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# OCCUPATIONAL HYGIENE IN AROMATICS PLANTS

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**Abstract**—After brief reference to the processes used at two plants manufacturing aromatic products. the importance of hygiene review in the design stage is emphasised.

Physical factors mentioned include noise. thermal conditions and lighting. Chemical factors include process chemicals and the aromatic products themselves.

A substantial part of the paper reviews experience in monitoring and controlling possible hazards from inhalation of benzene vapour. and makes reference to the routine analysis of phenol in urine.

Finally, a summary is made of the essential features of safe practice.

## INTRODUCTION

THIS PAPER is based on work undertaken to assist the medical and safety organisations of two plants. It presents a composite picture of hygiene experience at the aromatics plant of Esso Chemie N.V. located with the Esso refinery at Botlek, near Rotterdam, and at the recently commissioned aromatics plant of Esso Chemicals Ltd. at Fawley, Hampshire.

The Dutch plant came on stream in 1964 and its capacity, which has recently been doubled to make it one of the largest in the world, is now over 600,000 tons/year of aromatic products. The original unit, which is still in use, starts with Udex extraction of the $C_7/C_8$ feedstock followed by fractionation of toluene and xylenes. Hydrogen in powerformer tail gas is concentrated by cooling in a system with propane and ethylene and used to dealkylate toluenes and xylenes to produce benzene, separation being achieved by fractionation. Cyclohexane is produced by catalytic hydrogenation of benzene. The newly added plant includes a sulfolane extraction unit and separation and purification of *o*- and p-xylene. The complete process is shown in Fig. 1. The Fawley aromatics plant came on stream in 1968 and is based on sulfolane extraction from powerformate feedstock. Aromatics production is about 300,000 tons/yr.

The products are shipped principally by barge or coastal tanker, but road and rail transport are occasionally *used.* Toiuene and xylene are sold primarily for use as solvents, while benzene is a feedstock for the chemical industry-one customer being the Esso Chimie S.A. detergent plant at Port Jerome in France.

Hygiene aspects of both the original plants and the expansion at Botlek were reviewed at the design stage by the Medical Research Division of Esso Research & Engineering Company in New Jersey, and by Medical and Safety Departments at the plants. The importance of such reviews must be emphasised as they have ensured that most problems are controlled in the design of the plant. Even so, if a plant is

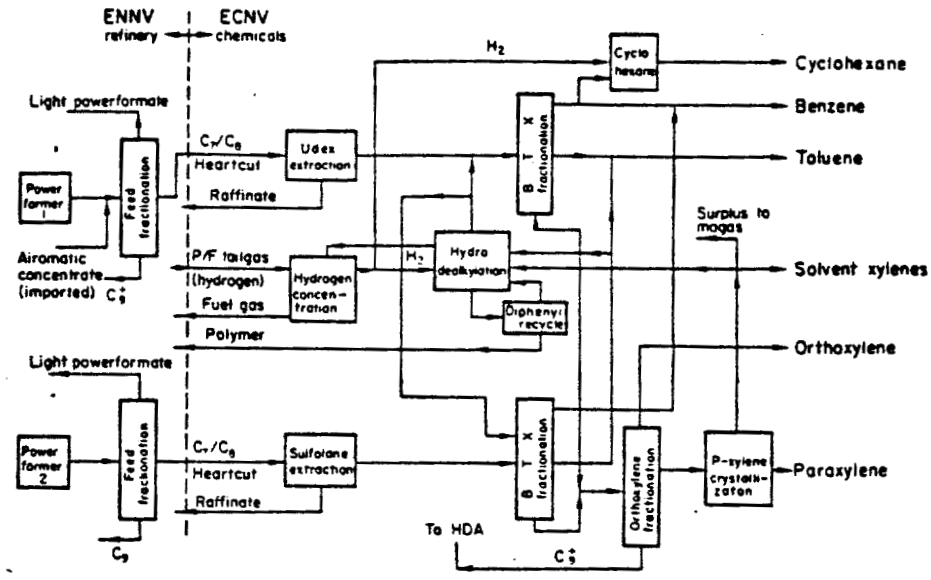


FIG. 1

to be economical in construction and operation, excessive hygiene precautions cannot be built in, so routine medical and hygiene reviews are made during and after start-up to determine the environmental conditions and the exposure of workers.

## NOISE

As there are no residential areas near either of the plants, no problems of neighbourhood noise have arisen. Speech interference has not proved a problem, though rather high noise levels existed in one centralised control room during reconstruction due to a standby electric generating plant running nearby.

As with most large scale processing plant, significant noise levels exist close to pumps and to major units. The levels at one plant were determined in 1965 and the results are shown in Table 1 together with recommended maximum exposure times based on criteria available at that time. Assessment by the new ACGIH standards adopted in the U.S. Waish–Healey Act is also shown and it can be seen that this standard is rather less stringent than those previously applied.

Subsequent attempts to determine actual exposure times of operators were unsuccessful due to the unreliability of the personal noise meters used, but routine audiometry has shown no evidence of occupational noise induced hearing loss. Billesholm glass down for ear protection is kept in the medical department and the plant control room and is widely used by operators. Ear muffs are also provided but are generally preferred less, as no completely successful Combination with the compulsory hard hats has been found.

TABLE 1. NOISE MEASUREMENTS AT OPERATING PLANT

| | Noise level dB scale | | | | Noise level (dB) in octave band centre frequency (cycles/sec) | | | | | | | | Recommended maximum exposure time hr/week | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | A | B | C | lin | 63 | 125 | 250 | 500 | 1000 | 2000 | 4000 | 8000 | (i) | (ii) | (iii) |
| Compressor house: | | | | | | | | | | | | | | | |
| near turbine set | 96 | 95 | 98 | 98 | 84 | 85 | 86 | 84 | 85 | 94 | 83 | 77 | 6 | 3·5 | 15 |
| near reciprocating compressor | 90 | 92 | 94 | 96 | 85 | 87 | 88 | 84 | 85 | 87 | 80 | 71 | 20 | 15 | 40 |
| Under airfin coolers | 90 | 94 | 98 | 100 | 92 | 92 | 91 | 88 | 83 | 80 | 73 | 69 | 15 | 30 | 40 |
| At pump,under T.101 | 97 | 100 | 101 | 102 | 88 | 89 | 98 | 95 | 91 | 89 | 82 | 78 | 6 | 6 | 15 |
| HDA pumps | 92 | 92 | 94 | 96 | 86 | 82 | 78 | 77 | 79 | 88 | 80 | 75 | 20 | 10 | 30 |
| Cyclohexane compressor house | 93 | 94 | 96 | 97 | 86 | 88 | 88 | 89 | 88 | 87 | 84 | 78 | 15 | 15 | 25 |
| Under UDEX furnace | 97 | 102 | 105 | 105 | 96 | 100 | 99 | 94 | 89 | 86 | 88 | 90 | 5 | 3·5 | 15 |
| Under hot oil furnace | 99 | 105 | 108 | 109 | 98 | 104 | 104 | 97 | 90 | 87 | 89 | 90 | 3 | 2·5 | 10 |
| Under HDA furnace | 90 | 93 | 97 | 97 | 87 | 87 | 90 | 83 | 84 | 82 | 82 | 78 | 20 | 40 | 40 |

Recommended maximum exposure times (i) JONES and CHURCH (1960).
(ii) draft ISO proposals (1961).
(iii) ACGIH (1969).

## THERMAL CONDITIONS

No special thermal conditions have been observed on either site, though in the course of the recent Dutch expansion the opportunity has been taken to provide full air conditioning for a centralised control room. Some sections of the Dutch plant contain products under extreme heat and pressure which present a straightforward safety hazard but, as the equipment is almost entirely in the open, no heat stress problems arise. More important is protection of operators against cold and wet in winter, for which normal modern outdoor protective clothing is provided in addition to the working coveralls.

## LIGHTING

The standards of artificial lighting on these plants are set by specifications incorporated in the company manuals on design practice and comply with the relevant American Standard (Amer. Standards Assoc. 1965.). In general, the quantity of light is universally adequate but minor alterations have been necessary to improve quality with particular reference to specular reflection.

## PROCESS CHEMICALS

The highly toxic and flammable substance carbon disulphide is injected in trace quantities into the feed for the Udex plant. The hazard is well recognised and extreme precautions arc taken in storage and handling. It is stored below ground level and pumped into the plant by small dosing pumps. Carbon disulphide vapour has never been detected during hygiene surveys, but the sensitivity of the Draeger Carbon Disulphide 0·04 indicator tubes used is limited to about the threshold limit value of 20 ppm (ACGIH, 1970). The characteristic odour of the vapour has never been detected even though the threshold of smell is reported as 1–2 ppm. In case an accidental release should occur additional compressed air breathing equipment is kept in the vicinity ready for immediate use.

Sulfolane, tetrahydrothiophene 1,1-dioxide is used at both Fawley and Botlek; it is a high boiling point (285°C) solvent that decomposes slowly above 220°C giving off sulphur dioxide. Its acute toxicity has been studied (Brown *et al.*, 1966) and it appears to present little hazard in normal industrial use. Even though the risk is low, eye and hand protection is always enforced during handling. In the sulfiner unit, concentrated sulphuric acid (98%) is used to remove sulphur compounds and traces of unsaturated hydrocarbons. Eye and skin protection is used when handling the acid and the alkali used to neutralise the products. The sewer system leads to a pit where aqueous waste products are neutralised before discharge to main sewers. Monoethanolamine solution is injected to neutralise acids formed during the distillation of the sulfolane. Although this substance has a low threshold limit value of 3 ppm which can just be sensed, no inhalation hazard has arisen as the vapour pressure is relatively low (boiling point 171°C) and all handling is in the open air. PATTY (1962) points out the apparent absence of injury in men despite wide use in industry. Operators are aware of the significant risk of eye damage, and precautions are taken to prevent contact with eyes and skin.

Diethylene and dipropylene glycols are used in the Udex process but have not given rise to hygiene problems. In industrial use they are of relatively low toxicity and have low vapour pressures. As with other chemicals, eye and skin protection is used.

Hydrogen is present in some process streams and presents a high potential flammability risk. To combat this, nitrogen is used as an inert gas for purging and to fill all vapour spaces. Although nitrogen is not commonly regarded as a toxic gas, the absence of oxygen in confined spaces makes the risk of asphyxiation serious. Although some use is made of oxygen measuring equipment, more emphasis is placed on preparing and enforcing safe working procedures.

## AROMATICS PRODUCTS

All the aromatic streams and products present potential toxicity risks but, in practice, few problems have arisen from exposure to toluene, xylenes or cyciohexane. Containment has proved relatively easy and, except for cyclohexane, the substances have good warning properties; none is considered to present any chronic hazard from long term low level exposure. Recommended threshold limits (ACGIH, 1970) for toluene, xylene and cyclohexane are 200, 100 and 300 ppm respectively. The corresponding odour thresholds (GERARDE, 1960) are 0·5, 0·2 and 300 ppm.

The principal chemical problems that have arisen in Holland have been benzene, and the heavy residual product from the Udex process. The latter contains over 70% diphenyl and can be expected to contain appreciable amounts of polycyclic hydrocarbons. It has a strong, and to some people unpleasant, odour and has an unknown cancer potential. Human contact is minimal as the material is used only as a refinery fuel but fume release has been a particular problem, as at this stage the process operates at high temperature and pressure, and the substance readily penetrates glands and gaskets. In the early years escapes of fume were common, and work in the pump area was difficult due to restricted space. During plant expansion one of the three pumps was moved elsewhere; the extra space available, together with improvements of gland and gasket materials and reduction of the numbers of joints, have now made the problem much less serious.

A single air sample taken over a period of 2·5 hr downwind of a leaking gasket indicated a fume concentration of 1·1 mg/m³ (probably mostly diphenyl oxide) and a diphenyl vapour concentration of 1·3 mg/m³, which is slightly above the threshold limit value of 1 mg/m³ (ACGIH, 1970). A unique problem that arises with this substance is the condensation of fume on respirator eyepieces which rapidly impedes vision when men make emergency repairs to serious leaks.

## BENZENE

By far the most potentially hazardous substance in the plants is benzene ($C_6H_6$) which represents both an acute hazard of asphyxiation and narcosis, and a chronic hazard of blood disease and possible genetic damage. As the vapour pressure at normal temperature is many times the accepted safe limits it is essential that exposure be properly monitored and controlled.

The essential philosophy in plant design has been the maintenance of strict containment. In normal operation the only points at which exposure to vapour can occur are where samples are taken for process control, and where products are loaded for shipment.

The risk of exposure is appreciably greater in maintenance work and special working procedures have been developed. For example, all lines containing more than 10% benzene are colour coded, and labelled "benzene". No lines may be broken unless breathing apparatus is worn and all components for removal (such as defective pumps) are purged and then steamed before work is started.

At the original plant in Holland, severe corrosion problems were encountered in the acid treatment of benzene and service conditions were such that it became impossible to maintain strict containment. The problems were enhanced as the plant had no separate sewer system so that acid and benzene spread through much of the main system. Further, to prevent benzene from freezing (melting point is 5·5°C), all lines were steam traced. To reduce the risk of skin burns, the steam was discharged into the sewers and led to the periodic release of benzene vapour from sewer openings at considerable distances from the plant. (For example, at an opening 300 yd from the plant a concentration of 86 ppm over 2.5 hr has been observed. As no men work near this point it represented bad practice more than a real health hazard.)

For both hygiene and operational reasons, the process was changed to clay contacting in May 1967, since when conditions have been much better as there is no routine loss of benzene to sewers. Additionally, a separate closed sewer system has now been constructed in the fractionation area.

Mechanical means for remote tank gauging were originally installed in Holland but these never proved satisfactory, and hand gauging had to be undertaken. Recently, a new system of remote tank gauging from the control room has been developed. In these modern plants routine exposure of men does not occur, and emphasis is placed on protection during accidental releases and in maintenance work.

Outside the operating areas benzene exposure may occur in laboratories and during loading for shipment. The only laboratory work found to cause significant exposure has been the hand washing of sample bottles and this practice has been discontinued. Exposure during loading operations still gives rise to concern; it is considered that some system for remote ullaging is needed. Investigations of exposure are at present in progress in marine operations which are less amenable to direct managerial control and skilled monitoring.

### *Evaluation of exposure*

Although significant concentrations of benzene are most unlikely to be met outside the property, it may well be that environmental assessments may be required in future to establish proof. Possible sources to be investigated would be tank venting and product loading and, under accident conditions, the liquid effluent plant.

Until now, emphasis has been placed on monitoring the exposure of men working on the plants. To identify points of vapour release and to make some estimation of the likelihood of exposure, simple methods have been used to determine air concentrations of benzene. These comprise colour detector tubes, such as the Draeger 0·05% Benzene and (where pure benzene is released) sensitive explosimeters such as

the MSA Model 40. While they can give no real indication of exposure, these methods serve a useful purpose in delineating areas where protection is required and can guide engineering requirements on plants. This is shown by the routine Draeger tube samples taken at fixed points on the Dutch plant. The results obtained in the periods before and after the change of process are shown in Table 2.

TABLE 2. COMPARISON OF ROUTINE DRAEGER TUBE SAMPLES BEFORE AND AFTER PROCESS CHANGE

| | Up to May 1967 (acid treatment) | Since May 1967 (clay contacting) |
|---|---|---|
| | % of all samples | % of all samples |
| Detectable (< 15 ppm) | 23 | 8 |
| Over 15 ppm | 15 | 0 |
| Over 25 ppm | 12 | 0 |
| No. of samples | 392 | 142 |

The exposure of individual workers to benzene vapour (or other hydrocarbons) may be determined by personal air sampling, by breath sampling, or from the concentration of the benzene metabolite, phenol, in urine. Development of suitable field methods has already been described (SHERWOOD and CARTER, *1970).*

At the present time a variety of standards for acceptable concentration$ of benzene in air have been published. The ACGIH (1970) recommended a ceiling value of *25* ppm; this figure has been adopted by HM Factory Inspectorate. The US Standard 2-37.4 (1969) recommends three figures; a peak of *50* ppm, a ceiling value of *25* ppm, and a time-weighted average of 10 ppm. The American Industrial Hygiene Association, Hygienic Guide (1970) also recommends a ceiling value of 25 ppm, and includes a "short-exposure tolerance" of 100 ppm. The German MAK is a time-weighted average of 10 ppm.

From this selection it is considered that for normal plant practice any measurement above 25 ppm should be investigated, and that for hygiene surveys a time weighted average of 10 ppm, with not more than 2% probability of 25 ppm being exceeded, should be taken as reasonable criteria that can be applied to air sampling results.

Only limited use has been made of personal air sampling on the aromatics plants as routine exposure is negligible and it has not been possible to investigate exposure that occurs during incidents. Results from personal air sampling undertaken during routine operations where exposure may occur, are shown in Table 3.

TABLE 3. SUMMARY OF PERSONAL AIR SAMPLING RESULTS FROM ROUTINE OPERATIONS

| Plant | Operation | Season | Concentration (ppm) | Duration (min) |
|---|---|---|---|---|
| Aromatics production | Plant sampling | Winter | 4 | 10 |
| | Plant sampling | Summer | 20 | 16 |
| | Tank dipping | Summer | 3 | 16 |
| Benzene feedstock | Plant sampling | Summer | <0·05 to 0·5 | |
| | Tank dipping | Summer | 2.4 | 6 |
| | Draining water from tank | Summer | 3·4 | 5 |

On other plants much use has been made of exhaled breath sampling after exposure to estimate the amount of benzene absorbed by operators but the technique has been little used at either of the aromatics plants as routine exposure of workers is minimal. On one occasion breath samples were taken from a contractor's workers employed on a new project while the existing plant was in operation; these showed Qat some men had recently been slightly exposed but to concentrations probably not exceeding 10 ppm.

Exposure of men has been routinely monitored by the Medical Department at the Dutch plant by fortnightly determination of phenol in urine. As benzene and phenol are rapidly eliminated from the body, this method does not detect every Occurrence of exposure, but the programme does provide a record of typical exposure of individuals. For over five years phenol has been determined by the non-specific colorimetric method described by WALKLEY et *al.* (1961) but the laboratory is now adopting the more specific and sensitive VAN HAAFTEN and SIE (1965) gas chromatographic technique with on-column acid hydrolysis.

Only a limited amount of information has been published relating benzene exposure to concentration of phenol in urine. DOCTER and ZIELHUIS (1967) in a literature review suggest that groups of workers exposed to 25 ppm over an 8-hr work period may produce 170-195 mg/l. phenol in urine, and with 10 ppm the excretion may be 70–80 mg/l. H.M. Chief Inspector of Factories (1970) has proposed a biochemical threshold of 100 mg/l. Values observed using the non-specific colorimetric method can be expected to be rather higher than those indicated above.

The number and proportion of apparent cases of over-exposure based on a threshold of 100 mg/l. before and after the change of process are shown for each group of workers in Table 4.

TABLE 4. NUMBER OF PHENOL IN URINE RESULTS EXCEEDING 100 mg/l.

| Group | Before May 1967 (No.) | (%) | *After* May 1967 (No.) | (%) |
|---|---|---|---|---|
| Process operators | 3 | 0·6 | 3 | 0·3 |
| Maintenance worken | — | — | 1 | 0·2 |
| Laboratory workers | 0 | <0·2 | 0 | <0·3 |

The 1600 results from 27 process operators have been statistically analysed (Zaworka, 1970) and the following conclusions drawn:

It is possible to determine for each man a concentration in urine which indicates a probable accidental exposure even at levels below the threshold limit. The actual value depends on the normal phenol concentration for each individual; phenol concentrations in the absence of benzene exposure more closely follow normal rather than log-normal distributions.

For the group of men concerned and using non specific colorimetric analysis, upper limits (99% confidence) for normal concentrations of phenol in urine varied between individuals from 28 to 60 mg/l.

Specific gravity correction (mean of all values 1.023) made no statistically significant reduction in the variation in results though it reduced the highest upper limit of 60 to 52 mg/l. . .

The effect of the process improvement in 1967 can be seen in the urine sampling results. Before that date 9·8% of samples probably indicate some exposure; this fell to 4·7% afterwards.

Where this analytical technique is used and insufficient results have been obtained from each individual for statistical analysis, normal limits (2 x S.D.) for phenol in urine can be predicted from the mean value for each man. Thus, for men whose exposure is intermittent, exposure incidents are probably indicated if individuals with normal mean concentrations of 10, 20 and 30 mg/l., show phenol concentrations of 15, 35 and 50 mg/l. respectively. When sufficient data has been collected similar analysis will be made on results using the more sensitive gas chromatographic techniques.

While the value of normalising to a constant specific gravity remains uncertain, it is recommended that specific gravity be determined, and results from any samples requiring correction by a factor greater than 2 should be rejected. Below this value, there is probably little biological significance in differences between normalised and measured concentrations.

At Fawley, to handle the very large numbers of samples during start up, a more specific colorimetric method using 4-aminoantipyrine was adapted for use on an autoanaiyser; the VAN HAAFTEN and SIE (1965) technique is now used with a Hewlett Packard automatic gas chromatograph. Excellent correlation has been found between this technique and the more definitive external hydrolysis method developed by Carter (SHERWOOD and CARTER 1970) in a comparative analysis of 32 urine samples from men exposed to benzene elsewhere (see Fig. 2).

The criteria at present applied to evaluate exposure to benzene are shown in Table 5.

TABLE 5. PROVISIONAL BENZENE EXPOSURE CRITERIA

| | Phenol in urine (mg/l.) | Benzene in breath (ppm) |
|---|---|---|
| Immediately after exposure to 25 ppm in air | 100 | 2 |
| Morning after exposure to 100 ppm-hr | 50 | 0·2 |

## RESPIRATORY PROTECTION

Respiratory protection is normally provided by means of self-contained breathing apparatus or airline masks connected to compressed air bottles on trolleys. Generally, the purity of both plant and instrument air is treated as suspect and these sources are not used. Canister respirators are never used but some use is made of carbon cartridge respirators for operators where slight exposure might arise, for example, when tank dipping.

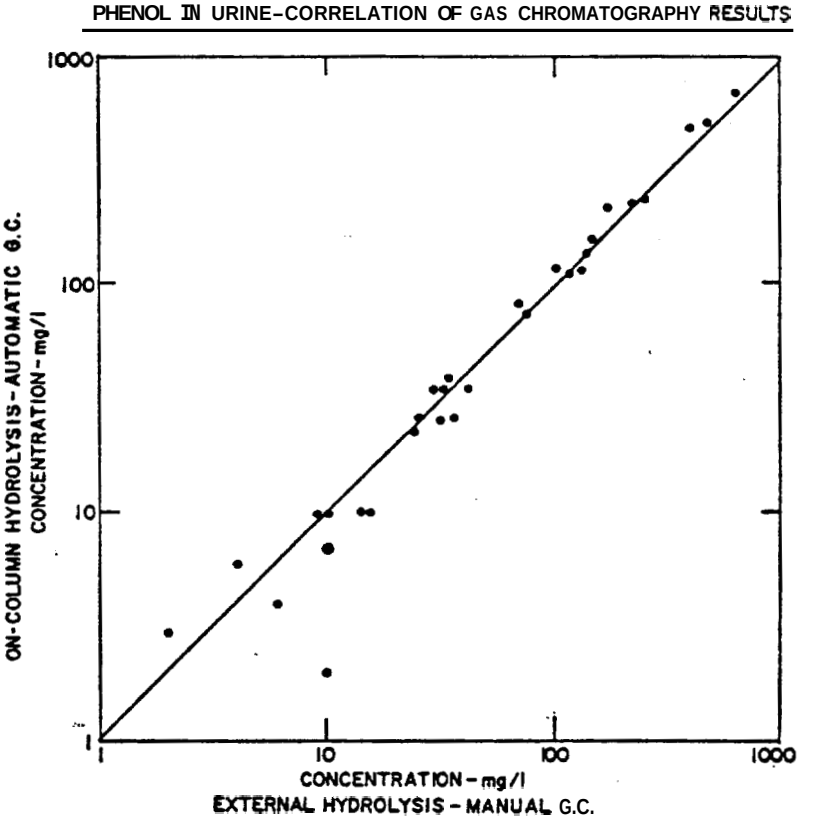


FIG. 2

## SAFE WORKING PROCEDURES

All plant operators are trained in the safe working procedures that have been developed. The key to training is a proper understanding of the hazard and an appreciation of the need for, and effectiveness of, the carefully prepared working methods. In addition to attendance at formal training courses, every man who may be in contact with streams containing 10% or more of benzene or who works in areas purged with inert gas is provided with a pamphlet outlining the hazards of these substances and the precautions to be taken and procedures to be followed.

## CONCLUSIONS

The principal potential hazard arises from the presence of large quantities of benzene on the plants. Although benzene must be respected as a volatile toxic substance, experience has shown that it can be handled with no greater risk to trained operators than that which arises in other process plants.

To achieve this, close attention must be given to safe practice. Essential features are:

Design the plant for effective containment in operation and simplicity in maintenance.

Prepare written safe working procedure for normal and emergency conditions.

Educate all personnel to appreciate the risk involved in exposure and to comply with prepared procedures. Train all operators to recognise hazardous conditions and to use monitoring and protective equipment properly: emergency practice is essential.

Provide and maintain reliable respiratory protection for emergency use.

Provide an effective investigation and monitoring service which should include medical surveillance and routine biological measurement.

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## REFERENCES

American Conference of Governmental Industrial Hygienists, Denver 1969.

American Conference of Governmental Industrial Hygienists, Committee on Threshold Limits. (1970) Threshold Limit Values of Airborne Contaminants adopted by ACGIH for 1970.

American Industrial Hygiene Association (1970) Hygienic Guide Series, Benzene.

American Standards Association Inc. (1965) American Standard Practice for Industrial Lighting. A11.1-1965.

BROWN, V. K. H., FERRIGAN, L. W. and STEVENSON, D. E. (1966) Br. J. *ind. Med.*, 23, 302.

DEPARTMENT OF EMPLOYMENT AND PRODUCTIVITY (1970) Annual Report of H.M. Chief Inspector of Factories, 1969. H.M.S.O. London.

DOCTER, H. J. and ZIELHAUS, R. L. (1967) *Ann. occup. Hyg.*, 10, 317.

GERARDE, H. W. (1960) *Toxicology and Biochemistry of Aromatic Hydrocarbons*. New York, Elsevier Publishing Co.

International Organization for Standardization (1961) Draft Secretariat Proposal for Noise Rating Numbers with Respect to Conservation of Hearing, Speech Communication and Annoyance. ISO/TC 43.

JONES, A. R. and CHURCH, F. W. (1960) *Am. ind. Hyg. Ass.*, 21, 481.

PATTY, F. A. (Editor) (1962) *Industrial Hygiene and Toxicology*. Vol. 2, 2nd rev. ed. Interscience Publishers, New York.

SHERWOOD, R. J. and CARTER, F. W. G. (1970) *Ann. occup. Hyg.*, 13, 125.

VAN HAAFTEN, A. B. and SIE, S. T. (1965) *Am. ind. Hyg. Ass. J.*, 26, 52.

WALKLEY, J. E., PAGNOTTO, L. D. and ELKINS, H. B. (1961) *Am. ind. Hyg. Ass. J.*, 22, 362.

ZAWORKA, 3 (1970) Personal communication.