DATA SHEET D-308
(D-Chem 47)

Benzene (Benzol)

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1. Benzol is the common name applied to the technical grade of benzene (C_6H_6), an organic liquid generally obtained by fractional distillation of coal tar.*

2. Benzene is supplied commercially in five grades according to the amount of impurities present. These are reagent, thiophene free, nitration, industrial pure, and industrial 90 per cent. Production employees are exposed to benzene in crude material and in the coal tar light oil from which it is distilled, as well as to these five grades.

This Data Sheet is one of a series published by the National Safety Council, reflecting experience from many sources. Not every acceptable safety procedure in the field is necessarily included. This Data Sheet should not be confused with American Standard Safety codes, federal laws, insurance requirements, state laws, rules and regulations, or municipal ordinances.

Characteristics and Uses

3. Benzene in its purest form is a pure colorless liquid with a rather pleasant aromatic odor somewhat like that of gasoline but readily distinguishable from it. The intensity of the odor varies considerably with the grade or purity of the benzene, but a person with a normal sense of smell can detect the vapor by odor in a concentration of about 75 to 100 ppm.

4. However, in an atmosphere containing benzene vapor the sense of smell quickly ceases to respond to that the odor is a very unreliable indicator of the concentration or even of the presence of benzene vapor.

5. Pure benzene boils at 80.1 C (176.2 F) and freezes at 5.5 C (41.9 F). The specific gravity at 20 C compared to that of water at 20 C is 0.88 for the liquid, and the vapor density compared to that of air is 2.73. Its flash point is —11.1 C (12 F), and the explosive limits are 1.5 to 8 per cent by volume in air. The ignition temperature is 538 C (1000 F).

6. The major impurities in commercial benzene are toluene and xylene. These substances are toxic but somewhat less volatile than benzene and somewhat less hazardous. Because the appearance and pleasant smell of benzene give no warning of its toxic effect and because a victim may become incurably poisoned before he feels ill, benzene is one of the most insidious poisons ever to find wide industrial use.

7. Benzene is an excellent solvent for fats, oils, resins, gums, rubber, and many other organic substances. It is therefore used to extract these materials from aqueous solutions or crude mixtures. It is used also in paints, varnishes, lacquers, adhesive cements, and paint removers.

8. In many of these applications its presence is often not declared upon the label, contrary to the agreement between the manufacturers and the United States Public Health Service.

9. The manufacturers of benzene under this agreement are obligated to apply labels like that shown below, to warn users against its hazardous characteristics. Under the agreement, similar labels must be applied to products for domestic consumption which contain 15 per cent or more of benzene.[1]

BENZENE (BENZOL)
Danger! Extremely Flammable
Vapor Harmful—Poison
Keep away from heat, sparks, and open flame.
Keep container closed.
Use only with adequate ventilation.
Avoid prolonged or repeated breathing of vapor.
Avoid prolonged or repeated contact with skin.

10. In the past, benzene has been used in large quantity in blends with gasoline for automotive fuel. The need for benzene as the starting material for an enormous variety of synthetic chemicals may largely eliminate its use as motor fuel.

11. A partial listing of industries and trades in which the use of benzene may be expected is given in paragraphs 12 through 21. The trades named are examples of those in which precautions against benzene poisoning should be taken. Each operation which uses benzene must be carefully studied, and precautions must be based on the specific conditions of use.

12. The *coke and gas industry* is the major source of benzene. Workers who may be exposed are:

benzene still men
by-product operators
laboratory workers
tank inspection and maintenance men
drum fillers
tank car loaders

* The name *benzene* must not be confused with the name *benzine*. The latter is still sometimes applied to a mixture of hydrocarbons obtained from petroleum, but it is archaic and misleading and should not be used.

13. The *chemical industry* consumes a large amount of benzene. Workers who may be exposed are:

nitrobenzene makers
aniline dye workers
explosives workers
nitrocellulose workers
phenol makers
pharmaceutical workers
denatured alcohol workers
maintenance men or others working in the benzol area

14. Because benzene is an excellent solvent for printer's ink, the *printing and lithographing industry* commonly uses benzene as a solvent and cleaner. Those who may be affected are:

layout men (from rubber cement)
lithographers
mimeograph operators
multigraph operators
photoengravers
pressmen and helpers
typesetters and cleaners

15. The *paint industry* uses benzene as a solvent in paints, especially quick-drying enamels and asphalt paints. Those who may be exposed are:

asphalt paint makers
enamel makers
enamelers
lacquer makers
varnish makers
varnishers
stain makers
lacquerers
paint makers
paint remover makers
shellac makers
stainers
airplane dope makers and users
painters

16. The *rubber industry*, especially those branches which make rubberized fabrics, has many operations in which there will be serious benzene poisoning unless complete protection is provided. Many rubber companies have substituted other solvents for benzene in the applications which are most difficult to safeguard. Workers who may be exposed to benzene are:

raincoat makers
cementers (rubber)
compounders (rubber)
dryers (rubber)
reclaimers
overshoe makers
rubber sheet makers
oilcloth makers
vulcanizers
rubber cement makers

17. The *dry cleaning industry* uses benzene to some extent, especially for "spotting." Dry cleaning workers and spotters may be exposed.

18. The *adhesives industry* incorporates benzene into certain glues and cements, usually those stated to be waterproof. Glue workers and adhesive workers may be exposed. Those using glues and cements which contain benzene should get a full description of their toxic hazards and set up suitable precautions for their use.

19. The *petroleum industry* blends benzene with fuels and uses it to extract certain products from petroleum oils. Those who may be affected are blenders (motor fuel) and paraffin wax makers.

20. *Laboratories* use benzene in various kinds of analytical work. Chemists and technicians may be exposed.

21. The *coatings industries* commonly use a great deal of benzene as a solvent. Workmen engaged in the production of artificial leather, patent leather, oilcloth, linoleum, and shade cloth may be exposed.

Benzene Poisoning

Acute poisoning

22. *Causes and characteristics.* Benzene poisoning may be acute or chronic. The acute form is incurred most commonly when men enter enclosed spaces such as tanks which contain very high concentrations of benzene vapor. It may also be caused by benzene stored in closed rooms. This form of poisoning is rare, and its dangers are more widely recognized and more immediately apparent than are those of chronic poisoning.

23. In acute benzene poisoning the symptoms result from the powerful anesthetic action of the vapor. The victim usually has little warning after entering the contaminated atmosphere. Although the odor may be very strong, it is not sufficiently irritating to force withdrawal from the closed space.

24. By the time the victim begins to feel dizzy and unable to control his movements, he is usually too weak to escape. He staggers, appears drunk, falls to the ground and rapidly becomes unconscious. If not rescued, he becomes more and more deeply anesthetized. In a short time, depending on the concentration of the vapor, his breathing becomes gradually slower until the respiratory center is paralyzed and death results.

25. If the victim is rescued before death occurs, he may be in any stage of unconsciousness or apparent drunkenness. He should be removed to fresh air, and if breathing has ceased, artificial respiration should be begun at once. A physician should be called immediately and oxygen administered as soon as it is available.

26. Recovery will exhibit the stages of acute poisoning in reverse. From a state of coma, the victim will progress to movements, muttering, and struggling. Upon regaining consciousness he will tend to become excited, irrational, and stubborn. He must be restrained at this time from running about. Dizziness and headache are the last symptoms to disappear. Medical supervision of all such cases is imperative to prevent severe after-effects.

27. *Prevention.* Workmen should never enter closed spaces where benzene vapor may be present until appropriate tests have shown that the air is safe to breathe. As an additional precaution, workmen entering such closed spaces should be equipped with hose masks or self-contained oxygen breathing apparatus and should wear safety belts with life lines.

28. The respirator and life line should be used even though the tank or other enclosed place has been thoroughly steamed out and has been shown by the benzene-

detecting instrument to be free from vapor. Even after steaming out, there may be a residue of benzene in sludge, under scale, or in crevices which will make the air in the tank toxic again when it is stirred up.

29. It is extremely important that the tank be properly cleaned and steamed before anyone enters it. The steps which should be taken are these:

a. See that there are no open flames, sparks, or other sources of ignition in the vicinity.
b. Use non-sparking tools.
c. Disconnect and blank off all pipelines.
d. Disconnect agitators.
e. Connect a steam line to the tank, and steam until the temperature is above the boiling point of benzene throughout the tank.
f. Connect a water line to the tank and flush with cold water at high pressure.
g. Ventilate the tank and test for vapors before entering.

30. When the tank is entered, the air supply equipment and life line of the men going into it should be attended by a man outside who has no other duties.

31. Waste benzene should not be discharged into sewers nor boiled off and released into the open air. It should either be distilled and recovered or burned in the open with precautions against uncontrolled fire or explosions.

32. Discharge into sewers may result in the accumulation of toxic or explosive quantities of benzene vapor in the sewer itself or in tunnels, work rooms, or other closed places drained by it. Discharge into the open air in the presence of adverse winds may lead to explosive or toxic conditions in adjacent buildings.

33. The same hazards will be encountered if benzene stills are operated beyond the capacity of their condensers. Vents on such stills, as well as on all storage tanks and other containers, should be equipped with flash arresters and should extend high enough above the nearest building that vapor cannot find its way to an inhabited place.

CHRONIC POISONING

34. *Causes and characteristics.* Chronic benzene poisoning occurs as the result of repeated or long-continued exposure to amounts of vapor smaller than those which produce acute poisoning. Many safety codes set maximum safe limits of benzene vapor as between 50 and 100 ppm. However, some very sensitive individuals can probably be harmed by smaller quantities of vapor after a long exposure.

35. Chronic benzene poisoning affects the blood and blood-forming organs, producing serious degeneration in the bone marrow. When slightly damaged by poison, the marrow can still regenerate after removal from the toxic agent. When the damage is severe, no known treatment will restore the marrow to normal or make it able to perform its vital functions of furnishing red blood cells, white blood cells, and blood platelets.

36. There is no way to determine the sensitivity of an individual beforehand. Cases of fatal poisoning have been recorded from very light exposures to benzene. Some individuals, on the other hand, are apparently well after prolonged and heavy exposure.

37. Some of this variation may be due to the very considerable difficulty in determining benzene concentrations in the air as well as to individual differences in susceptibility. In any case, safe practice dictates that any employee who shows signs of benzene poisoning should be transferred to work in which he will have no exposure.

38. Chronic benzene poisoning may be detected early by signs of absorption or late by symptoms of poisoning. Early benzene poisoning is indicated by changes in the composition of the blood, as determined by blood counts.

39. Such a blood examination should include a red cell count, a white cell count, a differential count, a measurement of hemoglobin (preferably by the Sahli or other accurate method; the Tallquist method is not accurate enough for this purpose), a hematocrit measurement, and a determination of mean corpuscular volume.

40. Medical authorities differ as to what change in the blood count is first found in chronic benzene poisoning. Possibly the change which occurs first varies from one individual to another. Some authorities believe that changes in the size and number of the red cells appear first, followed by a decrease in the number of white cells and a shift in the percentage of granulocytes, and still later by a depression of red and white cells and platelets.

41. In general, signs which should arouse suspicion of early chronic benzene poisoning in exposed individuals are the following:

a. Depression of a previously normal red cell count to below 4.5 million.
b. Depression of a previously normal white cell count to below 6,000.
c. Depression of a previously normal hemoglobin to below 12 grams per 100 cubic centimeters or 80 per cent by colorimeter.
d. The appearance of immature or abnormal red or white cells in the differential count.

42. *Prevention.* Pre-placement blood counts should be made, and if there is continuous or repeated exposure to benzene vapor, the counts should be repeated at intervals of from one to six months.

43. These counts should be so recorded that previous counts for an individual can be readily compared with the current count. The recording system should also permit easy calculation of the degree of normal variation among all the individuals in the exposed group and should permit the supervising physician to obtain a summary of conditions in the entire group for any period.

44. An experienced industrial physician should examine and evaluate all blood count results because many diseases and conditions not connected with benzene exposure, or with any industrial exposure, may cause changes in blood counts.

45. Chronic benzene poisoning can be prevented by a combined program of medical supervision, industrial hygiene, and safety organization. The industrial hygienist can furnish methods for testing the air throughout the plant to detect harmful concentrations of benzene vapor and can suggest the best methods of handling the material to prevent these exposures.

46. The safety organization can train workmen to avoid exposure and can acquaint them with the dangers of the chemicals so that they will promptly report any hazardous conditions to those charged with controlling them.

47. The medical supervisor can watch over the physical condition of the workmen through periodic examinations. These examinations will detect locations or processes where precautions are inadequate. No method of prevention can succeed without cooperation among all departments of the organization and on the part of the workmen, who must understand the reasons for the precautions which they are to observe.

48. The medical supervisor should not only study periodic blood counts but also give preplacement examinations and routine re-examinations. The preplacement examination should prevent persons with blood dyscrasias, severe liver or kidney damage, or lung or heart disease from having contact with benzene.

49. Pregnant women and young persons in general are believed by many to be unusually susceptible to benzene poisoning. At the discretion of the examining physician, they may be excluded from work requiring contact with benzene.

50. New workers who have already had contact with benzene or other agents likely to cause damage to the bone marrow (such as TNT, x-ray, or radium) should receive special scrutiny since they may already be suffering from mild damage.

51. New workers who show preplacement blood counts in the suspicious or abnormal range should be excluded from contact with benzene if only for the practical reason that their blood counts could not be reliable indices of bone marrow damage.

52. Some benzene is eliminated unchanged in the urine. Some is oxidized in the body to phenols and diphenols which, in turn, are conjugated in the liver with sulfate ions and excreted in the urine, thus increasing the ratio of ethereal or organic sulfates to total sulfates in the urine. This is the basis of a dependable control test to determine the severity of the overall daily exposure to benzene.

53. The ratio of inorganic sulfates to total sulfates in the urine is normally 85 per cent or above. Upon exposure to benzene this ratio is decreased, and the decrease is related quantitatively to the severity of the exposure to the point where nearly all sulfates are eliminated as organic sulfates.

54. Ratios of less than 70 per cent inorganic are abnormal and may be indicative of benzene exposure; they warrant investigation of exposure sources with a view toward correction. Ratios of 60 per cent or less inorganic indicate dangerous exposures warranting immediate correction and termination. Concurrent exposure to carbon tetrachloride, or any other material having an adverse effect upon the liver, may decrease the sulfate response so that ratios on the order of 70 per cent inorganic would indicate exposures of great significance.

55. The sulfate test must be made while the worker is on the job. It is not to be considered a method for diagnosing benzene poisoning, because the changes are merely indicative of exposure, not of poisoning nor of damage.

56. It is therein that the great preventive value of this test lies. The indication occurs in advance of demonstrable harmful effects, but forewarns of their coming if exposures are not reduced.

57. It seems logical to make urine sulfate tests, perhaps weekly, and periodic hematological studies of all workers coming in contact with benzene vapors. Air analyses for benzene in suspected atmospheres should be made frequently.

58. If these three control measures are consistently performed, and heeded, no fear need be entertained regarding use of benzene in industrial processes.

Skin Contact

59. Hands and arms should never be immersed in benzene or benzene solutions, nor should benzene be used to wash or rinse grease or other materials from the skin. Rubber gloves used to protect the operator should be frequently inspected for leaks. Protective creams insoluble in benzene but soluble in water may be used on exposed skin surfaces.

60. Benzene almost instantly dissolves fats and natural oils from the skin. It may cause reddening, dry scaling, and cracking, and predispose the skin to secondary infections. More prolonged contact may result in injuries resembling first and second degree burns.

61. Wetting of a large area of the skin with benzene is extremely hazardous and has caused fatalities in a very short time. Clothing wet with benzene should be removed immediately, and all portions of the body which have been wet with benzene should be thoroughly washed with soap and water.

Air Analyses

METHODS OF DETECTION

62. Of the several methods which may be used to measure the

concentration of benzene vapor in air one of the most sensitive depends upon the color produced when benzene is brought into contact with a solution of formaldehyde in sulfuric acid. The concentration of the benzene vapor is measured by the amount of air which must be drawn through the sulfuric acid formaldehyde mixture to produce a standard color.[2] Toluene and xylene also react in this test although it is not as sensitive to them as to benzene.

63. Another sensitive test and a somewhat more quantitative one is the "butanone test" in which the air sample is passed through nitrating acid. After neutralization, the dinitrobenzene formed is extracted with methyl-ethyl-ketone. When some alkali is added to the methyl-ethyl-ketone solution, a purple color is formed, the intensity of which is a measure of the amount of benzene in the sample.[3] As little as 10 ppm can be detected readily and measured with reasonable accuracy by this test.

64. A more rapid and convenient though less sensitive test is that obtained with the benzene detector. This is a very sensitive combustible gas indicator equipped with a special filter to exclude water vapor. It has a special low range to get the concentration of interest from a toxicological standpoint and provides instantaneous reading on a dial graduated in ppm.

65. If pure benzene is not in use, the instrument must of course be calibrated in terms of the particular mixture employed in the plant.

66. Another convenient instrument using an optical measurement is the organic vapor interferometer. This instrument measures the change caused by the gas or vapor in refractive index of the air. Since it will respond to any vapor present, it must be calibrated for the particular materials in use in the plant. It is also quite sensitive to sudden changes in temperature. Under good conditions it provides an extremely sensitive means of measurement.

67. The industrial hygiene survey should include air sampling at various strategic locations in all buildings where benzene is used, especially in the laboratory. The samples should be taken while regular operations are being carried on.

68. If the process is said to be entirely enclosed, special attention should be paid to the possibility of leakage at pumps, valves, gaskets, and other points of joining. If the benzene is used in open containers, the vapor content at the breathing level at each work station should be thoroughly investigated.

69. The values found in such surveys should be recorded on a floor plan of the workroom. Sources of contamination will usually become apparent on such a map, and the ventilation can be designed to eliminate the hazards.

Maximum Allowable Concentration

70. The American Standards Association has set 100 ppm for the maximum allowable concentration of benzene vapor in the air.[4] In spite of this standard there has been an almost continuous movement to lower the maximum allowable concentration, and lower values are used by various state authorities. The safety code of one state now goes as low as 35 ppm. Because of these wide variations, the legal requirements for control of benzene vapor should always be carefully investigated.

Exhaust Ventilation

71. Benzene vapor is most efficiently removed by suction as close as possible to the point of generation. Increasing general ventilation to dilute the vapor is generally a far more expensive and much less effective method. In fact, sweeping large amounts of air through workrooms may increase the pollution of the air and is sure to increase the cost.

72. Exhaust hoods should preferably be located just around the upper rims of tanks or around the edges of work tables. These fixtures should have narrow slots so placed as to assure even distribution of the exhaust around the working area. This method utilizes the high specific gravity of benzene vapor (nearly three times that of air) and tends to prevent the vapor from escaping from the point of operation.

73. Inasmuch as benzene vapor is heavy and has a tendency to settle, low points in areas in which benzene is used should be ventilated by suction. However, it should be noted that as the benzene vapor becomes more dilute, the tendency to settle becomes less and the tendency to mix uniformly with the air in the room becomes greater.

74. It is expensive to attempt to oppose the natural air circulation in the area. If heat in the process or some other influence produces a strong thermal movement, this movement should be utilized in the exhaust system rather than opposed. The air should, however, in every instance be exhausted away from the operator and never drawn past his face.

75. All rooms where benzene is used, even in small quantities, should have sufficient positive ventilation to keep atmospheric concentration below the safe limit in all occupied areas. Open windows cannot provide efficient positive ventilation because they may be closed during inclement weather and at the will of the operators.

76. The exhaust ventilation systems should conform to the regulations of the National Fire Protection Association.[5, 6]

77. The use of a fountain cup or some other type of closed container is suggested where benzene or benzene mixed with other ingredients, such as rubber, bakelite, or artificial leather "dope," is used. Where the operation requires that large vessels containing benzene remain uncovered, the vapors can readily be removed if the vessel is placed within a larger con-

tainer, at the bottom of which suction is applied.

Fire and Explosion

78. The fire and explosion hazards of benzene are similar to those of other flammable solvents of approximately the same boiling range. Because of its low flash point (12 F, "closed cup"), benzene is rated as extremely flammable. Benzene vapors when mixed with air in proper proportions are explosive if ignited. The Underwriters' Laboratories' fire hazard classification for benzene is 95 to 100 on a scale in which ether is the standard for 100.

79. One of the best fire prevention devices for this and other flammable solvents is a properly designed and operated exhaust system which will keep the vapor concentration throughout the plant well below the explosive range.

Prevention

80. Because of its low flash point (12 F) and low explosive limits (1.5 per cent), every precaution should be taken to prevent the ignition of benzene vapor.

81. Only non-sparking tools should be used in atmospheres which may contain this vapor. Windows and openings of buildings which house benzene processes should be carefully screened with copper or bronze screening to keep sparks from locomotives or other sources from entering and causing ignition.

82. Indirect heating systems are preferable to direct systems. No heating apparatus, whether direct or indirect, should be located close enough to the flammable liquid that splashes might strike the heated surface and be ignited.

83. The "no smoking" and "no matches" rule should be strictly enforced. Open flames, such as torches, heating and welding apparatus, stoves, or gas burners, should never be used in the same room with open benzene operations.

84. When open flame apparatus must be used in the vicinity or even in other rooms, the possibility of its acting as a source of ignition should be thoroughly investigated and the operation should be carried out only after proper precautions have been installed and a permit has been issued by the plant fire prevention department.

85. Electrical installations should be made in accordance with the National Electrical Code.[7]

86. Static discharges should be prevented by the use of electrical grounding and static brushes on all points where there may be static accumulations.[8]

Protection

87. Sufficient hand and automatic fire protection apparatus should be provided where open benzene processes are used. Carbon dioxide, foam type, or dry powder extinguishers furnish excellent protection. Steam has also been found satisfactory.

88. The location of the hand apparatus is very important; it should be outside the danger area but readily accessible to the place where the benzene is used.

89. Steam jets may be provided to extinguish vent fires caused by lightning.[9] Tanks and vats should have heat-actuated automatic covers; and other fire protection, such as sprinklers or other extinguishing media, should be automatic in operation.

Storing and Handling

90. Benzene, like other flammable solvents, should be stored and handled in accordance with the regulations of the National Fire Protection Association.[10]

91. The solvent piping systems in the plant should be painted and stenciled in accordance with American Standard A13-1928, "Scheme for the Identification of Piping Systems."[11] Containers and piping systems should be inspected frequently for breaks and leaks, and all such defects should be corrected at once. When such repairs are being made, the workmen should be carefully supervised.

92. Large quantities of benzene should be stored outside buildings, preferably in underground tanks, unless the structures are especially designed for benzene storage. Tanks should be vented through flame arresters.

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4. "American Standard Allowable Concentration of Benzene, Z37.4-1941," American Standards Association, 70 East Forty-fifth Street, New York 17, N. Y.

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6. Safe Practices Pamplets No. 32, "Exhaust Systems," and No. 91, "Spray Coating," National Safety Council, Chicago, Ill.

7. "Standard of the National Board of Fire Underwriters for Electric Wiring and Apparatus," NBFU Pamphlet 70, National Board of Fire Underwriters, 1947.

8. Safe Practices Pamphlet No. 52, "Static Electricity," National Safety Council.

9. "Standard of the National Board of Fire Underwriters for the Installation, Maintenance and Use of First Aid Fire Appliances," NBFU Pamphlet 10, National Board of Fire Underwriters.

10. "Standard of the National Board of Fire Underwriters for the Installation of Containers for Storing and Handling Flammable Liquids," NBFU Pamphlet 30, National Board of Fire Underwriters, 1941.

11. See also Safe Practices Pamphlet No. 88, "Identification of Piping Systems," National Safety Council.

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