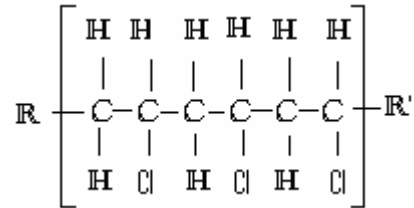


## Production of Chlorinated Polyvinyl Chloride from Polyvinyl Chloride

Molecular structure:

“PVC”:

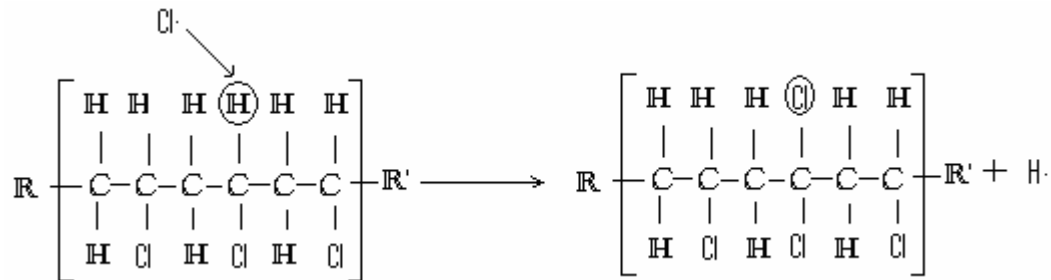


**PVC chlorination Reaction Chemistry:**

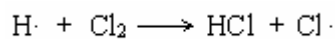
CPVC is produced by reacting suspension PVC resin with chlorine. The reaction is initiated by decomposing diatomic chlorine dissolved in water into highly unstable and reactive chlorine atoms,



With either high heat or ultraviolet radiation. Once this **initiation step** has taken place, a chlorine atom attacks a PVC chain at a random location and replaces a hydrogen atom at the attack position.

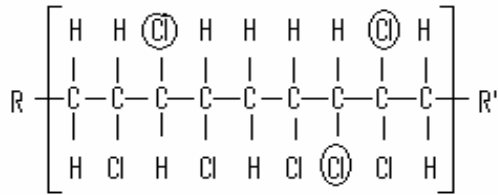


The liberated hydrogen atom reacts with a chlorine molecule to form a molecule of hydrogen chloride and another chlorine atom:



The new chlorine atom attacks a polymer molecule and replaces another hydrogen atom, and this **chain propagation sequence** continues as long as both chlorine gas and hydrogen atoms on polymer chains remain in the system. If enough chlorine is added to the reactor, a structure similar to the following one might be obtained (the added chlorines are circled):

### “67 % Cl CPVC”:



### Process Description:

#### Step 1:

Solid PVC resin is combined with water in a stirred tank to make a **slurry** (a suspension of solid particles in liquid) containing about 10 wt % PVC. The slurry is pumped to a continuous **chlorine absorber**, a vessel equipped with an impeller that keeps the content agitated. A stream of chlorine vapor at 25 °C also enters the absorber. The absorber operates at 25 °C.

The chlorine absorber is enclosed by a jacket through which a hot or cold fluid can be pumped to maintain the absorber contents at any desired temperature. A **pressure relief pipe** emerging from a point near the top of the absorber is equipped with a **rupture disk**, a thin metal membrane designed to break if the absorber pressure rises above a certain value. If this happens, gas flows from the absorber through the relief pipe to a **surge tank**, lowering a pressure in the absorber while containing the released gas.

#### Step 2:

The chlorine that eventually be fed to the absorber is stored in a tank as a liquid under pressure at 22 °C. Liquid is pumped from this tank through a **chlorine flow control valve** to a **chlorine vaporizer**, a tall tank about half of which is filled with chlorine liquid and the other half with chlorine vapor. The liquid and vapor are in equilibrium at 5 °C. Saturated steam at 2 bar absolute is fed to through a **steam flow control valve** into a coil submerged in the liquid in the vaporizer, and the heat transferred through the coil wall vaporizes chlorine. Chlorine vapor flows from the top of the vaporizer.

The pressure and liquid level in the chlorine vaporizer are controlled automatically. As vapor flows out the top, the pressure in the tank begins to decrease. A

pressure sensor detects the drop and sends a signal to the steam flow control valve. The valve opens and feeds more steam to the coil, causing more liquid chlorine to evaporate and raising the pressure back to the desired value. As the liquid evaporates, the liquid level in the tank begins to drop. A liquid level sensor detects the drop and sends a signal to the liquid chlorine flow control valve. The valve opens, and more liquid enters the tank to replace the liquid that evaporated, raising the liquid level back to the set point (desired) value.

**Step 3:**

The chlorine vapor leaving the vaporizer passes through an adiabatic **expansion valve**, then through a **chlorine vapor heat exchanger**. In the exchanger, the vapor comes in thermal contact with a hot flue gas from a furnace to be described in Step 15. The heat transferred from the flue gas is used to raise the temperature of the chlorine vapor to 25°C. The heated vapor is the chlorine feed to the absorber mentioned in Step 1.

**Step 4:**

The chlorine enters the absorber through a pipe in the bottom that ends in a **sparger** (something like a shower head nozzle) located close to the impeller. The chlorine comes out of the sparger in thousands of tiny bubbles, which are then dispersed by the impeller throughout the slurry in the absorber. Chlorine is soluble in water and even more soluble in the PVC resin and so dissolves in both the liquid and solid phases of the slurry.

The feed rate of chlorine to the absorber is automatically controlled to maintain the absorber pressure at a specified value. If pressure begins to fall, a pressure sensor detects a drop and sends a signal to the expansion valve described in step 3. The valve opens, causing the flow rate of chlorine to increase and raising the absorber pressure back to the set-point value. If the pressure rises above the set point, the pressure sensor sends a signal that adjust the control valve to decrease the flow rate of chlorine and the pressure comes back down to the set-point value.

**Step 5:**

The PVC resin slurry that leaves the chlorine absorber at 25 °C is heated to 50 °C in the **reactor preheater**. A very small amount of a chemical *initiator* is added to the heated slurry leaving the preheater. The amount of initiator added is small enough to be neglected in material balance calculations on the reactor.

**Step 6:**

The heated slurry flows to a **chlorination reactor**, which is a long jacketed pipe. In the reactor, the initiator – which is unstable at 50 °C and higher – decomposes and begins the PVC chlorination chain reaction described in the introductory section. As the slurry moves through the reactor, dissolved chlorine in the resin particles reacts with the polymer, producing hydrogen chloride as a byproduct. The HCl which is essentially insoluble in PVC and CPVC – diffuses out of the particles and into the liquid phase, forming hydrochloric acid (by definition an aqueous solution of hydrogen chloride), and the chlorine that had been dissolved in the liquid phase diffuses into the particles and reacts. All of the chlorine fed to the reactor is eventually consumed. The exit stream from the reactor is slurry of CPVC particles containing 67-68 wt % chlorine suspended in aqueous hydrochloric acid.

The chlorination reaction is highly exothermic. Some of the heat of reaction raises the slurry temperature to its exit value of 65 °C, and cooling water flowing through the reactor jacket removes the additional heat generated. (If the reactor temperature were to rise above 65 °C, the rate of chlorination reaction would become extremely high, chlorine dissolved in the liquid phase would all react near the outer surface of the particles rather than diffusing through the pores, and the quality of the final product would suffer.)

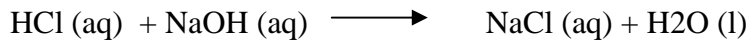
**Step 7:**

The CPVC slurry flows to the **reactor centrifuge**, a spinning horizontal drum. The solids are forced against the circular drum wall and are compressed there. Liquid hydrochloric acid (**waste liquor**) collects in the drum and overflows through an opening

at one end, and the **wetcake** retained on the wall, which contains 90 wt% CPVC resin and 10 % hydrochloric acid, is scraped out by a large interior screw conveyor.

### **Step 8:**

The waste liquor from the reactor centrifuge flows to a **waste liquor neutralizer**, where the HCl is neutralized with caustic soda (sodium hydroxide) solution:



A stream of CO<sub>2</sub> produced in the resin neutralizer (Step 10) also enters the neutralizer liquid through a sparger and reacts with sodium hydroxide:



The caustic solution fed to the neutralizer, which comes from the NaOH feed drum (Step 9), contains 10 wt % NaOH and also some dissolved NaCl and Na<sub>2</sub>CO<sub>3</sub>.

### **Step 9:**

The solution of sodium chloride and sodium carbonate leaving the waste liquor neutralizer is combined with the waste liquor from the product centrifuge (Step 12). The combined solution is split into two streams. One goes to a waste treatment facility, and the other goes to the **NaOH make up tank**, an agitated jacketed batch vessel. Solid pellets of sodium hydroxide are added to this tank to bring the NaOH concentration in the solution up to 10 wt %. Cooling water is circulated through the make up tank jacket to remove the considerable heat generated by the dissolution of NaOH. Batches of solution are pumped from the NaOH makeup tank to the **NaOH feed drum** (a holding tank), and solution is pumped from the feed drum to the waste liquor neutralizer (Step 8). The feed drum always contains enough inventory to provide a continuous feed to the neutralizer.

### **Step 10:**

The wetcake produced in the reactor centrifuge is conveyed to a **resin neutralizer**, another large, jacketed, agitated vessel, where the HCl in the resin is neutralized with sodium bicarbonate in the reaction



(Sodium bicarbonate, a weak base, is used because a strong base like sodium hydroxide can damage the resin.) A 10.0 wt % aqueous  $\text{NaHCO}_3$  solution at 21 °C pumped from the  $\text{NaHCO}_3$  feed drum (Step 11) is augmented by a clean water stream at 60 °C, and the combined stream is fed to the tank. Enough bicarbonate solution is fed to neutralize all the HCl in the wet cake, and enough additional water is added to make a 15.0 wt % CPVC slurry in the vessel.

A pH controller monitors the neutralizer vessel contents and sends a signal to a flow control valve in the bicarbonate solution feed line if more or less solution is needed. The resin remains in the neutralizer long enough for even the HCl trapped in the resin pores to be neutralized. The neutralizer exit stream is a slurry containing 15.0 wt % CPVC in an aqueous sodium chloride solution at 90 °C and pH = 7.

Steam fed to the vessel jacket maintains the contents at 90 °C. At this temperature, the reaction proceeds to completion and essentially all of the carbon dioxide formed in the reaction between HCl and  $\text{NaHCO}_3$  is driven out of the aqueous phase. The  $\text{CO}_2$  leaving the resin neutralizer is recycled to the waste liquor neutralizer (Step 8).

#### **Step 11:**

The sodium bicarbonate solution fed to the resin neutralizer (Step 10) is produced by dissolving  $\text{NaHCO}_3$  powder from 25 kg bags in clean water in the **NaHCO<sub>3</sub> makeup tank**, an agitated batch vessel. The makeup tank is not jacketed like the NaOH makeup tank, as the heat of solution of sodium bicarbonate is low enough for the heat generated in the tank to be neglected. Batches of solution are pumped from the make up tank to the  $\text{NaHCO}_3$  feed drum, and solution is pumped continuously from the feed drum to the resin neutralizer.

#### **Step 12:**

The slurry leaving the resin neutralizer goes to the **product centrifuge**. The dilute NaCl solution wrung from the resin in the centrifuge is cooled to 25 °C in a heat exchanger. The cooled solution combines with the effluent stream from the waste liquor neutralizer (Step 8).

**Step 13:**

The wetcake from the product centrifuge, which contains 90 wt% CPVC, is conveyed to a **rotary dryer**. This unit functions like clothes dryer. The resin is tumbled down an inclined, rotating drum with hot air flowing through the drum in the opposite direction. Heat transferred from the air vaporizes most of the remaining water in the resin. The CPVC product resin emerges from the dryer at 120 °C containing roughly 0.1 wt % moisture.

**Step 14:**

The humid air leaving the rotary dryer at 110 °C, 1.3 atm, and 20 % relative humidity is split into two streams. 10 % of the air is vented to the atmosphere, and the other 90 % is combined with **makeup dryer air**, heated in the **indirect contact furnace** described in the next step, and fed back to the rotary dryer (Step 13).

**Step 15:**

In the **indirect contact furnace**, natural gas containing 92.5 mole% methane, 4.8 mole % ethane, and the remainder propane is burned completely with excess air (**combustion air**). The dryer air feed stream (the combination of make up dryer air and humid air recycled from the dryer outlet) passes through metal channels within the furnace combustion zone and then out of the furnace to the rotary dryer air inlet. The hot gases in the furnace combustion zone heat the metal channel walls, and the walls in turn heat the dryer air.

**Step 16:**

The combustion products leave the furnace at 250 °C and flow through the chlorine vapor heat exchanger (this stream is the flue gas referred to in Step 3) and then to a **flare**, where any carbon monoxide and residual hydrocarbons in the gas are burned and the products released to the atmosphere. The flare is a safety precaution: if the furnace operates as intended, the CO and hydrocarbon content of the flue gas should be negligible,

## PROBLEMS

1. On an oversized page, draw a flow chart for this process. Label each stream with an identifying symbol (e.g. S1,S2,S3,.....) and known information about what the stream is and /or what it contains [e.g., slurry, 10 wt % PVC in water; wetcake, 90 wt % CPVC, 10 wt % HCl (aq); 10 wt % NaHCO<sub>3</sub> (aq)].
2. Neglecting the end groups, calculate the mass fractions of carbon, hydrogen, and chlorine in PVC and in the “67 % Cl” produced in this process. (The molecular structure of this product is shown in the section on PVC chlorination reaction chemistry)
3. The plant is to produce  $3.5 \times 10^6$  kg/year of “67 % Cl”. Assuming that the plant operates 300 days per year, 24 hours per day, calculate the required hourly feed rates (kg/h) of the 10 wt % PVC slurry and of Cl<sub>2</sub> (g) to the absorber and the production rate of hydrogen chloride (kg/h) in the chlorination reactor. (Suggestion: Write balances around the system composed of chlorine absorber and chlorination reactor.)
4. The CPVC wetcake leaves the product centrifuge at 80 °C and 1 atm and is fed to the elevated end of the dryer (a rotating cylinder inclined about 35° from horizontal). The flow rate of wetcake is 540.05 kg/h and its water content is 10 wt%. A fresh air stream at 27°C, 1 atm, and 60 % relative humidity is mixed adiabatically with an air stream recycled from the dryer exhaust, and the combined stream is heated in an air furnace and fed to the lower end of the dryer. Water evaporates from the wet cake moving downward in the rotating drum into the hot air moving in the opposite direction. The exhaust air leaves the dryer at 110 °C, 1.3 atm, and 20% relative humidity. *The dryer operates adiabatically.* 90% of the exhaust air is recycled, and the rest is vented to the atmosphere. The dried polymer resin leaves the dryer at 120°C containing 0.1 wt % water.
  - (a) In your own words, explain the purpose of this portion of the process.



Your explanation should include statements about why the dryer must be tilted, why the air temperature drops as the air moves through the dryer, and why the preheater (air furnace) is necessary.

- (b) Draw and fully label a flowchart of this portion of the process, substituting known variable values from previous calculations and including the required rate of heat transfer to the air in the preheater in the labeling. Use molar flow rates and mole fractions when labeling gas stream.
- (c) Use as references for enthalpy calculations solid CPVC at 80°C, liquid water at 0°C, and dry air at 110°C (all at 1 atm), neglect the contribution of sodium chloride to the energy balance, use the steam tables to determine vapor pressures and heat of vaporization of water, and use the following heat capacities: CPVC (s), 1.88 kJ/(kg °C); Dry air, 29.2 kJ/(kmol °C); H<sub>2</sub>O (l), 4.2 kJ/(kg °C); H<sub>2</sub>O (v), 34.0 kJ/(kmol °C). Do not perform the calculations in this part. Determine the unknown stream flow rates, component fractions and temperature of the air entering the dryer, and rate of heat transfer to the air in the furnace (kW).