Generic Scenario: Formulation of Water-Soluble Wood Preservatives

Background. Water-soluble preservatives have been used commercially to treat wood since 1832. Mercuric chloride, copper sulfate, and zinc chloride were the first water-soluble preservatives used, but these toxic preservatives were difficult to fix in the wood and were highly corrosive. The discovery that adding soluble chromate to copper, arsenic, or mercury solutions improved fixation and reduced corrosivity greatly increased the usefulness of water-soluble preservatives. Acid copper chromate (ACC) was first used in 1929; and, by 1940, chromated copper arsenate and ammoniacal copper arsenate had been introduced.

Unlike oilborne preservatives, water-soluble preservatives leave wood surfaces clean, paintable, and free from objectionable odors. They also decrease the danger of fire. Water-soluble preservatives are used in building foundations, building poles, utility poles, marine piles, and piles for land and fresh water use. Today the majority of wood in the United States is treated with water-soluble preservatives, particularly chromated copper arsenate (CCA) and ammoniacal copper zinc arsenate (ACZA). Other water-soluble preservatives include chromiated zinc chloride (CZC), bis-(tributyltin) oxide (TBTO), copper-8-quinolinolate (Cu-8), copper naphthemate, zinc naphtheuate, boric acid and borate, quaternary ammonium compounds (QAC), and ammoniacal copper/quaternary ammonium compounds (ACQ).

Chemicals Used. CCA contains chromium, copper, and arsenic and ACZA contains copper, zinc, and arsenic. Arsenic, available in large quantities as a by-product of mining operations, was first used in the 1930s to manufacture wood preservatives. The arsenic consumed in the United States is imported (24,000 metric tons in 1992), and most of the arsenic imported (17,900 metric tons) is used in wood preservatives. The total market in the United States is 140 million lb/yr; the total market value is $147 million dollars. The potential growth rate of the market is 2%/yr. Some preservatives may have a potential decline rate of up to 5%/yr.

The U.S. Environmental Protection Agency reguates the use of inorganic arsenic under provisions of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), and the use and disposal of arsenic and chromium under provisions of the Resource Conservation and Recovery Act (RCRA). The Occupational Safety and Health Administration has established standards limiting worker exposure to arsenic and chromium.

Production Process. Three companies in the United States produce water-soluble preservatives. These plants (about 10 to 15) normally operate 5 days a week, 16 hours a day, in two shifts of 3 or 4 workers. Two 4,500-gal batches (60,000 lb each) of water-soluble preservatives can be produced in an 8-hr shift.

Arsenical Preservatives: The arsenic used to produce CCA and ACZA is imported as arsenic trioxide, which is converted to arsenic acid to produce arsenical wood preservatives. CCA and ACZA are produced by mixing arsenic acid, copper oxide, and chromic acid (in the case of CCA) or zinc oxide (in the case of ACZA) in large agitated mixing vessels (e.g., 5,000 gal).

Chromic acid is received in solid form in 75-ton railcars. A total of 12,000 gallons of water is added to the railcar. The contents are then agitated for 12 hours to produce a 60% chromic acid liquid solution. The solution is transferred into storage tanks. Arsenic acid solution (75%) is produced on site and transferred to a storage tank in the CCA production area. The chromic acid, arsenic acid, and water are metered into the CCA mixing vessel via a transfer pump. Copper oxide is a powdery solid that is added to the vessel by mechanical means. The four ingredients are added and allowed to agitate for several hours. Batchs are analyzed and adjusted to ensure that the formulations are within specification. The standard formulations of these two preservatives are shown below.

The batches are filtered to remove insolubles and transferred to storage tanks. The diagram below depicts a typical manufacturing process.

Major Equipment for Arsenical Preservatives Manufacturing: The only major equipment involved is the mixing vessel, storage tanks, and associated valves, pumps and pipework. Mixing vessel dimensions vary by site from 3,000-10,000 gallons. For PMN purposes, the operating parameters are based on two 5,000 gallon mixing vessels.

Non-Arsenical Preservatives: Only one of the two main components comprising ACQ is produced by preservative prodcers, which is copper solution (CS), also known as copper ammonium carbonate. CS is produced by air oxidizing copper metal in an aqueous solution of ammonium carbonate and aqua ammonia.

The reaction is executed in two 12,000-gal agitated vessels which are vented to wet scrubber. Water, recycled scrap copper, 29% aqua ammonia are the raw materials. A total of 5,200 gal of water is added to a reactor, followed by 10,000 lb of copper and 5,900 gal of ammonia. The batch is then sparged with 10,800 lb of CO2 and then with air for 48 hours to complete the oxidation.

When oxidation is complete the solution is sampled and analyzed. Some minor adjustments in constituent concentrations, if necessary are performed. Upon lab approval, the solution is transferred to an intermediate storage tank. The solution is then filtered in to a secondary storage tank equipped with a pump to load tanker trucks. The diagram below depicts typical manufacturing process.

Major Equipment for Non-Arsencial Preservatives Manufacturing: The kit comprises 2 mixing vessels, 2 intermediate storage tanks, final storage tanks, and associated pumps, cartridge filters, and pipework.

Modes of Exposure. The chemicals used to produce water-soluble preservatives usually are in a liquid, flake, or powder state.

Hazardous vapors can be released during mixing and material transfer. Vapors or aerosol carryover and dusting also can occur during mixing material transfer.

Solid waste resulting from the production process includes gloves, coveralls, and rags as well as precipitated solids from the wastewater treatment system.

Liquid waste is minimal because most of the process materials are recycled. Small amounts may evade the collection system, in which case the chemicals may be introduced into the wastewater treatment system.

References:

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