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Interoffice Communication

To R. S. Matthews
From R. A. Frohreich
Date June 18, 1973
Subject Resin Development Program--D-300 Operation

Attached is the report covering the resin development test runs conducted earlier this year. We are distributing the report to Operations only at this time to solicit review and comment prior to wider distribution. Final issue of the report is planned for July 2, 1973, if no changes or additions are required.

The primary purpose of the test work on D-300 was to obtain the effect of polymerization time on the heat release curve and various operating parameters on resin quality.

We would like to extend our appreciation to the Aberdeen personnel for their cooperation in conducting the test runs and for providing analytical results.

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OPERATING MANUAL
OLD UNIT PVC REACTORS
ABERDEEN, MISSISSIPPI

I. INTRODUCTION

A. Operator Responsibilities

The purpose of this plant is to safely and economically convert vinyl chloride monomer (VCM) into a usable form of polyvinyl chloride (PVC). This is accomplished by a batch process in which VCM, water, initiator and colloid solution are charged into the reactor and under carefully controlled conditions PVC with the desired physical properties is produced. This chemical reaction, which changes VCM to PVC is called polymerization. PVC leaves the reactor in slurry form and is dried to product specification by centrifuging and drying with hot air.

The operator helps fulfill the plant's purpose by making sure that quality production is obtained from his equipment without endangering himself, his fellow workers, or his equipment. The operator is able to attain his goals in safety, job performance, and efficient operation through a training period, on the job experience, and passing written and field examinations.

The operator fulfills his responsibilities by:

1. Demonstrating understanding of how his equipment functions.
2. Being able to explain what role each piece of equipment plays in the process.
3. Keeping a close and regular check on equipment.
4. Being able to demonstrate troubleshooting and corrective measures.
5. Keeping his area of responsibility safe and clean.

I. INTRODUCTION (CONTINUED)

A. Operator Responsibilities (Continued)

6. Keeping complete and accurate records.
7. Reporting process or equipment problems to his supervisor promptly.

This operating manual will cover the normal responsibilities and duties of the old reactor unit lead and "A" operators. Each phase of the production method will be covered. In addition to normal operating methods it will also discuss operations under abnormal and emergency conditions. The operator must be prepared to meet these situations with temporary measures until the abnormal condition is corrected or the emergency crisis ceases to exist.

Safety takes second place to no other plant activity. The safety of the plant personnel and equipment is to be carefully considered before any job is started. The Conoco safety slogan "Our work is never so urgent or important that we cannot take time to do it safely" is an idea that can help make the work area safer for everyone when it is put into practice. Each operator is responsible for compliance to all plant safety rules as stated in the plant safety rulebook and for reporting any infractions of these rules by other personnel in their units. This includes keeping himself safe by following the VCM safety rules and wearing proper protective equipment as required.

Preventing the loss of raw materials and product in the area where he works is another responsibility of the operator. Each operator is

I. INTRODUCTION (CONTINUED)

A. Operator Responsibilities (Continued)

responsible for doing his job and producing resin without losing any raw materials or resin or, if product loss is absolutely necessary, by doing the job in a manner that minimizes such losses. Any loss of material, whether resin, VCM, or other raw materials, must be reported promptly by the operator to his Supervisor and corrective steps will be taken as soon as possible. Awareness of this problem, planning jobs before performing them, reporting losses that occur, and being careful when handling raw materials, will improve the plant vinyl efficiency and make the plant operation more profitable.

Any loss of VCM from any process equipment or piping requires special attention by the operator. VCM emissions are regulated by regulations from the Environmental Protection Agency (EPA) and the Occupational Safety and Health Administration (OSHA), because it is a suspected carcinogen (cancer causing agent). VCM losses must also be minimized because it is extremely flammable. The operator is responsible for stopping any VCM leak that he is aware of (including water leaks that have VCM in the water). If the operator cannot stop the leak himself, he must notify his Supervisor immediately. Any relief valve discharge, whether major or minor, from a piece of equipment that processes VCM is reportable to government agencies, and must be reported to a Supervisor immediately. Also, any VCM

I. INTRODUCTION (CONTINUED)

A. Operator Responsibilities (Continued)

discharge which exceeds one pound of VCM is reportable to government agencies within a few hours of its occurrence and must be reported to a Supervisor and to the Operations Supervisor immediately (this includes releases due to "O" ring failures and other miscellaneous losses of VCM).

Another important responsibility of each operator is energy efficiency in his operating area. Plant operating costs are heavily affected by energy usage and cost, and inefficient operation of process equipment is very unprofitable. The operator must be aware of the equipment that must be run to do his job and is responsible for shutting down energy using equipment that is not needed. Prompt reporting of steam leaks is also expected of each operator to reduce energy losses. The operator is responsible for notifying his Supervisor if a steam leak cannot be stopped, and the Supervisor will see that a work order is written and that the leak is tagged. Some other examples of energy inefficiencies that should be watched for and corrected include air leaks (write maintenance work orders for repair), steam tracing on in above freezing weather conditions, automatic cooling tower fan controls not running in automatic, an excessive number of cooling tower pumps running, recovery system pumps left running, aeration on to empty blend tanks, and dryers left running when there is no feed to them. The lead and "A" operators in the

I. INTRODUCTION (CONTINUED)

A. Operator Responsibilities (Continued)

affected area must be aware of such unprofitable energy usage and are responsible for correcting these and similar situations to minimize energy losses.

Good communication is one of the most important keys to effective and efficient plant operation. However, effective communication is not easily attainable. It must be worked toward on a day-to-day basis by each person involved and affected. The operator is responsible for keeping his Supervisor and affected co-workers informed of operating or mechanical problems in his area. The operator must also pass on pertinent information to his shift relief, in detail, so that plant operation can continue smoothly from shift to shift. Communications between the lead and "A" operators are most important and are essential to good plant operations. The lead operator initiates and coordinates "A" operator actions, and then the "A" operator must communicate back to the lead operator that the action has been completed as instructed.

Good housekeeping is also an important responsibility of each operator. It requires careful attention for safety reasons and for maintaining good working conditions. Cleaning up after a job is finished is the responsibility of the person doing the job. A job is not considered completed until all materials are picked up and properly stored.

I. INTRODUCTION (CONTINUED)

B. Process Information

1. Vinyl Chloride Monomer

Vinyl chloride monomer (VCM), also called vinyl chloride or vinyl, is the principal raw material used in the manufacture of poly vinyl chloride (PVC). It is a colorless, sweet-smelling gas at room temperature and pressure and may be condensed to a colorless liquid under moderate pressures (50-100 psig). It is an extremely flammable gas that emits highly toxic fumes (carbon monoxide and hydrogen chloride, an acid-gas) when burned.

Exposure to VCM is regulated by the EPA (Environmental Protection Agency) and OSHA (Occupational Safety & Health Administration) because it is a suspected cancer causing agent. Vinyl chloride liquid is lighter than water and the vapor is heavier than air. Liquid VCM will float on top of water in pressurized tanks, but the water will be saturated with VCM and is an exposure hazard. VCM vapors will collect in low spots and in the bottom of open tanks and sewers since it is heavier than air. This will be further discussed under VCM safety (below).

a. Manufacture and Use

Vinyl chloride is made from ethylene and chlorine. Ethylene is made from ethane and propane [that comes primarily from natural gas as LPG (liquified petroleum gas)] or from naptha (a refinery petroleum cut that is lighter than gasoline). In an ethylene plant, the ethane, propane, or naptha is "cracked" at temperatures from 1500°F to 2000°F breaking the raw mate-

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

1. Vinyl Chloride Monomer (Continued)

a. Manufacture and Use (Continued)

rials into many chemical gaseous products, and ethylene is the primary product that is distilled from the resulting gases.

Ethylene is a highly versatile gas that is reacted with other chemicals to make chemicals such as ethylene glycol (anti-freeze), polyethylene (plastics), and vinyl chloride. A vinyl chloride plant reacts ethylene with chlorine (which is made in electrolytic cells in a chlorine plant from very salty water known as "brine") to make ethylene dichloride which is then "cracked" at 800-900°F. Vinyl chloride is distilled from the resulting gases and is compressed and condensed (liquified) for shipment to PVC makers.

The primary industrial use of vinyl chloride at the present time is for manufacture of PVC. Vinyl was used in the past as a propellant in aerosol cans, but government regulations on VCM halted its use.

Most of the VCM that comes into this plant comes in tank cars from Conoco's VCM plant in Westlake, Louisiana. VCM also occasionally comes from PPG in Lake Charles, Louisiana, B. F. Goodrich in Calvert City, Kentucky, or from Uniroyal in Geismar, Louisiana. VCM tank cars typically hold 175,000

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

1. Vinyl Chloride Monomer (Continued)

a. Manufacture and Use (Continued)

pounds of VCM (about 23,000 gallons of liquid) and are unloaded into the tank farm sphere by the yard department as VCM is used by the reactor units.

b. Safety

Vinyl chloride is a hazardous chemical because it is highly flammable and because it is a suspected cancer causing agent.

Vinyl chloride mixes with air (oxygen) to form a very flammable and potentially explosive mixture. The explosive range for vinyl chloride is 3.6 to 33.0 percent or 36,000 to 330,000 ppm. Whenever vinyl is mixed with air and is in that range, it can ignite if there is an ignition source (from sparks, welding, static electricity, and other similar sources). VCM and oxygen burn and emit fumes which are highly toxic, including hydrogen chloride gas and other very dangerous chemicals.

Tests have shown that VCM may be linked to acroosteolysis, which is a finger bone disease, and to angiosarcoma, which is a rare form of liver cancer. Acroosteolysis can be prevented by avoiding or preventing direct contact with high concentrations of VCM. VCM was linked to this disease when a high percentage of workers who cleaned reactor internals over long periods of time without adequate protection were shown to

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

1. Vinyl Chloride Monomer (Continued)

b. Safety (Continued)

have a higher incidence of the disease. The direct contact with dried PVC resin product is not considered toxic because of the very low levels of VCM contained in the resin (less than 10 ppm).

Angiosarcoma was linked to VCM by studies showing that workers exposed to breathing high levels of VCM for many years had a high incidence of this rare form of liver cancer. The EPA and OSHA have regulations on VCM which must be followed by plant personnel. The plant has taken extensive measures to eliminate exposure of plant personnel to VCM. All safety rules concerning VCM must be followed by all employees while on the job, and are listed in the current Safety Rulebook or in the Engineering and Work Practices Control Plan. If any problem concerning VCM exposure develops that is not specifically covered by these rules, consult your Supervisor. Every employee is expected to control his exposure to VCM or other potentially hazardous chemicals used in the process in accordance with plant safety standards. It is important to use sound materials handling practices when using these chemicals to minimize the potential for skin and respiratory contact. This includes respiratory

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

1. Vinyl Chloride Monomer (Continued)

b. Safety (Continued)

- (3) The fixed point monitor computer records the hourly averaged levels of VCM for each Honeywell continuous monitor point and gives a report at the end of each shift. If the computer malfunction alarm comes on, the lead operators must record the VCM concentration at each monitoring point hourly on the continuous monitoring log sheet. An instrument maintenance work order should be filled out and turned in to repair the computer as soon as possible.

The computer also monitors the individual Honeywell points for EPA leaks. A "leak" is defined as three successive readings of 5 ppm VCM or more at any given fixed point. An alarm will go off in the control room and the lead operator that acknowledges the alarm must fill out a leak report form and have the "A" operator put on proper respiratory equipment and identify the source of the leak. Each leak will be given a successive number by the computer to enable the leak to be kept up with until it is fixed. If the leak is at the tank farm, the lead operator will notify the yard operator, who must put on proper respiratory protection and

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

1. Vinyl Chloride Monomer (Continued)

b. Safety (Continued)

protection, safe work practices, protective clothing and the like.

The following items warrant particular emphasis and explanation concerning VCM exposures:

- (1) Breathing protection must be worn in any area where the VCM concentration is greater than 1 ppm, as follows:
 - a. 1-10 ppm: VCM canister mask or air line respirator.
 - b. 10-1000 ppm: Air line respirator.
 - c. Above 1000 ppm or unknown concentration: Self-contained breathing equipment (Scott Air Pack).
- (2) The Honeywell continuous monitor alarm goes off in the control room when the VCM concentration at any of the 40 monitoring points exceeds 3 ppm, and the field alarm beacons also come on at 3 ppm. Whenever the lights come on, employees are required to either leave the area or put on a respirator. The lead operator will notify the "A" operator upon acknowledging the control room alarm, and will tell him the location and concentration of VCM at the site of the alarm. The "A" operator is then responsible for making sure all personnel that are not wearing proper respiratory equipment clear the affected area. Personnel who have a need to work in an area where a warning light is flashing are responsible for wearing proper respiratory equipment.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

1. Vinyl Chloride Monomer (Continued)

b. Safety (Continued)

identify the source of the leak.

NOTE: A VCM canister mask must be worn as the minimum protection in VCM leak detection operations. If the leak is 10.0 ppm or more as shown on the printout in the control room, an air-line respirator must be used when looking for the leak. The operator will use a properly operating HNU as a guide for what type of respiratory protection to use when checking for the leak in the field. Proper operation of the HNU must be verified before leaving the control room. The HNU can be tested using any organic vapors such as fumes from liquid paper, liquid paper thinner, a cigarette, tobacco, or lighter fluid.

- (4) Air line respirators, disposable coveralls, and rubber gloves must be worn when changing VCM filters or water filters that contain VCM (such as recovery seal water or scrubber water).
- (5) When VCM can be smelled by the human nose, the concentration is generally greater than 200 ppm. Thus, when an operator smells VCM an air line respirator or Scott Air Pack is a minimum requirement for breathing protection.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

1. Vinyl Chloride Monomer (Continued)

b. Safety (Continued)

The operator must evacuate the area and obtain proper respiratory protection before re-entering the area. Continued breathing of high concentrations of VCM can cause dizziness, tingling sensations on various body parts, unconsciousness, and can be fatal. Whenever VCM is detected in high concentrations, a serious fire hazard may be present.

- (6) Air line respirators are required for personnel who are on top of any large blend tank containing slurry and may be necessary on top of the small tanks if high residual slurry has been added and was just put on "aeration."
- (7) VCM canister masks are to be kept in the immediate area of each operating unit. Shift personnel who work in each area are responsible for knowing the location of the masks and for turning them in to their Shift Supervisor if used. Shift Supervisors are then responsible for collecting the used masks in the control room or putting them at the emergency equipment station (throw the canister away) and for notifying Safety personnel about where the canisters came from.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

1. Vinyl Chloride Monomer (Continued)

b. Safety (Continued)

- (8) Protective rubber gloves must be worn when cleaning culls from dump Sweco screens.
- (9) Air line respirators are required when any pipe or line that has contained VCM is broken or blanked (even if the line or vessel has been evacuated and/or steam stripped).
- (10) Special precautions should be taken before going into low lying areas, sewers, or areas like the 500 series activator pit. VCM is heavier than air and will collect in low lying non-aerated places and the oxygen level may not be adequate for life support. A man-hole watch must be present before entering such areas and the pit, sewer, or area to be entered must be sniffed with a HNU meter prior to entry.
- (11) Entry of any vessel or piece of equipment requires an authorized entry permit and checksheet. The Shift Supervisor is the only shift worker who can authorize an entry permit.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

1. Vinyl Chloride Monomer (Continued)

b. Safety (Continued)

(12) Air line respirators which have been used during a shift must be put into the proper receptacle for used respirators whenever they are no longer needed or at the end of a work period.

(13) After a Scott Air Pack is used it must be brought to the emergency equipment station for service. Safety personnel must be notified as soon as the emergency conditions have been corrected so the air pack can be serviced and returned to its normal storage location.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride

Poly Vinyl Chloride resin (PVC) is a dry granular white powder used to make various products including pipe, siding, wire and cable insulation, wall covering, car tops, seat covers, phonograph records, and other plastic products. It is a polymerized hydrocarbon made from vinyl chloride monomer (VCM). PVC is the second largest volume plastic sold in the United States, behind polyethylene. About 6 billion pounds of PVC are produced in the United States yearly and current U.S. plant capacity is 9 billion pounds. PVC resins produced today are very stable and without sunlight and heat will not environmentally degrade for hundreds of years. At elevated temperatures, however, PVC becomes unstable, begins to lose its physical properties, and becomes discolored.

a. Manufacture

PVC is produced by the polymerization of vinyl chloride monomer. Vinyl chloride is placed in the presence of very unstable free radical initiators. These initiators (commonly called catalysts in this plant) break down upon heating, forming free radicals which react with the monomer.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

a. Manufacture (Continued)

The free radicals activate the monomer molecule and it then combines with another monomer molecule, which then combines with another, etc., until very long chains of the monomer are put together or "polymerized". The "length" of the PVC chains (called the molecular weight) determines the viscosity or resin type. The reaction is highly exothermic, which means heat is produced from the reaction. One of the primary factors in producing PVC commercially is control of the heat released by the reaction. The polymerization reaction is ended by adding a killing agent. Any monomer left after killing is then recovered and the PVC is further processed until product specifications are met.

There are four processes used to polymerize VCM to PVC:

(1) Bulk or mass polymerization - VCM and initiator are put into a reactor and a very high purity PVC is produced since there are no other additives. This process is not very prevalent but is gaining in importance because it produces a very uniform particle size resin. The disadvantages of this process are high reactor pressures and reactor heat transfer control.

(2) Solution polymerization - In this process, monomer is polymerized in a solution containing other ingredients.

This is used by only one U. S. manufacturer to

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

a. Manufacture (Continued)

make a copolymer of vinyl acetate and vinyl chloride for a specialized application.

(3) Suspension Polymerization - VCM is suspended in water and suspending agent is used to stabilize the VCM droplets by coating them. The amount of suspending agent and the agitation mode determine the resin particle size. The water surrounding the particles facilitates heat transfer control. Disadvantages of this process are impurities in the resin from the suspending agent and investment in equipment and energy to remove the water from the resin.

(4) Emulsion Polymerization - VCM is polymerized in water using an emulsifying agent. This produces a very fine particle size resin which is then dried for use in plastisols and paints.

The Aberdeen Chemical Plant produces PVC using a batch suspension process in which VCM, water, suspending agent, and initiator are put into a reactor, controlled at between 115-155°F, and approximately 80% of the VCM in the reactor is converted to PVC. The plant reactor area has four 18,000 gallon reactors, four 22,000 gallon reactors and two 32,000 gallon reactors.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

a. Manufacture (Continued)

The PVC leaves the reactors in a slurry form (mixed with water) and most of the water is removed with centrifuges in the dryer area. Further drying occurs by mixing hot air with the resin in either the fluid bed dryer or one of the seven rotary dryers. If there were no VCM or resin losses, every pound of VCM polymerized should produce a pound of PVC. The plant efficiency usually is about 98 percent, meaning that two pounds of resin or VCM are lost for every 100 pounds of VCM brought into the plant (or 20,000 pounds lost out of every million pounds of VCM).

NOTE: If 20,000 pounds of material are lost per day at a typical price of about 20¢ per pound, then the plant would lose \$4,000 per day due to efficiency losses. This emphasizes the importance of minimizing resin and VCM losses in the reactor and dryer areas.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

b. Phases of Reactor and Dryer Operation

The phases of reactor operation at the Aberdeen plant and a brief description of each phase follows:

- (1) Evacuation - Steam ejectors are used to remove most of the air from the reactor. Too much air left in the reactor will cause safety and quality problems. Reactor evacuation requires 5-10 minutes depending on which evacuation system is used and the size of the reactor being evacuated.
- (2) Charge - Water, colloid, and VCM are charged into the reactor using an automatic charge sequencing system. Chain transfer agents, where required, and initiator (catalyst) are charged into the reactor by the field operator. Reactor charge takes about 10-15 minutes.
- (3) Polymerization - This is the time from initiator addition until most of the VCM has been converted to resin. Steam is added to the reactor jacket for the first hour of polymerization to heat the reactor contents to the desired polymerization temperature. At run temperature the reaction begins to generate its own heat as the

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

b. Phases of Reactor and Dryer Operation (Continued)

(3) Polymerization (Continued)

liquid VCM is polymerized to PVC. This heat is removed by cooling water in the reactor jacket and condenser. Reaction times vary depending on the catalyst loading which is dependent on weather and cooling water temperatures. Polymerization usually requires five to seven hours, except in the 32,000 gallon reactors where 3 to 4 hours is usually required.

(4) Recovery - The reaction is killed when it has reached the desired conversion, and then the un-reacted VCM must be removed from the reactor. A compressor-vacuum pump system pulls the vaporized VCM from the reactor while steam is added to the bottom of the reactor. The steam rises through the PVC and water slurry to "strip" the un-reacted VCM from the reaction mass.

Recovery requires about 55-65 minutes for the small reactors and 75-90 minutes for the extra large reactors.

(5) Dump - After recovery is complete, the water and PVC mixture (called "slurry") is gravity drained from the reactor through a screener and is pumped to slurry holding tanks called blend tanks. The dryer operation

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

b. Phases of Reactor and Dryer Operation (Continued)

(5) Dump (Continued)

begins at the slurry blend tanks. Reactor dump requires about 20-25 minutes except in the large reactors where it takes about 30-35 minutes.

(6) Clean and Rinse - After dumping, the reactor shell and condenser are either chemically washed or are rinsed with water according to an established schedule. This cleans the reactor internals which is very important to heat transfer control and to resin quality. Chemical washing and reactor rinsing each require about 20 minutes.

(7) Swirl - The reactor is filled with water which is agitated to further clean the reactor. This is also set up on a schedule according to the reactor cleanliness required to make a specified product. Reactor swirl takes 10-20 minutes depending on whether a half swirl or full swirl is required.

After reactor cleaning is completed, the reactor is ready to be evacuated and charged. The total batch cycle usually requires about 7 to 8 hours.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

b. Phases of Reactor and Dryer Operation (Continued)

The phases of dryer operation at Aberdeen and a brief description of each phase follows:

- (1) Blend Tanks - The blend tank system provides storage for slurry between the reactors and dryers. It consists of tanks and the associated slurry pumps which transfer slurry as needed to feed the centrifuges. Tank agitation is provided by air injected into the bottom of each tank that also strips VCM out of the slurry. In the larger blend tanks, several reactor batches can be dumped and blended together giving a more consistent and uniform product.
- (2) Centrifuges - The dryer centrifuges are fed slurry that contains 60 to 70 percent water and concentrates the slurry into a wet cake, containing 20 to 25 percent water. After removing most of the water, the centrifuge feeds wet cake into either a rotary dryer or the fluid bed dryer. This reduction in water shortens the drying time in the hot air dryers resulting in less energy used.
- (3) Dryers - The plant employs two different types of dryers to dry the wet cake from the centrifuges.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

b. Phases of Reactor and Dryer Operation (Continued)

(3) Dryers (Continued)

Both types mix hot air with the wet cake to dry the wet cake to a product containing 0.15 to 0.25 percent water.

The rotary dryers utilize an exhaust fan that pulls air through a gas-fired burner and through the rotating dryer. The wet cake drops into the dryer from the centrifuge and is dried as it mixes with the hot air and is swept through the dryer. The air and resin are separated in a filter (dust collector) and then the resin is screened to remove any oversize particles before being transferred to the product silos.

The fluid bed dryer has two sections and a common exhaust fan pulls air through the gas-fired burner for each section. Additional heat is provided in the first section by circulating water that is heated by direct steam injection. Wet cake is fed into the first section (backmix section) from the centrifuge where it is "fluidized" and dried to about one percent moisture. It then flows into the second section (plug flow section) where it is dried to product specification. The resin overflows a weir at the fluid bed discharge and drops

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

b. Phases of Reactor and Dryer Operation (Continued)

- (5) Silos - Resin for shipment is loaded from the silos into railcars or trucks, or is bagged. The vinyl department is responsible for bagging operations and the yard department loads the trucks and railcars.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

c. Miscellaneous Raw Materials and Additives

Some of the raw materials and additives used in making PVC in the Aberdeen vinyl department and a brief description of each follows:

- (1) Water - The process water used by the plant is pumped from wells that are on the plant premises. Process water is used as reactor charge water and rinse water, rinse water for process lines, high pressure service water (HPSW) and mechanical seal purge water (MSPW), water for making up methocel and chemical wash solutions, and is used for numerous other plant activities. Well water also feeds the cooling towers which supply reactor and process cooling water. City water is the back-up for the process water systems and is used as needed for process water as the demand for well water exceeds the supply.
- (2) Methocel - The suspending agent or colloid changed into the reactors is a solution of Methocel* and water. Methocel* is a granular white powder that comes into the plant in 50 pound bags. Its chemical name is hydroxypropyl methylcellulose. A 1.5% solution is made up for charging into the reactors.

*Registered Trademark

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

c. Miscellaneous Raw Materials and Additives (Continued)

(2) Methocel (Continued)

The colloid or suspending agent solution is referred to by plant personnel as methocel or PVA, and will be referred to in this manual as methocel. PVA (poly vinyl alcohol) can be used as a suspending agent for VCM polymerization but is not currently used in this plant. The amount of methocel charged into the reactor is one of the biggest factors affecting the resin particle size. Too much methocel will cause small (fine) particles to be formed in the reaction. Not enough methocel will cause large (coarse) particles to be formed. Methocel solution makeup is also very important and very critical for consistently producing good resin particle size.

NOTE: Dust masks must be worn while handling the Methocel* powder. This is to prevent inhalation of the fines (dust) from the Methocel*.

(3) Initiator - The initiator charged in the reactors decomposes at reactor temperature and reacts with the VCM causing the monomer to become reactive and start long chains of polymer (polymerization). Initiators used by the plant are generally peroxydicarbonates and peroxyesters, and come into the plant in one gallon

*Registered Trademark

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

c. Miscellaneous Raw Materials and Additives (Continued)

(3) Initiator (Continued)

plastic bottles. The initiators are very unstable and must be kept below 10°F. Heat or impact can cause the material to decompose rapidly and explode. Plastic disposable gloves must be worn when handling initiator bottles or cases. Initiators are commonly called catalysts by plant personnel and will be hereafter referred to as catalysts in this manual to facilitate better communications.

Catalysts decompose faster or slower according to temperature and usually only one type of catalyst is charged into a reactor. However, some of the resins are made at an "in between" temperature where one type of catalyst is too fast and the next higher type is too slow. Dual catalyst, or two types of catalyst, are charged for these resins and one catalyst controls the "front end" or first few hours of the reaction and the other catalyst controls the "back end" or last few hours of the reaction. Whether a catalyst reacts fast or slow is temperature dependent, for example, L-223 reacts faster the last few hours of polymerization with 5385 resin, but with 5305 resin that is made

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

c. Miscellaneous Raw Materials and Additives (Continued)

at a higher temperature it is a "front end" catalyst, reacting faster the first few hours of polymerization.

- (4) Chain Transfer Agents (CTA) - The use of a chain transfer agent allows low molecular weight (small chain length) PVC to be made at lower temperatures and pressures than are required without the CTA. The CTA reacts with the polymer chain causing it to stop growing before it reaches the normal length. This gives chains that are shorter than normal and results in low molecular weight resins. 5265 and 5305 are made using the chain transfer agent 2-ethylhexaldehyde. It comes into the plant as a clear liquid in 55 gallon drums and has an irritating odor that will not easily wash off of skin or out of clothing, so direct contact with it should be avoided.
- (5) Odorless Mineral Spirits (OMS) - Odorless mineral spirits are charged into reactors with some products to lower the dry time, which is a measure of plasticizer absorption. It comes into the plant in 55 gallon drums and is a clear liquid. Chemically, OMS is a refinery cut of hydrocarbons.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

c. Miscellaneous Raw Materials and Additives (Continued)

- (6) Alpha-methylstyrene (AMS) - AMS is used to kill or terminate the PVC polymerization. It reacts with the reactive growing polymer chains in the reactor and deactivates them, ending the reaction. It is a clear liquid that comes into the plant in 55 gallon drums. It will irritate or burn the skin and should be immediately washed or flushed off of the skin if contacted. Plastic gloves must be used when killing reactors to avoid contact with AMS. The amount of AMS put into the reactor is critical. Some residual AMS is apparently carried over into the recovery system during reactor recovery and stays with the recovered VCM (RVCM) that is charged into subsequent reactor batches. Too much AMS in the RVCM will inhibit or slow down the polymerization and may cause erratic particle size. On the other hand, too little AMS put into a reactor will not entirely kill the reaction and some of the RVCM will still contain reactive monomer molecules which will react in the recovery system, recovered receivers, or in VCM charge lines, causing troublesome polymer buildup problems.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

c. Miscellaneous Raw Materials and Additives (Continued)

- (7) Naugard - Naugard 492 is an antioxidant which is added to the resin to give it improved heat stability. As mentioned previously, PVC degrades and discolors at elevated temperatures which is partially due to impurities in the resin such as catalyst residue. An antioxidant is a material that reacts with the impurities in the resin and prevent resin degradation. Naugard is a very viscous light yellow liquid and comes into the plant in 55 gallon drums. It is chemically a blend of a substitutive phenol and an organic phosphite, and may cause skin irritation if direct contact is not avoided.
- (8) Nitric Oxide (NO) - Nitric Oxide is used as an emergency reactor killing agent. The mechanism of reaction termination is similar to AMS. It is stored in pressurized cylinders and is a yellowish-brown vapor when emitted to atmosphere. NO is very dangerous to breathe and Scott Air Packs must be worn while using it.
- (9) Antifoam (Bubble Breaker) - DF-160 LC is an antifoam that is used in the reactors during recovery to reduce reactor foaming. It is important that the antifoam be

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

c. Miscellaneous Raw Materials and Additives (Continued)

(9) Bubble Breaker (Continued)

be added to every reactor batch to prevent resin carryover into the recovery systems. DF-160-LC is a mixture of various oils and is a light tan colored liquid that comes into the plant in 55 gallon drums.

- (10) Hydroquinone - Hydroquinone is an antioxidant and polymerization inhibitor. It will react with reactive monomer molecules and deactivate them, keeping them from polymerizing in lines and vessels. Hydroquinone is a light tan powder that is made up with water as a 5% solution and added to the recovery system seal water. The powder comes into the plant in 100 pound fiber drums and should be kept dry.

- (11) Calcium Stearate - Calcium stearate is a material used to reduce torque on the bird centrifuges, reduce static on the dried resin, and to increase resin bulk density. Calcium stearate also helps resin customers process the resin easier and is required by customers that make PVC siding.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

B. Poly Vinyl Chloride (Continued)

c. Miscellaneous Raw Materials and Additives (Continued)

(11) Calcium Stearate (Continued)

Chemically, the material is a neutralized dispersion of calcium stearate in water and comes into the plant as a white liquid in 55 gallon drums. Calcium stearate solution will freeze below 40°F and will not go back into solution, so it must be stored in a warm place.

(12) Glycerine - Glycerine is added in the dryer area to some resins to reduce static on the dried resin. Static makes the resin particles repel each other due to electrical charges and the resin will not flow easily. Glycerine comes to the plant in 55 gallon drums as a clear liquid. Its chemical name is glycerol. A 10% solution of glycerine in water is made up by the dryer operators and is sprayed as a fine mist onto the resin as it leaves the rotary dryers.

(13) Caustic - A caustic solution is used to chemically wash the reactors according to a set schedule and procedure. The reactors are then rinsed for an extended period of time and very little if any caustic should remain in the reactor. Caustic is a solution of sodium

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

c. Miscellaneous Raw Materials and Additives (Continued)

(13) Caustic (Continued)

hydroxide (NaOH) which is brought into the plant in bulk as 50% caustic and is diluted to 22% caustic by the compound department. Further dilution may occur in the vinyl chem wash tank prior to reactor cleaning. Caustic is very dangerous and will cause severe burns if it contacts the skin. Caustic will cause coarse batches if it gets into a reactor. It may also increase the pH of the resin to unacceptable levels and cause discoloration (yellowing) of the resin.

d. Resin Quality and Uses

Several types of resins are produced in the Aberdeen Chemical Plant vinyl department. The molecular weight of the resin, which is indicated by the viscosity of the resin in solution, determines the resin type. There are five types produced at the present time. In order of increasing viscosity, they are:

- (1) 5265 - Used for injection molding (pipe fittings, such as valves, couplings, and tees). The low molecular weight (viscosity) gives better and faster flow which allows the molds to be filled more easily.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

- (2) 5305 - Used in injection molding and in calendering, where resin films are made between heated rollers. Examples of calendered PVC include wall covering and plastic wrappers that go around grocery and drug products.
- (3) 5385 - Used for pipe, for PVC siding, and for general extrusion applications.
- (4) 5425 - Used for wire and cable insulation, calendering, and PVC foam products.
- (5) 5465 - Used for wire and cable insulation, vinyl tape, and for various specialty applications.

The middle two numbers of each type of resin indicate the specific viscosity (e.g., 5385 has a specific viscosity of 0.38). The viscosity measured in the plant is inherent viscosity, which is not the same as the specific viscosity.

Most of the PVC made in this plant used to be pipe grade resin. About 40% of all PVC made in the U.S. in 1981 went into PVC pipe. Generally, pipe grade resin (Type III 5385) is much easier to make than Type I resins which must have better quality. The PVC marketplace is becoming more and more diversified as more uses are found for the plastic and the monetary rewards and profits are very appealing in these

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

other markets. However, resins produced for these markets require much stricter quality control and more attention to keeping the resin quality within the quality specifications. Pressure is also being applied by the marketplace as more non-5385 resins are required since there are very few outlets for low quality non-5385 resin.

The most important factor to making good quality resin consistently is for each step of the production process to be done the same way by every operator every time. Each quality parameter is affected by some process variable in the reactors or dryers. It is important for each operator to know how each production step affects resin quality and for operating procedures to be followed consistently. Consistent resin quality is one of the most important factors customers look for as they buy resin and use it to make finished products for the market place.

Each of the resin quality parameters, how it is tested and what process variable(s) affects it is listed below. The resin specification sheet gives the specifications for each resin type (Figure 3 in the Appendix). Some customers are even more specific, and resin specs tighter than the pub-

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

d. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

lished ones must sometimes be met. The spec sheets show the quality specifications for the various types of resin that are prime grade such as type I, type III, BC, and S. BC stands for "Blendable into Compound" and this resin can sometimes be used in the compound department for rigid (dry blend) or flexible (compound) applications. "S" stands for siding which has special specifications for contamination and bulk density. The spec sheet shown in the Appendix does not show 5265 specifications, which are the same as 5305 except for viscosity and bulk density. 5265 must have a 0.66-0.71 inherent viscosity and the bulk density must be 0.538 - 0.634 g/cc.

Most of the quality tests are conducted on dryer "regular" samples, which are samples taken off the dryers by the dryer "A" operator for every reactor batch dumped into the blend tanks. The regular samples show blended results from the blend tanks but will give indications of quality problems according to the trend of each parameter. Corrective action can then be taken to resolve the problem before a result is out of specification.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

- (1) Viscosity - Resin viscosity is a measure of the resin molecular weight. The higher the reactor run temperature the faster the monomer will react, causing shorter chains of polymer and a lower molecular weight (viscosity) resin. Thus, reactor run temperature should be lowered to produce higher viscosity resin and raised to produce lower viscosity resin.

NOTE: The vapor pressure of VCM is dependent on temperature; therefore, the reactor temperature will determine the reactor pressure. Raising the reactor run temperature will raise the run pressure and lowering the run temperature will lower the run pressure. Generally, for each one degree Fahrenheit rise in temperature, there will be a two psig rise in reactor pressure. Relief valves on the small reactors start relieving at 185 psig and at 205 psig on the extra large reactors. These maximum pressures limit the

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(1) Viscosity (Continued)

reactor run temperatures and the viscosity that can be produced in the plant's reactors.

The viscosity of the resin is a measure of how fast it will flow when put in solution. Solutions of shorter chains will flow with less resistance than solutions of longer chains, thus the viscosity of lower molecular weight resins is lower. The Instrument Development Lab puts the resin in solution and measures the solution viscosity in an apparatus called a viscometer. Viscosity specs range from .066 inherent viscosity for 5265 resin to 1.14 inherent viscosity for 5465 resin.

The resin viscosity (molecular weight) is important to the customer because low molecular weight resins process easier and faster, fuse at lower temperatures and are less viscous in the melted state. High molecular weights give the finished article better physical properties such as higher tensile strength, more resistance to cutting, and better impact strength.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(1) Viscosity (Continued)

Resin viscosity is measured daily from the samples taken from the dryers by testing one sample from the dryer regularly for each product dried, and is tested daily on each reactor from the residual samples taken by the reactor "A" operator when the reactor is dumped. In addition, all railcars and many truck shipments are tested for viscosity. Viscosity tests are very sensitive and time consuming. A single sample takes three hours to test for viscosity.

- (2) Particle Size Distribution - Dried resin is put into a set of screens with an antistatic agent, shaken for a given length of time, and then the amount of resin on each screen is weighed. Typically, the specs are that less than 20% of the resin must go through the 140 mesh screen with less than 5% being on the pan (which is under the 200 mesh screen). On 5305 and 5265 resins, 25% is the maximum through the 140 mesh screen, and resins for compound and dry blend can exceed the normal.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(2) Particle Size Distribution (Continued)

specifications as indicated on the spec sheets. The maximum amount on the 40 mesh screen is 0.1% for all resins. Typically, the internal specs are that any result over 10% on the 60 mesh screen (which is under the 40 mesh screen) or over 18% through the 140 mesh screen requires rechecking, resampling, and possible corrective action.

Resin particle size distribution affects compound processing and bulk handling properties. Fine particles produce dusting problems both in bulk handling and in processing. On the other hand, oversize (coarse) particles may not process properly causing gels or fish eyes in the finished product because they do not absorb an equal amount of plasticizer during blending.

Particle size is primarily controlled by the amount of methocel charged into each batch. For this reason, methocel makeup is very important because the methocel

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(2) Particle Size Distribution (Continued)

batch concentration will also affect particle size.

Methocel concentration must be 1.40-1.60% solids when tested according to both the scope test and the oven test in the QC lab. Methocel with less than 1.40% solids should never be charged, as coarse batches may result. Other things which affect particle size distribution are:

(a) Catalyst Loadings and Polymerization Times - Generally, the longer a batch runs the more the chance of it going coarse. Guidelines are set up on each product for how long it can run before killing it (see Polymerization Operating Procedures). Batches with excessive catalyst loadings that are killed early because of temperature or pressure runaway will generally be fine but should be able to be blended off if dumped into the extra large blend tanks (502 or 747).

(b) Amount of RVCN Charged - When a 50% RVCN batch is charged, 5 gallons less methocel should be charged.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(2) Particle Size Distribution (Continued)

When an all fresh charge (NO RVCM) is made, 10 gallons more methocel should be added. This is why it is important that the same amount of RVCM is charged on every charge. 5265 and 5305 resins are charged with no recovered VCM due to its affect on particle size.

(c) Water in the RVCM Charged - This will cause the amount of VCM in the charge to be shorted and a broadened particle size may result that can cause coarse and/or fine batches. Excessive amounts of water in the RVCM receivers will cause coarse batches.

(d) Charge Temperature - The charge temperature is defined as the reactor temperature at the end of the water charge. If the charge temperature is too cold, the particle size distribution tends to "flatten" and the amount on both the coarse and fine ends of the particle size distribution increases. If the charge temperature is too hot, the methocel may come out of solution and a coarse batch may result.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(2) Particle Size Distribution (Continued)

- (e) Heatup Time - Heatup time is defined as the time from the end of charge until the reactor reaches run temperature. Batches with abnormally long heatup times usually have "fine" particle size results, while batches with short heatup times (usually caused by high charge temperatures) may result in coarse batches.
- (f) Impurities in the RVCM - Too much AMS, CTA, or other impurities in the RVCM may cause erratic particle size. 5265 and 5305 resins charged with CTA must be charged with no RVCM due to the affect of the CTA in the RVCM on resin particle size.
- (g) Water to Monomer Ratio - Higher water to monomer ratios (weight of water divided by weight of total VCM charged) give "tighter" particle size distributions (less through the 140 mesh screen and less on the 40 and 60 mesh screens) while lower water to monomer ratios will give "flatter" particle size distributions. This is inversely proportional to increasing productivity as high water to monomer ratios give better quality but low production, and

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(2) Particle Size Distribution (Continued)

lower water to monomer ratios give higher production but the resin has a more spread out particle size distribution.

(h) H over T (H/T) - The height of liquid in the reactor (H) divided by diameter of the reactor (T) is also a controlling factor in particle size distribution. Changing batch size (which changes "H") can therefore affect particle size.

(i) Agitation - Reactor agitation is very important to particle size. This is measured by the power to volume ratio in the reactor. Agitator blade size and configuration will determine the motor horsepower put into the reactor, which is divided by the total liquid volume in gallons to calculate the ratio. Higher power to volume ratios give tighter particle size distribution but involve using more energy to make the resin.

(j) Baffles - Size, configuration, and number of baffles in the reactor will affect resin particle size.

(k) Chem Wash Left in the Reactor - The chem wash (caustic) destroys the effectiveness of the methocel and will cause a batch to go coarse if it is

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(2) Particle Size Distribution (Continued)

left in the reactor. Correct rinsing of the reactor is important to flushing all the chem wash out of the reactor and maintaining consistent particle size.

Resin particle size is tested off the dryers for every batch that is dumped into the blend tanks as a dryer regular sample by the dryer "A" operator. If particle size begins to shift (get finer or coarser), slurry samples off of the reactors may be caught as each reactor is dumped and the slurry can be dried in the lab and tested for particle size.

A new method of testing particle size is being used by the lab using the Leeds and Northrup (L & N) Microtrac Analyzer. This machine, called the "L & N", uses a laser to record the size of resin particles passed through a cell and gives a printout that may be related to screen particle size distribution. The L & N result utilizes three numbers, showing the micron size that 20% of the sample is less than, showing the median particle size (50% micron size), and showing the micron size that

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

80% of the sample if less than. To be within specifications, the 20% value must be greater than 100 microns, (95 microns on 5265 and 5305), the 50% value should be about 140-150 microns, and the 80% value must be less than 240 microns. L & N samples are taken by the reactor "A" operator on each reactor as it dumps, and are analyzed by the lab once per shift and printed out to the vinyl control room.

(3) Bulk Density

Bulk density is the weight of dry resin per some given volume. It can be measured as pounds per cubic foot or as grams per cubic centimeter. The lab pours the resin into a small container with an antistatic agent and weighs the container to give a measure of the bulk density. It is reported in grams per cubic centimeter (to convert g/cc to lb/cu. ft., multiply by 62.4). Conoco resin specs run from 27-39 lb/cu. ft. or 0.438 to 0.624 g/cc, depending on the type of resin.

The shape and particle size distribution of the resin will affect the resin bulk density, which gives a measure of how closely the resin particles will pack

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(3) Bulk Density (Continued)

and how much void space is around the particles. Static charge on the resin will also affect bulk density, making the bulk density low because like charges on the resin repel each other. The bulk density is sometimes an indicator of the resin viscosity, but this may sometimes give misleading results. Low molecular weight resins will generally give high bulk densities.

The bulk density is important to customers because higher bulk densities allow maximum compounding and processing rates. Additives such as calcium stearate are used to make resin bulk densities higher. This is important because of high processing rates required for some uses such as siding. Some customers also require that a fluff test be run. The fluff test gives a measure of how much static charge can be put on the resin. The resin is mixed or "fluffed" in a blender in the lab and then the bulk density is remeasured. The amount of calcium stearate in the resin also affects the results of the fluff test.

Bulk density is sampled on the dryer regular sample

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(3) Bulk Density (Continued)

taken by the dryer "A" operator for every reactor batch that is dumped. Fluff tests are run on every 5385 blend tank every shift on fluff test samples taken by the dryer "A" operator. A low bulk density or fluff test result may require that additional calcium stearate be added to the blend tanks.

- (4) Dry Time - The dry time is a measure of how long it will take a given amount of resin to absorb a given amount of plasticizer. This is important to the customer because it affects the processing time. The more absorbent the resin is, the shorter the dry time. Dry time is measured on a machine in the lab called a Brabender Torque Rheometer using a "sigma" head which mixes the plasticizer and resin. One customer, Southwire, requires a special dry time test that must be run on 5425 resin and that has no numerical testing results. The resin is either "OK", "Marginal", or "Wet", according to how it "cakes" together or flows when mixed with plasticizer with a mixing blade.

The resin dry time is determined by the reactor pressure drop allowed before killing the reactor. As the batch

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

pressure drops, the outside or "crust" of the resin particles contracts and hardens, allowing less plasticizer absorption after longer pressure drops. To lower the dry time, a shorter or small pressure drop is required, and longer or larger pressure drops will give higher dry times. The amount of "back end" catalyst when using dual catalysts also affects dry times because too much "back end" catalyst causes a faster reaction and a faster pressure drop at the end of the batch.

Dry time is sampled by the dryer "A" operator on dryer regular samples which come off of each reactor batch dumped.

- (5) Gels - Gels are resin particles which will not absorb plasticizer. In a finished plastic product they may be observed as small spots or windows. They degrade and discolor more than the surrounding resin because of plasticizer and stabilizer deficiency.

The lab tests for gels by milling out a sheet of plasticizer resin, then observing for "holes" or spots in the sheet over a lighted box. The gel rating is given

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(5) Gels (Continued)

according to how many holes are counted, for example, 1-4 holes is given a 1 gel rating, 5-9 holes is a 2 gel, and 10-13 holes is a 3 gel, etc. A three or less gel rating is required for Type I resin (except on 5265 and 5305 where gels are not counted).

Reactor cleanliness is the main factor affecting gels. Polymer buildup on reactor internals will go through several batches and then "flake off" into a batch being produced and will cause gels.

Reactor chem washing, rinsing, and swirling is used to keep the reactor internals clean. The frequency or length of time on these may need to be increased if gels become a problem. Another problem may be that the reactor and condenser sprayheads are not functioning properly. These are pipes that extend into the reactor and that are designed to evenly spread or "spray" the chem wash or water onto the reactor condenser or walls. The sprayhead pattern can be visually checked through the reactor manway during rinse to verify that the sprayhead is working properly. Resin or impurities

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(5) Gels (Continued)

that are charged into the reactor with raw materials will also cause gels. The charge filters on the raw materials (water, or fresh or recovered VCM) can be changed out, if needed, to prevent gels in the resin.

Resin gels are checked off the dryer on the dryer regular sample taken by the dryer "A" operator. If there is a problem with gels, a gallon slurry sample may be required to be taken by the reactor "A" operator when dumping each reactor to have the lab dry the slurry and check for gels from each specific reactor.

(6) Color - The color of the resin is affected by the heat history of the resin. At elevated temperatures PVC is inherently unstable and will have discoloration, increased melting viscosity, embrittlement, sticking, and loss of HCl (which may damage process equipment). Customers desire resin with good color to reduce their color matching problems and give the finished product consistent outward appearance and color.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(6) Color (Continued)

The lab measures color on a Gardner Colorimeter which gives a "L", "a", and "b" value for the resin sample.

They have the following meanings:

- (a) "L" - White (high value) vs. Gray-Black (low value).
- (b) "a" - Red (high value) vs Green (low value).
- (c) "b" - Yellow (high value) vs. Blue (low value).

High "L" values are desirable and the "a" and "b" values should be between the respective red and green or yellow and blue ends of the ranges. The spec sheet gives the acceptable results for each resin type.

The color of the resin is controlled by reactor stripping conditions when recovering a reactor and by the amount of antioxidant added to the reactor. Naugard is presently used as the antioxidant and is added when killing a reactor, which is just before reactor recovery begins. The operator must be sure that the proper amount of Naugard is added to each batch to keep the color and heat stability within specifications.

Stripping temperature and the length of time the batch is held at high temperatures affects color and heat

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(6) Color (Continued)

stability because of the amount of heat the resin is subjected to. Stripping conditions are set up that will allow the resin to remain within specifications, but the stripping procedures must be closely followed or the batch will become discolored.

The vinyl department normally goes by the "b" color value to determine whether the resin is within specification. Usually, if the "b" value is good, the "L" and "a" value will also be within specification. If the color results are out of specification more Naugard may be added to subsequent batches to give lower color results so that the high color slurry can be blended off in the large blend tanks. The reactor temperature controllers may also need to be checked and any malfunctions repaired by instrument maintenance if color results are high.

Resin color may also be affected by the dryers if the resin is allowed to stay in contact with high temperatures for extended periods. A good example of this is that resin backing up in a dust collector

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

6. Color (Continued)

may become discolored if it is not transferred out or if the heat is not shut off of the dryer promptly. The dryer inlet temperatures must also be watched closely to keep resin color within specification.

Color results are run off the dryers on every dryer regular sample taken by the dryer "A" operator. If the "b" value is too high, further sampling may be required to determine if the slurry from the reactor had a high color or if the dryers caused the bad result. This can be checked by drying a slurry sample in the lab and running the color test. The sample would be taken by the reactor "A" operator when the reactor is dumped.

- (7) Heat Stability - Resin heat stability tests are run by the development lab once per week off of random dryer regular samples from each product produced. A strip of plasticized resin is put into a Metrastat oven and the strip feeds out of the oven, allowing a progressive heating of the strip from one end to the other. This is then compared to standard control resins to determine if heat stability is equivalent to the standard. A heat

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(7) Heat Stability (Continued)

stability value of 3.0 means the tested resin was the same as the control resin. A value of more than 3.0 indicates that heat stability is worse than the control. Values less than 3.0 indicate resin heat stability that is better than the control resin.

Bad heat stability gives resin customers burned products which cannot be reprocessed, and causes the addition of extra heat stabilizers which are expensive and affect the customer's operating cost. The heat stability is affected by steam stripping, but also largely reflects the heat history of the resin, including temperature peaks during polymerization or heat kicks (runaway) at the end of the polymerization time. These problems can usually be controlled by changing the reactor catalyst loadings or by improving heat transfer to the reactor cooling water (i.e., more flow, cooler water, or cleaner condensers).

- (8) Contamination - Contamination in the resin may be any small pieces of foreign matter or particles of burnt resin. These particles will not absorb plasticizer or fuse and will appear as black "specs" in a finished

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(8) Contamination (Continued)

vinyl article. This is objectionable from an appearance standpoint and can also lead to weakening of the finished product. For instance, in wire and cable insulation the burnt resin particle will be highly conductive and may lead to spark failures when the cable is tested.

Contamination is tested every two hours off of each dryer (except on some products where it may be required every hour as specified by the Shift Supervisor) and guidelines are set up for what procedures to take if the contamination level is out of spec. Contamination results are reported as black contamination and brown contamination. The internal specification for brown contamination is a maximum of 100 except on certain customers such as Southwire where brown contamination is more critical (brown contamination maximums are not shown on the spec sheet). The lab tests for contamination by putting a resin sample in a soap solution and the heavier brown and black particles will settle to the bottom and can be counted.

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(8) Contamination (Continued)

Another method of checking the contamination is by spreading a resin sample on a small vibrating trough and counting the contaminated particles as the resin moves down the trough. This test is required for Southwire.

Contamination is usually a measure of dryer cleanliness. The rotary dryers will have some resin particles build up on the baffles and the inlet portion of the dryer and as these discolor and "flake" off, resin contamination is caused.

Going into and cleaning the dryer will usually clear up the contamination. Occasionally the contamination may come from the reactors, which may be determined by running a contamination test on a slurry sample after it is dried in the lab. The source of contamination must then be isolated and the contamination can be stopped. Resin that gets in the chem wash and is left in the reactors is one source of reactor contamination, usually causing brown contamination.

(9) Moisture - Moisture in the resin comes from water that is not removed from the wet cake in the dryers. The

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(9) Moisture (Continued)

maximum moisture specification for all the resins produced is 0.30 weight percent as measured by the Anacon moisture analyzer on a resin sample. The analyzer uses infrared light to determine the moisture content of the resin. Moisture content can also be determined by drying a weighed resin sample in an oven and then reweighing it after completely drying. The internal vinyl department resin moisture spec is changed from season to season. In the winter, the spec must be lowered insure that moisture levels are very low in the resin product.

Excessive moisture in the product causes resin transfer problems in the customer's transfer systems. The moisture in a railcar will tend to migrate to the bottom of the compartment, causing unloading problems because the wet resin will not flow. In winter conditions moisture is an even bigger problem because the resin can freeze and the railcar will not unload. Moisture mixed with the other raw materials when the resin is processed can also cause porosity or various other processing problems

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(9) Moisture (Continued)

in the finished product. Water turns to steam in hot processing equipment causing venting problems, bubbles, and rough surfaces on their finished products.

Moisture in the resin is sampled every two hours off of every dryer that is running. If the result is above a given maximum moisture level, the dryer conditions must be adjusted to make the resin more dry and the resin from the dryer must be resampled in one hour. If a moisture problem continues for more than 4 hours on any dryer, the lead operator must notify the Shift Supervisor and follow his instructions for correcting the problem.

- (10) Residual VCM - The residual VCM maximum on all resins produced is 10 ppm. Residual VCM is tested by the Instrument Development Lab on all shipments and is tested off of the dryers on every 5265 and 5305 dryer regular sample. The specification of 10 ppm is set by industry standards because excessive VCM in the resin may be hazardous to human health and the environment. Excessive VCM in the product can also cause problems

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(10) Residual VCM (Continued)

for the resin customer because when the resin is heated, the VCM may form gaseous bubbles giving impurities in the finished product, and may give off hydrogen chloride acid-gas which can damage process equipment.

The residual VCM content in the resin is controlled by reactor recovery and stripping conditions and by blend tank aeration. The plant has established reactor stripping conditions that will give acceptable amounts of VCM in the slurry that is dumped from the reactors. The EPA has set a limit on the amount of residual VCM that can be contained in the slurry, which must be less than 400 ppm averaged over all the batches dumped in a 24 hour period. Lack of compliance to this regulation could lead to fines or plant shutdown, so stripping according to the established procedures is essential. A sample for residual VCM must be taken off of every batch dumped from the reactors to comply with government regulations.

Lengthy aeration times are necessary in the blend tanks on some resins such as 5265 and 5305 which are harder

I. INTRODUCTION (CONTINUED)

B. Process Information (Continued)

2. Poly Vinyl Chloride (Continued)

d. Resin Quality and Uses (Continued)

(10) Residual VCM (Continued)

to strip. These resins must be dumped into separate blend tanks and aerated for a given length of time prior to drying the slurry so that the 10 ppm residual VCM requirement for the dried resin can be met.

- (11) Volume Resistivity - Volume resistivity tests are run once per month on 5425 and 5465 to check the electrical properties of the resins. The tests are run by the Development Lab and the resins are compared to a previously run control resin. Impurities of any type in the resin and/or poor heat stability can affect resin volume resistivity. Too much or too little additives in the resin will also affect volume resistivity. The volume resistivity is important to electrical customers in wire and cable applications where resin is used to insulate electrical wires and cables.