pennsylvania
DEPARTMENT OF ENVIRONMENTAL PROTECTION

ODORS FROM PAPER MILLS

Paper mills can at times produce very unpleasant smells. The distinctive odor of sulfur, similar to rotten eggs, is characteristic of many industrial processes, including the kraft pulp mill process used in the manufacture of paper. Sewage treatment plants, gas wells, coke manufacturing plants, refineries, chemical manufacturing, and leather making also may emit sulfur compounds. This odor is primarily caused by hydrogen sulfide and to a lesser degree by several other reduced sulfur compounds collectively referred to as 'total reduced sulfur' (TRS) compounds. The human nose is particularly sensitive to TRS compounds and is capable of detecting them at concentrations as small as 0.1 parts per million (ppm) of air.

ORIGIN OF TOTAL REDUCED SULFUR IN PAPERMAKING

Wood has two major components—cellulose and lignin. Lignins are organic compounds that bind the wood cellulose fibers together. To make cellulose usable for paper manufacture, the lignins must be separated from the cellulose, a process known as pulping.

Kraft pulping is the most commonly used paper pulping process in the United States. Wood chips are cooked in a digester under pressure in a solution of sodium sulfide and sodium hydroxide known as white cooking liquor to separate the lignin and cellulose. The cellulose (pulp) is then filtered, washed, bleached, pressed, and dried into paper.

The sodium sulfide in the white cooking liquor is the source of the sulfur in the TRS compounds. Although hydrogen sulfide is generally the main TRS compound emitted from kraft pulping, several other compounds are formed during digestion as the sodium sulfide reacts with the lignin in the wood and with process gases. One of these compounds is methyl mercaptan, the highly odiferous substance that natural gas companies purposely add to odorless natural gas to facilitate the detection of gas leaks.

Although most TRS compounds are emitted from the digester, other parts of the process, such as older design evaporators (in which spent cooking liquor is concentrated for reuse), recovery furnaces, and pulp washing and processing can also be sources of TRS emissions. Temporary process upsets or even weather changes can sometimes cause unusually strong but transient TRS odors in the vicinity of these plants.

CONTROLLING TRS COMPOUNDS

The Department of Environmental Protection (DEP) adopted federal TRS emission standards (25 Pa. Code § 129.17) for kraft pulp mill systems in 1991. The standards affect facilities constructed, reconstructed or modified after September 24, 1976. The standards limit emissions from digesters and other parts of the papermaking process. Also, emissions from furnaces, digesters, and evaporators must either be monitored continuously to ensure that emission limits are being met or that emissions are being adequately incinerated. In addition to complying with these standards, the owners or operators of the facilities must also comply with DEP's regulations relating to odor emissions (25 Pa. Code § 123.31).

The owners or operators of the facilities in Pennsylvania have used various technologies to meet the state and federal standards for TRS. Modifying the papermaking process should reduce the potential for TRS emissions. For example, spent cooking liquor can be isolated from the furnace exhaust gases that supply the heat for concentration. Emissions can be incinerated and exhaust routed to scrubbers and other control equipment. However, all TRS produced by a plant may not be effectively collected and routed to control equipment.

In addition to the regulations that specifically target TRS emissions, the federal air toxics regulations affecting paper pulp mills reduce TRS emissions indirectly by requiring collection and treatment of

pulping and combustion emissions for hazardous air pollutants (see 40 CFR 63, Subpart S). These regulations began to take effect in 1998; the final deadlines occurred in 2006. While controlling these other compounds, additional reductions of TRS are achieved.

HEALTH EFFECTS

Most available health effect information on TRS focuses on hydrogen sulfide. Studies of hydrogen sulfide have not shown this compound to cause cancer in humans.

Noncancer health effects of TRS compounds vary with exposure concentration and the sensitivity, age, and physical condition of the exposed populations. Eye irritation has been reported in workers exposed to concentrations as low as 2 to 5 ppm. Other health effects noted at similar concentrations include irritation to throat and respiratory pathways, fatigue, nausea, insomnia, headache, and dizziness.

TRS compounds can pose a potential acute threat to human health at concentrations that could be encountered by workers involved in certain manufacturing processes. The current Occupational and Safety Health Administration (OSHA) standard for hydrogen sulfide exposure includes a ceiling level limit (i.e., an exposure concentration not to be exceeded*)* of 20 ppm of hydrogen sulfide or a maximum allowable peak of 50 ppm for 10 minutes once per work shift if no other measurable exposure occurs during that workday. The American Conference of Governmental Industrial Hygienists (ACGIH) recommends a threshold limit value (TLV) of 1 ppm as an 8-hour time-weighted average (TWA) and a short-term exposure limit (STEL) of 5 ppm (for 15 minutes). The TLV of a chemical is considered to be the ambient concentration to which a worker can be exposed day after day for a working lifetime without adverse effects.

Human noses are so sensitive to TRS that people can smell hydrogen sulfide at levels considerably lower than the most protective workplace standard. While TRS odors emitted from Pennsylvania's papermaking facilities can be unpleasant to experience, they are unlikely to cause health problems. DEP monitoring in areas around kraft paper mills indicates that residents may be exposed to concentrations around 50 to 100 parts per billion for short periods of time. This exposure concentration range is well below protective occupational exposure levels.

For more information, visit www.dep.pa.gov.

PRIMARY TOTAL REDUCED SULFUR (TRS) CHEMICAL COMPOUNDS

Hydrogen Sulfide (H_2S) is a colorless, flammable gas with an offensive odor similar to rotten eggs. Hydrogen sulfide emissions originate from the breakdown of sodium sulfide, a component of the kraft cooking liquor.

Methyl mercaptan (CH_4S) is a flammable, water soluble gas having a very disagreeable odor described as decayed cabbage. Methanethiol is another name for this compound. One use of CH_4S is as an odorant to make natural gas detectable.

Dimethylsulfide [$(CH_3)_2S$] is formed primarily through a chemical reaction with the lignin component of the wood. It is also known as methylthiomethane and methylsulfide.

Dimethyldisulfide [$(CH_3)_2S_2$] is formed by the oxidation of methyl mercaptan throughout the recovery system. It is also known as methyldisulfide and methyldithiomethane.