2-5-54
K. Shaffert

OPERATING INSTRUCTIONS

2,4,5-TRICHLORPHENOL

1.00 METHOD OF MANUFACTURE

1.01 1,2,4,5 tetrachlorobenzene is fused with flake caustic soda in the presence of methyl alcohol to produce sodium 2,4,5-trichlorphenate. This reaction takes place at a pressure of 360 - 400 psi gauge and a temperature of 180 - 186°C.

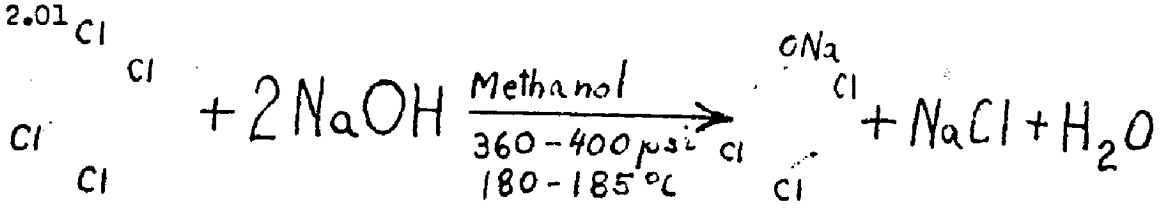
1.02 The methanol is stripped off and recovered.

1.03 The reaction mass is diluted to a 5% solution with water in order to precipitate out the organic impurities (chiefly unreacted 1,2,4,5-tetrachlorobenzene and 2,4,5-trichloroanisole). The pH of this solution is adjusted to 7.5 - 8.5 with 96°Be' sulfuric acid in order to facilitate subsequent filtration. The water-insolubles are allowed to settle and the supernatant liquid is filtered.

1.04 The filtered sodium trichlorphenate solution is heated and acidified. After settling, the phenol layer is withdrawn and the acid water discarded.

1.05 The trichlorophenol is again dissolved in aqueous caustic soda and stored as a 35% solution of sodium 2,4,5-trichlorophenate.

2.00 CHEMISTRY

2.01 

2.02 

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3.00 HAZARDS

3.01 The caustic fusion reaction is highly exothermic. The rate must be checked at the proper point during the induction period by turning cooling water on the jacket. If this is not done the pressure will rise uncontrollably and then only the pressure relief valves and/or rupture discs can prevent autoclave failure.

3.011 If a pressure release through the rupture disc lines appears imminent, all personnel should be evacuated from the river front, HCB unit, pilot plant areas.

3.012 A danger of equipment failure exists due to recoil from a franging disc. This force is calculated by the equation:

$F = 2Ap$, where F = force (opposite to direction of release) in pounds

A = cross sectional area of

p = gauge pressure at time of rupture in psi

In the case of #1 Autoclave this force would be equal to 6.71 p. For the #2 Autoclave the force is 14.79 p.

3.013 If actual autoclave failure due to excess internal pressure is anticipated it should be borne in mind that the main chlorine line runs just to the right of the #1 autoclave.

3.02 Methyl Alcohol

A flammable liquid and dangerous fire hazards. Open cup flash point 60°F. Autoignition temperature 800°F. Explosive limits 6.0 to 36.5% by volume in Air. Toxic. Ingestion and absorption causes central nervous system damage, especially to the optic nerve. Symptoms of intoxication may be delayed 9 to 36 hours. Maximum allowable concentrate in air is 200 parts per million.

3.03 2,4,5-Trichlorophenol

Toxic. Can cause conjunctivitis and irritation more marked than that caused by phenol. Vapors severe lachrimator. Wash burns with alcohol to remove all phenol, then wash with bicarbonate of soda.

3.04 Caustic Soda and Sulfuric Acid.

Plant-wide handling methods to be applied. Flake caustic is hygroscopic and when strewn about will form little alkaline pools which can drip or splash.

4.00 PROCESS

4.01 Fusion

4.011 The charges are as follows:

For #1 Autoclave: 900 lbs. 1,2,4,5-tetrachlorobenzene
400 lbs. flake caustic soda
215 gals. methanol (new and recovered)

For #2 Autoclave: 2250 lbs. 1,2,4,5-tetrachlorobenzene
1000 lbs. flake caustic soda
540 gals. methanol (new and recovered)

The tetrachlorobenzene is loaded through a chute into the handhole of the autoclave. The flake caustic soda follows. Then the chute is removed, the handhole sealed, and, with the vent line open, the methanol is forced in by air pressure.

4.012 Greasing. The stuffing boxes must be greased regularly and properly. They function on the basis of grease pressure spreading chevron packing rings, thus providing a pressure seal around the agitator shaft.

The #1 autoclave has three grease fittings. The lowest section is provided with a vent which should be opened. Pump grease until a solid stream of undiluted grease comes out of this vent. The middle section is greased until 200 psi have built up. The increment over kettle pressure is maintained throughout the batch. The top section is greased until grease issues from between the retainer ring and the shaft.

The #2 autoclave has two grease fittings, each provided with a reservoir. Nitrogen pressures of 600 and 550 psi respectively are maintained on the lower and upper reservoirs. The nitrogen pressure has to be regulated for every batch (when the kettle pressure has reached its maximum) but grease is added only occasionally. Inability to maintain nitrogen pressure on the reservoir indicates the need for replenishing grease.

4.013 The stuffing boxes of both autoclaves require water cooling. Before starting a batch the flow should be checked. The temperature of the overflow water should never be above 60°C.

4.014 After the autoclave is sealed, the vent and all other valves are closed, the agitator is started and 120 psig steam pressure is applied to the jacket. When the temperature in the autoclave reaches 132°C. the steam is shut off and the jacket is drained. The temperature and pressure continue to rise. At 166°C. cooling water is applied to the jacket, causing the temperature to level off between 180 - 185°C. The jacket is drained again and the reaction is allowed to proceed for 4-1/2 hours from the time that the temperature reached 160°.

It is sometimes necessary to

use steam during the second half of the reaction in order to maintain the temperatures over 160°C.

At the end of this time the batch is cooled.

4.02 Distillation

4.021 #1 Autoclave:

Cooling water is applied to the #1 condenser and #1 receiver is vented. When the cooling cycle has reached the point where the pressure is below 50 psi, the blow-leg valve is cracked open slowly and the batch is blown into the still. The agitator is shut off when about two thirds of the batch has blown over. Then the blow-leg is closed and steam is applied to the still coil. The distillation rate is controlled so that pressure in the receiver never rises above 2 psi.

When the batch has been brought to a temperature of 130°C. no more distillate comes off. Steam is shut off, and 150 gallons of water are metered in. The batch is agitated by air sparging and then blown to the dilution tank with 10 psi air pressure.

4.022 #2 Autoclave:

Methanol is distilled right in the reaction vessel.

When cooling has reduced the pressure to 50 psig at the end of a fusion cycle, water is turned on the #2 condenser, the #2 MeOH receiver is vented and the distillation valve is cracked open. In the meantime, water is drained from the autoclave jacket and steam is applied. The rate of distillation is controlled so that there is never more than 2 psi pressure on the receiver. The agitator is left running during the procedure. Again, the distillation is complete at a temperature of 130°C. Then the batch is

cooled and 500 gallons of water are metered in. Air pressure is applied and the batch is forced through the blow-leg into the dilution tank M3.

4.03 Dilution, Settling and Filtration

4.031 The concentrated sodium salt is diluted with water in a ratio of 20:1. This means diluting to 1500 gallons in the case of #1 dilution tank and 3300 gallons in the case of the larger system. The batch is agitated with air. Sulfuric acid is added until a pH of 7.5 - 8.5 is attained in order to facilitate filtration.

After settling for one hour, the diluted sodium salt is filtered through a plate and frame press fitted with cotton cloths.

A constant heel is left in the dilution tanks. When enough solids have built up here to overflow (about 10 batches) the trichlorophenol is extracted by adding water and raising the pH to 8.5 - 9.0. This is filtered and acidified. The extracted sludge is discarded.

The press discharges into the acidification tank.

The drip pan contents are recycled to #1 dilution tank.

4.04 Acidification

As the dilute sodium salt solution filters into the acidification tank it is heated by a steam coil and a live steam sparger. When the tank is full and the temperature has reached 50°C. sulfuric acid is added until the batch is acid to congo red paper (pH $<$ 4). The agitator is shut off while the phenolic layer settles out. The trichlorophenol is separated visually (through a sight glass) into a separating drum.

The supernatant acid water is pumped to a wooden catch tank on the roof where any suspended phenolic particles settle

out while the clear water overflows to discard.

Periodically, the water layer is syphoned off this tank, the trichlorophenol is melted and dropped by gravity to the #1 dilution tank, where it is converted to sodium salt, diluted and treated in a fashion similar to the autoclave batches.

4.05 The trichlorophenol is stored (and used for 2,4,5-trichlorphenoxyacetic acid condensations) as a 35% sodium salt solution. This is prepared in tank T2.

Pump 40% caustic solution into the make-up tank to an outage of 63". After the trichlorophenol from 11 separations has been added adjust the pH to between 8 - 9. Then add water until a specific gravity of 1.25 ± 0.02 is attained. The solution is tested by the laboratory (see Section 5) and pumped to the storage designated by the supervisor.

5.00 QUALITY CONTROL AND SPECIFICATIONS

5.01 Quality of 2,4,5-trichlorophenol

5.011 Set point - sample must first be dried by heating for 10 minutes in the presence of calcium chloride. Reported set point is 61 - 63°C. Plant material (undistilled) should be above 55°C.

5.012 Caustic solubility test - The most objectionable impurities (in view of the end use of the trichlorophenol) are those not soluble in water at a high pH. These are mainly unreacted 1,2,4,5-tetrachlorobenzene and 2,4,5-trichloro-anisole, the methyl ether formed as a byproduct in the fusion process.

An empirical method for finding the degree of excess of these impurities consists of dissolving 20 g of sample in 50 ml of 40% caustic solution and then diluting with 200 ml of water. The degree of turbidity is a measure of the impurity.

N.B. - Ignore the color of the solution in determining the translucency, but consider only the amount of suspended material.

Batches should test either "clear" or "slightly cloudy".

5.02 Specifications for 35% sodium trichlorophenate.

5.021 The specific gravity must be 1.25 ± 0.02.

5.022 A sample is diluted and titrated with N/2 sulfuric acid first to thymophthalein and then to a congo red end point. The first end point is an indication of the free caustic present, while the second is a measure of the concentration of trichlorophenol. There must be 1 to 2% excess caustic present and 35 ± 1% trichlorophenol.