Regulations and Background Information for Proposed Standards, and (b) public review of those draft documents before the National Air Pollution Control Techniques Advisory Committee (NAPCTAC). Based on the public hearing proposals, some modifications to the draft proposed standards are anticipated prior to the next stages of final agency clearance and publication in the Federal Register. Since changes are likely and the proposed regulations lengthy, the specifics will not be detailed, but the general approach summarized.

VOC fugitive emissions reduction will result from two types of proposed control techniques:

1. Implementation of systematic monitoring, maintenance, and record keeping programs, and
2. Compliance with equipment, design, and operational requirements.

Additionally, technically feasible processing equipment control options have been analyzed from the standpoint of two important economic considerations:

1. Whether the control technology is to be applied (a) in the design of a new plant or installation or (b) retrofitted into existing facilities, and

2. Cost effectiveness--the balance between VOC fugitive emission reduction obtainable through application of seals and fittings control choice versus the cost of installation throughout a chemical production facility.

The background information reviews present detailed cost breakdowns for a series of processing equipment control option alternatives. The alternatives consist of various groupings of the following chemical processing equipment seals and fittings choices together with the estimated costs of initial application to existing facilities and annualized operating charges. Technically feasible control options (not necessarily economically feasible) for obtaining maximum reduction of approximately 90 percent in both VOC and benzene fugitive emissions comprise the following:

<u>Fugitive Emissions Source</u>	<u>Equipment Specification</u>
Pumps	Double mechanical seals (with degassing vent control)
Valves	
In-line	Packless (diaphragm or sealed bellows)
Open-end	Packless (diaphragm or sealed bellows plus caps, etc., on open end)
Compressors	Double mechanical seals (with degassing vent control)
Pressure Relief Valves (primarily gas service)	Rupture disc added--degassing vent control--to flare or combustion unit.
Drains	Covered and check valved
Sampling Assemblies	Closed loops--thru sampling bomb
Product Accumulation Tanks	Degassing vent control

Based on cost effectiveness analyses for retrofitting existing facilities, the Emission Standards and Engineering Division selected the alternative grouping which includes all the above listed equipment specifications except substitution of packless valves and enclosed drains. In lieu of such substitution, existing valves and drains would have at least monthly inspection using approved fugitive emission detector instruments with detailed repair scheduling, and record keeping mandatory. The EPA proposed regulations would apply uniformly to all the designated seal and fitting components located throughout a chemical production facility.

In existing facilities where worker exposure to toxic or carcinogenic VOC

fugitive emissions (PEL's less than 10 ppmv) is possible, these EPA proposed regulations should be considered to be minimum requirements. Hence in large outdoor areas of chemical processing facilities, operators and maintenance men on occasional extended visits should wear approved respirators as a precautionary measure. In those processing areas where workers are normally stationed, retrofitting of process equipment seals and fittings should exceed the EPA proposed regulations to include sealless valves, enclosed drains, and possibly sealless pumps in all applications where these are technically feasible. Fixed point monitoring is also advisable in these populated processing areas, preferably with automatic sensors located at each possible emission source. Additionally, operator personal sampling should be periodically conducted by industrial hygiene personnel to double check effectiveness of such automatic monitoring systems.

For planning and design of new chemical processing facilities where worker exposure to fugitive emissions with PEL's under 10 ppmv is possible, all of the listed seals and fittings control choices should be incorporated wherever they are technically feasible.

GENERAL CONTROL PRINCIPLES AND EXAMPLES OF INDUSTRY ADVANCES

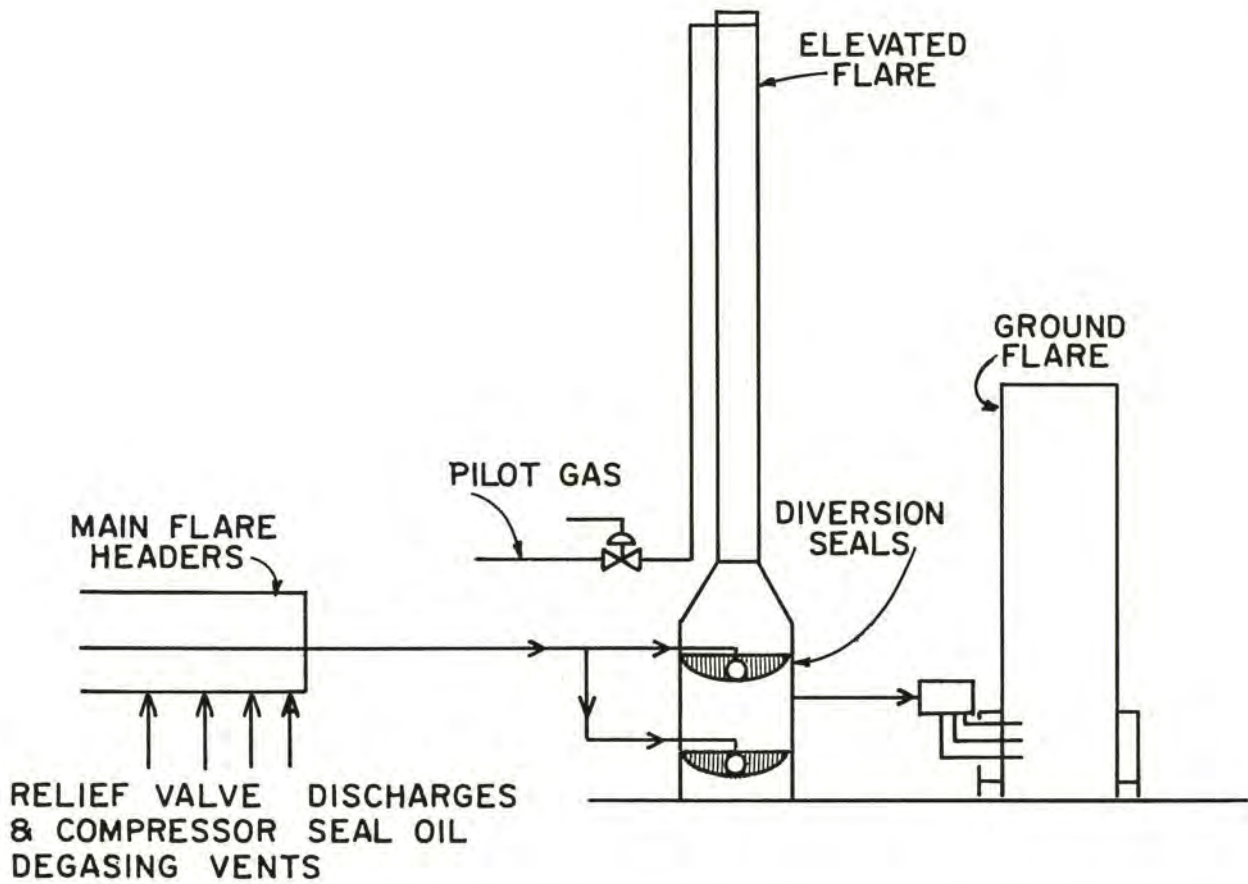
NIOSH recommended control technology measures for minimizing occupational exposure of industrial production and maintenance workers are outlined^{2f} in Table 6. Of the three routes of possible worker exposure (inhalation, skin contact, and ingestion), inhalation and skin contact occur with fugitive emissions of toxic or carcinogenic compounds from the seal and fitting components of chemical processing equipment. Examination of these measures indicates they: 1) were envisioned primarily in the context of manufacturing industries operating within building enclosures; 2) may or may not (depending on the individual measure) reduce environmental pollution. A number of industry personnel have privately advanced their opinions that NIOSH recommendations covering worker occupational exposure sometimes appear to be at cross purposes with EPA recommendations and standards for environmental pollution control. Currently, industrial planners and design engineers in formulating plans for new and/or expanded industrial installations feel they must start by correlating all pertinent requirements (guidelines, regulations, worker exposure limits issued by the different agencies concerned) and synthesize overall solutions that best meet the range of governmental requirements.

To modify this industry perception, NIOSH and EPA liaison and information exchange should be sufficiently close to ensure recommendations and standards proposed for fugitive VOC emissions control are mutually beneficial in reducing or eliminating both worker exposure and environmental pollution. NIOSH control technology assessments (particularly for manufacturing operations within building enclosures) should emphasize the control techniques serving both functions.

Means of reducing and/or controlling fugitive emissions from the seals and fittings components of chemical processing equipment can be effective in minimizing both worker exposure and environmental pollutions. Of the worker exposure control measures listed in Table 6: 1) most are compatible with and of active assistance in reducing environmental pollution; 2) some are neutral—neither help nor hinder; and 3) a few are detrimental unless modified or augmented. The principles marked with an asterick belong in the latter two categories. The following discussion includes the modifications and/or additions needed to make them mutually beneficial.

Isolation of the Source

This includes the following possibilities: 1) substitution of emission-proof seals and fittings; 2) process equipment enclosures; and 3) where feasible, rearrangement of processing equipment (emitting toxic or carcinogenic compounds) within a limited area of the whole installation. If 2) or 3) are accomplished, the addition of a suitable local vent system coupled with pollutant removal (i.e., a baghouse and flare disposal (Figure 12), enclosed combustion device, or carbon adsorption bed for particulates and VOC respectively) will both minimize worker exposure and reduce environmental pollution.



Reprinted, with permission, from EPA, Reference 9, Page III-4.

Figure 12. Diagram of Simplified Closed Vent System with Dual Flares

Table 6. Principles of Control Technology for Controlling Worker Occupational Exposure+

POINT OF APPLICATION OF THE CONTROL MEASURE	CONTROL MEASURE
At or near the hazard zone	Substitution of non-hazardous or less hazardous material Process modification Equipment modification Isolation of the source* Local exhaust ventilation* Work practices (housekeeping)
To the general workplace	General dilution ventilation* Local room air cleaning devices Work practices (housekeeping)
At or near the worker	Work practices (housekeeping) Isolation of workers* Personal protective equipment*
Adjuncts to the above controls	Process monitoring systems Workplace monitoring systems Education of workers and management Surveillance and maintenance of controls Effective process--people interaction and feedback

+Reprinted, NIOSH Symposium, Reference 2f, Table 1, page 19.

Local Exhaust Ventilation

A successful local vent system for toxic or carcinogenic VOC can become environmentally effective with the pollutant removal additions listed above.

General Dilution Ventilation

This was considered a feasible means of controlling worker exposure within building enclosures when energy costs were low and emissions only moderately hazardous (PEL values in an approximate 10 to 200 ppmv range). General dilution ventilation alone is not satisfactory when toxic or carcinogenic compounds (PEL's less than 10 ppmv) are present. Currently, high energy costs plus environmental pollution limits strongly favor exhaust air recirculation, with worker exposure limits forcing pollutant removal before recirculation. Effectiveness of pollutant removal from exhaust air is the major consideration. Particulate removal has been proven to be technically feasible, but adequate removal of nonparticulate carcinogenic compounds is questionable. NIOSH's current recommendation is that recirculation should not be employed if carcinogens are present.

Isolation of Workers and Personal Protective Equipment

These two are discussed together since isolation of workers covers any means of separating the worker from a hazardous environment, while personal protective equipment provides a specific form of such separation. Generally, environmental pollution is unaffected by any of the means of worker isolation. NIOSH and OSHA regard personal protective equipment as suitable only when engineering controls are clearly inadequate or the situation is in the nature of an emergency (e.g., a maintenance worker making repairs). Personal protective equipment should not be used on a continuing daily basis as its use puts the major responsibility on the individual worker.

Control measures that are generally most successful and frequently cost effective fall in the categories of equipment modification, process modification, and substitution of nonhazardous chemicals. The rigorous "systems approach" adopted by the PVC manufacturing industry provided control technology that satisfactorily deals with emissions from both point sources (stacks and vents) and nonpoint sources (fugitive emissions) as well as satisfactorily guarding against serious fire and explosion safety hazards. This comprehensive system approach was followed in design of a new high-containment batch polymerization plant^{2a} to successfully meet rigorous OSHA and EPA VCM regulatory limits for worker exposure and environmental pollution. Most importantly, specific emission characteristics of the volatile toxic or carcinogenic chemicals to be handled in a proposed installation should be determined prior to plant design. Shroy^{2g}, who helped develop such emission characteristics information for VCM and acrylonitrile, presents the technique and equations for developing such emission characteristics for other hazardous chemicals from either literature data (if available) or laboratory investigation. Fugitive emissions are not solely dependent on the design features of chemical process equipment seals and fittings. For any individual seal or fitting, the extent of fugitive emissions from different processing streams will be dependent also on:

1. Physical properties of the chemicals being handled (boiling point, vapor pressure, viscosity, etc.).
2. Process operating conditions (temperature, pressure, etc.)

For any specific situation, the basic approach is to define pollutant profiles around seals and fittings seal points (both static and dynamic) in terms of both distance and prevailing air velocity. Emission rates (lb/hr) need to be established for both individual chemicals and stream mixtures containing them. Concurrently, these emission rates need to be correlated with 1) detection instrument readings (ppmv) taken at the seals and fittings interface, and 2) ambient air pollutant concentrations established by analysis of contents of personal samplers which have been situated at strategic points in the local area surrounding the fugitive emission source. Methods and procedures for obtaining this information have been outlined ^{2b,16,20}.

If the emission characteristics of hazardous chemicals are not determined before full scale equipment design and installation, the lack of such information can unfortunately result in:

1. Installing unnecessary high cost engineering controls in a new installation.
2. Costly retrofitting-after plant startup demonstrates the need for added controls.

Specific examples of successful industrial equipment modification, process modification, and substitution of nonhazardous chemicals follow.

EQUIPMENT DESIGN

Barley^{2c} cites an example of positive design changes to eliminate worker occupational exposure, i.e., the unitized double mechanical seal assemblies now available for agitators. The first requirement is for initial installation of a shaft, coupling, seal, and gear drive assembly that permits the agitator to be supported from outside the reactor when a seal is being replaced. Hence the maintenance worker does not have to remove the drive nor enter the reaction vessel. Second, a cartridge-type double mechanical seal assembly is employed. The old seal is quickly removed, and a new or reconditioned unitized unit is inserted. This quick change markedly reduces the maintenance worker's exposure time at the reactor. During the seal interchange, a portable leak detector is used to check the pollutant concentration level. Maintenance personnel need to be trained in use of NIOSH-approved protective respiratory equipment and clothing for use during such emergency maintenance work.

PROCESS EQUIPMENT OPERATION MODIFICATION

Both fugitive emissions from PVC batch polymerization reactors and the VCM gas within the reactors can cause production worker exposure. In past operation, reactor fouling (buildup of a tenacious film of PVC on the reactor walls)

required opening of the reactor after each batch for manual cleanout by operators entering the reactor through the opened reactor manhead. This labor-intensive operation exposed the workers to carcinogenic VCM vapor both by inhalation and skin contact. The required chipping also damaged the inside walls of the reactors, making cleanout progressively more difficult with succeeding batches. The first improvement--high pressure (4,000 to 6,000 psig) rotating water jets for wall cleaning--improved the operation and reduced worker exposure, but jet cleaning was not completely effective. Therefore, with advent of OSHA's 1 ppm VCM exposure limit, alternative means had to be developed and applied. Goodrich Chemical Company^{2h}, and Air Products and Chemicals, Inc.²ⁱ followed two completely different yet successful routes. Goodrich developed a proprietary precoating solution and application method that has essentially eliminated reactor wall fouling. Air Products and Chemicals researched and installed their patented solvent cleaning operation to largely eliminate wall fouling.

SUBSTITUTION OF NONHAZARDOUS MATERIALS

In spray painting of home appliances, use of high solvent (VOC) content paints causes both worker exposure and environmental pollution problems. Spray painter exposure was brought under control by one or more of the following means:

1. Installation of local ventilation units (properly designed spray booths).
2. Adoption of automatic spray equipment, including use of robot sprayers.
3. Substitution of electrostatic spray guns for compressed air guns.

All of these means contribute to minimizing worker exposure, either by reducing pollutant content in the spray painter's breathing zone or eliminating the spray painter. However, only the third, substitution of electrostatic spray guns, is mutually beneficial in reducing worker exposure and environmental pollution. The mutual benefits (plus a bonus of significant cost reduction) result from substantially lower paint usage providing equally satisfactory coverage.

While these controls essentially eliminated worker exposure problems, environmental pollution still exceeded EPA point-source standards. To comply with these air quality standards, the appliance manufacturers now had two basic alternatives:

1. Install equipment to capture and/or destroy the solvent vapors (VOC) from plant stacks and vents.
2. Reformulate the paints to substantially reduce or eliminate their solvent contents.

The latter alternative, favored by the economics of the situation, was advantageous, provided essentially equal surface coating performance, and esthetics could be maintained. Cooperative investigation by both paint and appliance manufacturers led to development and adoption of water-base paint formulations. To maintain film durability and esthetics, a minimum content of higher boiling solvent is still required. This solvent content, however, is generally sufficiently low to meet air quality standards. Both the development and capital costs of the required modifications have been substantial; yet, in the long term, the shift to water-base paints will probably be found to be cost effective.

A relatively recent development is electrostatic spraying of solvent-free powder coatings. This technique and coating material is being successfully employed in high-output assembly-line finishing installations. Additionally, water base bath applications, substitutions for spray painting, are being developed and installed for some surface coating operations. A corollary effect of the recently lowered OSHA PEL 8-hour TWA worker exposure limit of 0.05 milligram per cubic meter (mg/m^3) for inorganic lead, is that appliance manufacturers have been collectively phasing out lead-pigment based colors and substituting alternative colors based on less toxic pigments.

CONCLUSIONS

A major source of worker exposure to hazardous chemical compounds in petroleum refineries and other chemical processing industries is from the VOC fugitive emissions (gaseous and liquid) from seal and fitting components of the chemical processing equipment employed. This is true whether manufacturing operations are conducted within building enclosures or in large outdoor installations. Because these fugitive emissions are frequently unexpected (unpredictable as to timing, emission rates, and individual items identification), it is difficult to identify hazardous areas and predict the extent of worker exposure. The most critical health exposure problems (whether by inhalation or skin contact) are posed by those toxic or carcinogenic chemicals for which prior research and past industrial experience have demonstrated that very low permissible exposure limits (PEL's less than 10 ppmv) are necessary. Prominent among such chemicals are vinyl chloride monomer, acrylonitrile, and benzene.

The EPA contract studies undertaken to provide up-to-date fugitive emission factors for different categories of chemical processing equipment seals and fittings has provided information needed to define and develop cost effective means for minimizing worker exposure to these fugitive emissions. The following summary provides approximate percentages of VOC fugitive emissions caused by each category of seals and fittings in the petroleum refining industry. It also recommends the available seal and/or fitting within each category that best controls VOC fugitive emissions for both petroleum refineries and other chemical processing industries.

Type of Seal and Fitting	Approx. % of Total Fugitive Emissions (EPA Model Refinery)	Choice of Types within Categories to Provide Minimum Worker Exposure
Pumps	9	1. Sealless 2. Double mechanical seals (with degassing vent control)
Valves	65	Packless (diaphragm or sealed billows)
Compressors	4	Double mechanical seals with degassing vent control)
Flanges	7	--
Pressure relief valves	3	Rupture disc plus relief combination (with degassing vent control to flare or combination unit

Drains	12	Covered and check valved
Sampling Assemblies	Not estimated	Closed loop through sampling bomb
Product Accumulation Tanks	Not estimated	Degassing vent control

The listed fugitive emission percentages and calculated emissions factors (see Table 1) for petroleum refining processing equipment seals and fittings may not be exactly applicable to the other chemical processing industries.¹⁹ Possible reasons for variation are:

1. The extent of fugitive emissions is strongly influenced by the properties of the chemicals being handled (gas or liquid) and, if liquid, their volatilities (vapor pressure) at the processing conditions.
2. There are differences in: (1) processes and processing equipment; 2) scale of operations in petroleum refineries versus other chemical processing industries, and 3) effectiveness of maintenance programs.

Use of improved types of seals and fittings is technically feasible for all the listed categories except possibly certain types of valves. Unfortunately, leaky valves are a major source of fugitive emissions in the petroleum refining and other chemical processing industries. This situation is partly due to valves not being optimally selected (particularly in older installations) to minimize leakage. Additionally, the packless (leak free) valves currently commercially available have limitations, both operational and cost, which have restricted their application. Development work by valve manufacturers is needed to provide both: 1) improvements in existing valve design, and 2) moderate-cost, long-life packless valves for handling toxic or carcinogenic chemicals.

Effectiveness of maintenance programs in controlling VOC fugitive emissions from processing equipment seals and fittings is as important in minimizing worker exposure to fugitive emissions as the original choice of the most effective seals and fittings. The EPA results demonstrate that a relatively small percentage of the total units in any seals and fittings category provide the major share of VOC fugitive emissions from that category. For example, in petroleum refining gas service, 4 percent of the valves were shown to cause 92 percent of the total valve emissions. The key to controlling fugitive emissions from the existing seal and fitting components of chemical process equipment is to:

- o Provide an effective monitoring program for locating the small percentage of high leakers.
- o Develop directed maintenance programs that (1) prevent or reduce initial leakage and (2) provide quick, satisfactory repair that forestalls recurrence after the maintenance work is completed.

Either fixed point or complete source monitoring (regularly scheduled) are required to locate the high leakers. Only fixed point monitoring provides the rapid alerting of production workers to either evacuate or don protective

breathing apparatus and clothing. The quoted Exxon petrochemical plant results²⁶ on special versus routine maintenance on valves show impressive improvement.

The present EPA/NIOSH investigative status (6/80) on VOC fugitive emissions from the seal and fitting components of processing equipment in the petroleum refining and other chemical processing industries is:

- o Fugitive emissions in the petroleum refinery industry have been investigated (EPA/Radian). Detection results (ppmv of VOC have been correlated with emission rates (lb/hr) for three different refinery streams (complex chemical mixtures) and for different refinery categories of seals and fittings.
- o The effects of different levels of maintenance on fugitive emission occurrence and rates in the SOCFI is currently being investigated (EPA/Radian). Both optimum frequency of scheduled maintenance and added manpower requirements and costs are being established.
- o Levels of ambient VOC being emitted from specific processing areas of a petroleum refinery (i.e., catalytic cracking, aromatics extraction, coking, asphalt processing, and API separators have been preliminarily assessed (EPA/Radian). Monitoring was conducted within: 1) the aforementioned sections, 2) the total installation area, and 3) outside the installation perimeter. Study results are to be officially released.
- o An industrial hygiene characterization of petroleum refineries study is underway (NIOSH/Enviro Control, Inc. contract 210-78-0082). The study encompasses occupational exposure for both production and maintenance personnel (working within catalytic cracking, coking, and asphalt processing areas) to known and suspected carcinogenic chemicals (i.e., benzene, biphenyl, anthracene, other polynuclear aromatics, etc.).
- o A control technology assessment of the petroleum refining industry is being initiated (NIOSH).

As a result of this work and private industry investigations, the equipment, techniques, and procedures are available for conducting basic engineering studies to develop predictive design methods for characterizing worker occupational exposure to toxic and carcinogenic VOC's in the petroleum refining and other chemical processing industries. Industry views of how to conduct such studies are summarized on pages 50 and 51. In using information from this report, the reader must remember the different approaches used to safeguard the environment and prevent occupational hazards. Evaluation of occupational hazards involves as a major consideration the location and activities of individual workers (i.e., dermal contact by maintenance workers). The EPA information, summarized in this report, provides a valuable reference source in assessing occupational exposure hazards. However, it is not sufficient to guarantee adequate protection for occupationally exposed workers in the petroleum refining and other chemical processing industries since VOC fugitive emission rates must be correlated with both worker location and air movement data.

RECOMMENDATIONS

Compliance by the petroleum refining and other chemical industries with EPA proposed regulations for reducing the VOC fugitive emissions for the seals and fittings components of chemical processing equipment should provide major improvement over current environmental pollution and worker exposure conditions in many existing chemical processing facilities. The improvement will be occasioned by both types of control techniques being included in the proposed regulations:

1. Implementation of systematic monitoring, maintenance, and record keeping programs.
2. Compliance with equipment, design, and operational requirements.

Systematic monitoring with approved leak detection equipment, directed maintenance within specified time periods, and record keeping of maintenance results for difficult to control emission sources are the means of upgrading the unglamorous but vital maintenance function in chemical processing industry. Compliance with the equipment requirements encompasses retrofitting existing seals and fittings components of chemical processing equipment with technically feasible replacements which do not require excessive initial installation and annual operating costs (see page 45 for specific items).

The EPA proposed regulations apply uniformly to all the designated seals and fittings components located throughout a chemical production facility. From the stand point of worker exposure to highly toxic or carcinogenic VOC fugitive emissions (PEL's less than 10 ppmv, i.e., vinyl chloride monomer, acrylonitrile, benzene, etc.) a greater degree of flexibility is needed. Where worker exposure to such hazardous VOC fugitive emissions is possible, these EPA proposed fugitive emission regulations should be considered as minimum requirements. Hence in large outdoor areas of hazardous chemical production facilities, operators, pumpers, and maintenance men making extended visits should wear approved respirators as a precautionary measure. In those processing areas where workers are normally stationed, retrofitting of existing processing equipment seals and fittings should exceed the EPA proposed regulations to include sealless valves, enclosed drains, and possibly sealless pumps in all applications where these are technically feasible. Fixed point monitoring is advisable in such populated processing areas, locating automatic sensors at each possible seals and fittings emission source. Additionally, periodic personal sampling of workers in such locations should be conducted by industrial hygiene personnel to double check operating effectiveness of such automatic monitoring systems.

In design of completely new chemical production facilities or substantial additions to existing facilities to handle such hazardous VOC's, the EPA

proposed seals and fittings standards should be augmented throughout the entire new chemical production facility with sealless pumps, sealless valves and enclosed drains in all applications where these are technically feasible.

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