IN-DEPTH SURVEY REPORT:

OCCUPATIONAL HAZARD CONTROL OPTIONS FOR CHEMICAL PROCESS UNIT OPERATIONS

AT

U.S. Steel Corporation
US Steel Chemicals Division Site
Haverhill, Ohio

REPORT WRITTEN BY:
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NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
Division of Physical Sciences and Engineering
Engineering Control Technology Branch
4676 Columbia Parkway
Cincinnati, Ohio 45226
PLANT SURVEYED: USS Chemicals Division Site
Haverhill, Ohio

SIC CODE: Group No. 281, Industry No. 2865

SURVEY DATE: June 11 through 15, 1984

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I. INTRODUCTION

The Occupational Safety and Health Act of 1970 (PL-91-596) was enacted to "assure safe and healthful working conditions for men and women." The Act established the National Institute for Occupational Safety and Health (NIOSH) in the Department of Health and Human Services. NIOSH was charged by this Act (Sections 2 and 20) with the duty and responsibility to conduct research and develop guidance for preventing or reducing exposure of workers to harmful chemical and physical agents. In response to this legislative mandate, NIOSH has conducted major programs to document, develop, and disseminate information regarding the health effects of such agents. To complement these ongoing programs, NIOSH has instituted a major effort to prevent occupational health and safety problems through the assessment and application of hazard control technology in the workplace.

Two of the main policy objectives of this Federal Act are to:

- Encourage employers and employees in their efforts to reduce the number of occupational safety and health hazards at their places of employment; also, to stimulate employers and employees to both institute new control techniques and to perfect existing programs for providing safe and healthful working conditions.

- Provide for research in the field of occupational safety and health with a view to developing innovative methods, techniques, and approaches for dealing with occupational safety and health.

The Institute's Division of Physical Sciences and Engineering is now conducting a study titled "Occupational Hazard Control Options for Chemical Process Unit Operations." Objective is to obtain and disseminate information on principles, equipment, and techniques employed in the chemical processing industries to successfully minimize or eliminate worker exposure to hazardous compounds. This project is being conducted by NIOSH personnel on an in-house basis.

Preliminary site visits are made to a number of chemical processing facilities to obtain information on effective control technology. NIOSH defines control technology as encompassing not only engineering controls, but also work practices, monitoring, and use of personal protective equipment. In most processing situations, optimum control will normally include application of all four means, but the emphasis on each will probably vary from situation to situation. Later, in-depth studies, which may include area and personal monitoring and monitoring of emission sources for specific materials, are conducted on a minority of these facilities—selected on the basis of the effectiveness of controls observed during preliminary site visits.

The reports from these surveys are the basis for preparing technical reports and journal articles on effective hazard control measures. The information from these research activities builds the data base of publicly available information on hazard control techniques for use in preventing occupational exposure to hazardous chemicals.
A preliminary survey of the USS Chemicals Division, Haverhill, Ohio, site was performed by the Dynamac Corporation on June 14th and 15th, 1982. At that time, the project was under contract and the preliminary survey report (issued July 12, 1982) was prepared by Dynamac personnel. Mr. Van Wagenen, NIOSH, was present during this preliminary survey, which covered the entire site; separate outdoor facilities for producing (1) oxo alcohols, (2) phenol and acetone from cumene, (3) bisphenol-A, and (4) aniline.

With expiration of the Dynamac Corporation contract in late FY 1982, the investigation has been continued as an in-house NIOSH project. This in-depth survey was conducted by DPSE Division personnel.
II. SUMMARY

A. General Site Description

This large processing site (Figure 1) is one of the USS Chemicals Division chemical processing sites which provide approximately 1.5 billion dollar sales for the parent corporation, U.S. Steel. It is located adjacent to the north bank of the Ohio River at Haverhill (near Ironton, Ohio) and encompasses 565 acres. Of these, about 125 acres are occupied by separate outdoor processing facilities for five different chemicals and the remaining acreage leased as farmland.

Figure 1. Haverhill Site (Haverhill, Ohio — on Ohio River)
USS Chemicals Division
U.S. Steel Corporation

The site was developed in 1961 as a joint venture of Amoco and Pittsburgh Chemical Company. These original owners installed a facility for making Oxo alcohols from alkenes in 1962. USS Chemicals purchased the site and its existing processing facilities in 1965. The polystyrene unit had been shut
down permanently prior to the preliminary visit of June 1982. The Oxo alcohol facility, operating during the preliminary visit, was permanently mothballed prior to this June 1984 in-depth survey. The processing facilities installed by USS Chemicals Division since 1965 and now operating are:

1. **Phenol and Acetone From Cumene**

   Phenol I (cumene and oxygen reactants) 1969
   Phenol II (cumene and oxygen reactants) 1979
   Rated capacities — phenol approximately 520 mm pounds yearly
   acetone approximately 325 mm pounds yearly

2. **Bisphenol-A**

   (phenol and acetone reactants) 1980
   Rated capacity — bisphenol-A approximately 120 mm pounds yearly

3. **Aniline**

   (ammonia and phenol reactants) 1982
   Rated capacity — aniline approximately 200 mm pounds yearly

Figure 2 demonstrates the interrelationship of the raw materials and finished products and the vertical integration within the site. During the recent recession, national phenol consumption and prices were so reduced that a number of producers dropped out of the business; companies having substantial internal usage of phenol, fared better. Today, the Haverhill phenol production is split approximately 50-50 between internal usage and bulk sales to outside customers. USS Chemicals is considered the largest phenol merchant producer in the U.S.

![Figure 2. Raw Materials and Products
USS Chemicals, Haverhill, Ohio](image)
All processing facilities operate on continuous 24-hour, 7-day-per-week, and 50-51-week-per-year basis with four crews rotating to handle three 8-hour shifts. Currently, this site has approximately 220 employees (all non-union). Site maintenance is performed by an outside contractor, Catalytic, Inc. Each chemical production facility has its own separate repair and maintenance building manned by these maintenance personnel. The approximately 80 unionized maintenance personnel are a very stable, long-term, and experienced maintenance group, Catalytic, Inc. being the maintenance contractor since site startup in 1961-62.

The majority of both raw materials and finished products are received and shipped in bulk by barges, rail cars, and tank trucks. Barge service, via the Ohio River, is an important feature of the site operation (discussed in detail later). Barge operations are handled by an independent contractor, using USS Chemicals operating personnel to assist in a number of loading and unloading situations. Pipelines run 1 mile from the various facilities to the riverside barge terminal (Figure 1). All barge operations are conducted in accordance with U.S. Coast Guard regulations. A railway spur gives access to the nearby railroad right of way. A company trackmobile moves rail cars within the site complex. Easy access to U.S. Highway 52 and the flat terrain assist tank truck transport. The only sizable non-bulk material handling in the entire site is the packaging of bisphenol-A prills. Fifty-pound net multiwall polyethylene-lined bags are filled and palletized for shipment, plus special 2,000-pound flexible palletized containers.

Process steam is generated onsite by boilers adapted to using oil, gas, and coal as fuel. The site also has a large experimental solar unit for steam generation. This industrial test unit was primarily funded by the U.S. Department of Energy.

In lieu of a full-time industrial hygienist, laboratory personnel have been trained and are performing industrial hygiene sampling under the direction of the Corporate Senior Environmental Health Engineer (based at the Pittsburgh, Pennsylvania, corporate headquarters). There is a well-equipped fire and safety department with a fire brigade of site operators manning a foam-equipped fire engine. The safety department has an agreement with the local Green Township for both fire and ambulance assistance service as necessary, but has rarely used the same.

There is no in-house medical or nursing staff. A number of Safety Department personnel are qualified emergency medical technicians (EMT) and operate a rescue and first aid squad. Yearly physical examinations are provided to all hourly personnel via an area medical van unit coming to the Haverhill site.

USS Chemicals provides all the safety equipment and personal protective equipment required by the company safe job procedures. This varies among the production facilities depending on the nature of the chemicals to which personnel may be exposed.

Group safety meetings of facility supervisors and foreman are held monthly. Foremen discuss safety and operation information with each shift crew on a weekly basis. The shift crews are sometimes called in early for these
meetings which are held prior to taking over operation from the outgoing shift. At this site, employing satisfactory work practices basically means practicing the Safe Job Procedures outlined for the various specific jobs within each facility. A good indication of management follow-up on work practices and concern for safety and occupational exposure to hazardous chemicals is the general state of both site and individual facility housekeeping. Compared to other chemical installations previously visited, Haverhill housekeeping is rated as very good.

To protect the customers and users of their products, USS Chemicals supplies material safety data sheets (MSDS) and product technical information brochures. These are an excellent source of chemical usage and health hazard information.

B. NIOSH Activities, Including Sampling, During this In-Depth Survey

Five days were occupied in both observing and discussing chemical processing operations and exposure hazards in the phenol/acetone, bisphenol-A, and aniline facilities. Personal and area exposure samples were taken in cooperation with company personnel. Specific subjects covered in discussions with USS Chemicals personnel were general engineering controls, quality control and product sampling, equipment sealing and gasketing, equipment selection, equipment decontamination procedures, maintenance management and practices, safety and medical programs, job training and work practices, and monitoring. Personal and area samples (taken near potential emission points) were obtained in both Phenol I and II units. Tank car loading of phenol and aniline were also subjects of short-term sampling. Many of these samples were duplicated by USS Chemicals personnel. Mr. Stockton furnished NIOSH with a detailed summary of the industrial hygiene sampling results previously obtained on the currently operating Haverhill facilities by corporation personnel over the period 1976 through 1982. Additionally, Mr. John R. Weinert, USS Chemicals Division Manager of Environmental Engineering, provided a copy of a comprehensive survey of the aniline manufacturing operation of the five American aniline producers. This industry report (August 8, 1983) was prepared by the Synthetic Organic Chemical Manufacturing Association, Inc. (SOCMA) in response to EPA Toxic Substances Control Act (TSCA) Section 4 activities. These industrial hygiene exposure results will be discussed in detail later under the individual chemical products sections. Unfortunately, industrial hygiene exposure results could not be obtained by NIOSH in either the bisphenol-A or aniline facilities. Corrosion induced failure of a major heat exchanger in the bisphenol-A facility forced a production shutdown for equipment replacement. For the aniline facility, completely filled finished aniline storage tanks plus a temporary dearth of company dedicated tank cars necessitated production stoppage. This latter occurrence emphasizes the need for any chemical processor to be able to track dedicated tank car locations in order to shorten turnaround time and aid speedy return.

C. Brief Description of Haverhill Site Chemical Processing and Hazardous Chemicals

This section provides a brief summary of the chemical reaction steps occurring in the various operating facilities and the hazards of the raw materials,
intermediates, and finished products handled in each facility. Occupational exposure hazard limits shown are OSHA 8-hour permissible exposure limits (PEL). Subsequent individual facility discussions provide more detailed information.

1. Phenol/Acetone From Cumene Facility

In two parallel phenol production units (identified as Phenol I and II), cumene is oxidized with compressed air to form cumene hydroperoxide. The hydroperoxide is cleaved with sulfuric acid to provide crude phenol, acetone, and by-products (alpha methyl styrene (AMS) and acetophenone). Finally, a complex series of fractionations provides high quality phenol and acetone for either captive use in making bisphenol-A and aniline or for bulk sale. The following hazard information covers the raw material, intermediates, and product chemicals handled in this facility:

**Table I**

Hazards and OSHA Limits for Chemicals in Phenol/Acetone From Cumene Facility

<table>
<thead>
<tr>
<th>Chemical</th>
<th>OSHA-PEL (8-hour TWA)</th>
<th>Flash Pt. (°F)</th>
<th>Hazards</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cumene</td>
<td>50 ppm (skin)</td>
<td>111</td>
<td>Eye and skin irritant, respiratory damage, fire and explosion</td>
</tr>
<tr>
<td>Cumene hydroperoxide</td>
<td>No limit</td>
<td>175</td>
<td>Similar to cumene</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>1 mg/m³</td>
<td>NA</td>
<td>Eye and skin burns, respiratory damage</td>
</tr>
<tr>
<td>Sodium hydroxide (Sol'n)</td>
<td>2 mg/m³</td>
<td>NA</td>
<td>Eye and skin burns, respiratory damage</td>
</tr>
<tr>
<td>Sodium bicarbonate (Powder)</td>
<td>No OSHA limit ACGIH*</td>
<td>NA</td>
<td>Skin and eye irritant</td>
</tr>
<tr>
<td></td>
<td>nuisance dust (Respirable)</td>
<td>5 mg/m³</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>5 ppm (skin)</td>
<td>175</td>
<td>Eye and skin burns, respiratory damage, fire at high temp.</td>
</tr>
<tr>
<td>Acetone</td>
<td>1,000 ppm</td>
<td>-4</td>
<td>Fire and explosion</td>
</tr>
<tr>
<td>Alpha methyl styrene (AMS)</td>
<td>100 ppm</td>
<td>129</td>
<td>Eye and respiratory irritant, fire and explosion</td>
</tr>
</tbody>
</table>

* American Conference of Governmental Industrial Hygienists Threshold Limit Value (TLV)
2. **Bisphenol-A**

Bisphenol-A (EPA) is produced by the catalyzed exothermic reaction of high purity phenol and acetone (using a large excess of phenol) in a sequential series of agitated reactors. After the reaction is completed, the HCl catalyst is stripped from the BPA/phenol reaction mass, concentrated, and recycled back to the reactors. BPA is separated from the stripped BPA/phenol mass by crystallization. The crystals are separated, then melted, stripped of phenol, and finally solidified into finished product prills in a huge prilling tower. The following hazard information covers the raw material and product chemicals handled in this facility:

<table>
<thead>
<tr>
<th>Chemical</th>
<th>OSHA-PEL (8-hour TWA)</th>
<th>Flash Pt. (°F)</th>
<th>Hazards</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>5 ppm (skin)</td>
<td>175</td>
<td>Eye and skin burns, respiratory damage, fire</td>
</tr>
<tr>
<td>Acetone</td>
<td>1,000 ppm</td>
<td>-4</td>
<td>Eye and skin irritant, Fire and explosion</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>5 ppm</td>
<td>NA</td>
<td>Eye and Skin burns, respiratory irritant</td>
</tr>
<tr>
<td>Bisphenol-A</td>
<td>No OSHA limit</td>
<td>NA</td>
<td>Skin and eye irritant, fire and explosion</td>
</tr>
</tbody>
</table>

* American Conference of Governmental Industrial Hygienists Threshold Limit Value (TLV)

3. **Aniline**

Aniline is produced by a high-pressure catalyzed reaction of phenol with ammonia. This proprietary process does not (1) require catalyst regeneration, (2) produce by-product sulfuric acid, or (3) pose the health hazards of handling benzene, as does the standard reaction of benzene and nitric acid to form nitrobenzene with subsequent hydrogenation to aniline. The following hazard information covers the raw material and product chemicals handled in this facility:
### Table III

Hazards and OSHA Limits for Chemicals in Aniline Facility

<table>
<thead>
<tr>
<th>Chemical</th>
<th>OSHA-PEL (8-hour TWA)</th>
<th>Flash Pt. (°F)</th>
<th>Hazards</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>5 ppm (skin)</td>
<td>175</td>
<td>Eye and skin burns, respiratory damage, fire</td>
</tr>
<tr>
<td>Ammonia</td>
<td>50 ppm</td>
<td>NA</td>
<td>Severe irritant of eyes, skin, and respiratory tract</td>
</tr>
<tr>
<td>Toluene</td>
<td>200 ppm</td>
<td>39</td>
<td>Eye and respiratory irritant</td>
</tr>
<tr>
<td>Diphenylamine</td>
<td>No OSHA limit</td>
<td>307</td>
<td>Similar to aniline but less severe</td>
</tr>
<tr>
<td></td>
<td>ACGIH*—10 mg/m³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aniline</td>
<td>5 ppm (skin)</td>
<td>158</td>
<td>Skin absorption to give blood cell damage, fire and explosion</td>
</tr>
<tr>
<td></td>
<td>ACGIH—2 mg/m³ (Skin)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*American Conference of Governmental Industrial Hygienists Threshold Limit Value (TLV)*

Diphenylamine (DPA) is a by-product of the aniline making reaction. When low aniline sales occurred during the late recession, diphenylamine was manufactured in the later stages of the aniline facility by reacting aniline with phenol under optimum conditions for diphenylamine output.

### D. Haverhill Site General Control Technology

#### 1. Principles of Control

Occupational exposures can be controlled by the application of a number of well-known means, including engineering controls, work practices, personal protective equipment, and monitoring. These means may be applied at or near the hazard source, to the general workplace environment, or at the point of occupational exposure to individuals. Controls applied at the source of the hazard include engineering controls (material substitution, process/equipment modification, isolation or automation, local ventilation) and work practices. These are generally the preferred and most effective means of control in terms of both occupational and environmental concerns. Controls which may be applied to hazards that have escaped into the workplace environment include dilution ventilation, dust suppression, and housekeeping. Control measures may also be applied near individual workers, including the use of remote
control rooms, isolation booths, supplied-air cabs, work practices, and personal protective equipment.

In general, a system comprised of the above control means is required to provide worker protection under conditions of process upset, failure, and/or maintenance, as well as during normal operating conditions. Process and workplace monitoring devices, personal exposure monitoring, and medical monitoring are important mechanisms for providing feedback concerning effectiveness of the controls in use. Ongoing monitoring and maintenance of controls to ensure proper use and operating conditions and the education and commitment of both workers and management to occupational health are also important ingredients of a complete, effective, and durable control system.

In the various Haverhill site facilities, occupational exposure is most likely for the workers involved with tank car or truck loading, process and quality control sampling, equipment disassembly and decontamination, laboratory analysis, and process control instrumentation repair and maintenance. Hazard controls successfully employed will be discussed under the following component headings: engineering controls, training and work practices, monitoring, and personal protective equipment. In this summary section, controls which are generally applied in all site facilities will be discussed; while control measures more specific to each individual facility will be detailed in later individual facility sections.

2. Engineering Controls

The engineering control principles of isolation and automation are employed here. Extended spacing of the various outdoor processing facilities is combined with all-weather process design and construction. The only enclosed processing buildings comprise the bisphenol-A packaging and warehousing operations and the ventilated and positively pressurized control stations for each of the three facilities. The degree of automation is high throughout the site, particularly with the newer Phenol II and aniline facilities which utilize sophisticated computer control of processing operations. Operators are both few in number and spend a substantial share of their working hours inside the control buildings. Also, occupational exposure over 8-hour work shifts is substantially reduced both by the open air processing setup and the fact that all the chemicals present in the site, other than acetone and toluene, have relatively low volatility. Since airborne contamination is a function of volatility, these chemicals do not generate, at ambient temperatures, the emission levels of volatile chemicals. Several major site emission control improvement projects have been completed to meet EPA ambient air concentration limits.

The engineering control principle of material substitution is exemplified by the choice of the route for making aniline; the use of the high-pressure reaction of phenol with ammonia rather than the usual benzene reaction with nitric acid to form nitrobenzene followed by hydrogenation to aniline. Thus, use of benzene, a known carcinogen, was avoided. While the choice of this processing route was influenced by the internal economic advantages, other producers may make a similar choice when aniline production expansion occurs.
Process equipment modification is typified by the bisphenol-A facility. Important equipment improvements have reduced maintenance requirements, and extended the useful life of specific equipment items. The results have been reduction in frequency of repair-and-turnaround needs, reduced unit production costs, and improved product quality. Such modifications include (1) providing gravity flow (bisphenol-A facility) between a sequential series of reactors (thus eliminating pumping requirements), (2) use of more corrosion resistant materials in some equipment (Incoloy® 800 and E-Brite® replacing Type 304 and 316 stainless steels), (3) using Teflon®-lined pipes and agitators to minimize corrosion, and (4) replacement of original pump, agitator, and flange seals and gaskets with equivalents made of more effective materials.

Because of the continuous operating schedules, most site pumps are spared. The choice of pump seals depends on the particular service. While packed seals are used for water service, essentially all other processing pumps and reactor agitators are equipped with mechanical seals. Single mechanical seals predominate, but double mechanical seals are employed in special situations. O-ring inserts in the mechanical seals are Teflon® or Viton®. Most site flanges have spirometallic (Reiestoflex) Teflon®/stainless steel gaskets. An exception is the ammonia lines in the aniline facility for which blue asbestos gaskets are now standard. Viton® gaskets are also used in special situations. Maintenance supervisors and site engineering staff constantly check with suppliers for better performing equipment and fittings. This is particularly true for the bisphenol-A facility, which is considered to be the area for greatest potential for improvement (hence, reduced potential occupational exposure).

The facility operators are responsible for equipment decontamination prior to maintenance repairs by the Catalytic, Inc. maintenance specialists. This is true for either in-place repair or, preferably, repair performed in the separate facility maintenance shops (i.e., pump seals). Facility operators do lubricate pumps periodically and check spare pumps for rotational freeness before starting them. Basically, pumps are operated until the seals fail, then the spares are activated. The seal replacement factor for this site is about 1 seal per pump each 2 years compared to an industry average of about 2 seals per pump annually. Average replacement cost of a seal unit lies in a 250-500 dollar range and requires about 2 hours of shop time. Total cost and time per seal failure (equipment decontamination, pump dismantling, transportation, shop work, and pump reinstallation) is much higher.

3. Training and Record Keeping

A major factor in USS Chemicals processing operations is the emphasis placed on safe operation by the parent corporation. The basic essentials of the company-wide safety program, which has the dedicated support of top management, are Safe Job Procedures, Basic Training, Individual Contacts, Employee Records, Accident Investigations, Awareness Charts, Physical Conditions and Inspection Reports, Activities Reports, and Audit Reports.

The interrelationship of these essentials is illustrated in the following diagram taken from the corporate safety program manual (Figure 3).
Safe Job Procedures cover every area of facility operation and are the basic element for instruction, training, and continuing operation by facility operators. They are developed initially and revised as needed through the use of a group discussion method. A shift or general foreman works with two or more experienced operators to make a systematic and objective analysis of each job situation and to pool their experience about possible hazards, ways to eliminate and avoid them, and the most advantageous sequence of procedural steps into a preliminary Safe Job Procedure. Input of other management personnel and company hazard experts is incorporated to provide the finished printed Safe Job Procedure. A typical Procedure is included as Figure 4. Besides listing the detailed procedural steps which must be performed, each Safe Job Procedure includes the operation title, the chemical and physical hazards which are present, and the personal protective equipment which must be worn by the operator while carrying out these steps.
A foreman or job trainer instructs new employees, step by step, in the approved method of doing each job. Since each operator regularly rotates through all facility jobs during each shift cycle, they must become conversant with a substantial number of these Safe Job Procedures. The trainer must observe the new operator perform each job correctly and must be certain that the operator understands the whys' and hows' of each Safe Job Procedure. Subsequently, the shift foreman must make at least one contact per week for each employee under his supervision so as to continue the operator's training and consolidate his safety knowledge. These contacts are recorded in the Individual Employee Contact Record. Additionally, each shift foreman is required to make at least two planned Safety Observations for each employee per month. These observations are planned so they systematically cover all Safe Job Procedures on which the employee has received training. The shift foreman writes up these observations for each employee in a Supervisor's Safety Observation Report and also in the Individual Employee Contact Record. The Individual Contact and Safety Observation requirements continue indefinitely after completion of regular training.

4. Monitoring

Personal and area monitoring for possible occupational exposure of operating personnel to hazardous chemicals is conducted by laboratory technicians. These employees have been trained by and report results to industrial hygiene specialists from the corporate Environmental Health Division. They also measure sound levels of various processing units (i.e., the air compressors in the phenol/acetone facility), and perform audiometric tests on operators. An important factor in occupational health exposure to antiline, phenol, and cumene (the latter two to a lesser extent) is that all three are absorbed through the skin. Hence, if absorption occurs, health problems can develop even though airborne levels are within the OSHA permissible limits. Medical monitoring, good work practices, and the use of effective personal protective equipment are important in ensuring that health problems do not develop from skin absorption.

This site has no in-place ambient monitoring systems for the detection and activation of an alarm in the event of excessive fugitive emissions from the processing equipment. However, a Bendix chromatographic instrument is employed to monitor and control the composition of various process streams in the phenol/acetone from cumene production facility. This eliminates potential worker exposure which might have occurred during the manual sample taking and the subsequent analytical laboratory analyses. Maintenance personnel use IRD spike energy monitoring equipment to measure vibration on rotating equipment. Data from the monitoring of the bearing performance of rotating equipment, when compared with prior performance information can provide a good prediction of when such equipment must be taken out of service for overhaul. With this information, equipment maintenance can be performed on an "as needed" basis rather than "on set time" sequence scheduling.

Management monitoring and reporting of the manner in which site operators conduct their jobs is an important responsibility of shift and general foreman. The overall responsibilities of both the shift and general foreman are presented in detail in Table IX (Appendix). Employee deficiencies are
discussed by the foreman with the employee and entered into his Employee Record. Any accident is subjected to an Accident Investigation. In the Accident Investigation Reports, management must identify and define causes of accidents in the same manner that potential hazards were recognized and noted in the Safe Job Procedures. The extent of the level of management hierarchy involved in an Accident Investigation depends on the severity of the accident. Site Awareness Charts are kept by site management personnel to record the extent of injuries, violations, and unsafe acts as reported by the individual facility supervisors. This mechanism provides a means of establishing and taking corrective action - a management tool providing continuous self-policing of the effectiveness of occupational health and safety activities. Such action can involve further instruction of the employee in question, revision of Safe Job Procedures, preparation of a new Safe Job Procedure, redesign and improvement of equipment if this is a factor, and lastly, disciplinary action if warranted. Recurrence of operator deficiencies are considered as insubordination and result in disciplinary action (i.e., short-term suspension).

Physical equipment safe operation is based on the following three requirements: (1) Safety Standards are established and enforced in the design and specification of equipment, (2) newly installed or modified equipment is inspected and approved for safety prior to facility use, and (3) specific responsibilities are established for periodic inspection and for prompt correction of deficiencies or immediate shutdown of equipment if a serious hazard is found. Physical Condition and Inspection Reports are compiled and issued after the monthly equipment inspections have been completed within the different facilities. The corporation maintains an up-to-date series of manuals which include guidelines covering these requirements. Also, guidelines for prevention or control of occupational exposure to noise, ionizing radiation, and concentrations of dusts, gases, or fumes from toxic chemicals have been developed and are kept current by the corporate Environmental Health Division.

Finally, on a monthly basis, the various individual Health and Safety Reports (already discussed) are consolidated in an overall Facility Safety Activity Report. In turn, the various Facility Safety Activity Reports are summarized in a single Site Safety Activity Report. In addition to the latter, the site superintendent and his staff conduct Personnel Safety Audits which emphasize quality as well as the quantity of safety activity.

Medical monitoring is conducted by means of annual physical examinations for most site hourly employees. A major hazard in the aniline facility is skin absorption of aniline (resulting in possible blood cell damage). Consequently, aniline facility employees are monitored each six months with comprehensive blood and urine tests.

5. Personal Protective Equipment

The Safe Job Procedures itemize mandatory personal protective equipment items for facility operators to wear for each job. The company provides each operator with the equipment required for all of the facility jobs. Personal protective equipment requirements depend on the chemicals encountered and
their specific hazards. Hard hats and safety glasses must be worn throughout all processing facilities, except within the control rooms and other auxiliary buildings. Because of the outdoor construction, site operators are provided with full length rubber raincoats and rubber boots. Other items furnished are various types of gloves, goggles, face shields, and respirators. Except in the aniline facility, operators provide their own work clothing and shoes; safety shoes may be purchased at subsidized prices. Full face respirators are provided (i.e., MSA Comfo II ammonia canister type for ammonia, Dustfio for nuisance dust, and Scott Air Pack and airline respirators with bottled air for emergencies). Ear protection, except where required by the Safe Job Procedures, is provided on request.

E. Occupational Health Exposure Results

During this in-depth survey, area monitoring samples were obtained by NIOSH in the Phenol I and II areas to determine airborne phenol concentrations. The sampling equipment was positioned (1) adjacent to the single mechanical seals of pumps handling phenol and bottoms process streams at approximately 300°F and 50-150 psig pressure, and (2) at the hatch during tank truck loading. Personal samples were taken to determine phenol concentrations in the breathing zones of day shift operators performing various outside jobs in the same areas. Also, an additional personal sample was obtained to estimate the airborne cumene concentration. USS Chemicals personnel duplicated the area monitoring samples. The NIOSH phenol samples were collected in bubblers containing dilute NaOH solution and the cumene sample was collected on a charcoal tube. Analyses were performed in accordance with NIOSH Method S330 using a gas chromatograph equipped with a flame ionization detector (FID). Table VI results show four of seven NIOSH phenol area samples in a 1.0–2.7 ppm range, well below the OSHA PEL ceiling of 5 ppm phenol. The other NIOSH phenol area samples (including tank truck loading) and all the operator personal samples were below 0.4 ppm. The USS Chemicals area sample results were comparable to those of NIOSH. The cumene sample indicated a 0.35 ppm level; for comparison, the OSHA PEL is 50 ppm.

An aniline tank car loading was monitored by NIOSH using silica gel tubes. Analysis was by NIOSH Method S310 employing a gas chromatograph equipped with a FID. An area sample, located a foot downwind of the hatch, tested at 2.0 ppm aniline, while the loading operator's personal sample indicated a 0.4 ppm level. Both results, calculated “as is” for their 83-minute time duration, are well below the OSHA PEL of 5 ppm for aniline.

Results of prior USS Chemicals occupational exposure monitoring surveys for phenol and aniline were supplied to NIOSH. March 1976 and February 1977 survey reports on airborne phenol levels are summarized in Table X (Appendix). Two of 26 samples were in a 1.0–1.4 ppm phenol range and all others were under 0.3 ppm. Table VII contains the airborne aniline results (March 1982 Survey). These company results confirm the prior conclusion that both aniline and phenol airborne exposure levels at the Haverhill site are well below the OSHA PEL's of 5 ppm for phenol and aniline.
A. Facility and Process Description

About 94 percent of the U.S. phenol and 67 percent of the acetone are produced by oxidation of cumene, using compressed air as the oxygen source. The process steps, following Hercules technology, are successively:

1. Oxidation of cumene to cumene hydroperoxide (CHP)
2. Cleavage of the hydroperoxide
3. Neutralization of cleaved products
4. Distillation to provide high purity phenol, acetone, and alpha methyl styrene (AMS).

Approximately 0.4 pounds of acetone, 0.6 pounds of phenol, and 0.04 pounds AMS are produced from one pound of cumene in accordance with the following equation:

\[
\text{Cumene} + \text{O}_2 \xrightarrow{\text{Acid} \Delta} \text{OH} + \text{CH}_3\text{C}=\text{O} \\
\text{CH}_3\text{C-O-OH} \quad \text{Cumene Hydroperoxide} \\
\text{CH}_3 \quad \text{Phenol} \\
\]

By-Products

\[
\begin{align*}
\text{CH}_3\text{C}=\text{O} & \quad \text{Acetone} \\
\text{C}=\text{CH}_2 & \quad \text{Methyl Styrene} \\
\text{C}=\text{CH}_3 & \quad \text{Acetophenone}
\end{align*}
\]

All raw materials and finished products are handled in bulk. The facility receives cumene from Gulf coast producers in barge lots. Sodium carbonate is received as a powder via rail hopper cars, sodium hydroxide as a 50 percent solution by rail or truck tankers, and 93 Be' sulfuric acid (98 percent concentrated liquid) in the same manner. In addition to the phenol and acetone products, both the cumene hydroperoxide intermediate and the alpha methyl styrene by-product are sold in bulk quantity. Other by-products (acetophenone, dimethyl phenol carbinol, cumyl phenols, and acetaldehyde) are handled internally for disposal. Economics of the process are heavily dependent on the price obtained for the acetone.

As sales and internal use of phenol expanded, output of the original Unit I was augmented by construction of an essentially parallel facility, Unit II. For this phenol expansion program, the number of oxidation reactors in Unit I was almost doubled, so that both units could operate on cumene hydroperoxide from the Unit I oxidizer train. Figure 5, a simplified process flow sheet, demonstrates how the two units share several process unit operations. Heavy ends taken from the bottom of phenol distillation columns in both units are also processed in Unit I. The newer Unit II has somewhat more sophisticated
Figure 5. Phenol and Acetone from Oxidation of Cumene
fractionation equipment, computerized control, and produces slightly higher purity phenol than Unit I.

Operating conditions of the oxidation reaction are critical to obtaining high overall yield and minimizing by-product formation. The oxidation reaction is very sensitive to traces of phenol; a phenol concentration above 50 ppm in the oxidizers will inhibit the reaction. Also, acidic pH and elevated reaction temperatures promote hydroperoxide degradation. To maintain stable alkaline pH conditions and neutralize any acidic by-product which would inhibit oxidation, a 2-3 percent sodium carbonate solution is charged into the top of each of the seven oxidizers. Maximum reaction conditions of approximately 200°F and 80 psi pressure are maintained in the oxidizers. Cumene hydroperoxide can reach concentrations of 32-35 percent. However, the reactors are operated to attain about a 25 percent concentration which results in better product separation during distillation and less by-product formation. Because of recirculation, the reaction yield of CHP is normally in a 90-95 percent range based on the cumene charged. High humidity has an adverse effect on reaction yield. A Bendix chromatographic instrument is now employed for in-line analysis of process streams whereas previously a refractometer and density meters had been employed. The oxidizers are equipped with both normal cooling coils and extra coils which can be used for emergency cooling.

From the final oxidizer, the product stream goes to surge tanks where it is degassed and carbonate is settled out. The CHP containing liquor leaving the surge tanks is split into two streams for parallel processing in Units I and II (Figure 5).

Excess cumene is stripped off as overheads, condensed, and recycled back to the oxidizers. The bottoms from the stripper, containing about 92 percent cumene hydroperoxide, go to the cleavage reactor. Here, water and sulfuric acid are added to cleave the CHP into phenol and acetone. The acid content of the cleavage reaction outlet stream is neutralized with sodium hydroxide solution. The cleavage reaction and subsequent neutralization are hazardous and the temperature must be carefully controlled. The cleavage reactors have high temperature alarms and excess cooling coil capacity. If necessary, water can be added directly. The next unit operation is fractionation at atmospheric pressure. The two outlet streams from this fractionator are overheads of acetone and alpha methyl styrene (AMS), and bottoms of phenol and heavy ends.

Each stream now goes through successive fractionation columns to provide high purity products. The acetone overheads stream is purified by passage through two successive fractionation columns. In addition to high purity acetone as the main product, other component streams are water, acetaldehyde plus, and alpha methyl styrene. The acetone, coming off overhead, is condensed and stored in carbon steel tanks. The AMS goes to bulk storage to await truck and/or rail tank car shipment to customers.

The crude phenol bottoms stream from the atmospheric pressure splitter is purified by passage through a series of three fractionation columns. Other
component streams are water, light hydrocarbons, and heavy ends (hydrocarbons). Heavy ends from both Units I and II are combined and split in a separate unit operation. The phenol product (99+ percent pure with a minimum melting point of 106°F) is stored in epoxy-lined tanks and maintained at 120°F by means of continuous circulation through external heaters.

Phenol I and Phenol II, with their separate control rooms, each have a shift foreman and five to seven operators per shift. One operator is stationed within each control room at all times, while the other operators have a multitude of duties outside the control rooms, i.e., sampling, bulk product truck and tank car loading, etc.

B. Barge Shipments and Handling

Separate 8-inch diameter pipelines run from the various storage facilities to the riverside barge terminal to receive cumene and permit shipment of acetone, phenol, alpha methyl styrene, and aniline finished products by barge to customers.

The barge terminal operations are performed by a full-time tankerman and a part-time assistant; both are employees of an independent contractor. Additionally, a contract employee of an independent third party gauges compartments, takes stainless steel thief samples of each compartment on the cumene barges, and prepares a composite sample for analytical purposes. Barges are generally of two capacities: 10,000 barrels (approximately 2.9 million pounds) and 20,000 barrels (common on the Gulf Coast runs). Because the barges carry the equivalent capacity of a multitank car freight train, both the economic savings and the reduction in labor requirements (thereby minimizing potential occupational exposure) are substantial.

After the barges are unloaded, they are taken upriver to South Point for thorough cleaning by McCinnis, Inc. They are then either returned to the USS Chemicals terminal to pick up finished products or sent to other nearby processor plants to pick up loads for return to the Gulf Coast ports. Three to five barge loads of cumene are received weekly, and approximately two barge loads of acetone per week and one of alpha methyl styrene per month are returned to the Gulf Coast.

The survey team observed a cumene barge being unloaded. The workers wore hard hats, rubber gloves, safety glasses, and life preservers. Because of the flammable nature of cumene and acetone, the following safety features were evident: flame arrestors on vents, no worker smoking in the area, electrical lines were grounded, and nonsparking tools were used. No vapor recovery or other means of vapor control are employed. However, potential vapor emission points are minimal and the vapor pressure of cumene is low (10 mm Hg at 101°F). The close operator teamwork, careful attention to physical hazards and work practices, efficient use of mechanical aids in handling the large, heavy flexible hoses, pipes, and valves, and the overall scale of the operation were most impressive. The cumene was unloaded using a large diesel motor-driven pump mounted on the barge. Acetone and AMS finished products are transferred to the barges via pumps located in the tank farm storage areas.
C. Control Technology

The major occupational exposure problems in this facility are the hazard of eye and skin contact (burns and irritation) and skin absorption (possible systemic effects). Both phenol and cumene have low vapor pressures at the temperatures used to maintain them in the liquid state ready for pumping (2.4 mm Hg at 122°F for phenol and 8 mm Hg at 68°F for cumene). Since airborne contamination is normally proportional to vapor pressure, there may be less likelihood of occupational exposure during loading, unloading, and sampling operations than during processing operations in which fugitive emissions of hot vapors and liquids may escape from seals and fittings of otherwise tightly sealed equipment. For cumene and phenol, the human nose is a reasonably acute detector. The sweetish odor of phenol provides an odor threshold of 1-5 ppm compared to the OSHA PEL of 5 ppm; for cumene a sharp aromatic odor provides an odor threshold of approximately 1 ppm compared to its OSHA PEL of 50 ppm.

Besides proper selection of equipment seals and fittings (engineering control) in preventing vapor and liquid emissions from potential emission points, other control technology mainstays are work practices and personal protective equipment. These two (detailed in the appropriate Safe Job Procedures) are particularly important when obtaining and handling both process control and finished product samples. Sampling is done essentially by opening taps and collecting aliquot samples in sample containers. Eye wash fountains and safety showers are mounted at strategic locations in this outdoor facility, with tempered water supplied. These stations have been retrofitted with remote control alarms in the two control rooms to alert other operating personnel and gain their assistance.

Until about 4-5 years ago, most of the volatile emissions from facility processing equipment were exhausted directly to the environment. Such vapors, classed as volatile organic compounds (VOC), are now subject to Environmental Protection Agency (EPA) regulations and enforcement under the Federal Clean Air Act. VOC's are basically non-methane hydrocarbons falling into the C₂-C₄ range and are generally photochemically reactive. To develop background and support data for EPA generic regulations, production plants making approximately 40 major, high-volume organic chemicals have been investigated in-depth by EPA to establish the extent of VOC emissions from these plants and to define control techniques or devices which can minimize them. Results of an in-depth study of phenol/acetone from cumene facilities conducted under an EPA contract by IT Envirosence, Inc., of Tennessee were reported in 1980 (Table IV). The focus was on the following emission sources: process vents, storage tank vents, fugitive emissions (those leaks from seals and fittings components of otherwise tight processing equipment), and secondary sources (liquid, solid, and aqueous waste treatment operations that can emit VOC). EPA distinguishes between "point source" and "fugitive" emissions. "Point source" emissions are the VOC emissions from vents and stacks of operating chemical processing equipment. They are generally well characterized as to composition and reasonably consistent as to the rate of discharge to the environment. Contrarywise, fugitive emissions are unpredictable as to timing, leakage rate, and individual source identification. The real world of imperfect and variable performance of
various types of seals and fittings makes it difficult to detect and quantify fugitive emissions and identify resultant occupational health exposures.

Table IV lists the EPA estimated levels of emissions from the various unit operations of a model phenol/acetone from cumene facility employing Hercules technology and scaled to typical plant output capabilities of 200,000, 120,000, and 10,500 mg per year of phenol, acetone, and alpha methyl styrene (AMS), respectively. Important comparisons are estimated levels of emissions before and after installation of EPA-recommended control devices and percent reductions resulting from the use of these controls. This Haverhill facility has installed most of the EPA-recommended control measures.

The airstream currently exiting the oxidation reactors is collected and piped to parallel activated carbon adsorption beds. The two beds are alternated and regenerated each four hours. Regeneration involves heating the beds, air blowing them to remove the adsorbed liquids, and recycling these liquids back to the reactors. Incidentally, the value of the recovered chemicals pays a major share of the recovery operation cost. The activated carbon has an effective life of 12 to 18 months. Facility management is considering the possibility of returning the spent carbon to the supplier for reprocessing.

Close worker proximity to product emissions occurs during bulk tank car and tank truck loading or unloading. Occupational exposure by either skin contact or inhalation must be guarded against. In bulk loading of phenol, the facility loaders wear hard hats, safety glasses, and neoprene-coated gloves as the minimum required personal protective equipment. The elevated loading platform is designed to permit loading from either side. The tank truck or tank car is spotted on the downwind side of the loading platform. The loading platform itself is completely open to the wind and located away from other processing equipment or buildings. A venturi blower is turned on and positioned so as to assist the prevailing wind in directing vapors away from the operator. Liquid phenol, heated to about 120°F (vapor pressure ca 2.4 mm Hg), is pumped from the epoxy-lined storage via a tank farm delivery pump at 450–500 gallons per minute. The loader controls the amount of phenol pumped with an indicating flow meter and remote control pump cutoff switch (no automatic cutoff). Tank car loading was observed and both personal and area monitoring samples obtained.

EPA does not recommend any control measures for secondary emissions, possibly because they are only a small part of the total uncontrolled emissions. However, this facility does treat the waste water stream to remove phenol prior to final disposal by deep well injection. First, water insoluble material is skimmed from the waste water surface as it passes through API-type separators. Then anthracite fines (carbon) are mixed with this outlet waste water stream to adsorb the phenol and are later removed by Enzinger filters. This treatment presents a potential occupational exposure hazard as operator contact with phenol can occur during filter cleaning unless the required personal protective equipment is worn and proper work practices are observed.

A major source of fugitive emissions (both liquid and vapor) are the seals on process pumps and valves, and pressure relief units. Seals and fittings on sampling devices, process controllers, agitators, compressors, and a wide
<table>
<thead>
<tr>
<th>Emission Source</th>
<th>Composition of Emissions</th>
<th>Control Device or Technique</th>
<th>Uncontrolled (kg/hour rate)</th>
<th>Weight % of Total</th>
<th>Controlled (kg/hour rate)</th>
<th>Reduction in Uncontrolled Emissions Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin oxidation</td>
<td>N₂, CO₂, Benzene, H₂O, Lt. H.C.'s</td>
<td>Carbon adsorption</td>
<td>52.8</td>
<td>30</td>
<td>11.9</td>
<td>77</td>
</tr>
<tr>
<td>Cold water separation</td>
<td>Benzene, H₂O, Inert gases</td>
<td>Refrigerated condenser</td>
<td>1.8</td>
<td>1</td>
<td>0.3</td>
<td>86</td>
</tr>
<tr>
<td>IP concentration</td>
<td>Benzene, H₂O, Inert gases</td>
<td>Refrigerated condenser</td>
<td>27.3</td>
<td>16</td>
<td>0.6</td>
<td>98</td>
</tr>
<tr>
<td>IP cleaning</td>
<td>Mostly Acetone</td>
<td>Vent scrubber</td>
<td>10.5</td>
<td>6</td>
<td>0.4</td>
<td>96</td>
</tr>
<tr>
<td>Light ends column</td>
<td>Lt. H.C.'s, Acetone, Phenol, Misc.</td>
<td>Combustion in existing boilers</td>
<td>6.9</td>
<td>5</td>
<td>0.0</td>
<td>approx. 100</td>
</tr>
<tr>
<td>Acetone finishing column</td>
<td>Lt. H.C.'s, Acetone, Phenol, Misc.</td>
<td>Vent scrubber</td>
<td>14.3</td>
<td>8.5</td>
<td>0.6</td>
<td>96</td>
</tr>
<tr>
<td>Distillation columns</td>
<td>Lt. H.C.'s, Acetone, Phenol, Misc.</td>
<td>No controls identified</td>
<td>1.4</td>
<td>0.8</td>
<td>1.4</td>
<td>0</td>
</tr>
<tr>
<td>Storage and handling</td>
<td>Two-thirds Acetone</td>
<td>Vent scrubber on acetone emitting vents</td>
<td>20.8</td>
<td>12</td>
<td>5.0</td>
<td>76</td>
</tr>
<tr>
<td>Output Emissions</td>
<td>Misc.</td>
<td>Detection and correction of</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>major leaks from seals and fitting components of processing equipment</td>
<td>37.8</td>
<td>21.9</td>
<td>10.9</td>
<td>71</td>
</tr>
<tr>
<td>Secondary Emissions</td>
<td>Phenol</td>
<td>None</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waste water treatment</td>
<td>Phenol</td>
<td>None</td>
<td>0.6</td>
<td></td>
<td>0.6</td>
<td>0</td>
</tr>
<tr>
<td>Incineration of sludge and residual</td>
<td>None</td>
<td>None</td>
<td>0.2</td>
<td></td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td></td>
<td>175.7</td>
<td>100</td>
<td>31.9</td>
<td>82</td>
</tr>
</tbody>
</table>

**Notes:**


2) Table II information has been abstracted from Table IV-8 (Page IV-8) and Table IV-2 (Page V-5) of the IT Envirosience, Inc., report.
variety of flanges also contribute. Table IV shows fugitive emissions as being the second largest source of uncontrolled VOC emissions from the model plant at 21.5 weight percent. Packed seals require low controlled seal leakage to reduce frictional heat and lubricate the rotating shafts, hence are not suitable on chemical transfer pumps. Single mechanical (Durametallic) seals have provided satisfactory service on most site process pumps. Clean seal flush fluid is a requisite for extending mechanical seal life. To ensure clean seal flush fluid, condensed product vapor is used rather than pump discharge fluid. The site also extends mechanical seal life by automatic activation of the seal flush system when the pump is started. Basically, pumps are operated until the seals fail, then the spares are started. Seal replacement is about one seal per pump each two years compared to an industry average of about two seals per pump yearly.

All the hazardous chemical emissions from this Haverhill facility are capable of causing injury through worker occupational exposure. The degree of potential exposure is difficult to quantify for both point and fugitive emission sources because of factors of variable wind velocity and duration in open air processing equipment and the changing proximity of operating personnel to these emission sources during normal work patterns. Based on the EPA model information and past experience, the various emission sources of this phenol/acetone from cumene facility can be grouped into two categories - greater and lesser risk - as follows.

Table V

Quantification and Rating of Importance of Various Toxic Chemicals Emission Sources as Occupational Exposure Hazards for Phenol/Acetone From Cumene EPA Model Plant (Hercules Technology)

<table>
<thead>
<tr>
<th>Emission Sources</th>
<th>Estimated Weight Percent of Total Uncontrolled Emissions</th>
<th>Estimated % Reduction in Uncontrolled Emissions Through Application of EPA-Recommended Control Devices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greater Risk</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Storage and Handling</td>
<td>12</td>
<td>76 weighted average reduction</td>
</tr>
<tr>
<td>Fugitive Emissions</td>
<td>21.5</td>
<td>71</td>
</tr>
<tr>
<td>Secondary Emissions</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>Subtotals</td>
<td>34.0</td>
<td>72</td>
</tr>
<tr>
<td>Lesser Risk</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidation Reactors</td>
<td>30</td>
<td>77 weighted average reduction</td>
</tr>
<tr>
<td>Oxidate Wash and CHP</td>
<td>17</td>
<td>97</td>
</tr>
<tr>
<td>Concentration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHP Cleavage</td>
<td>6</td>
<td>96</td>
</tr>
<tr>
<td>Distillation Columns</td>
<td>13</td>
<td>91</td>
</tr>
<tr>
<td>Subtotals</td>
<td>66.0</td>
<td>86</td>
</tr>
</tbody>
</table>
The most recent and an ongoing facility project for reducing occupational exposure concerns handling of sodium carbonate employed for pH control in the oxidation reactors. Sodium carbonate is received at the facility in special hopper cars. The powder is air lifted from the car to a mixing tee located at the top of a solution storage tank (approximately 20 feet above the truck pad). Here it dissolves in recirculating hot water to provide a concentrated solution which will be diluted prior to entering the reactors. During this unloading and solution step, some undissolved carbonate dust escapes through the solution storage tank pressure equalizing vent. A scrubber installation has been designed and will be installed after the vent to minimize carbonate dust escape to the environment.

D. Emission Exposure Sources and Monitoring Results

On June 13th and 14th, the following phenol and cumene monitoring samples were taken in both Phenol I and II processing areas:

1. Six phenol area samples - samplers were positioned adjacent to single mechanical seals of pumps handling phenol and bottoms streams at approximately 300°F and 50-150 psig pressure.

2. Five phenol personal samples - samplers worn in their breathing zone by operators performing various outside jobs.

3. A cumene personal sample - sampler worn by the operator working near oxidation reactors in the Phenol I area.

4. Area and personal sampling during phenol truck loading - a personal sampler on operator during loading of several tank trucks and an area sample taken during one truck loading (20 minutes).

NIOSH phenol sampling involves drawing a measured volume of workplace air by means of a duPont P-125 pump through a vertical bubbler containing 15 ml of 0.1 N sodium hydroxide solution. Bubbler personal samplers were mounted vertically on the operator's clothing within the breathing zone. Operators were careful to prevent spilling of the caustic solution even though it was physically constraining. Bubbler area samples were strapped to vertical braces near the mechanical seals of pumps selected as operating under the most severe process conditions. The NIOSH Method 8-330 analysis employs a Hewlett-Packard Model 5711A gas chromatograph equipped with a FID to quantify the amount of phenol present. Limit of detection is 0.01 milligrams of phenol per sample. USS Chemicals mounted silica gel tube samplers adjacent to the NIOSH area bubblers. Their procedure included use of low airflow pumps (200 cc/min), phenol desorption with acetone, and passage through a DC 550 gas chromatograph equipped with an FID. Temperatures were 250°F injection, 150°F column, and 300°F FID. USS Chemicals duplicated the NIOSH area samplers but not the operator personal samplers.

NIOSH employed silica gel tubes to capture the cumene vapors, and carbon disulfide to desorb the tube contents. NIOSH Method 8-23 analysis employs a Hewlett-Packard 5711A gas chromatograph equipped with a FID to determine the amount of cumene present.
Table VI presents the air concentration results along with information identifying the individual sampler locations, etc. All the results are well below the OSHA PEL of 5 ppm phenol and 50 ppm cumene. For tank truck loading of phenol, the open hatch area sample indicated the exposure was 0.13 ppm over the 20-minute exposure period; the operator's personal sample for a series of truck loadings over a 176-minute period showed 0.40 ppm. In contrast, the highest area concentrations found were 2.7 and 2.2 ppm near phenol process pumps handling phenolic material at high temperatures (300-400°F).

A substantial number of earlier occupational exposure test results for phenol (area and operator personal samples taken and analyzed by USS Chemicals in a similar manner as NIOSH employed) are summarized in Table X (Appendix). These results verify the NIOSH conclusion that phenol-air concentrations near process stream pumps, operator personal samples, and tank car and tank truck loading operations are below the OSHA PEL of 5 ppm.
<table>
<thead>
<tr>
<th>Unit</th>
<th>Type of Sample</th>
<th>Description</th>
<th>Function</th>
<th>Collection Time (Minutes)</th>
<th>Material</th>
<th>PPM Air Concentration (For Times Shown)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol I</td>
<td>area</td>
<td>Wilson Synder pump</td>
<td>Product pump</td>
<td>118</td>
<td>phenol</td>
<td>0.65</td>
</tr>
<tr>
<td>Phenol I</td>
<td>area</td>
<td>Durco Buriron pump</td>
<td>Ry end column reboiler pump</td>
<td>113</td>
<td>Ry ends</td>
<td>1.62</td>
</tr>
<tr>
<td>Phenol I</td>
<td>area</td>
<td>Wilson Synder pump</td>
<td>Phenol splitter column bottoms pump</td>
<td>108</td>
<td>phenol, H.C.</td>
<td>1.09</td>
</tr>
<tr>
<td>Phenol I</td>
<td>area</td>
<td>Wilson Synder pump</td>
<td>Phenol reboiler pump</td>
<td>103</td>
<td>phenol</td>
<td>0.05</td>
</tr>
<tr>
<td>Phenol II</td>
<td>area</td>
<td>Wilson Synder pump</td>
<td>Crude phenol column bottoms</td>
<td>99</td>
<td>phenol</td>
<td>2.20</td>
</tr>
<tr>
<td>Phenol II</td>
<td>area</td>
<td>&quot;Uaicon&quot; union vertical pump</td>
<td>Bottoms pumps</td>
<td>97</td>
<td>H.C.</td>
<td>2.66</td>
</tr>
<tr>
<td>Phenol I</td>
<td>personal</td>
<td>Fractionation operator</td>
<td>Outside operator</td>
<td>205</td>
<td>phenol</td>
<td>0.13</td>
</tr>
<tr>
<td>Phenol I</td>
<td>personal</td>
<td>Tank car loader</td>
<td>Outside operator</td>
<td>444</td>
<td>phenol</td>
<td>0.09</td>
</tr>
<tr>
<td>Phenol II</td>
<td>personal</td>
<td>Fractionation operator</td>
<td>Outside operator</td>
<td>435</td>
<td>phenol</td>
<td>0.35</td>
</tr>
<tr>
<td>Phenol II</td>
<td>personal</td>
<td>Fractionation operator</td>
<td>Outside operator</td>
<td>360</td>
<td>phenol</td>
<td>0.12</td>
</tr>
<tr>
<td>Phenol loading</td>
<td>personal</td>
<td>Tank truck loader</td>
<td>Outside operator</td>
<td>176</td>
<td>phenol</td>
<td>0.40</td>
</tr>
<tr>
<td>Phenol loading</td>
<td>area</td>
<td>Tank truck - open hatch</td>
<td>Outside operator</td>
<td>20</td>
<td>phenol</td>
<td>0.13</td>
</tr>
<tr>
<td>Phenol II</td>
<td>personal</td>
<td>Oxidation operator</td>
<td>Outside operator</td>
<td>433</td>
<td>cumene</td>
<td>0.35</td>
</tr>
</tbody>
</table>
V. **Bisphenol-A Facility**

A. **Facility and Process Description**

High purity phenol (preferably from phenol unit 2) and acetone (from the phenol/acetone from cumene facility) are reacted in a continuous hydrochloric acid catalyzed reaction in accordance with the following equation:

\[
\begin{align*}
\text{Phenol} + 2 \text{Acetone} & \xrightarrow{\text{HCl Catalyst}} \text{Bisphenol-A} \\
\end{align*}
\]

There are four stages to bisphenol-A (BPA) processing:

1. Reaction and HCl removal
2. BPA crystallization
3. Excess phenol removal and prilling
4. Automated filling of bags and bulk containers

The first three stages are shown in Figure 6, a simplified process flow chart. This processing is based on Rhone-Poulenc technology. After 4–5 years of operation, this facility underwent a major retrofitting and modification program to provide the current level of effective operation. Two grades of bisphenol-A prills are produced: epoxy grade and polycarbonate grade, with the polycarbonate grade being much purer. Variations in crystallization operations during BPA purification account for the two levels of purity and product color.

The highly exothermic reaction (Figure 6) is carried out in a gravity-fed sequence of eight 2,000-gallon Pfauider glass-lined agitated reactors. The heat of reaction is removed by means of the reactor cooling jackets and Teflon-lined external cooling loops. After the reaction is completed, the hydrochloric acid (catalyst) is stripped from the bisphenol-A phenol reaction slurry. This slurry, BPA-phenol particles suspended in excess phenol, is pumped from the final reactor to crystallizers, where BPA-phenol particles are separated from the mother liquor. In turn, these particles are heated to 300°F (350°F maximum) to both drive off the excess phenol (which is dried and returned to the reactors) and to liquify the bisphenol-A. The molten BPA is introduced into the top portion of the prilling tower through spray nozzles. The resultant small liquid droplets congeal and solidify into solid spheres as they drop through a countercurrent flow of cool air entering the bottom of the tower. The prills are pneumatically conveyed to storage bins to await gravity packing.

Conveying and packing the BPA prills generates dust, which causes concern from two standpoints: (1) inhalation as nontoxic nuisance dust by facility
Figure 6. Process Sequence
Bisphenol-A Processing
operators and (2) dust explosions. Because the dust is potentially explosive, nitrogen (rather than air) is used as the conveying medium. The bisphenol-A packing and warehousing operation is impressive both from the standpoint of size and of the array of automated, bagging, palletizing, protective wrapping, and strapping equipment.

During normal operation, this facility has four, 8-hour shift crews, each comprising a shift foreman and eight men (six unit operators and two warehousemen). The day shift additionally has a material handling foreman, two packaging operators, and a facility supervisor. Because this facility was shut down and bisphenol-A packing not operative during the in-depth survey week, neither personal nor area sampling were possible.

B. Control Technology

The bisphenol-A facility has had severe equipment maintenance problems during the 8 years since its startup, mainly due to the extreme corrosivity of the hydrochloric acid catalyst and the high melting point of the bisphenol-A product.

In the glass-lined Pfaudler reactors, hydrochloric acid permeates the glass lining and reacts with the carbon steel shell. This causes nascent hydrogen to build up between the shell and the lining. The hydrogen pressure increases until glass lining failure results. This was especially severe for the top-mounted, glass-coated agitators and agitator shafts. Replacing the glass-coated agitators and pipes between the reactors with Teflon-coated equivalents has improved the operating situation. However, over a long period of time the Teflon also becomes permeable to the hydrogen chloride vapors. Early on, the original packed seals on the agitator shafts were replaced with double mechanical seals. Even with these mechanical seals the high melting BPA droplets formed during reaction tend to work under the O-ring shaft seal from the reactor side, solidify, and thereby raise the O-ring to allow further leakage. Eventual seal failure is partly due to shaft surface erosion. Treated the shaft surfaces with hard chrome and adopting Teflon O-rings has improved the situation. Still, the facility maintenance supervisor and site engineering staff continue investigating other options for upgrading reactor linings and agitator seal performance. Similar problems have occurred with the single and double mechanical seals on a number of the facility BPA-phenol slurry pumps.

The control of hydrogen chloride vapor emissions from the reactors has proven difficult. Rupture discs in pressure relief valves have been a problem, both from the standpoint of finding suitable corrosion resistant materials and the difficulties of equipment decontamination required prior to maintenance work. Installation of graphite pressure relief discs has helped. To ensure that hydrogen chloride vapor does not escape to the environment if vent line pressure relief discs open, all HCl vent lines will be directed to a packed scrubber now being installed. It has been sized to accommodate the potential discharge of the largest existing rupture disc. Because of possible plugging in BPA phenol slurry lines, flow shut off is accomplished through use of plug valves rather than conventional block valves.
Bisphenol-A prills are packed and shipped in 50-pound net bags, one ton "supersacks," and special hopper cars (both rail and truck). The lower purity BPA (epoxy grade) generates more dust than the polycarbonate grade when using the same equipment. The ventilation of the bag packing station includes both local exhaust ducts and a moving eductor. The eductor is automatically inserted into the bag to remove the displaced air as the bag fills and is withdrawn just before the bag is automatically sealed. Both the local exhaust and eductor dust streams are connected to a large baghouse for dust removal.

There are occasions, despite the continuing efforts to prevent dust dispersal, that the operators need and use dust masks supplied by the company.
VI. **ANILINE FACILITY**

A. **Facility and Process Description**

Phenol and ammonia are continuously reacted under high temperature and pressure over a proprietary catalyst to make aniline in accordance with the following equation:

\[
\text{OH} \quad \text{Catalyst} \quad \Delta \quad \text{NH}_2
\]

Phenol + Ammonia \rightarrow Aniline + By-product (Diphenylamine)

Figure 7 is a simplified process flow chart for this Halcon SD proprietary process (developed in the 1960's by Halcon International, Inc.). Although this is the first U.S. installation to use this process, a Japanese facility, operated by Mitsui Petrochemicals Industries (MPI), has been operating since 1970. USS Chemicals personnel were trained in Japan prior to startup of the Haverhill facility. This facility was designed, installed, and started up under supervision of the Scientific Design Corporation in conjunction with MPI engineers.

Four pressure bullets store ammonia (as received by special rail cars) at about 45°F and 65 psig. Ammonia from the bullets is compressed by an Elliott 2-stage compressor from 65 psig to 200 psig in the first stage and then from 200 to 265 psig in the second. A furnace and heat exchangers bring reactants to 760°F. The reaction, in two parallel reactors, occurs over a proprietary catalyst using a large excess of ammonia. Almost 100 percent of the phenol feed to the reactors is converted to aniline and diphenylamine. From the reactor, the crude product stream goes through heat exchangers and an ammonia stripper (packed column at 65 psig and 45°F). The excess ammonia is recovered, then recycled via the compressor back to the reactor. The resultant crude aniline contains about 90 percent aniline, 5 percent diphenylamine, 1-1.5 percent phenol, and water. The water is removed by means of azeotropic distillation in a 40-tray column with water-free aniline leaving at the bottom of the column and the toluene-water azeotrope at the top. The next column, an 84-tray unit operating under vacuum, fractionates the dry crude aniline stream to provide pure aniline (less than 5 ppm phenol content) from the top of the column and a diphenylamine, triphenylamine, and phenol containing stream near the bottom. These bottoms are redistilled in a third column with phenol overheads recycled back to the process. The resultant fluid bottoms are burned as boiler feed - a safe means of disposal. Waste aqueous streams go to the site waste treatment unit for cleanup and are disposed of by deep well injection.
Figure 7. Aniline by Halcon SD Process
(Reaction of Phenol and Ammonia)
Because the aniline facility is highly automated and computer controlled, it functions satisfactorily with few personnel. Included on each shift are a shift foreman and two operators. One of the two operators is the control board man and spends 100 percent of his time inside the pressurized control room. The second operator, the field man, spends up to 80 percent of his time outside the control room—checking gages and valve settings, doing minor lubrication, loading tanks and tank trucks, taking requisite control samples, etc.

B. Control Technology

The major occupational exposure problems in this facility are exposure to phenol, aniline, and ammonia. Due to the high reaction temperature and pressure, proper selection of equipment seals and fittings are critical to preventing vapor and liquid emissions. An important hazard of aniline is skin absorption resulting in adverse blood composition effects. Hence, proper work practices and use of effective personal protective equipment are critical components of successful control technology.

The open air, all-weather construction of the aniline facility as well as its location away from other operations minimizes worker exposure. While major shutdown operations are automatically controlled, startup and shutdown of the various distillation columns must be done carefully to prevent ammonia vapor escaping to the environment. Past worker complaints were chiefly about emissions of ammonia vapor. Ammonia's pungent odor, low-odor threshold, high volatility, and difficulty in finding satisfactory gasketing material presented a startup problem. Spirometalllic (Resistoflex) Teflon®/stainless steel gaskets, found satisfactory in eliminating most fugitive emissions from flange joints, did not contain ammonia regardless of the care taken in installing and torquing the 12-14 inch diameter ammonia pipe and furnace flanges. The solution was use of 1/8-inch thick blue African asbestos gaskets (Gordon Gasket Company) and torquing flanges to uniform pressure.

To decontamination distillation columns, the columns are drained to appropriate storage containment, then boiled out at total reflux for about 6-8 hours. This boiling out continues until Draeger tube samples, taken from bottom bleed valves, show aniline content is below 100 ppm. Next, the columns are drained completely, then steamed until residual aniline content (Draeger tube testing) is below the OSHA PEL of 5 ppm. Finally, the columns are cooled by sucking air from the top of the columns. The lines to the column are blinded before column entry for maintenance, in accordance with Safe Job Procedure requirements. Carbon steel is normally used in aniline equipment with stainless steel standard for phenol equipment. For carbon steel equipment cleanout, hot water (steam/water mixture) is employed; and for stainless steel equipment cleanout, hot condensate (steam/condensate mixture) is used. Packed column decontamination is accomplished by steaming. The various cleanout water streams drain to the pad.

Samples are taken through needle valves to pressure bombs or sample bottles. All sampling points are at grade and they have enclosures to reduce risk of operator contact with process materials. Pressure bomb samples are cooled before delivery to the laboratory for analysis and for those containing free
and dissolved ammonia in addition to aniline and/or phenol, the ammonia is allowed to bubble off under laboratory hoods prior to analysis. Formerly a number of gas samples were taken for process control, but this practice was eliminated when it was found that the analyses were not sufficiently accurate for control purposes.

At the end of a run or other planned shutdown, excess ammonia is removed from the front end of the process, directed through the compressor, sparged (and condensed), then pumped back to the ammonia feedstock storage bullets. A water scrubber captures ammonia vent gases released if the ammonia storage bullets are overpressured. One or more of the four pressure relief valves on each ammonia storage bullet opens to relieve overpressure. Corrosion of the springs in these pressure relief valves, a past maintenance problem, has been solved by employing specially coated corrosion resistant springs.

Work practices and personal protective equipment employed in the facility are spelled out in detail in the Safe Job Procedures. These have been carefully prepared to cover all normal operation situations, startup and shutdown sequences, and also emergency situations which have either already occurred or have been conceived as possible occurrences. Some of the startup and shutdown procedures may vary somewhat with the season (winter versus summer). In addition to the basic requirements for hard hats and safety glasses, outside operators are required to wear rubberized coveralls and rubber shoes. Depending on the specific job procedures, the operators must also wear rubber gloves, face shields, goggles, and/or full face respirators. In some areas, the outside operators may wear leather shoes. All this equipment and wearing apparel is furnished by USS Chemicals. A service company supplies and cleans the clothing and workers change as required. Experience has demonstrated that butyl rubber is much more resistant to aniline than neoprene. If leather shoes become contaminated by aniline, they are disposed of as hazardous waste. The appropriate canisters for the full face respirators are provided as required, i.e., an ammonia canister for ammonia.

A feature of this facility is the permanent placement of large sturdy signs in each area detailing the exposure hazards and the required personal protective equipment. Housekeeping in all areas of this facility was found to be excellent. Facility personnel thoroughly decontaminate all worn or damaged equipment which can be transported (either whole or disassembled) to the facility maintenance shop, where contract maintenance specialists do the repairing. When maintenance must be done in place, i.e., flanges, the contract maintenance personnel do the work in accordance with facility work practices and wear the required personal protective equipment.

The facility is not equipped with an in-place ambient monitoring system for detection and automatic alerting when fugitive emissions escape from the processing equipment. However, medical monitoring is conducted. Each six months both blood and urine samples are obtained from each aniline employee by medical personnel who visit the facility in a special medical van. An elaborate series of tests run on those fluids determines if blood cell damage or other health impairment due to occupational exposure has occurred.
The aniline facility was not operating during the week of this in-depth survey, thwarting initial plans for getting both personal and area samples to establish aniline, phenol, and ammonia ambient air concentrations during normal operation. However, an aniline tank car loading was monitored.

C. Emission/Exposure Sources and Monitoring Results

Tank car loading of aniline is carried out in a similar manner as for phenol (previously described). Whereas phenol must be held at 120°F to maintain liquidity, aniline may be pumped at ambient air temperatures (freezing point is 21°F and vapor pressure at 68°F is 0.6 mm Hg). Its weak amine odor provides good warning properties; the odor threshold is approximately 1 ppm compared to the OSHA PEL of 5 ppm or the ACGIH recommended 2 ppm TLV.

A tank car loading took 83 minutes from the initial hatch opening until it was closed and sealed. The operator had a personal charcoal tube sampler attached to his lapel to sample his breathing zone as he followed the Safe Job Procedures on aniline tank car loading, and an area charcoal tube sampler was suspended from the tank car railing approximately 1 foot directly downwind of the open hatch. Weather conditions were a warm summer day with a minimal 0-5 mile per hour breeze blowing across the open hatch. The two charcoal sample tube samples were analyzed in accordance with NIOSH Method 8-310. Sample desorption was done with 95 percent ethanol and analysis by gas chromatography (Hewlett-Packard Model 5710 equipped with a FID). The operator personal sample showed an air concentration of less than 0.4 ppm aniline and the area sample, 2.0 ppm.

Table VII lists results provided by USS Chemicals (personal sampling of aniline facility personnel for successive days during the period March 21-April 2, 1982).

<table>
<thead>
<tr>
<th>Job</th>
<th>Number of Personal Samples (8-hour)</th>
<th>ppm Aniline (8-hour TWA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline operator (field)</td>
<td>8</td>
<td>All non-detectable</td>
</tr>
<tr>
<td>Aniline technician</td>
<td>3</td>
<td>All non-detectable</td>
</tr>
<tr>
<td>Aniline foreman</td>
<td>3</td>
<td>All non-detectable</td>
</tr>
<tr>
<td>Aniline maintenance man</td>
<td>12</td>
<td>All non-detectable</td>
</tr>
<tr>
<td>(working in processing area)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aniline chemist (laboratory)</td>
<td>3</td>
<td>All non-detectable</td>
</tr>
<tr>
<td>Aniline analyst (laboratory)</td>
<td>3</td>
<td>All non-detectable</td>
</tr>
</tbody>
</table>

35
A SOCMA (Synthetic Organic Chemical Manufacturers Association, Inc.) report of August 8, 1983, summarized exposure information supplied by the five major U.S. manufacturers of aniline for 1982 production operations. As for results in Table VII and this NIOSH in-depth survey, air sampling was performed using silica gel tubes. Table VIII presents the SOCMA summary of employee exposures.

### Table VIII

SOCMA Summary of Aniline Manufacturing Plant Employee Exposure Results

<table>
<thead>
<tr>
<th>Function</th>
<th>Number of Employees</th>
<th>Level of Exposure ppm range (TWA 8-hour)</th>
<th>Worker Hours per Year (1982)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operations</td>
<td>184</td>
<td>0.001 - 0.86</td>
<td>280,285</td>
</tr>
<tr>
<td>Maintenance</td>
<td>215</td>
<td>0.001 - 1.4</td>
<td>129,530</td>
</tr>
<tr>
<td>Quality Control</td>
<td>112</td>
<td>0.001 - 0.4</td>
<td>119,882</td>
</tr>
<tr>
<td>Warehouse/Shipping</td>
<td>47</td>
<td>0.01 - 0.6</td>
<td>37,283</td>
</tr>
<tr>
<td>Other*</td>
<td>78</td>
<td>0.01</td>
<td>34,024</td>
</tr>
</tbody>
</table>

* Other includes supervisory and engineering personnel.

The airborne aniline-in-air concentrations shown in Tables VII and VIII demonstrate that the OSHA PEL of 5 ppm is unlikely to be exceeded.
VI. CONCLUSIONS

The Haverhill, Ohio, site of USS Chemicals is characterized by the large scale of operations, the widely dispersed open air, chemical processing facilities for manufacture of a number of hazardous chemicals; the extensive use of river barges as a major transportation component; the degree of product integration providing internal use of basic chemicals to make other downstream chemicals; the excellence of overall site housekeeping; and the marked corporate emphasis on conducting all operations in a safe manner in accordance with written Safe Job Procedures to minimize occupational exposure to hazardous chemicals. It was apparent during this NIOSH in-depth survey that the managers and workers were a veteran group, very familiar with their job duties, and performing them with a high degree of skill.

Considering all these aspects, this Haverhill site represents a well operated chemical processing complex compared to other sites that have been visited. Noteworthy were the candid admissions and explanations of both the operating and processing problems encountered, and the remedial actions taken to solve these problems. While emphasis was on solving production problems and improving production efficiency, hazardous working conditions were considered and modifications instituted were also effective in minimizing occupational exposure to the many hazardous chemicals either employed or produced. Additionally, improvement programs are ongoing activities.

With the exception of acetone and toluene, the chemicals the site handles are relatively non-volatile (having low vapor pressures). This is advantageous from the inhalation hazard standpoint during unloading, sampling, and storage operations. Complicating the health exposure situation is the fact that aniline (and to a lesser extent, phenol and cumene) are absorbed by the skin. The low volatility (and evaporation rate) exacerbates this condition. If absorption occurs, health problems can develop even though airborne levels are within the OSHA permissible limits. USS Chemicals' systematic application and strong enforcement of their written Safe Job Procedures is of particular value in this regard since worker protection against skin absorption of chemicals is heavily dependent on good work practices and wearing of effective personal protective equipment.

NIOSH air sampling results obtained in the phenol and aniline facilities during the survey as well as the many test results previously obtained by USS Chemicals during past years (many included in this report) indicate that employee exposure via inhalation to airborne phenol and aniline was well below the current OSHA PEL value for these chemicals at the time of the survey.

Good housekeeping was observed throughout the site; the Phenol II and aniline facilities were particularly well kept. Service to chemical customers was also well handled. Information was presented by the company in the form of Material Safety Data Sheets and excellently written and attractively presented brochures covering product characteristics, safe handling procedures, and product end use discussions.

A Haverhill practice which would be helpful to other chemical processors for use during bulk loading of product tank cars and tank trucks is the use of
Venturi blowers positioned on the loading platforms so as to augment existing wind currents to rapidly disperse any vapors rising from loading batches and pipe closures.

River barge transportation is a very important factor in Haverhill site operation. The two-way traffic with cumene receipts and acetone and alpha methyl styrene product shipment provides economic savings via lower transportation costs and reduces site labor and handling requirements; which in turn markedly reduces total potential occupational exposure.

Adequate reduction of fugitive vapor and liquid emissions from pumps and agitator seals has been accomplished in all three Haverhill processing facilities through employment of mechanical seals based on the conditions observed during the survey. Only a few double mechanical seals have been required; single mechanical seals are successfully used over a wide range of pumping applications. USS Chemicals claims to have an average pump seal life of two years per pump. They compare this to a chemical industry average of two seals per pump per year for continuous processing operations. This amounts to an approximate one to four seal replacement advantage - accounting for a major savings in maintenance operations and reduction of potential occupational exposure.
APPENDIX
Table IX

FOREMAN - Responsibilities and Training Functions

I. The responsibility for the safety of assigned employees and the safe condition of the assigned work area is vested in the Foreman who is accountable to the General Foreman.

II. The minimum requirements will be met when the Foreman fulfills the administrative, control, and training functions listed below.

A. Administrative Functions

1. Each employee to receive at least one individual Safety Contact a week.

2. Each Foreman shall:
   a. Enforce Safe Job Procedures as developed by Job Safety Analyses.
   d. Participate in Job Safety Analysis conferences.

3. Instructs each employee in all Safe Job Procedures pertaining to assigned work, and records instruction.

4. Makes at least one Safety Observation per day, with each employee being observed twice a month.

5. Reviews accident causes as shown on Awareness Charts and directs daily safety activities to correct these causes.

6. Conducts weekly instruction of employees in Safe Job Procedures, safety rules and regulations; records instruction; and enforces all Safe Job Procedures, safety rules and regulations at all times.

7. Makes daily inspections of assigned work area and takes immediate steps to correct unsafe or unsatisfactory conditions; reports to General Foreman conditions which cannot be immediately corrected; instructs employees on housekeeping standards; and requires Maintenance or Service employees to maintain these standards while in assigned work area.

(continued)
8. Instructs employees that tools are to be inspected before each use; makes daily spot checks of tool conditions; inspects each tool in assigned work area monthly; uses a check list for recording tool inspections; and submits check list to the General Foreman, noting type of defect and action taken.

9. Instructs employees in visual inspection before using wire rope, slings, chains, clevises, pins, spreaders, etc.; makes spot checks daily of such devices in service; inspects weekly each such device in assigned work area; and reports to General Foreman.

10. Requires powered mobile material-handling equipment operators to submit reports at the end of each turn; reviews reports and takes prompt corrective action; transmits reports to General Foreman with comments on action taken; and inspects such equipment weekly in assigned work area.

11. Requires crane operators to submit reports at the end of each turn; reviews reports; takes corrective action; and submits reports to General Foreman with comments and action taken. Maintenance Foreman will be assigned specific cranes for inspecting biweekly. Operating Foreman makes cranes available for maintenance inspection; requires cranesmen to report crane collisions or severe contact with runaway bumpers; and takes such cranes out of service until inspection is made.

12. Maintains the identification of utilities in assigned work area according to plant requirements.

13. Takes action leading to the elimination or guarding of pinch points.

14. Instructs personally each new employee in assigned work area on job safety requirements; completes check list promptly; and forwards it to General Foreman.

15. Enforces the plant Medical Department's recommendations with respect to employee's physical limitations; reports employee's apparent physical limitations to General Foreman; and requests physical examination.

16. Enforces wearing of protective apparel; makes spot checks to determine that protective apparel is being used; and makes periodic checks to appraise condition of apparel.

(continued)
17. Sees that injured employee receives prompt medical attention; isolates area or shuts down equipment, as necessary; and immediately reports to the General Foreman the facts regarding employee's accident or illness and action taken. In near serious accident cases, Foreman determines cause; takes immediate steps to correct condition; and isolates area and/or shuts down equipment, as necessary. Foreman immediately reports facts and action taken to the General Foreman.

18. Makes thorough investigation of all accidents, near serious accidents, and medical cases occurring to employees in assigned work area. Immediately after the accident and before leaving plant, he prepares a complete Foreman's Accident Report for the General Foreman.

B. Control Functions

1. Checks, at the start of each turn and before relieving the on-duty Foreman, changes in operating practices, procedures, and conditions, noting facts related to safety which have occurred since last turn worked.

2. Makes, at the start of each turn, an immediate check to determine absentees. If plant injury is claimed, an immediate investigation is instituted and General Foreman notified.

3. Makes daily spot checks and takes the necessary corrective action regarding housekeeping, Unsafe Acts, Violations, unsafe conditions, tools, ladders, wire rope, chains, clevises, pins, spreaders, etc., and adherence to safety rules and Safe Job Procedures.

4. Reviews crane operators' inspection reports daily and takes necessary action.

5. Reviews powered material-handling equipment operators' inspection reports daily and takes necessary action.

6. Submits to General Foreman a written report monthly of inspections of tools, ladders, and wire rope, chains, clevises, pins, spreaders, etc.

C. Training Functions

1. Attends all scheduled and assigned safety training meetings.

2. Instructs personally or provides on-the-job instruction to employees in safe and efficient performance of assigned jobs.

3. Participates as assigned in Job Safety Analysis Conferences.
Table X
Results of Full Shift Phenol Vapor Evaluations
Conducted by USS Chemicals

<table>
<thead>
<tr>
<th>Date</th>
<th>AREA SAMPLES</th>
<th>No. of Samples</th>
<th>Results, ppm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/1-6/76</td>
<td>Bottoms pump, near phenol finishing column</td>
<td>3</td>
<td>0.16 0.04 0.08</td>
</tr>
<tr>
<td>3/1-6/76</td>
<td>Reboiler pumps, near crude phenol column</td>
<td>3</td>
<td>0.03 0.00 0.01</td>
</tr>
<tr>
<td>3/1-6/76</td>
<td>Reboiler pumps, near phenolic flash drier</td>
<td>3</td>
<td>0.08 0.05 0.07</td>
</tr>
<tr>
<td>3/1-6/76</td>
<td>Bottoms pump, near splitter column</td>
<td>3</td>
<td>0.16 0.06 0.13</td>
</tr>
<tr>
<td>3/1-6/76</td>
<td>AMS section pump</td>
<td>3</td>
<td>0.00 0.00 0.00</td>
</tr>
</tbody>
</table>

PERSONAL SAMPLES

Phenol Loading Area

<table>
<thead>
<tr>
<th>Date</th>
<th>AREA SAMPLES</th>
<th>No. of Samples</th>
<th>Results, ppm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2/8-10/77</td>
<td>Approximate breathing zone, loader, while loading one phenol tank truck (5,000 gal.)</td>
<td>2</td>
<td>0.0 0.0 0.0</td>
</tr>
<tr>
<td>2/8-10/77</td>
<td>Approximate breathing zone, loader, while loading one phenol tank car (20,000 gal.)</td>
<td>4</td>
<td>1.4 0.3 0.9</td>
</tr>
<tr>
<td>2/8-10/77</td>
<td>Breathing height, along RR car loading dock, between phenol cars (background sample)</td>
<td>2</td>
<td>0.0 0.0 0.0</td>
</tr>
<tr>
<td>2/8-10/77</td>
<td>Breathing height, under RR car loading dock, between phenol cars (background sample)</td>
<td>1</td>
<td>- - 0.2</td>
</tr>
</tbody>
</table>

Phenol Plant Proper

<table>
<thead>
<tr>
<th>Date</th>
<th>AREA SAMPLES</th>
<th>No. of Samples</th>
<th>Results, ppm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2/8-10/77</td>
<td>Approximate breathing zone, Fractionation</td>
<td>1</td>
<td>- - 0.3</td>
</tr>
<tr>
<td></td>
<td>Man tending pumps</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2/8-10/77</td>
<td>Approximate breathing zone, Auxiliary II</td>
<td>1</td>
<td>- - 1.2</td>
</tr>
<tr>
<td></td>
<td>Man, during Thursday afternoon sampling run</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Parts phenol vapor per million parts of air by volume. Phenol air samples collected in vertical impingers containing dilute caustic solution as the collection medium.