OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ANILINE

INTRODUCTION

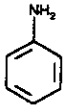
This guideline summarizes pertinent information about aniline for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_5NH_2$

- **Structure**



- **Synonyms**

Aminobenzene, aminophen, aniline oil, benzenamine, blue oil, kyanol, krystallin, cyanol, phenylamine

- **Identifiers**

1. CAS No.: 62-53-3
2. RTECS No.: BW6650000
3. DOT UN: 1547 57
4. DOT label: Poison

- **Appearance and odor**

Aniline is an oily, colorless to brown, combustible liquid that darkens on exposure to air and light. It has the characteristic aromatic amine-like odor. The odor threshold is reported to be 1.1 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 93.12
2. Boiling point (at 760 mm Hg): 184°C (363°F)
3. Specific gravity (water = 1): 1.02 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of aniline): 3.22
5. Melting point: −6.3°C (20.7°F)
6. Vapor pressure at 20°C (68°F): 0.68 mm Hg
7. Solubility: Moderately soluble in water; miscible with alcohol, benzene, chloroform, and most organic solvents
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame. The vapors of aniline form explosive mixtures with air.
2. Incompatibilities: Fires and explosions may result from contact with halogens, acids (including nitric and sulfuric acids), oxidizing agents (perchlorates, peroxides, perchromates, etc.), ozone, and trichloromelamine or hexachloromelamine.
3. Hazardous decomposition products: Toxic gases (such as ammonia, carbon oxides, and nitrogen oxides) may be released when aniline is heated and/or decomposes.
4. Special precautions: Liquid aniline attacks some coatings and some forms of plastic and rubber.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to aniline.

1. Flash point: 70°C (158°F) (closed cup)
2. Autoignition temperature: 615°C (1,139°F)

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Public Health Service Centers for Disease Control
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3. Flammable limits in air (% by volume): Lower, 1.3; upper, 11

4. Extinguishant: Use carbon dioxide, dry chemical, Halon®, water spray, or standard foam to fight fires involving aniline; never direct a solid stream of water into burning pools of liquid aniline because this will scatter and spread the fire. Water may be used to disperse vapors or to protect persons attempting to stop the leak.

Fires involving aniline should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny entry to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Cylinders of aniline may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of cylinders. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving aniline. Chemical protective clothing that is specifically recommended for aniline may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by aniline.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) PEL for aniline is 2 ppm (8 mg/m^3) as an 8-hr time-weighted average (TWA) concentration. The OSHA PEL also bears a "Skin" notation, which indicates that percutaneous absorption is a route of exposure (including mucous membranes and eyes) [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has recommended that aniline be designated a potential occupational carcinogen and that exposure be limited to the lowest feasible concentration. Contact with the worker's skin should be minimized [NIOSH 1990, 1992b].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned aniline a threshold limit value (TLV) of 2 ppm (7.6 mg/m^3) as a TWA and has also assigned aniline a "Skin" notation [ACGIH 1991b].

• Rationale for limits

OSHA and ACGIH limits are based on the risk of methemoglobinemia associated with exposure to aniline. The NIOSH cancer designation is based on significant evidence of increased bladder cancer in humans [NIOSH 1990].

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to aniline can occur through inhalation and by absorption through the eyes or skin.

• Summary of toxicology

1. *Effects on Animals*: Aniline causes methemoglobinemia in animals. Head-only versus whole-body exposure of rats for 4 hr resulted in LC_{50}s of 839 ppm and 478 ppm, respectively. These data demonstrate the significant extent to which dermal absorption occurs during ambient exposures. The dermal LD_{50} in rabbits is 820 mg/kg [NIOSH 1992a]. The oral LD_{50} in rats is 250 mg/kg, and the lowest lethal concentration in the same species is 250 ppm for 4 hr [NIOSH 1992a]. Dogs, rats, guinea pigs, and mice were exposed to 5 ppm daily for 6 months; no adverse effects were seen in these animals, except that rats developed a moderate degree of methemoglobinemia [Oberst et al. 1956]. At autopsy, rats given aniline for 5, 10, or 20 days showed splenic congestion, increased hematopoiesis, and bone marrow hyperplasia [NLM 1990]. The threshold for methemoglobinemia in rats required an exposure of 90 ppm for 4 hr. In vivo experiments with aniline induced DNA damage in the livers and kidneys of rats, and sister chromatid exchanges in the bone marrow cells of mice [NLM 1990]. In a single oral bioassay in mice and rats, aniline hydrochloride caused a significant increase in the incidence of hemangiosarcomas, sarcomas, and fibrosarcomas of the spleen and of fibrosarcomas and sarcomas of multiple body organs [NCI 1978; IARC 1987]. Based on this evidence, the International Agency for Research on Cancer (IARC) has concluded that the evidence for the carcinogenicity of aniline in animals is limited [IARC 1987].

2. *Effects on Humans*: Exposure to aniline causes the formation of methemoglobin, which results in a functional anemia that interferes with the ability of the blood to carry oxygen. Aniline is particularly dangerous because of the ease with which this substance is absorbed by the body after inhalation of the vapors or after contact of the skin with either the vapors or liquid. The oral aniline dose estimated to be lethal to 50% of exposed individuals is between 15 and 30 g, although as little as 1 g has caused mortality [Proctor et al.

1988]. Several deaths have been reported in workers acutely poisoned by aniline; cyanosis preceded death from asphyxiation [ACGIH 1991a]. Human volunteers exposed to aniline concentrations in the range of 7 to 53 ppm showed mild signs of cyanosis; increasing the concentration to 100 or 160 ppm for 1 hr caused serious signs and symptoms [Proctor et al. 1988]. Oral administration of 25 to 65 mg to adult volunteers caused a significant dose-dependent elevation in methemoglobin in the blood [Proctor et al. 1988]. Some studies suggest that chronic exposure to low concentrations of aniline is associated with the development of anemia, digestive disturbances, lack of energy, and headache [Proctor et al. 1988]. Early studies of workers exposed to aniline and to other chemicals, including some known bladder carcinogens, showed an excess of bladder cancer deaths. Studies in workers exposed to aniline alone have shown no excess risk of bladder cancer, although these studies are generally methodologically inadequate in various respects. Based on this evidence, IARC has concluded that the epidemiologic evidence of carcinogenicity is inadequate for aniline [IARC 1987]. An epidemiologic study of workers exposed to aniline and o-toluidine showed an increased risk of bladder cancer among exposed workers [NIOSH 1989, 1990]. The effects of o-toluidine and aniline could not be separated epidemiologically.

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to aniline can induce bluish discoloration of the lips, nose, earlobes, and nailbeds; headache; weakness; irritability; drowsiness; dizziness; ringing in the ears; difficult breathing; lethargy; incoordination; rapid heart beat; and unconsciousness. The onset of these signs and symptoms may be delayed as long as 4 hr after exposure. Hemolytic anemia, jaundice, and wine-colored urine may occur after severe overexposure, and these signs may be delayed for as long as 1 week after exposure.

2. *Chronic exposure*: Chronic exposure to aniline may cause headache, anemia, gastrointestinal disturbances, and lethargy. Workers who have been exposed to aniline should be notified that they may be at increased risk of bladder cancer, and they should be alerted to its signs and symptoms. These include (1) blood in the urine, (2) other changes in the appearance of the urine, (3) changes in urinary habits, (4) lumps in the groin or lower abdomen, and (5) pain in the lower abdomen or back [NIOSH 1990].

- **Emergency procedures**

WARNING!

Exposed victims may die!
Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Immediately rinse concentrated solutions, vapors, mists, or aerosols of aniline from the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Aniline can be absorbed through the skin in lethal amounts. ***Immediately*** remove all contaminated clothing and wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure*: If vapors, mists, or aerosols of aniline are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if aniline or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve aniline and may result in worker exposures to this substance:

—Manufacture of rigid polyurethanes; chemical synthesis of intermediates for dyestuffs and rubber processing; production of methylenediphenyl isocyanate and polymethylene polyphenylisocyanate

—Synthesis of pharmaceuticals, intermediates for pharmaceuticals, hydroquinone for photographic processing, and intermediates for agricultural chemicals

—Manufacture of cloth-marking inks, indelible inks, and lithographic and other printing inks

—Production of monomers for use in nylon fiber manufacture and synthesis of resins

—Manufacture of perfumes, varnishes, black shoe polishes, solvents, paint removers, optical whitening agents, laboratory reagents, and wood stains

The following methods are effective in controlling worker exposures to aniline, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to aniline, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the cardiovascular system, blood, liver, and kidneys. A complete blood count also should be performed.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to aniline at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with cardiovascular system, blood, liver, or kidney diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to aniline exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of aniline on the cardiovascular system, blood, liver, and kidneys. A complete blood count should be performed. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Since aniline is a potential bladder carcinogen, exposed workers should have an annual urine analysis, including microscopic examination for microhematuria and cytologic examination for neoplastic cells [NIOSH 1990].

Biological monitoring involves sampling and analysis of body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. p-Amino-phenol, a metabolite of aniline, can be measured in the urine of exposed workers. A concentration of 50 mg of total p-aminophenol per liter of urine correlates with an airborne exposure to

2 ppm. The sample should be collected at the end of the exposure period or in the first few hours after the cessation of exposure [ACGIH 1986]. A second method of monitoring for aniline exposure is to measure the methemoglobin concentration of the blood; methemoglobinemia is the first sign of excessive aniline exposure. A methemoglobin level of 1.5% in a specimen taken at the end of the exposure period or shift is a nonspecific indicator of exposure to aniline or other methemoglobinemia-inducing agents [ACGIH 1986].

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne aniline is determined by using silica gel tubes (150/75-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 30 liters is collected. The sample is then treated with 95% ethanol to extract the aniline. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg per sample. This method is described in Method 2002 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Incidents involving dermal exposure to aniline should be treated as an emergency. Workers should flush the affected areas immediately with plenty of water for 15 min and then thoroughly wash with soap and water. All areas of the body, including the scalp, hair, fingernails, and toenails, should be scrubbed carefully.

Clothing contaminated with aniline should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the contaminated clothing should be informed of the hazardous properties of aniline, particularly its potential for being absorbed through the skin in toxic amounts.

A worker who handles aniline should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where aniline is handled, processed, or stored.

STORAGE

Aniline should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred. Containers should be inspected regularly for leakage. Containers of aniline should be protected from physical damage and should be separated from oxidizers, acids, and other incompatible chemicals, sunlight, heat, sparks, and open flame. Because containers that formerly contained aniline may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving aniline, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate atmosphere to reduce concentration.
5. Protective clothing and respiratory equipment must be worn by cleanup personnel to prevent any skin and eye contact or vapor inhalation; cleanup personnel also should work upwind or use optimum exhaust ventilation.
6. Absorb spilled material with clay, vermiculite, or other noncombustible absorbent material and place the material in a covered container for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities for hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Employers owning or operating a facility with 1,000 lb or more of aniline onsite must comply with EPA's emergency planning requirements [40 CFR 355.30].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the

event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for aniline is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of aniline per calendar year are required [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of aniline emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Aniline is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. U012. Aniline is approved for land disposal as long as its concentration in the waste or treatment residual does not exceed 14 mg/kg. Aniline may also be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limits. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of aniline exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Because aniline can be readily absorbed through the skin, protective clothing should be worn to prevent any possibility of skin contact with liquid aniline or aniline vapors. In work areas where there is a potential for dermal exposure to aniline, gloves, boots, aprons, and gauntlets should be worn. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by aniline and may provide protection for periods greater than 8 hr: butyl rubber and polyvinyl alcohol. Materials that may withstand permeation for more than 4 hr but fewer than 8 hr are Teflon®, Saranex®/Tynek®, and polyethylene/ethylene vinyl alcohol (e.g., 4H® or Silver Shield®). Natural rubber, neoprene, nitrile rubber, polyvinyl chloride, and Viton® have demonstrated poor resistance to

permeation by aniline. Polyethylene has questionable value as a protective material.

If aniline is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which aniline might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with aniline. Contact lenses should not be worn if the potential exists for aniline exposure.

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