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INTRODUCTION TO PVC RESIN TECHNOLOGY

Only a small number of polymers with a particularly advantageous combination of properties have found a major place in commerce. Although PVC as a polymer has found a significant position in today's marketplace, this polymer is chemically one of the least stable of the common polymers; and its exploitation came about only through the development of proper technology for handling the resin and the discovery of suitable stabilizers. The factors responsible for the rapid growth of PVC are considered to be:

- low cost
- the ability to be compounded into a wide range of flexible and rigid forms
- good physical, chemical, and weathering properties
- utility and a broad range of large volume application
- processability by a wide variety of techniques

Poly(vinyl chloride) (PVC) was first characterized more than 100 years ago, but did not start to gain commercial importance until the 1930s. One of the earliest applications utilized a vinyl chloride-vinyl acetate copolymer as a coating for the interior of beer cans. The problems caused by its inherently poor thermal heat stability were overcome by the development of suitable stabilizer systems. Progress in PVC technology has involved a complex interaction between resin development, effects of additives, and equipment design, as well as market demands. Today, PVC is the second largest volume thermoplastic used in the U.S. and is the lowest priced of the five leading plastics. This low cost, along with its great versatility, is one of the major reasons for its large share of the plastics market.

PREPARATION OF VINYL CHLORIDE

The phenomenal growth in PVC production has been largely due to the availability of low cost monomer. Current commercial processes for production of vinyl chloride can be placed into two classes. The first class involves the gas phase reaction of acetylene with hydrogen chloride using mercuric chloride or other heavy metal

$$HC{=}CH + HCl \xrightarrow{HgCl_2} CH_2{=}CHCl$$

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halides as catalyst. The advantage of this acetylene process is that no hydrogen chloride is produced. With the second class of processes, ethylene dichloride (EDC) is first produced by the reaction of ethylene with chlorine which is then subsequently pyrolyzed to yield vinyl chloride and hydrogen chloride. Manufacturers employing the ethylene route with the resultant HCl by-product could combine this with the acetylene process in order to utilize the HCl.

$$2HCl + 1/2\ O_2 \longrightarrow Cl_2 + H_2O$$

$$Cl_2 + CH_2{=}CH_2 \longrightarrow CH_2Cl{-}CH_2Cl$$

$$CH_2Cl{-}CH_2Cl \xrightarrow{heat} CH_2{=}CHCl + HCl$$

Our Lake Charles Vinyl Chloride Monomer plant uses the newer oxychlorination process in which hydrogen chloride is oxidized using air or oxygen to produce chlorine in water. The chlorine then reacts with ethylene to give you EDC. This EDC is then pyrolyzed at higher temperatures to give you vinyl chloride plus HCl. The HCl is then reacted with oxygen to convert it back to chlorine.

PROPERTIES OF VINYL CHLORIDE

The following table lists the physical properties of vinyl chloride monomer. Because vinyl chloride is gaseous at normal atmospheric temperatures, it is normally stored under pressure as a liquid.

Color	Colorless, water clear
Odor	Pleasant, sweet
Molecular Weight	62.5
Boiling Point	-13.7°C
Freezing Point	-153.8°C
Density @ -20°C	0.983 g/ml
@ 20°C	0.910 g/ml
Refractive Index D^{15}	1.398
Viscosity @ -20°C	0.274 cps
@ 25°C	0.193 cps
Surface Tension @ 20°C	22.27 dyn/cm
Flash Point, COC	-78°C
Explosive Limits in Air	4-22% by vol.
Vapor Pressure @ 0°C	25.1 psi
@ 20°C	49.2 psi
@ 40°C	87.6 psi
Solubility of Water in VCM	0.11%
Solubility in Water @ 1 atm.	0.5%
Heat of Polymerization	720 BTU/lbs

Vinyl chloride may be stored in ordinary steel cylinders, tank cars, and storage tanks. Although vinyl chloride is stable under normal conditions, nevertheless, over a considerable period of

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time, polymer can build up in storage tanks and pipelines and, therefore, need to be inspected and cleaned at regular intervals. Many problems caused by the presence of impurities in monomer have been largely eliminated. Some of these impurities encountered are acetylene, iron, hydrochloric acid, oxygen, water, acetaldehyde, butadiene, and residual EDC.

Under normal production routine, vinyl chloride is used without further purification. However, even a trace of oxygen in the monomer will react to form peroxides, which may cause difficulties. The initial reaction product appears to be a monomeric material soluble in the vinyl chloride monomer. Subsequent decomposition or rearrangements lead to a polymeric peroxide of limited solubility which can initiate further polymerization. The presence of trace amounts of water and acid in the monomer accelerates this formation of peroxides and polymer. Thus, it is quite necessary to maintain the monomer free of air, water, and acid, both to obtain the best quality resins and to minimize handling difficulties.

CHEMISTRY OF VINYL CHLORIDE POLYMERIZATION

Vinyl chloride monomer (M) is polymerized efficiently in the presence of a free radical source ($I^{\bullet}$). The general reaction scheme and initial kinetics are typical of a free radical chain reaction and is shown below in Figure 1.

- **Initiation** $\quad I\text{-}I \xrightarrow{K_1} 2I\cdot$

  $I\cdot + M \xrightarrow{K_2} IM\cdot$

- **Propagation** $\quad IM\cdot + M_x \xrightarrow{K_3} IM_xM\cdot$

- **Termination**
  - **Chain Transfer To Monomer** $\quad IM_xM\cdot + M \xrightarrow{K_4} IM_xM + M\cdot$
  - **Chain Transfer To Other Chemical** $\quad IM_xM\cdot + C \xrightarrow{K_5} IM_xM + C\cdot$

Figure 1. The chemistry of vinyl chloride polymerization.

The rate of initiation (K_1 and K_2) is dependent on the type and concentration of initiator(s) and the temperature of polymerization. The rate of propagation (polymerization, K_3) is also dependent on initiator(s) and temperature, but it becomes complex because of the presence of the precipitating polymer phase. The molecular weight of the polymerizing PVC chain is dependent on the rate of termination (K_4) by transfer to monomer which is temperature dependent. In addition, molecular weight can also be affected by chain transfer to another chemical (chain transfer agent), and

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this rate of termination (K_5) is dependent on temperature, type, and concentration of chemical additive. Because K_5 is much greater than K_4, the resulting polymer chain will be of lower molecular weight.

Experimental work has shown that the free radical polymerization of vinyl chloride is thought to strongly favor a head-to-tail structure. The low order of crystallinity is attributed to the non-regular positioning of the chlorine and hydrogen atoms about the carbon atom. The degree of crystallinity of commercial PVC is estimated to be about 8-10%. Chain branching is believed to be low. What branching does exist is attributed to free radical transfer from a growing chain to the back of the same or another polymer molecule.

$$-CH_2-\overset{Cl}{CH}-CH_2-\overset{Cl}{CH}-CH_2-\overset{Cl}{CH}-$$

Four types of processes are used for the commercial manufacture of PVC: suspension, mass, emulsion, and solution polymerization. About 83% of all PVC is produced by the suspension process, about 8% by the mass process, about 8% by the emulsion process, and about 1% by the solution process.

SUSPENSION POLYMERIZATION PROCESS

The suspension polymerization process involves the mechanical dispersion of vinyl chloride in an aqueous medium. Suspending agents, or protective colloids, which are water soluble polymers are used to help stabilize the monomer droplets. Monomer soluble initiators, such as peroxypercarbonates, peresters, and peroxides, are used to initiate the polymerization.

Figure 2 illustrates a typical suspension PVC process flow diagram. The process begins with the charging of the process ingredients, as shown in Figure 3. While being agitated, the mixture of these ingredients is brought to the desired polymerization temperature, usually by circulating hot water through the reactor's jacket. Since the polymerization of vinyl chloride is an exothermic reaction, the heat of reaction must be removed in order to maintain the desired polymerization temperature. This heat can be removed by circulating cooling water through the reactor jacket. Refrigerated water and specially designed cooling baffles can improve heat removal. Also, stainless steel-lined carbon steel reactors have an advantage over solid stainless steel or glass-lined reactors. Several producers have developed reflux condenser technology to improve the reactor's heat removal capacity.

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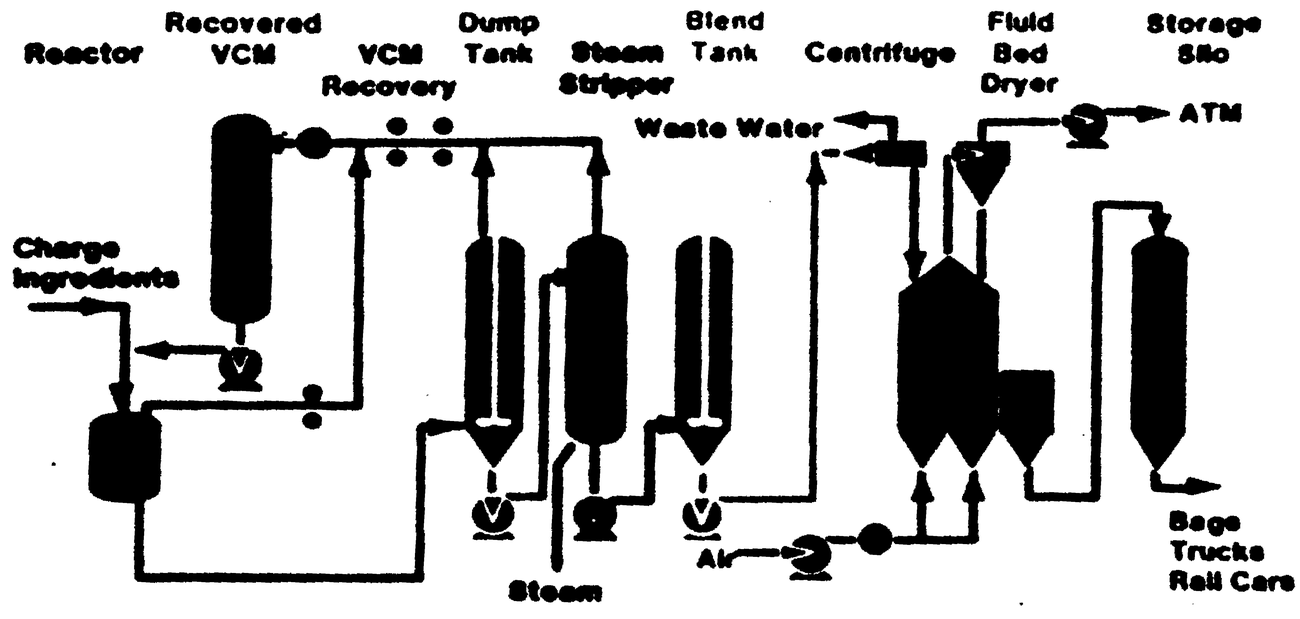

Figure 2. Typical suspension PVC process flow diagram.

Ingredients	Parts By Weight
Vinyl Chloride	100
Process Water	150
Suspending Agents	0.05
Chemicals	0.01-2.0
Initiator	0.05

Figure 3. Typical suspension PVC recipe.

The pressure in the reactor is the sum of the partial pressures of vinyl chloride and water at the polymerization temperature.

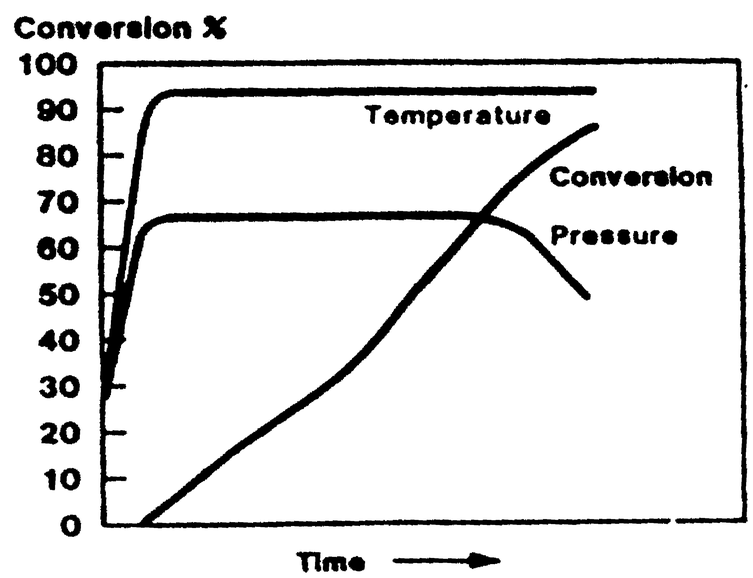

Figure 4. Conversion rate for vinyl chloride polymerization.

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As shown in Figure 4, the temperature and pressure remain constant during polymerization up to about 70% conversion, at which time the reactor pressure begins to drop because of the absence of liquid monomer. The rate of conversion increases throughout the polymerization, but begins to decrease at pressure drop. The polymerization time is dependent upon the amount of initiator charged. The reaction is then terminated at a specific conversion depending on product quality requirements. The unreacted monomer and PVC slurry are then transferred to a dump tank, and the unreacted monomer is degassed into the recovery system and stored in a separate tank to be recycled back into the reactor with the other charge ingredients.

The discovery in 1973 that exposure to vinyl chloride resulted in the increased incidence of a rare form of liver cancer (angiosarcoma) resulted in fundamental changes in the PVC industry. In addition to air emission and water discharge regulations in general, PVC producers must now comply with OSHA employee vinyl chloride exposure standards and the EPA vinyl chloride emission standards. These standards are met by additional monomer recovery in a stripping process where the slurry is heated and stripped of very small amounts of residual vinyl chloride by contact with steam. Continuous steam stripping is carried out in a trayed stripping tower by injecting steam directly into the slurry. This stripping process is carried out in such a way as to minimize heat exposure of the resin to avoid resin degradation.

The reactor is then rinsed with water. In order to meet OSHA and EPA regulations, employee exposure and reactor opening emissions are eliminated by using high-pressure-water cleaning equipment that operates in a closed reactor. Then the reactor's internal surfaces are treated with chemicals to prevent polymer buildup. The reactor is then ready to be recharged. Although the suspension polymerization of vinyl chloride is a batch process, after the reactor is emptied, the downstream processes can be carried out in a continuous manner.

The stripped slurry is then held in a blend tank before being centrifuged to produce a wet cake having a water content of 18-25%. A two-stage fluid bed dryer is used to dry the resin to below 0.3 wt% water. The resin is then stored in silos and is usually shipped in bulk by either rail cars or trucks, or packaged in bags or gaylords.

PVC plants before the 1970s contained many small batch reactors. Large reactor technology allowed the reactor size to be increased from 2,000-10,000 gallons to 15,000-50,000 gallons. These large reactors increased productivity, lowered plant costs, improved product quality and uniformity, and reduced vinyl chloride exposure and emissions. More and more older small reactors have been shut down and replaced with modern large reactors.

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MORPHOLOGY OF PVC

In the suspension polymerization of vinyl chloride, the bulk monomer phase is dispersed in water by vigorous agitation, and the droplets produced are stabilized by the presence of a suspending agent. The correct amount of this suspending agent is used so that the monomer droplets undergo controlled coalescence during polymerization to give rise to an irregularly shaped **grain** having an average particle size of about 150 microns (Figures 5 & 6). The size, shape, and porosity of this grain is very dependent on the type and concentration of the suspending agent used and on the type of agitation (e.g. stirrer speed, agitator type, size and shape of baffles).

Microscopic examination of this PVC grain shows it is composed of an agglomeration of **sub-grains** which are about 40 microns in average size (Figures 7 & 8). These are the stabilized monomer droplets which, during the initial phase of polymerization (about 5-15% conversion), coalesce to form the PVC grain. Further microscopic examination of these sub-grains show they are made up of primary particle **agglomerates** which are about 5 microns in average size (Figure 9). These are formed during the early stages (2-5% conversion) of polymerization by coalescence of **primary particles.** These primary particles are about 0.7 microns in size and are formed at very low conversion (less than 2%).

Within the monomer droplet suspended in the water, the first aggregate of polymer chains that precipitate, about 50 in number, form the smallest PVC species identified so far, the **microdomain,** which is about 0.02 microns in size. These microdomains coalesce to form a **domain.** A domain is the nucleus of the primary particle, contains about 1,000 microdomains, is about 0.2 microns in size, and is only observed at very low conversions (less than 2%). This term is only used to describe the 0.2 micron species because it immediately starts to grow to become the primary particle. The microdomain and domain are not features of PVC morphology at high conversions since a growth of these species with conversion obliterates all memory of them, leaving only the observable primary particle.

From this discussion, it can be shown that the formation of suspension PVC takes place through a series of interconnected aggregation steps which can be represented by the scheme in Figure 11.

Suspension PVC particles usually possess a pericellular "skin" or "membrane" which extends almost continuously over the entire outer surface of the grain. This skin is formed during the early stages of polymerization (less than 5% conversion) and has been shown to be a copolymer of vinyl chloride and the suspending agent(s). Since this skin is semi-permeable, it does contribute to the overall porosity of the resin, but not nearly to the extent as does the primary particle agglomerate.

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Several different types of PVC grains can be obtained during the suspension polymerization process. The most desirable grain has a semi-permeable skin and good porosity where the pores are open and evenly distributed throughout the grain. A less desirable grain contains closed pores which are not connected to the skin. The least desirable grain is the solid grain containing little or no porosity. The production of these different types of grains is mainly determined by the choice of suspending agents.

REACTOR PROCESS VARIABLES AFFECTING THE PROPERTIES OF SUSPENSION PVC

Molecular Weight

The various different grades of commercial PVC are mainly determined by their molecular weight. In the absence of other active chemicals, the molecular weight of PVC is almost entirely determined by the polymerization temperature; the higher the polymerization temperature, the lower the molecular weight.

In the presence of chain transfer agents, the molecular weight is lowered depending on the type and concentration of agent. Thus, low molecular weight resin can be produced at lower polymerization temperatures using chain transfer agents. In the opposite manner, the use of chain extending agents will allow the production of high molecular weight resins at higher polymerization temperatures.

Particle Size

Particle size is important for various PVC applications. For rigid extrusion, a more coarse resin is desired so that all of the grains are well fused in the extruder and no unfused fines are left to cause weaknesses in the final product. For plasticized applications (calendering, blown film), a finer resin is preferred so that there are no large unfused grains which will cause imperfections in the finished product.

Within a given reactor with a given agitation system, the particle size of PVC is dependent upon the type(s) and concentration(s) of the suspending agent(s); the higher the concentration of suspending agent(s), the finer the resin. Since the PVC grains are a distribution of sizes, particle size is usually described as an average particle size and the broadness (or narrowness) of the distribution is described as the coefficient of variation (the standard deviation divided by the average particle size); the smaller the coefficient of variation, the more narrow the particle size. Particle size can also be expressed as the percent through a set of standard mesh screens (ASTM test method D-1705-82).

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Porosity

The porosity of PVC is most important in controlling not only the absorption of plasticizers but also the desorption of vinyl chloride during the recovery/steam stripping process. A good understanding of the mechanism for the development of porosity in PVC is necessary to insure good quality resin. The various grades of PVC can be further divided into porous (for flexible applications) and non-porous (for rigid applications) resins.

The process of plasticizer absorption is generally believed to occur by a diffusion mechanism in which two separate mechanisms exist. The first process is a very rapid capillary filling of the intergrain (pores between the resin grains) and intragrain (pores within the resin grains) pores. The second process involves the diffusion of the plasticizer molecules into the molecular PVC chains. This second process is the rate-determining step in the absorption of plasticizer and is controlled by the size of the sorbing sphere, the primary particle agglomerate. Since it is known that one way to increase the absorption rate of a fluid into a solid is to reduce the size of the solid particle, it can be concluded that as the diameter of the agglomerate increases, the porosity of the resin decreases. Thus, controlling the size of the agglomerate is the important step in establishing the porosity of a PVC resin.

There are several process variables that affect the porosity of PVC. These are as follows:

Polymerization Temperature - For a given set of polymerization conditions, reaction temperature has a very large effect on porosity; the higher the reaction temperature, the lower the porosity. This is because the agglomerate size increases as the reaction temperature increases.

Conversion - Conversion is also found to have a very large effect on resin porosity; the higher the conversion, the lower the porosity. Again, this is due to the agglomerate size. Resins polymerized to a higher conversion have larger agglomerates than those polymerized to a lower conversion.

Agitation System - Agitation is of fundamental importance in the PVC suspension process. Together with the suspending agent system, it determines the particle size of the finished product and other properties, such as porosity. Generally, the more power (e.g. higher speed) the agitation system puts into the reaction mixture, the higher the porosity. Also, different agitator blades and baffles can affect resin porosity.

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Suspending Agent System - Given a particular type of agitation system, a particular polymerization temperature, and a reasonable conversion (75-85%), the suspending agent system has a great influence on resin porosity. The **primary suspending agent** is usually a water soluble organic polymer, such as a polyvinyl alcohol, a substituted cellulose, or a mixture of the two. Generally, the lower the surface tension of the suspending agent(s), the higher the porosity of the resin.

The primary suspending agents are chosen not only for their ability to control particle size but also for their ability to produce porous resin. However, the degree of surface activity for these chemicals is limited, thus additional **secondary suspending agents** are used to further increase porosity. A variety of materials can be used, such as nonionic or anionic surfactants and low molecular weight polyvinyl alcohols of very low degree of hydrolysis. These secondary suspending agents increase porosity by either lowering the surface tension between the vinyl chloride and the aqueous phase or by stabilizing the primary particle agglomerates during polymerization.

There are several ways of measuring and expressing the porosity of PVC. Among these are the following:

Porosity - This is measured by mercury intrusion and expressed as cc/g (ASTM D-2873-70). Also other descriptions of the porosity of the resin are available from this single measurement: void volume (cc/g), a measurement of the intergrain pores (volume between the resin grains); average pore size (microns), a measurement of the diameter of the pores within the grain, and distribution of pore sizes.

Cold Plasticizer Absorption (CPA) - The amount (%) of plasticizer that a resin will absorb at room temperature (ASTM D-3367-75). This is a measurement of both inter- and intragrain porosity and should be about the same value as the mercury intrusion porosity measurement.

Brabender Dry Time - Under a given set of test conditions, this measures the time (min) that it takes a given amount of resin to fully absorb (giving a dry powder) a given amount of a particular plasticizer at an elevated temperature (about 80° C) using a torque rheometer for mixing (ASTM D-2396-79). This is primarily a measure of the filling of the inter- and intra-grain pores and the rate of hot plasticizer absorption (diffusion into the resin molecules), but measures, to some extent, the capacity of the resin for plasticizer.

Gel Test - In this test, a plasticized milled sheet is prepared under given conditions and the number of gels (fisheyes, hard particles, glassies) are counted in a given area (ASTM

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D-3596-77). A gel is a PVC grain which does not absorb plasticizer at the same rate as the other grains. This is usually due to the inaccessibility of the pores to the plasticizer. The number of gels will decrease to a constant number as the length of time on the mill increases.

Microscopic Examination - A simple technique for qualitatively examining the porosity of PVC is placing the resin on a microscope slide and immersing it in a liquid having a refractive index similar to PVC and, after equilibrium, viewing it at low magnification (100x) with transmitted light. The internal morphology of each grain can clearly be observed.

Bulk Density

Generally, the bulk density (g/cc) of PVC (ASTM D-1895-69) is in opposition to its porosity; as porosity decreases, bulk density increases. Thus, all of the process variables that affect porosity also affect bulk density. The most important process variable is probably the choice of the suspending agent system.

For rigid extrusion applications, the rate of output of the extruder (especially twin-screw extruders) is directly dependent on the bulk density of the dryblend which feeds the extruder. Thus, it is important that this dryblend have a high bulk density.

Electrical Properties

For wire and cable applications, the electrical conductance of the PVC resin is an important property. PVC must be produced which has extremely low conductivity (or very high resistivity). Generally, this is done by using deionized (DI) water as the process water and not contaminating the resin with non-DI water or resin made with non-DI water.

STEAM STRIPPING AND DRYING PROCESS VARIABLES AFFECTING THE PROPERTIES OF SUSPENSION PVC

Color

The color of PVC resin is usually measured by a colorimeter and is described by a L-, a-, and b-value. The L-value is a measure of its whiteness; the a-value is a measure of its pinkness; and, the b-value is a measure of its yellowness. In order to assure a white, non-pink, non-yellow resin, antioxidants and killing agents (to prevent further polymerization at high temperatures) can be added to the slurry before steam stripping and drying to prevent degradation.

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Heat Stability

Good heat stability of PVC is maintained by the proper care given to the steam stripping and drying processes. Too high a temperature or too long a residence time will decrease resin heat stability. Again, the addition of antioxidants and killing agents will aid in maintaining good heat stability.

Heat stability is usually measured in these three ways:

Static Oven Heat Stability - PVC is milled into a given plasticized compound and subjected to a given temperature in an air-circulating oven. Coupons (or chips) are removed from the oven over a given period of time until the milled sheet has degraded to black (ASTM D-2115-67). The resins are compared to a standard resin of the same molecular weight and similar quality. If the time-to-black is less than the standard resin, then the heat stability of that resin is poor.

Dynamic Mill Heat Stability - PVC is mixed into a given rigid dryblend and placed on a two-roll mill at a given speed and temperature. Coupons (or chips) are removed from the mill at given intervals of time until it turns dark or sticks to the mill. Again, the resins are compared to a standard and judged to be less stable if the milled sheet turns dark or sticks to the mill before the standard.

Brabender Heat Stability - PVC is mixed into a rigid dryblend and placed in a torque rheometer at a given speed and temperature. The amount of time it takes from fusion to degradation is a measure of its heat stability.

Percent Volatiles and Contamination

Both of these properties are mainly dependent on the proper use of the dryer. If the dryer temperature is too low, then an excess of volatiles will be present in the resin: if the dryer temperature is too high, the amount of contamination (dark specks which are usually burnt resin) will be too high. Also, contamination can be caused by a dirty dryer.

Static

Even if the PVC is dried to the proper dryness, there may be static built up on the resin which will cause poor flow properties. The static can be eliminated or reduced in the drying process by the addition of an antistatic agent (e.g., dry steam).

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MASS POLYMERIZATION PROCESS

Elimination of the requirements for suspending agents and other additives prompted considerable effort to develop a suitable commercial process to polymerize vinyl chloride by a mass process. Extensive research efforts were undertaken during the 1940s and 1950s to develop a successful mass polymerization process because of its potential for both cost savings (reduced raw material usage and elimination of the centrifuging and drying operations) and product improvement (reduction of chemical residues and elimination of the pericellular skin). Initial attempts followed the fairly conventional approaches of using a single reactor. A major breakthrough came in 1963 when Pechiney-Saint Gobain (later to become a part of Rhone-Poulenc and now a part of Chloe Chemie) developed a two-stage process. Licensees are now producing PVC by this patented process in Europe, Japan, United States, and other countries.

The first reactor is vertical and fitted with a high intensity turbine-type agitator to give vigorous agitation to obtain the desired particle-size distribution. Only monomer and initiator are charged, and polymerization proceeds to about 10% conversion at which point the formed particles are dispersed in the bulk of the liquid monomer as a sort of PVC slush in monomer. A monomer soluble initiator is used, and the particle size is controlled by the speed of the agitation. Then the free-flowing mass is transferred to a horizontal reactor fitted with a "ribbon blender"-type agitator. More monomer and initiator are added and the polymerization continues being slowly stirred. At about 20% conversion, all of the liquid unpolymerized monomer is absorbed into the porous structure of the grains leaving only a dry powder. The second reactor is about twice the size of the first which feeds up to five second-stage reactors. The heat of polymerization is removed through reflux condensers, and polymerization continues to about 70-80% conversion. The unreacted monomer is recovered, followed by high-temperature stripping; and the reactor is emptied by means of an air flow. The product is transferred to a large classification system which screens out the oversize particles (about 3-8% of the yield) and then is transferred to silos without the need for centrifuging or drying.

Continuous updating of the process has occurred with a progressive increase in reactor size. A very significant development has recently occurred with the introduction of a vertical second-stage reactor which is easier to empty and clean, produces less oversize particles, and gives higher-quality product.

PROPERTIES OF MASS PVC

PVC grains produced in the mass process are very round and uniform in nature. They have the same morphology as suspension PVC grains

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except for the semi-permeable skin. They have an average particle size about the same as suspension PVC, but have a very narrow particle-size distribution. Since there is no suspending agent present, they do not have a pericellular skin, as seen in Figure 10. They have about the same porosity as suspension PVC and the same reaction variables (except suspending agent) affect porosity (e.g. polymerization temperature, conversion, agitation). Chemicals can be added to increase porosity and also to improve heat stability.

A very positive feature of mass PVC, especially in rigid extrusion applications, is its high bulk density resulting in a high dryblend bulk density which gives high extrusion rates. In the U. S., most of the mass resin is used in rigid applications.

Mass PVC is very similar to suspension PVC, and they compete in almost the same application areas; however, they are not compatible. Mixing the two leads to powder-flow problems. Thus, they must be used separately and can not be mixed in the same storage silos.

EMULSION POLYMERIZATION

As in suspension polymerization, emulsion polymerization involves the dispersion of vinyl chloride in an aqueous medium. The most important characteristics of an emulsion process as distinguished from suspension polymerization are the use of wetting agents or soaps as emulsifying agents and a water-soluble initiator. Agitation, though necessary, is not as important as it is in a suspension process since the soap is present to maintain an emulsion or latex. Protective colloids are usually used to ensure latex stability. The PVC particles obtained by the emulsion technique are about one micron in diameter, which is about 100 times smaller than those made in the usual suspension process. As in a suspension process, there is a distribution of particle sizes. Also, as in the suspension polymerization technology, the amount of emulsifier will affect the final size of the latex particles.

Emulsion polymerization may be described in the following manner: At the concentration employed, most of the soap exists in the form of micells. These tiny micells serve to stabilize a portion of the vinyl chloride which is only slightly soluble in the water. The remainder of the monomer exists as small droplets. A free radical generated from the water-soluble initiator enters the micell, meeting a monomer-rich environment; and a rapid polymerization takes place on a small scale. Polymerization, therefore, takes place primarily in the monomer solubilized in the soap micells rather than in the dispersed droplets of monomer because the free radical formed by the initiator goes into these micells. As polymer forms, the monomer in the micells is replenished by migration from the droplets; thus, the emulsion polymerization can be described as taking place in the water phase rather than in the

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monomer-droplet phase. As these micells grow and the further polymer is produced, these small particles are then protected by the soap used for the polymerization. When the polymerization is complete, which is usually at about 30 percent solids, the residual monomer is removed, and the latex is generally spray-dried to give a fine powder which is packaged.

SOLUTION POLYMERIZATION

The Union Carbide Corporation was responsible for the development of solution polymerization techniques for vinyl chloride/vinyl acetate copolymers. The methods employed produce highly uniform copolymers of various molecular weights. Applications are mainly solution coating resins where the high quality and uniformity justify the higher manuafacturing cost.

Polymerization is carried out in solvents in which the polymer is insoluble, resulting in precipitation of the resin during polymerization. These copolymers do not contain suspending agents and are also free of homopolymer impurities.

COPOLYMERIZATION

In the copolymerization of two monomers, either monomer can add to itself or the other monomer present. The composition of the copolymer obtained from a specific mixture of monomers is determined by the two reactivity ratios of the corresponding monomers. The polymer thus formed at any instant will be different from the monomer mixture. Where the reactivity ratios of each monomer are both less than one, the polymer tends to alternate. If one of the reactivity ratios is greater than 1, and the other reactivity ratio is less than 1, the polymer will be richer in monomer of the reactivity ratio greater than 1. To prevent formation of a polymer with a wide distribution of composition, it is generally necessary to add the more reactive monomer during the course of the polymerization.

The limitations of PVC, as recognized early in its development, led to efforts for modification by copolymerization. Improvements were required in heat stability, melt viscosity, solubility, and processing temperature. Copolymers have thus become an important part of the total consumption PVC. The chloride-vinyl acetate copolymer predominates as the most useful copolymer of vinyl-chloride, and its applications include coatings, floor coverings, and phonograph records. The vinyl acetate content of most commercial copolymer ranges from 1/2 to 15 percent. The greatest flexibility in solubility is obtained at the higher levels. The major applications for the vinyl chloride/vinyl acetate copolymers are those in which low melt viscosity, low processing temperatures, freedom from external plasticizers, and solubility are required.

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The reduction in melt viscosity and increased flexibility are attributed to interference by the bulky acetate groups with intermolecular associations. Copolymerization with vinyl acetate reduces tensile strength, heat distortion temperature, chemical resistance, abrasive resistance, and heat stability. Another important group of copolymers is that formed by the copolymerization of vinyl chloride with olefins. The introduction by Air Products of a vinyl chloride-propylene copolymer is directed towards improved processing characteristics, permitting higher production rates and a lower processing temperature. The reduced processing temperature allows lower stabilizer requirements and permits less expensive nontoxic stabilizers for application, such as blow-molded bottles. The propylene content in this copolymer is about 3 to 5 percent. These copolymers have been approved by the FDA for food applications and may be used for packaging at temperatures up to 150°F.

Another modified PVC which is not strictly a copolymer is chlorinated PVC. An early attempt to change the chemical structure of PVC to improve processibility, solubility, and heat stability was through chlorination. Chlorinated PVC is obtained by chlorinating PVC particles in a water suspension. A patent was issued to B. F. Goodrich describing this process.

REFERENCES

Since this is only meant to be an introduction to PVC resin technology, a complete bibliography is not included. If the reader is interested in further pursuing this subject matter, then the following references will be very useful and current. If the reader wishes to delve even deeper into the literature, these books have many more references than what would have been found here.

R. H. Burgess, **Manufacturing and Processing of PVC,** MacMillan Publishing Co., Inc., 1982.

G. Butters, **Particulate Nature of PVC, Formation, Structure and Processing,** Applied Science Publishers, Ltd., 1982.

W. V. Titow, **PVC Technology, Fourth Edition,** Elsevier Applied Science Publishers, 1984.

VAB.0001130517

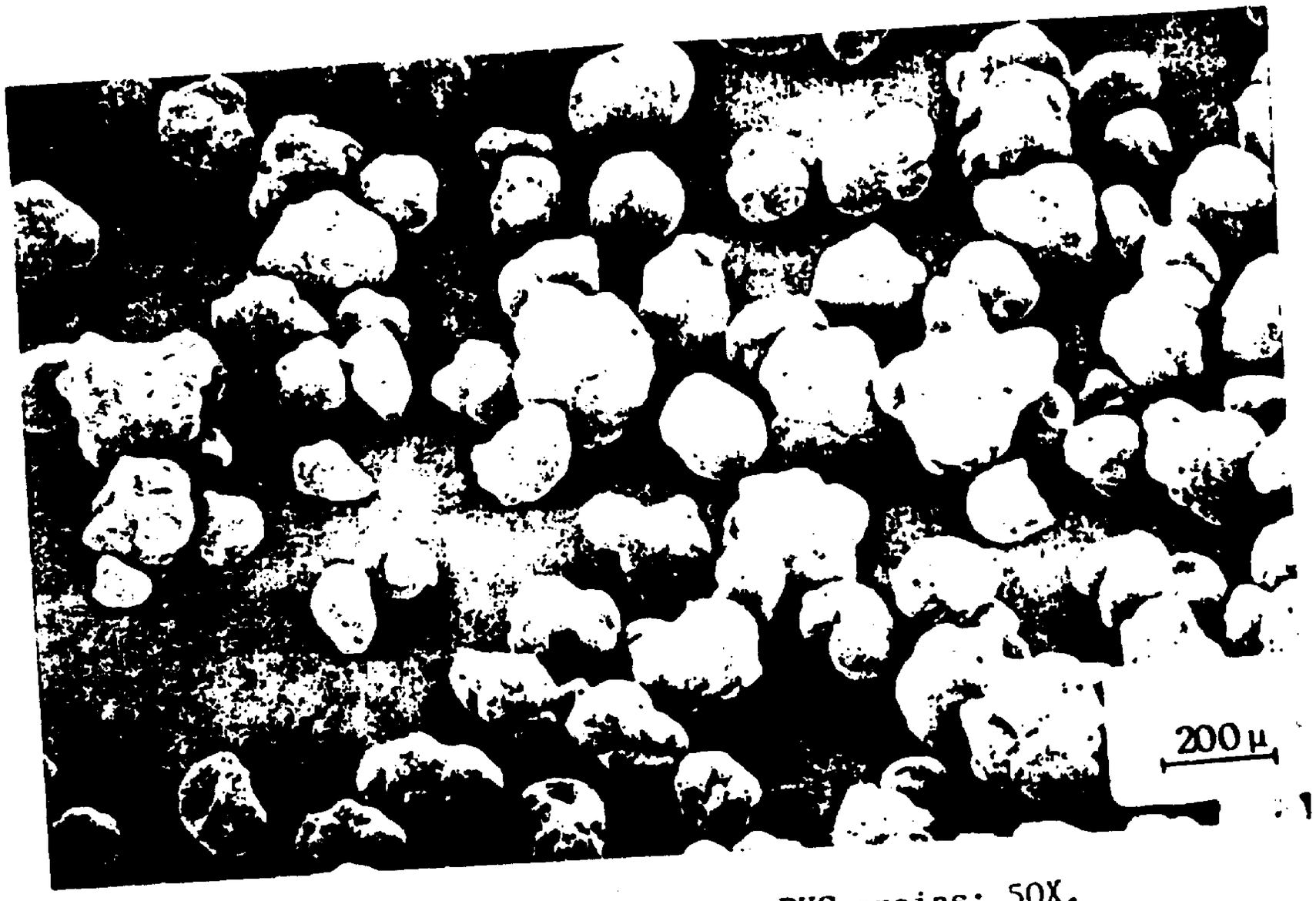

Figure 5. Suspension PVC grains: 50X.

Figure 6. Suspension PVC grains: 250X.

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Figure 7. Suspension PVC grain: 800X.

Figure 8. Interior structure of a suspension PVC grain: 800X

VAB.0001130519

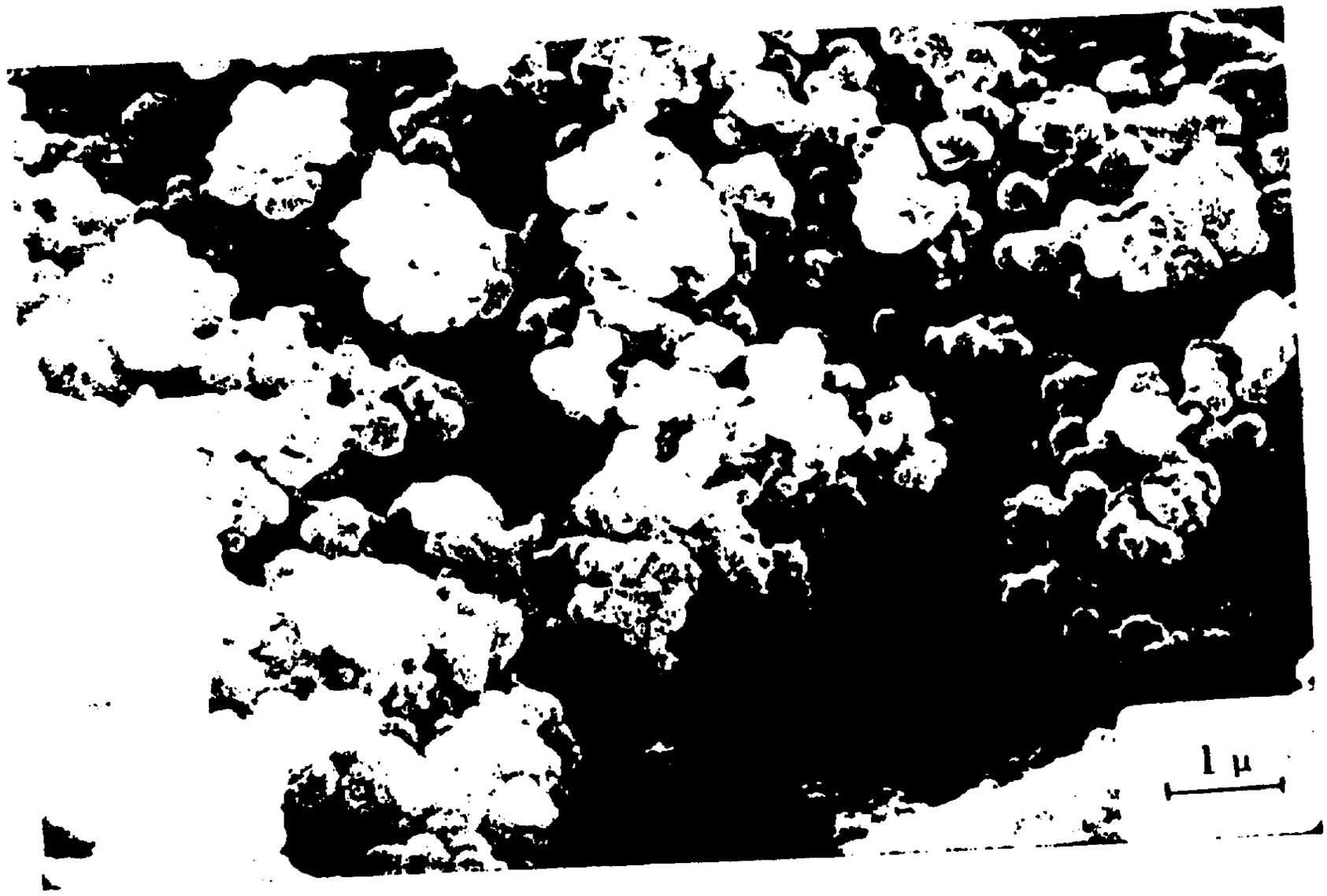

Figure 9. Interior structure of suspension PVC grain: 10,000X

Figure 10. Mass PVC grains: 250X

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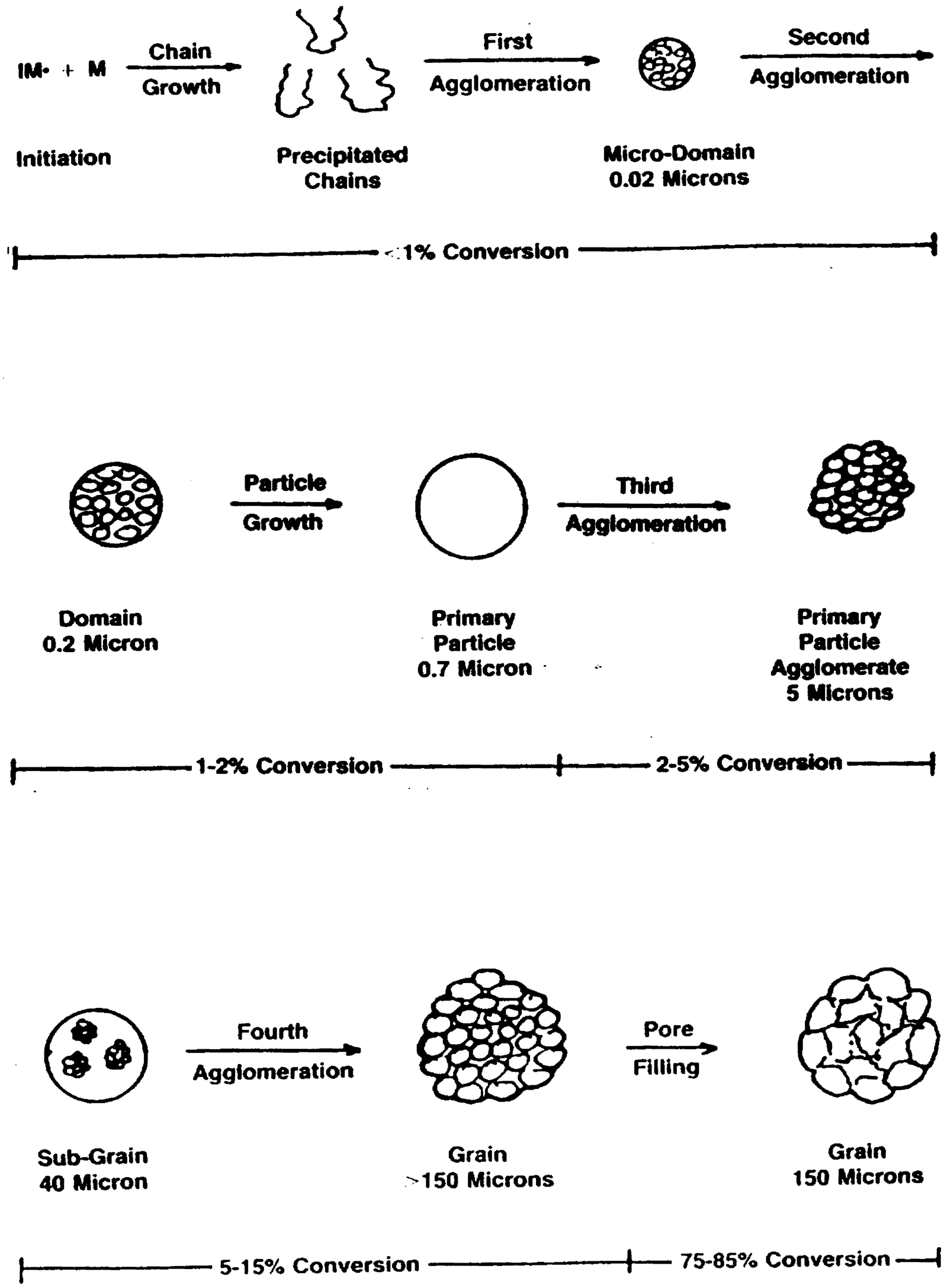

Figure 11. Schematic representation of the formation of suspension PVC

Aberdeen Class - RBQ

A

PVC IN-DEPTH RESIN TRAINING SCHEDULE

WEDNESDAY, OCTOBER 14, 1987
ABERDEEN, MS

7:30 Welcome & Introduction

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12:00 Lunch

1:00 Resin Morphology

1:30 Effect of Process Variables on Resin Properties

2:30 Break

2:45 Research Projects

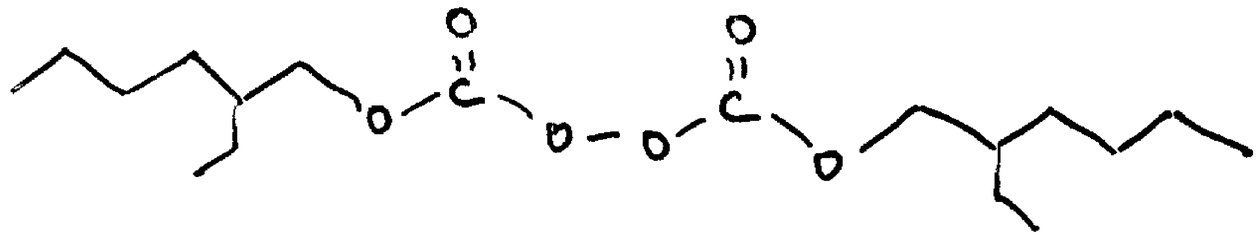
1. VCM Absorption
2. Hard Particles
3. CTA's
4. IR

4:00 Adjourn

A

INITIATORS

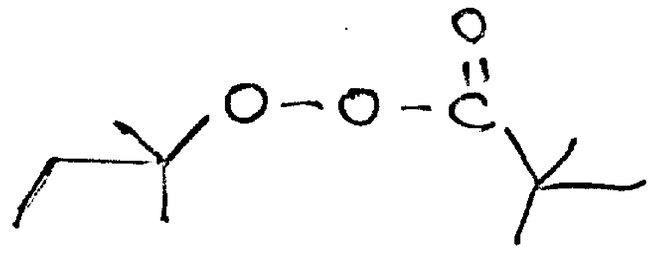
L-223
840M



5535
(5265)
5415
5465

Di-2-Ethylhexylperoxy dicarbonate

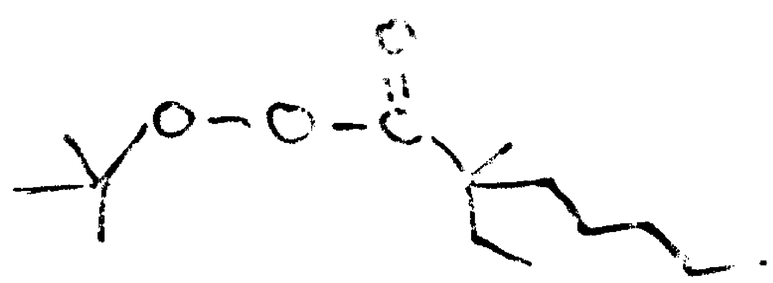
L-554



5265
5305

t-amyl peroxy pivalate

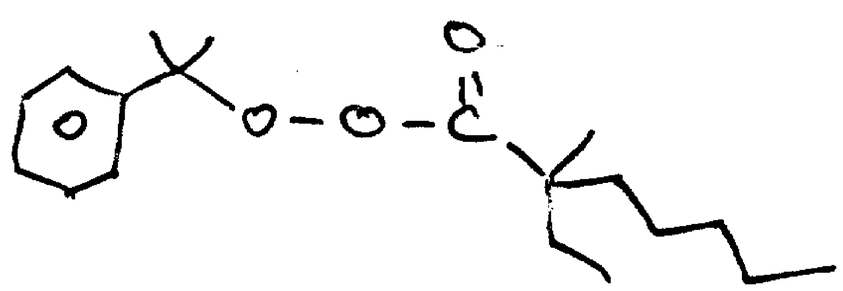
L-10



5305
5265

t-butyl peroxyneodecanoate

L-188
E-939



5415
5465

α-cumyl peroxy neodecanoate

To _____

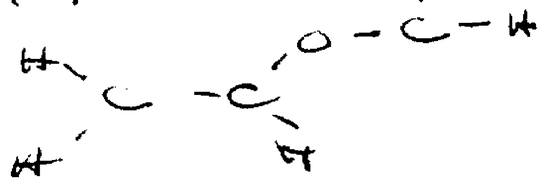
From _____

Calculation Sheet

VISTA

A

Vinyl Acetate



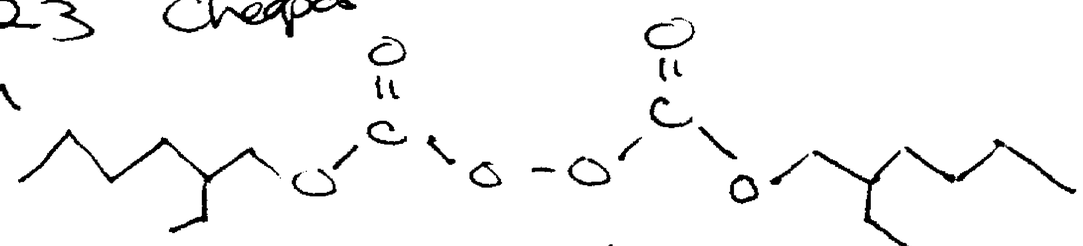
used in conjuction w/ PVC

Records copolymer of vinyl acetate and PVC

Back End Init

L-223 Cheapest

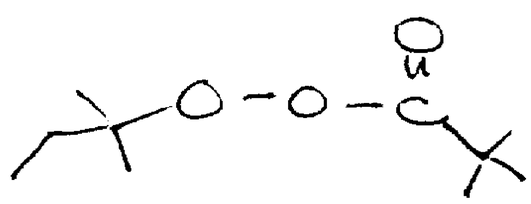
840-M



Di-2-Ethylhexyl peroxy dicarbonate

5385
5265
5415
5465
dual

L--554

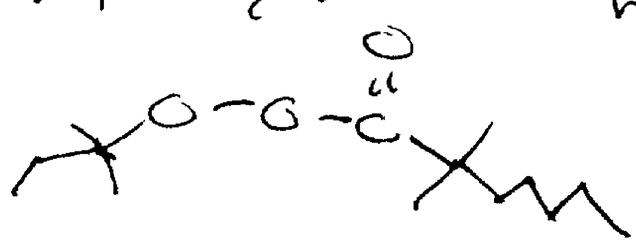


t-amylperoxy-pivalate

t-amylperoxy- pivalate 5265 5305

high temp. initiator, most stable hottest initiator needs high temp to break down

--10



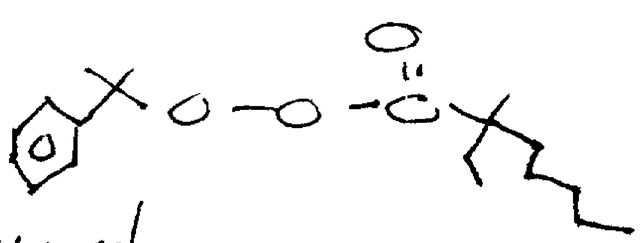
t-butyl peroxyneodecanoate

5305
5265 dual

Front end Initiator

L-188

E-939



α cumyl

5415, 5465
coolest initiator

5265 5305

L.-554

L.-223

Made By _____

Date _____

Page _____ of _____

V3-20G-S

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Calculation Sheet

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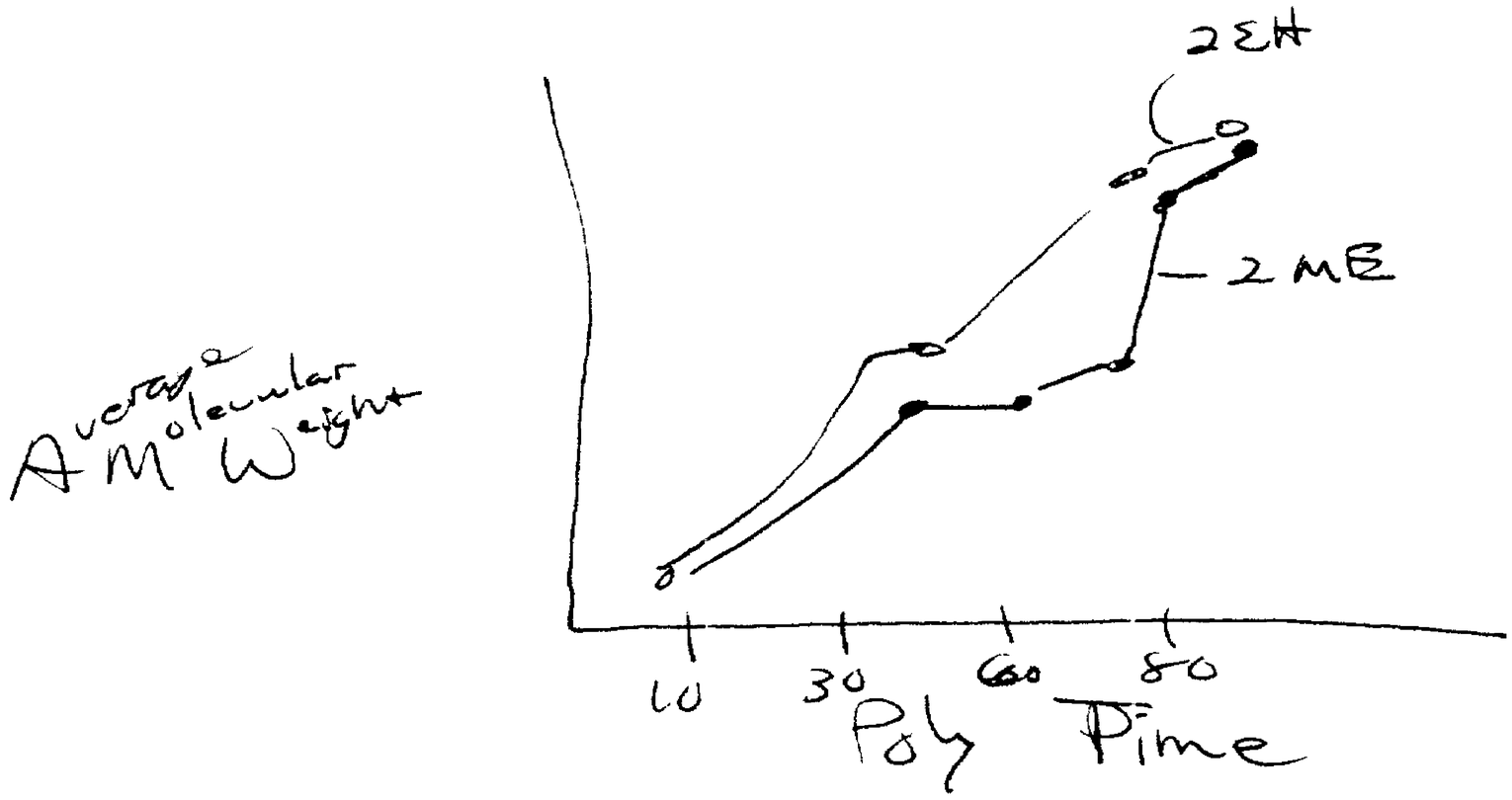

— Membrane Technology

Wastewater Treating

Removal of oils/plast. from wastewater

Temp	150	150	124	127	119	134	150
I.V	0.74	0.74	1.04	1.02	1.19	.92	.66

— Recipes

	5305		5415		5465	5385	5265
	old	New	Old	New			
Anti-Oxidant BHT							
Sonox	*	*	*	*	*	*	*
SA F2-50	*	*	*	*	*	*	*
C.H-20		*					
H 72.5				*			
Post A. 72.5				*			
Initiator							
L-654	*	*					*
L 223			*	*	*	*	*
L-10		*					
L-188			*	*	*		
Buffer (STP)		(*) no longer used		(*)			
CTA	*						*
Il Agent Ans	*		*	*	*	*	*
BPA		*					
Fat Enhancer		* .02PHM		(*)			
Anti bact Cost		*		*		*	
CMS		*			*		*

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Date _____

Page (S202) of _____

V3-2013-S

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Title _____

VAB.0001130526

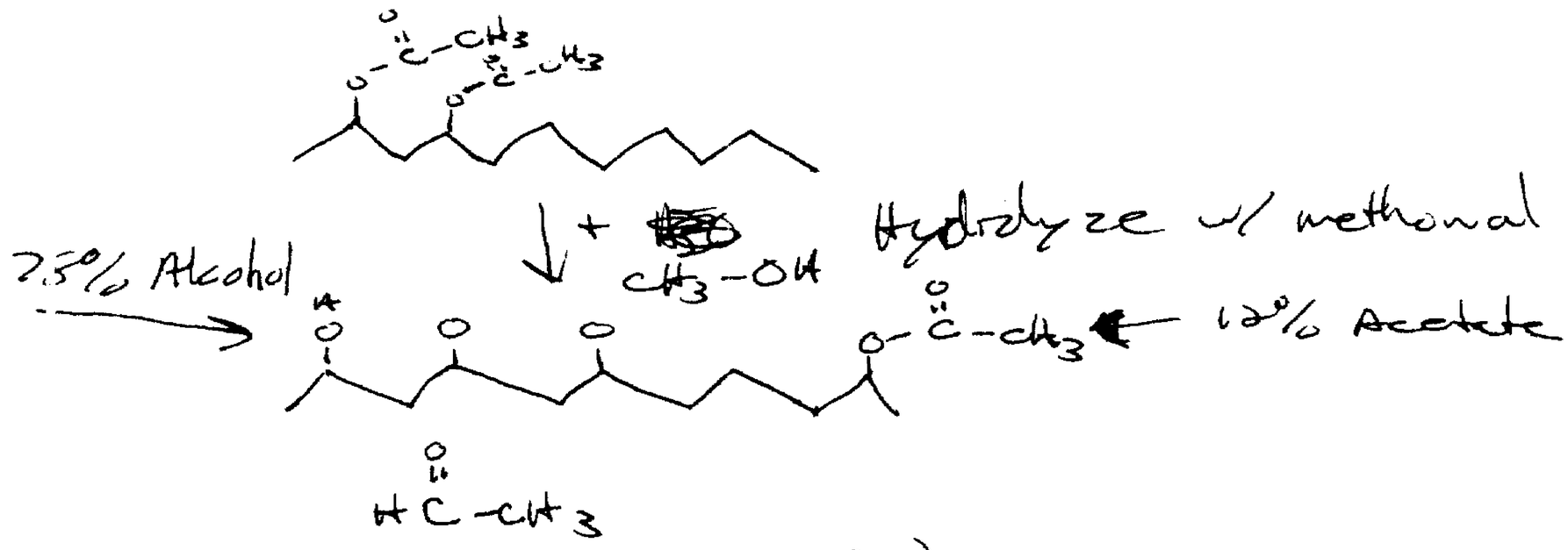
To _____

From _____

Calculation Sheet

VISTA A

Polyvinyl Alcohol (Acetate)

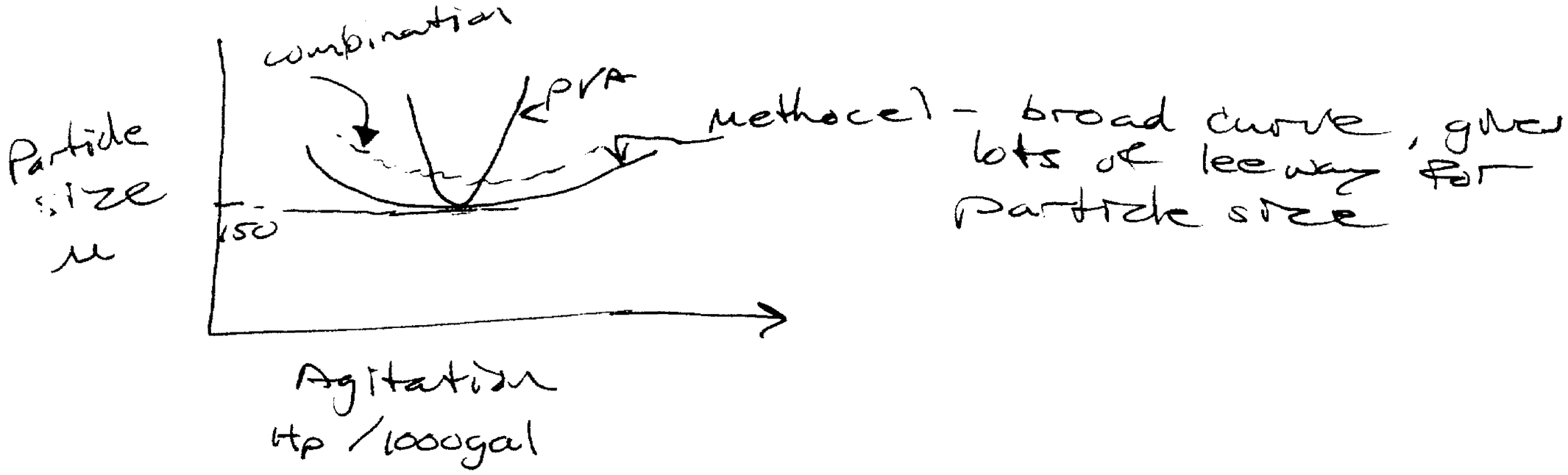


(PVA's)

2nd suspending Agent acts to inhibit Micro-Domains from aggregating together

The longer you keep the micro domains separate the better porosity you have

Porosity - consistent porosity
Not necessarily high porosity



Porosity enhancer - More Polyvinyl acetate than Alcohol

STP - Advantages of adding
1. Buffer - buffers water to pH above 7
2. Clean wall agent
3. Some porosity enhancing effect Some particle size effect

Made By _____

Date _____

Page _____ of _____

Job No. _____

Title _____

VAB.0001130527

V3-2(G-S

A

VISTA CHEMICAL COMPANY

RESEARCH & DEVELOPMENT DEPARTMENT

PVC PROCESSING TECHNOLOGY AREA

RICK QUY
MOREY OSBORN
CHARLIE MCDONALD
RICHARD LAHIERE
ALAN WARDWELL
ROD HAMMONS
BETH LEVEN

A

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2. Hard Particles
3. CTA's
4. IR

4:00 Adjourn

08/04/87

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History of PVC Technology

HISTORY OF PVC

1835	FIRST RECORD OF VCM	LIEBIG
1845	VINYL CHLORIDE APPEARED IN LEHRBUCH DER ORGANISCHEN CHEMIE	KLOBÉ
1836	WHITE POWDER FORMED WHEN VCM EXPOSED TO SUNLIGHT	REGNAULT
1872	FIRST CONFIRMED PVC	BAUMANN
1900s	ACADEMIC INTEREST ONLY	

1906-1913	VCM FROM ACETYLENE + HCL AND POLYMERIZED WITH HEAT AND PEROXIDES	KLATTE & ROLLETT
1916	SOLUTION PVC WITH HEAT AND U.V.	OSTROMUISLENSKII
1928	COPOLYMERS	REID & WILEY
1929	PVC PLASTICIZED	SEMON

1930-1940	BREAKTHROUGHS PVC PASTES PVC/PVAC - WATERPROOFING STABILIZERS EMULSION SUSPENSION - EASY PROCESSING	
1937	FULL-SCALE PRODUCTION	GERMANY
1939	SMALL PRODUCTION	
1940-1960	USE DOUBLED EVERY THREE YEARS	
1960	UNPLASTICIZED USES SURPASSED PLASTICIZED BECAME CHEAPEST POLYMER ON COST PER UNIT WEIGHT BASIS	

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A

SELECTED U.S. RESIN MARKETS

(MILLION LBS)

	Domestic Demand		Sales of Domestic Resin	
Resin	1985	1986	1985	1986
LDPE	8143	8491	8790	8769
PVC	6806	7087	6720	7197
HDPE	5823	6197	6661	7017
PP	4413	4697	5275	5790
PS	4054	4392	4108	4452
ABS	981	1035	1015	1074

FACTORS RESPONSIBLE FOR PVC GROWTH

1. LOW COST.
2. CAN BE COMPOUNDED INTO WIDE RANGE OF FLEXIBLE AND RIGID FORMS.
3. GOOD PHYSICAL, CHEMICAL, AND WEATHERABLE PROPERTIES.
4. UTILITY AND BROAD RANGE OF LARGE VOLUME APPLICATIONS.
5. PROCESSABILITY BY A WIDE VARIETY OF TECHNIQUES.
6. LESS ENERGY INTENSIVE OVERALL.

VAB.0001130536

PVC USES

40%	PIPE/FITTING
11%	FLOORING
11%	COATINGS
7%	WIRE & CABLE
8%	FILM & SHEET
1%	BOTTLES
3%	RECORDS
8%	MISCELLANEOUS EXTRUSION
2%	MISCELLANEOUS MOLDING
5%	EXPORTS
8%	OTHERS

ALSO

CONSTRUCTION	60%
PACKAGING	10%
ELECTRICAL	7%
FURNISHING	6%
AUTOS	4%
RECREATION	3%
APPAREL	3%
MEDICAL	2%
MISCELLANEOUS	5%

A

MAJOR U.S. PVC PRODUCERS

(MILLION LBS/YR)

Supplier	Total	Suspension	Dispersion
BFGoodrich	1545	1370	175
Occidental	1520	1360	160
Formosa	1038	952	86
Shintech	1000	1000	-
Georgia Gulf	850	800	50
VISTA	715	715	-
Borden	660	605	55
Air Products	500	500	-

HISTORY OF VISTA'S PVC ACTIVITIES

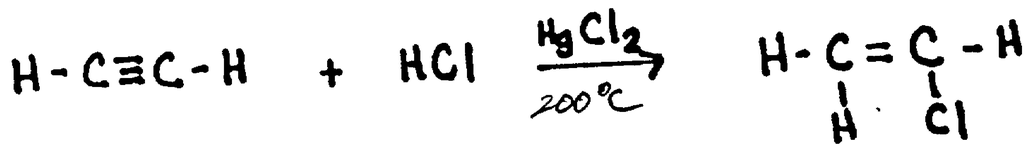
1963	ACQUIRED CARLON PVC PIPE CO.
1964	ACQUIRED APEX TIRE AND RUBBER CO. (COMPOUND) AND THOMPSON CHEMICAL CO. (PVC RESIN) FROM FAIN FAMILY.
1964	EXPLOSION AND FIRE AT THE HEBRONVILLE MASS. PVC PLANT.
1964	ABERDEEN MISS. PLANT STARTED-UP AND THE ASSONET MASS. PLANT BUILT.
1967	R & D MOVED FROM PONCA CITY TO ASSONET MASS.
1968	VINATEX (ENGLAND) CAME INTO EXISTENCE.
1968	FTC MADE CONOCO DIVEST OF ITS ASSONET MASS. PLANT (SOLD TO OLIN INDUSTRIES), COMPOUNDING FACILITIES IN RHODE ISLAND (SOLD BACK TO THE FAIN FAMILY [TECKNOR-APEX]), AND BUY OUT STAUFFER PORTION OF THE VCM PLANT.
1968	CONOCO PLASTICS FORMED FROM CARLON PIPE AND PVC PLANT IN ABERDEEN AND HEADQUARTERED IN WILTON, CONN., INCLUDING R & D.
1970	LARGE REACTOR PLANT STARTED-UP IN OKLAHOMA CITY.
1972	SOLD CARLON TO INDIAN HEAD INDUSTRIES, SHUT DOWN THE WILTON FACILITIES, MOVED R & D TO PONCA CITY, AND FORMED CONOCO CHEMICALS.
1975	ALL SMALL REACTORS SHUT DOWN.
1976	DIVESTED OF OUR HOLDINGS IN VINATEX.
1978 to 1981	PVC RESIN, DRY BLEND, AND COMPOUND CAPACITIES INCREASED.
1984	VISTA POLYMERS INC. FORMED.

Chemistry of Polymerization

YAB.0001130541

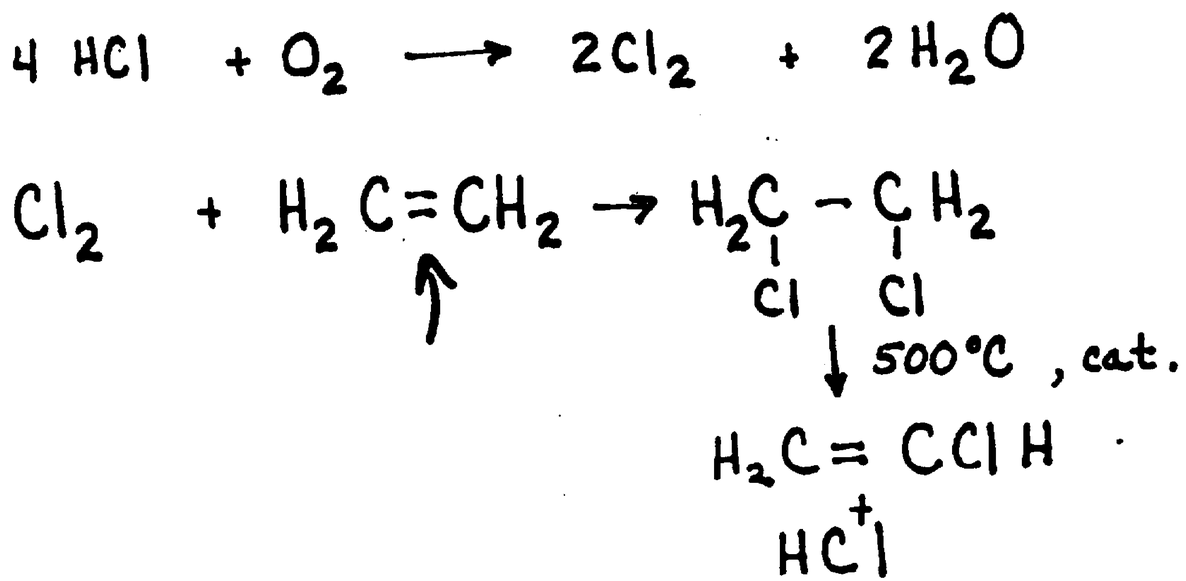
PREPARATION OF VINYL CHLORIDE

Hydrochlorination of acetylene



After 1960:

oxychlorination/cracking of dichloroethane



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PROPERTIES OF VINYL CHLORIDE

Color	Colorless, Water Clear
Odor	Pleasant, Sweet
Molecular Weight	62.5
Boiling Point	-13.7°C
Freezing Point	-153.8°C
Density @ -20°C	0.983 g/ml
@ 20°C	0.910 g/ml (7.60 lbs/gal)
Refractive Index R_D^{15}	1.398
Viscosity @ -20°C	0.274 cps
@ 25°C	0.193 cps
Surfact Tension @ -20°C	22.27 dyn/cm
Flash Point, COC	-78°C
Explosive Limits in Air	4-22% by vol.
Vapor Pressure @ 0°C	25.1 psi
@ 20°C	49.2 psi
@ 40°C	87.6 psi
Solubility of Water in VCM	0.11%
Solubility in Water @ 1 atm.	0.5%
Heat of Polymerization	720 BTU/lbs

Polymerization Steps

1) Initiation

2) Propagation

3) Chain Transfer

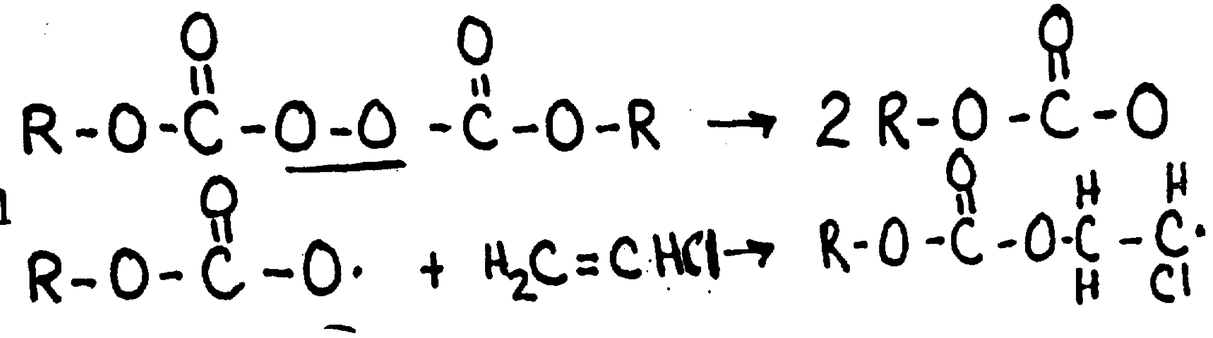
4) Termination

MECHANISM OF POLYMERIZATION

$R-C(=O)-O-O\cdot \rightarrow R-O\cdot + CO_2$

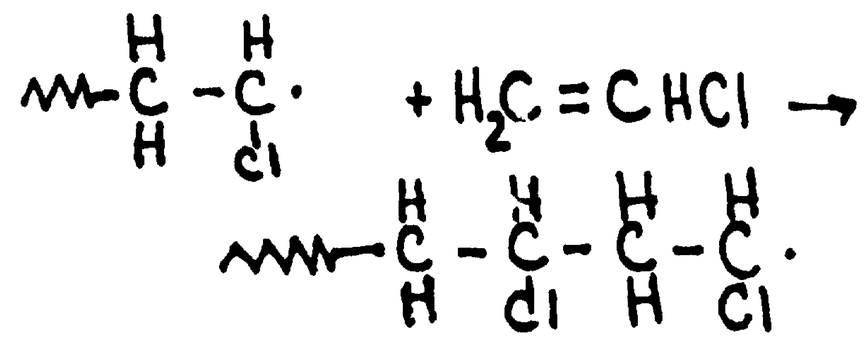
1.INITIATION

free radical formation



2.PROPOGATION

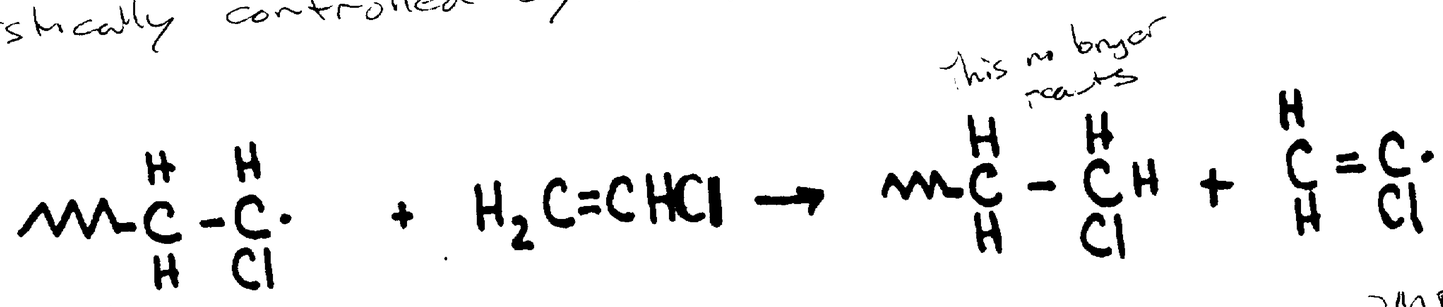
note head to tail addition



3.CHAIN TRANSFER

statistically controlled by Temp.

Chain transfer agents make this happen faster



free radical takes this H off

$H-S-CH_2-CH_2-OH$ 2ME

$\cdot S-CH_2-CH_2-OH$

2ME .7 gal 5305

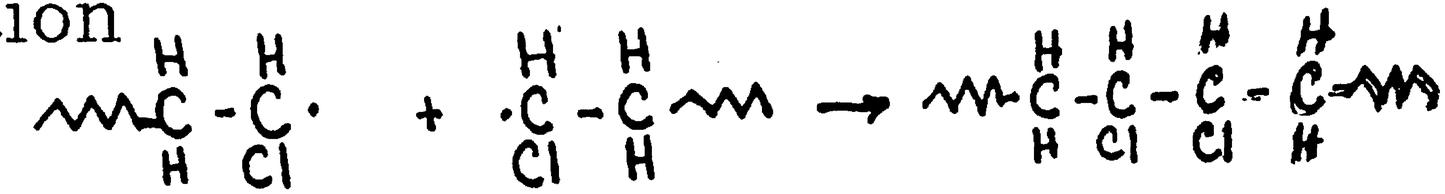
2.4 gal 065

shortening of avg. chain length

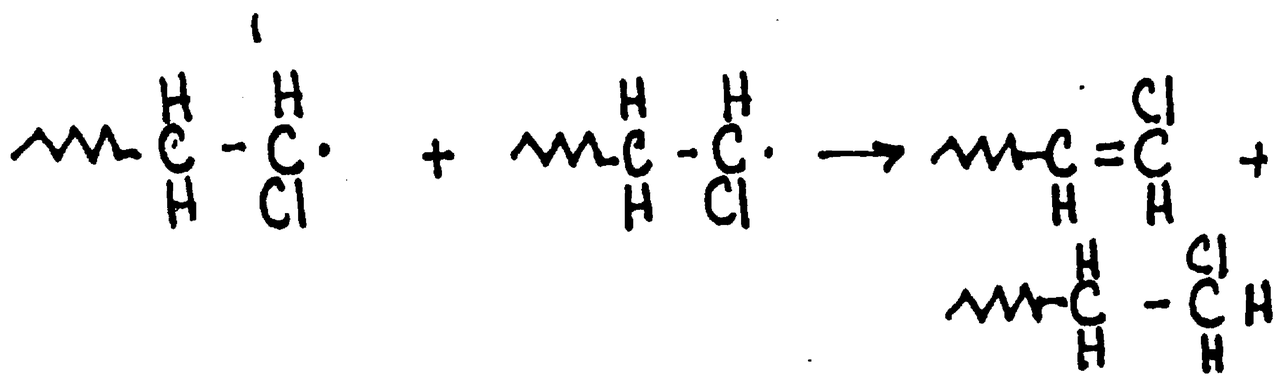
VAB.0001130545

4. TERMINATION

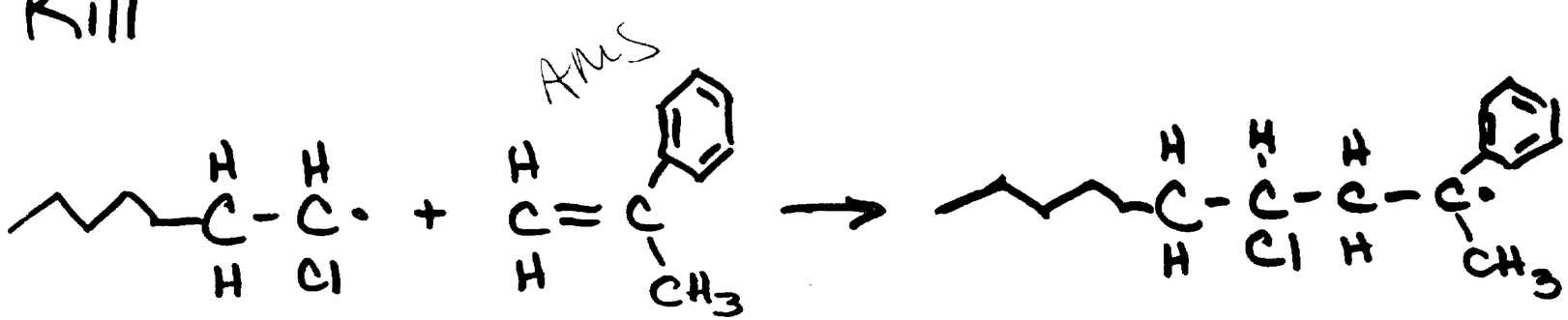
Recombination



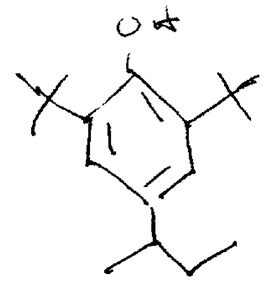
disproportionation



Kill

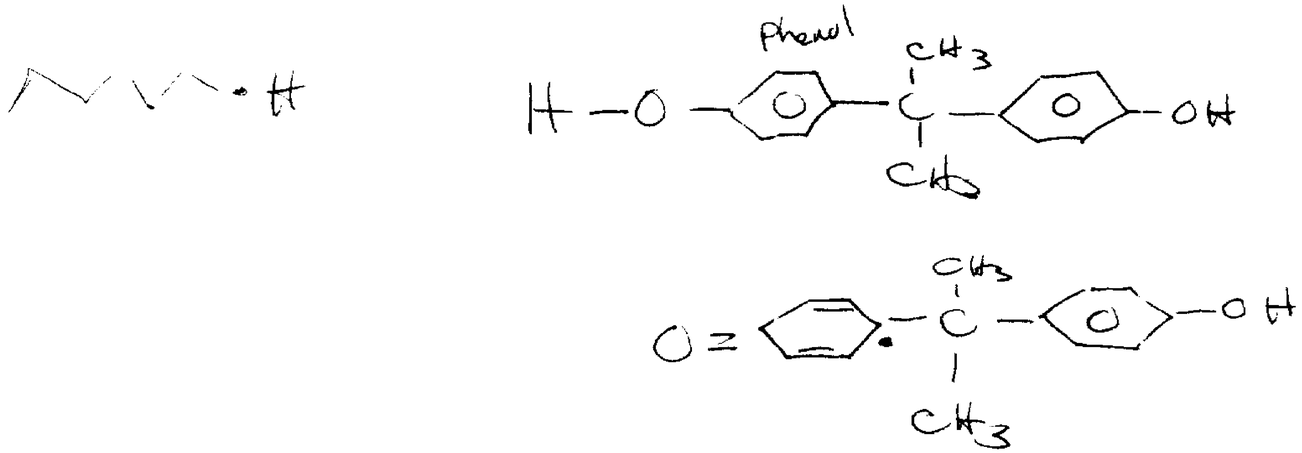


Isonox more stable than BHT



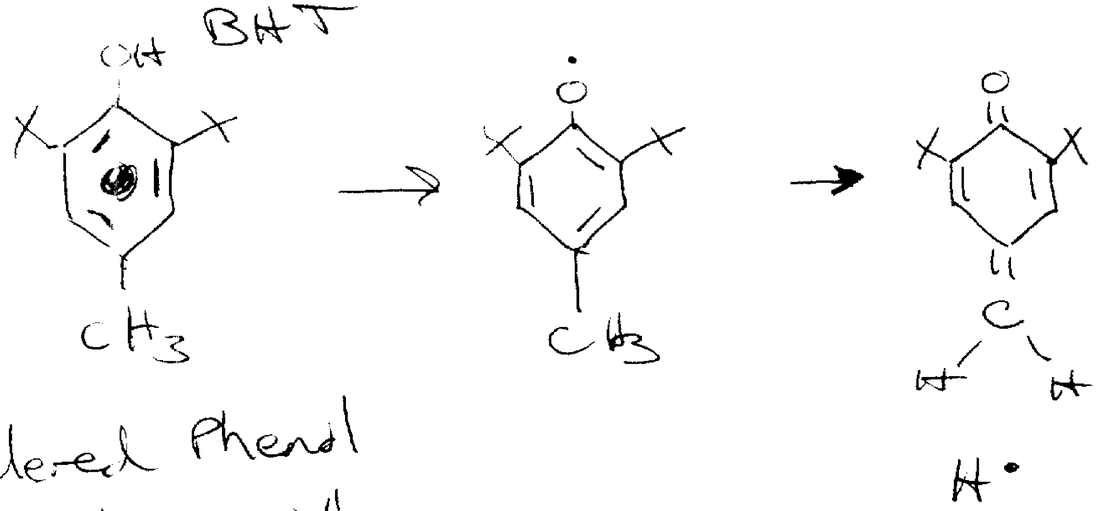
This is OK in Fluid Bed

BPA Kill



Solid Mat'l which stays on molecule

~~Isonox~~ BHT



Hindered Phenol make H on OH group less reactive

In Fluid Bed when pH is High changes color from white

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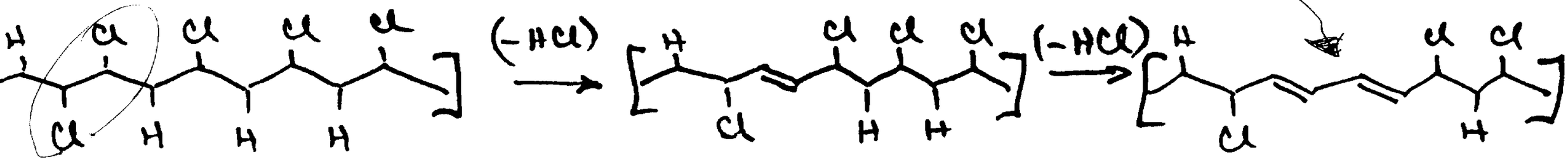
. PROBLEMS

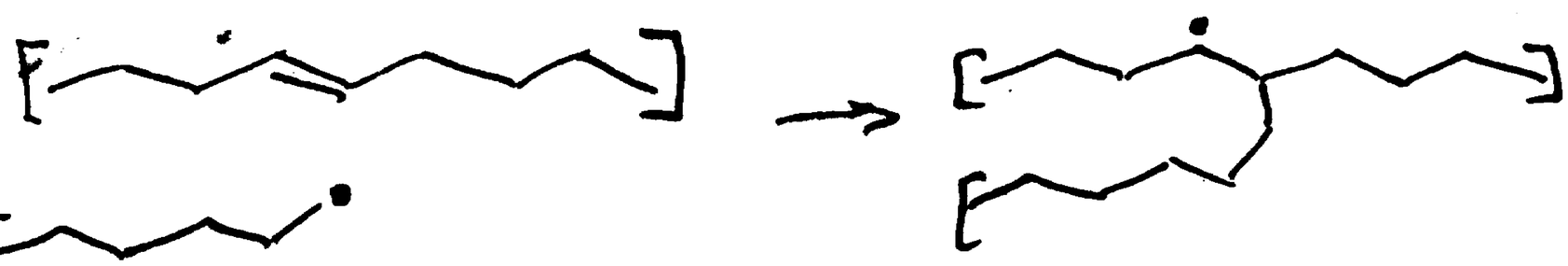
EHYDROCHLORINATION - cause color problems as double bonds increase



happens 1.2% of time

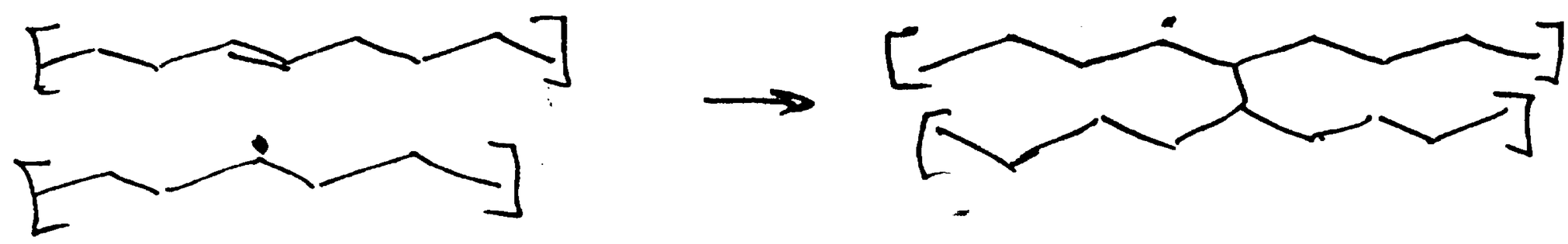
would be a problem w/ deionized water

BRANCHING - make PVC less fusable



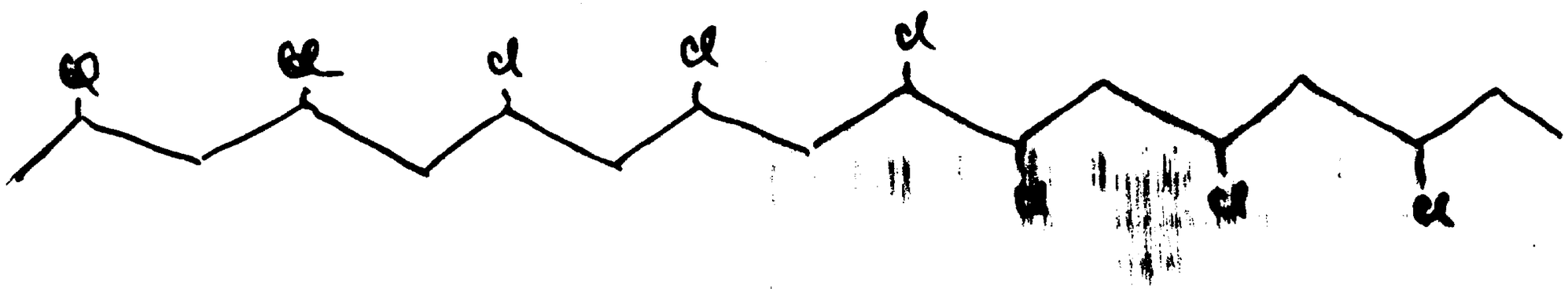
at end of reaction, this is one reason why you kill

CROSSLINKING



STRUCTURE OF PVC

98% HEAD TO TAIL



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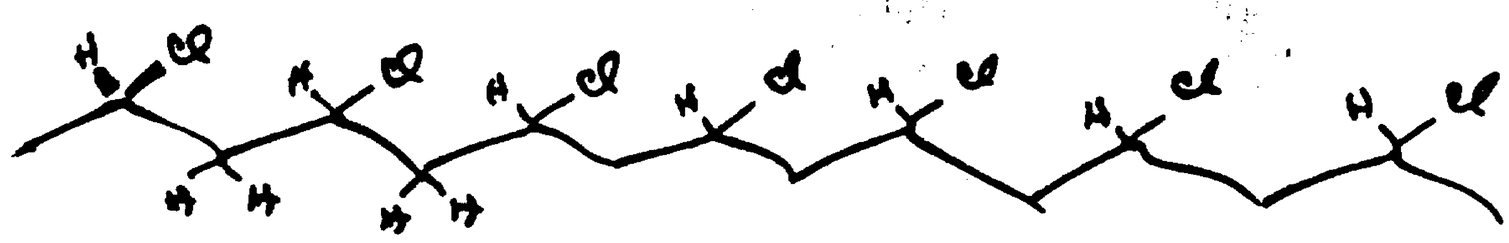
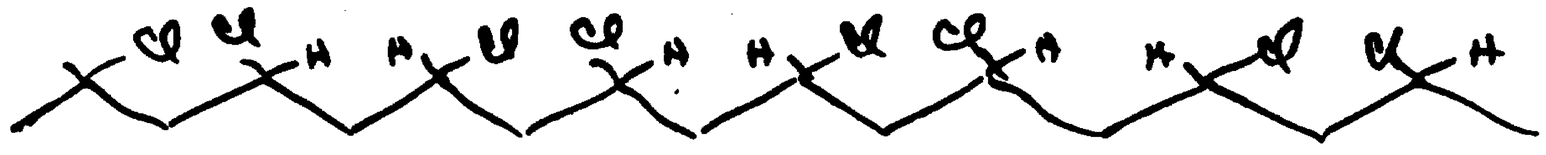
TACTICITY

ISOTACTIC



SAME

SYNDIOTACTIC



ALTERNATE

ATACTIC

RANDOM

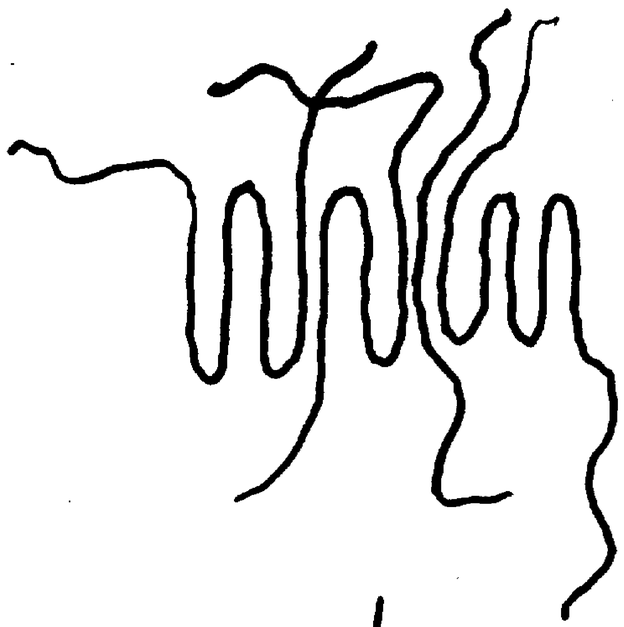
interferes with crystalinity

PVC is this

CRYSTALINITY

PVC: 7-10% CRYSTALLINE
90% + AMORPHOUS OR GLASSY

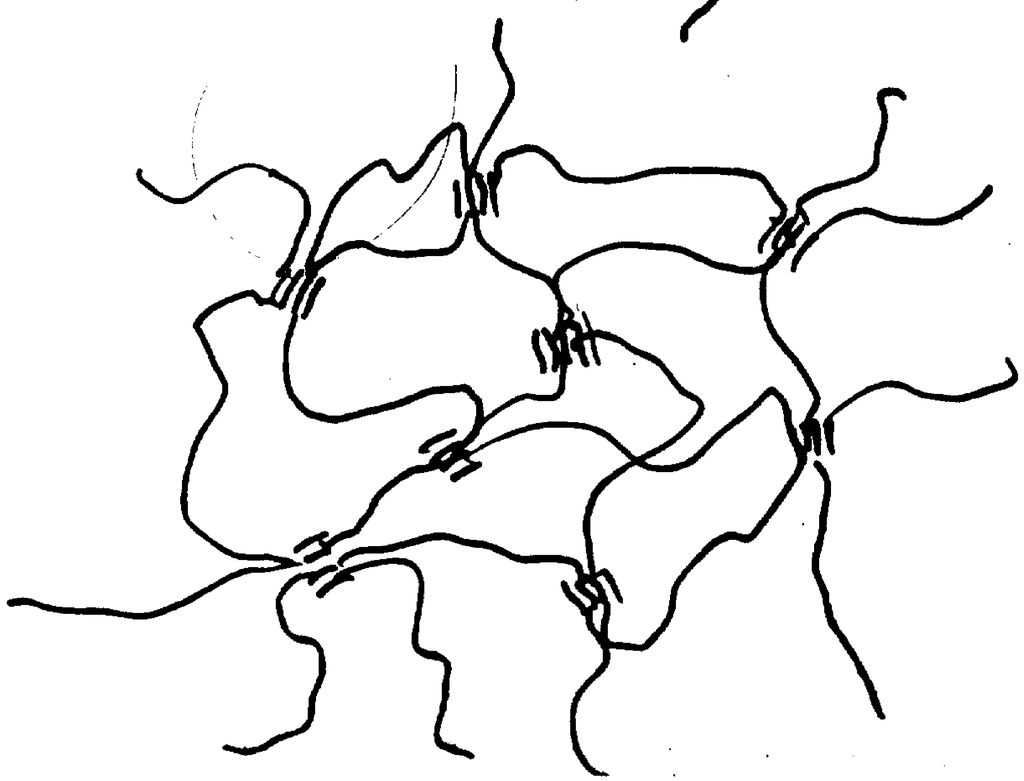
CRYSTAL:



Glass Transition Temp
≥ 70-80 °C

when you go above this (crystallinity) you form more glassy structures

MASS



Go above when
steam strip
dryer
Intens mixer
compounder

GENERAL PROPERTIES OF RIGID VINYL POLYMER AND COPOLYMER
(POLYVINYL CHLORIDE--POLYVINYL CHLORIDE ACETATE)

POLYMER PROPERTIES	TYPICAL VALUES
1. GLASS TRANSITION TEMPERATURE, T_g (°C)	75-105
2. COMPRESSION MOLDING TEMPERATURE °F	285-400
3. COMPRESSION MOLDING PRESSURE PSI	750-2,000
4. INJECTION MOLDING TEMPERATURE °F	300-415
5. INJECTION MOLDING PRESSURE PSI	10,000-40,000
6. SPECIFIC GRAVITY	1.30-1.58
7. TENSILE STRENGTH PSI	6,000-7,500
8. ELONGATION PERCENT	40-80
9. COMPRESSIVE STRENGTH PSI	8,000-13,000
10. FLEXULAR STRENGTH PSI	10,000-16,000
11. IMPACT STRENGTH FT-LB/IN (1/2 IN x 1/2 IN NOTCHED BAR, IZOD TEST)	0.4-20
12. HARDNESS, ROCKWELL	65-85 (SHORE D)
13. FLEXULAR MODULUS 10^5 PSI, 73°F	3-5
14. TENSILE MODULUS 10^5 PSI	3.5-6.0
15. THERMAL CONDUCTIVITY 10^{-4} CAL/SEC/SQ. CM./1 (°C/CM)	3.5-5.0
16. SPECIFIC HEAT, CAL/°C/GM	0.25-0.35
17. THERMAL EXPANSION, 10^{-5} IN/IN/°C	5.0-10.0
18. DEFLECTION TEMPERATURE °F AT 264 PSI FIBER STRESS	140-170
66 PSI FIBER STRESS	135-180
19. WATER ABSORPTION 24 HR., 1/8 IN THICK PERCENT	0.04-0.4
20. EFFECTS OF SUNLIGHT	VARIES WITH FORMULATION
21. EFFECTS OF WEAK ACIDS	NONE

22.	EFFECTS OF STRONG ACIDS	NONE TO SLIGHT
23.	EFFECTS OF WEAK ALKALIES	NONE
24.	EFFECTS OF STRONG ALKALIES	NONE
25.	EFFECTS OF ORGANIC SOLVENTS	RESISTS ALCOHOLS, ALIPHATIC HYDROCARBONS, OILS; SOLUBLE OR SWELL IN KETONES AND ESTERS; SWELLS IN AROMATIC HYDROCARBONS

Bulk density 33 lb/ft^3

PVC very insoluble in VCM

PVC colorless + transparent

POLYMERIZATION TECHNOLOGY

1)Mass

2)Solution

3)Emulsion

4)Suspension

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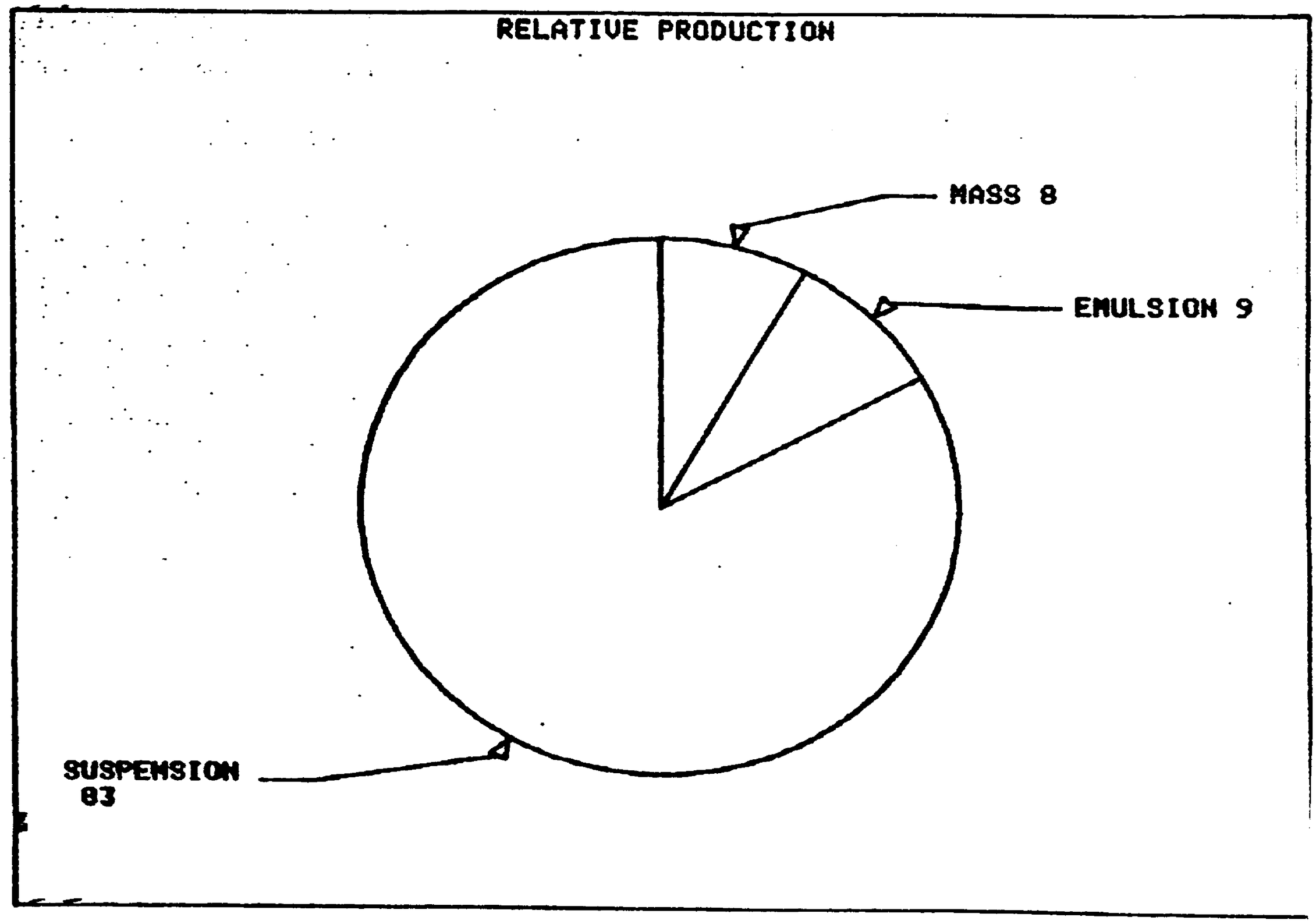

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POLYMERIZATION

MASS (BULK)

Manufacturer: Pechiney St. Gobain

Two-step batch

Polymerization starts in VCM phase, then precipitates.

Advantages:

1. Very uniform, porous particles.
2. High bulk density.
3. Free of suspending or emulsifying agents.

Disadvantages:

1. Difficult to control temperature.
2. More expensive than suspension.

Market: Same as suspension except for molding

SOLUTION

Manufacturer: Union Carbide

Polymerization in a solvent then precipitates form copolymers.

Advantages:

1. Same properties as bulk.

Disadvantages:

1. High Cost — 44¢/lb.

Market: Very limited (beer can liners)

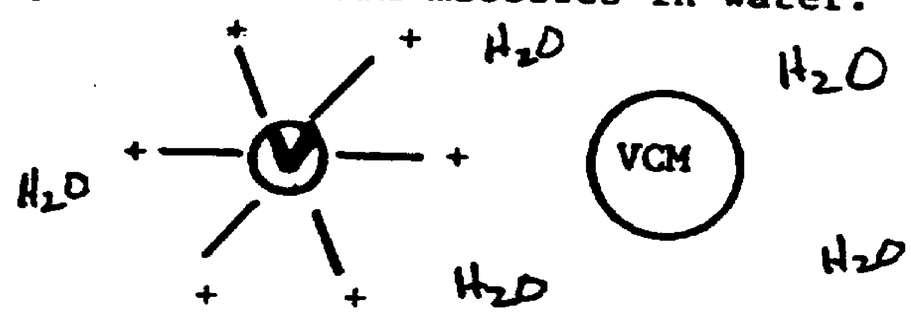
EMULSION

Manufacturer: BFG

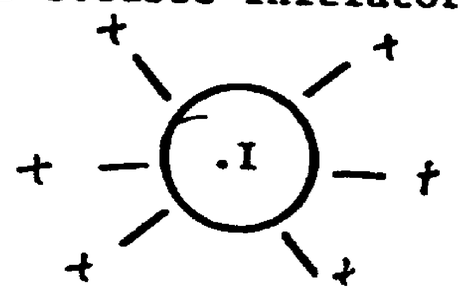
Partical size 1-3 microns
very fine mat'l

1. Soaps used to form micelles in water.

1μ



2. Water-soluble initiator encounters VCM in micelles.



3. Diffusion from droplets replaces polymerized VCM.

Advantages:

1. Prepare high MW resin.
2. Produces very small nonporous resin.

Disadvantages:

1. High contamination level of soap.
2. Poor heat stability.
3. High Cost — 57¢/lb.

Market: Plastisols, used for coatings

Ex is rubber gloves, dashboards

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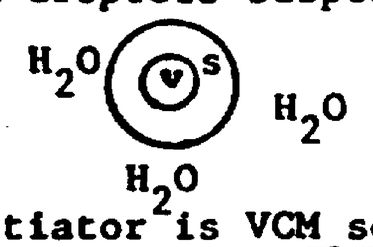
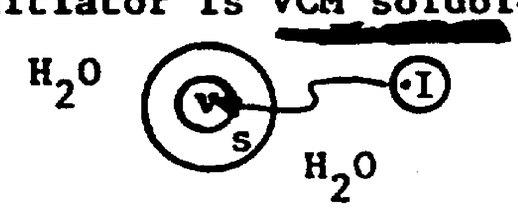
SUSPENSION

Manufacturers: Conoco and many others

1. VCM droplets suspended in water



2. Initiator is VCM soluble.



Advantages:

1. Easily controlled temperature.
2. Easily filtered and dried.
3. Cheap — 27¢/lb.

Disadvantages:

1. Small change in conditions alters properties.
2. Not as pure as mass or solution.

Market: Extrusion, molding, calendering

CHARACTERISTICS OF PVC POLYMERIZATION PROCESSES

	Resin Polymerization Type			
	Suspension PVC	Emulsion PVC	Mass or Bulk PVC	Solution PVC
Ingredients:				
Monomer(s)	VCM	VCM	VCM	VCM/Vinyl Acetate
Initiator Solubility	VCM	Water	VCM	VCM
Suspending Agent	Protective Colloid	Soap	None	None
Reactor Agitation	Low Shear	High Shear	High then Low	Low
Market Rank (Lb. Basis)	1st	2nd	3rd	Distant 4th
Mean Particle Diameter	150 μm	10 μm	150 μm	Solution
End Use	Rigid Flexible Extrusion Film Blown Calender Molding	Pastes Latex Dispersions Creams	Rigid Flexible Extrusion Film Blown Calender	Beer Can Liners

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VISTA POLYMERIZATION PROCESS TECHNOLOGY

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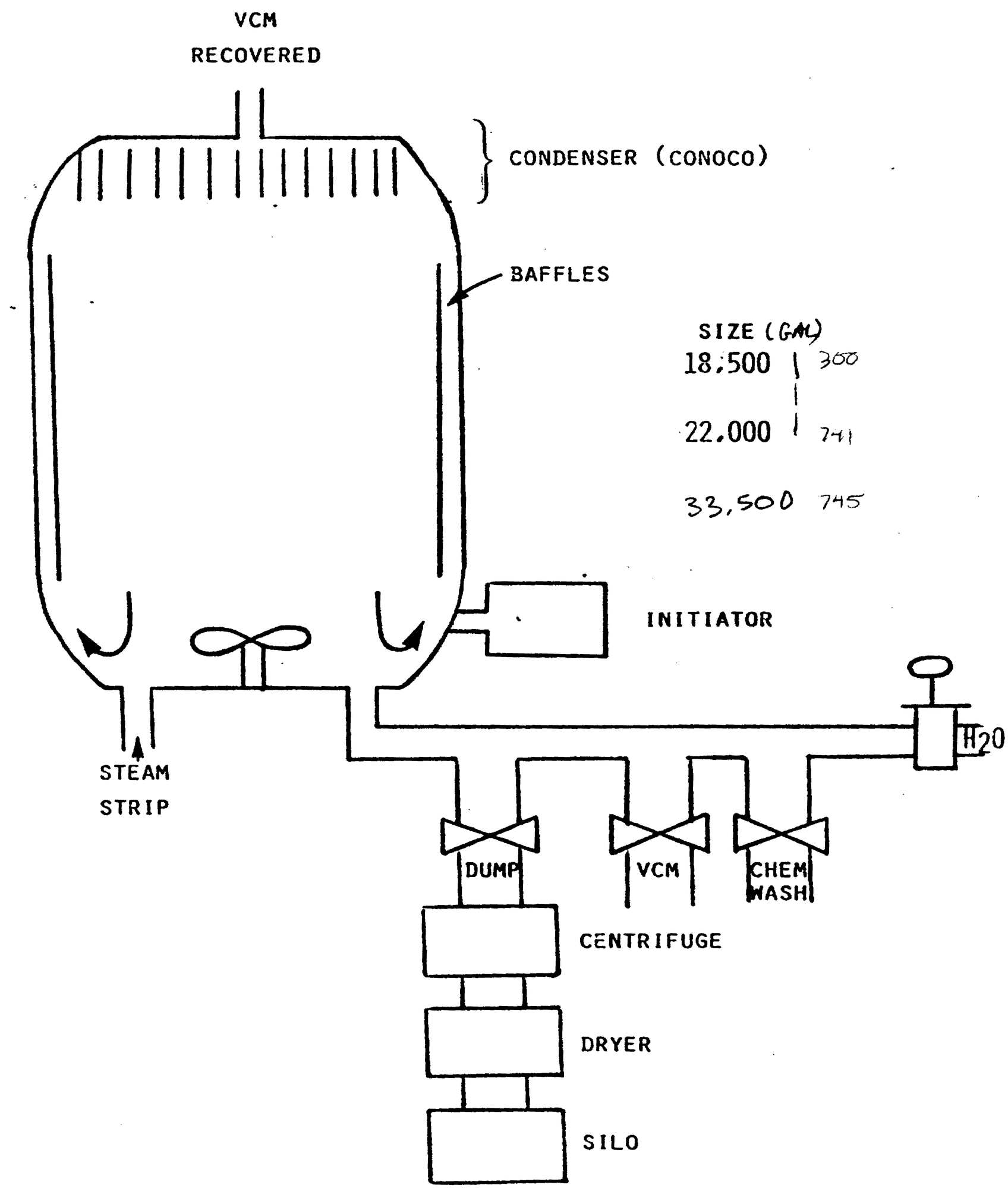
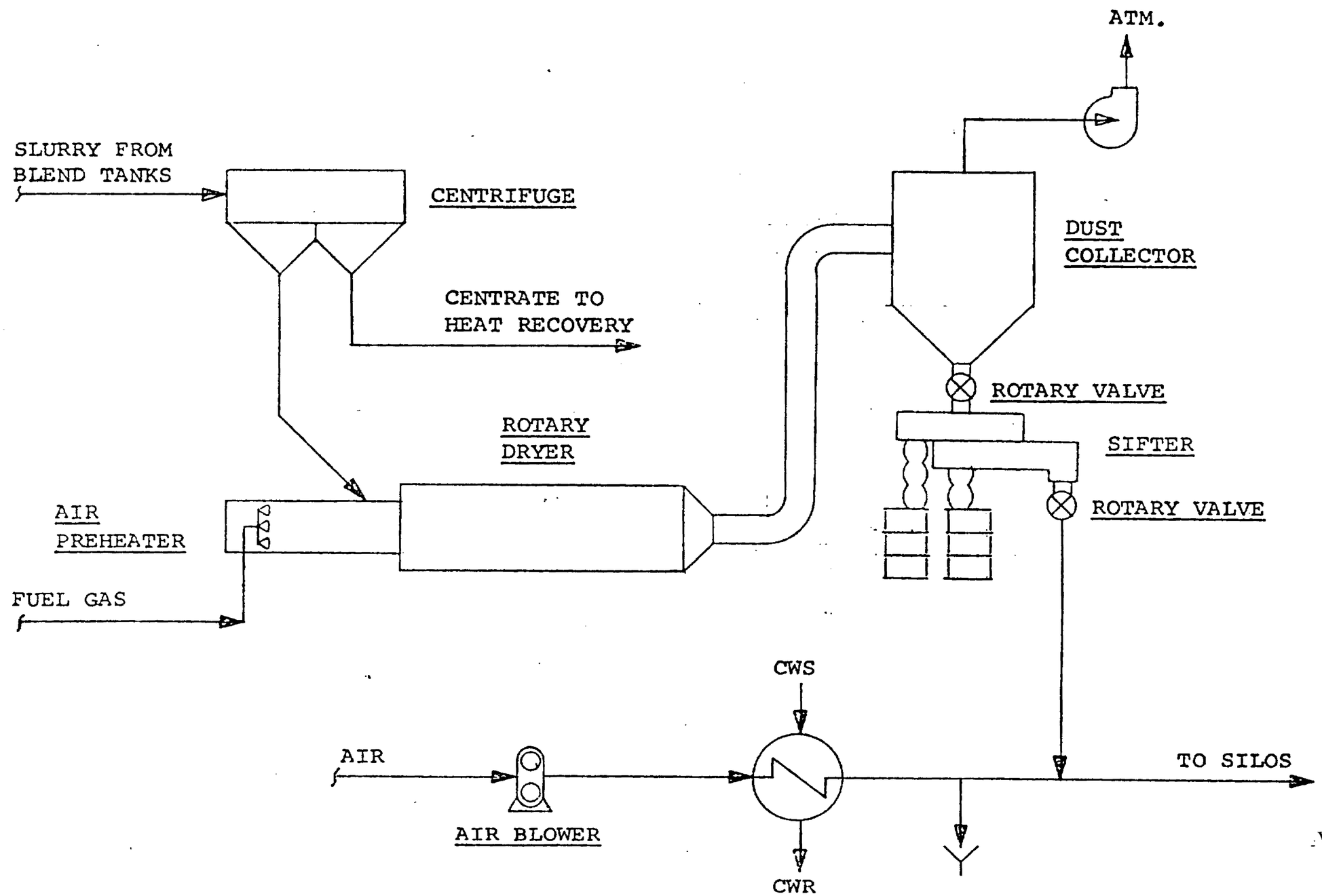

VCM
RECOVERED
CONDENSER (CONOCO)
BAFFLES
SIZE (GAL)
18,500 300
22,000 741
33,500 745
INITIATOR
H2O
STEAM
STRIP
DUMP
VCM
CHEM
WASH
CENTRIFUGE
DRYER
SILO

RESIN DRYING SECTION

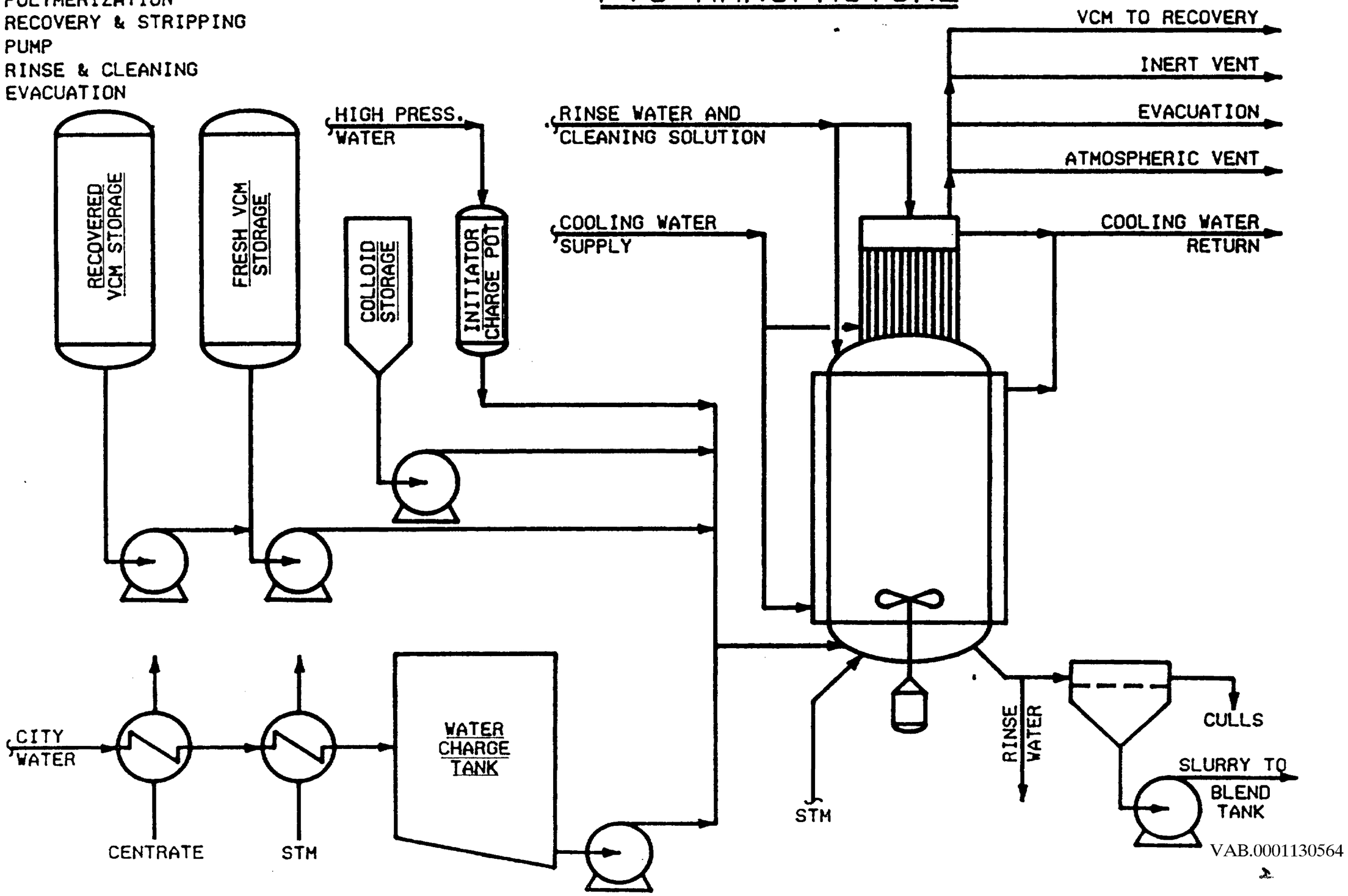
PVC MANUFACTURE



POLYMERIZATION CYCLE

CHARGE
POLYMERIZATION
RECOVERY & STRIPPING
PUMP
RINSE & CLEANING
EVACUATION

POLYMERIZATION SECTION
PVC MANUFACTURE



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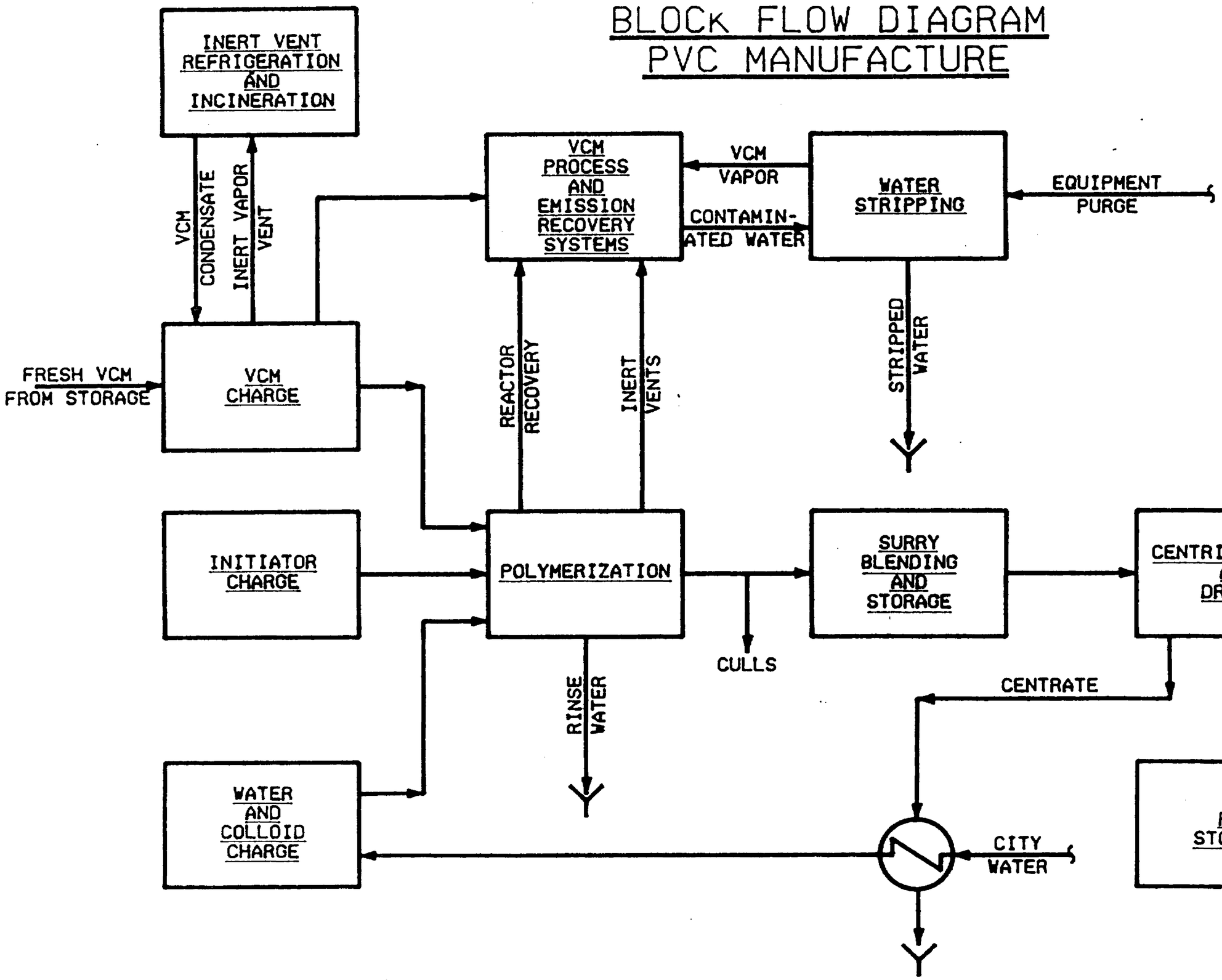
BLOCK FLOW DIAGRAM
PVC MANUFACTURE



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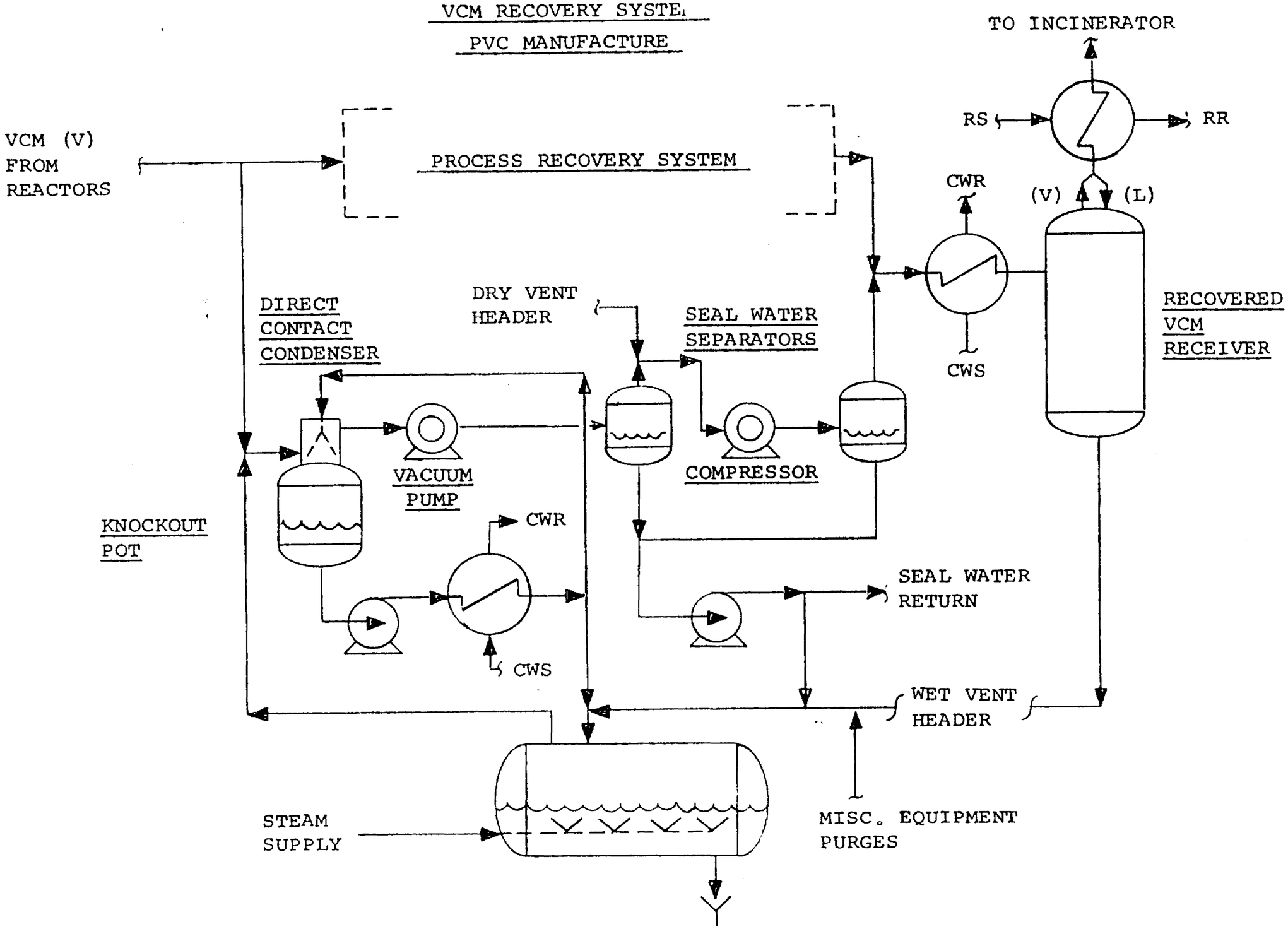
VCM RECOVERY SYSTEM

PVC MANUFACTURE



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REACTOR SIZE

ABERDEEN	OKC
FOUR 18,000-GAL	SIX 18,000-GAL
FOUR 22,000-GAL	
TWO 33,500-GAL	

CAPACITY

ABERDEEN - 425 MM LBS

5465	5.0%
5425	13.7
5385 TYPE 1	22.5
5385 TYPE 3	35.0
5305	11.3
5265	12.5

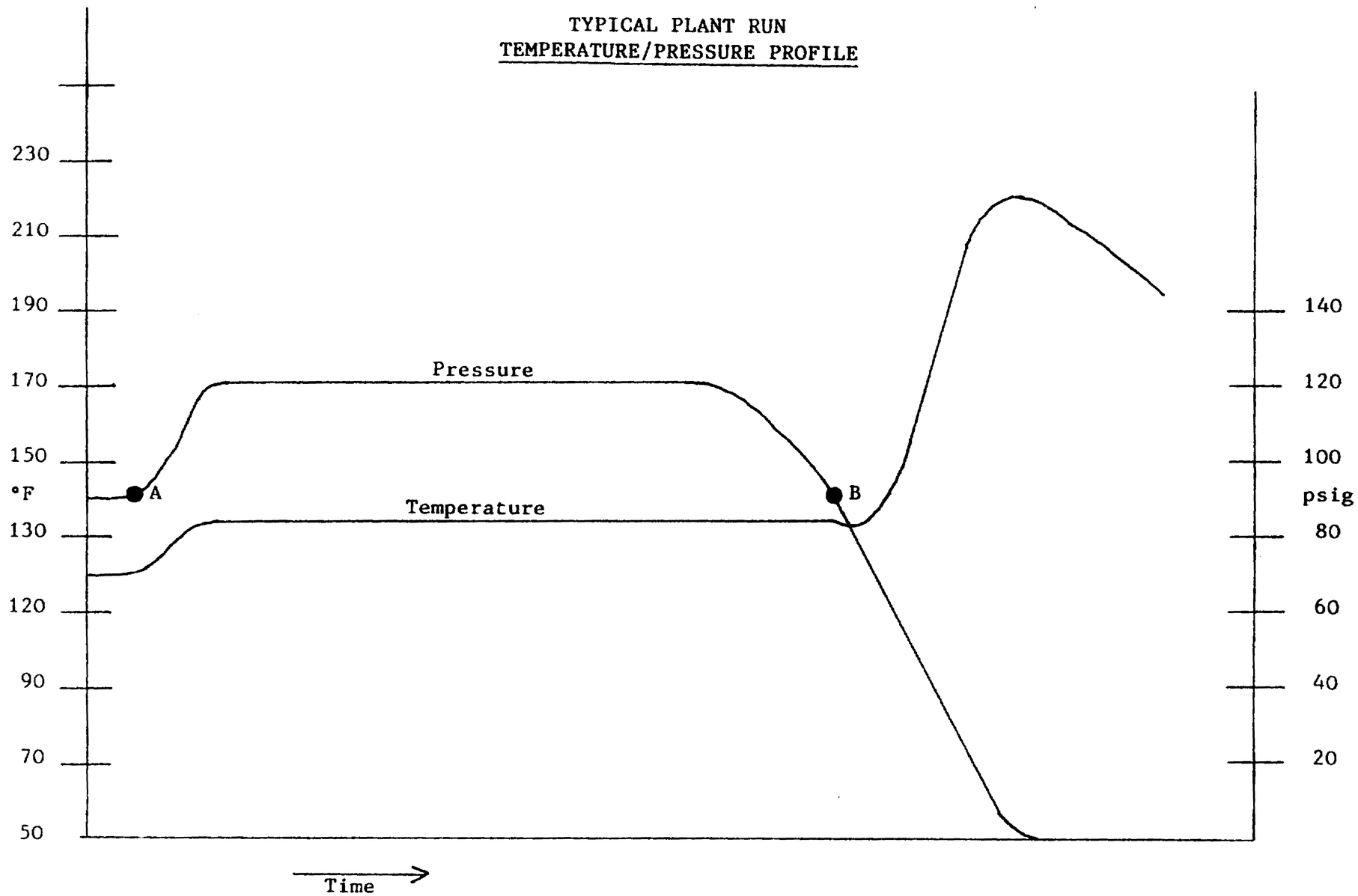
OKC - 2~~6~~90 MM LBS

5385	100.0%

TYPICAL CHARGE SIZE

ABERDEEN

	18,000 (LBS)	22,000 (LBS)	33,500 (LBS)
VCM	47,000	47,000-58,000	78,000
WATER	56,000	56,000-69,600	98,000



Legend:
A. Charge complete heatup started.
B. Pressure at 90 psig KA/AO added and steam injection started.

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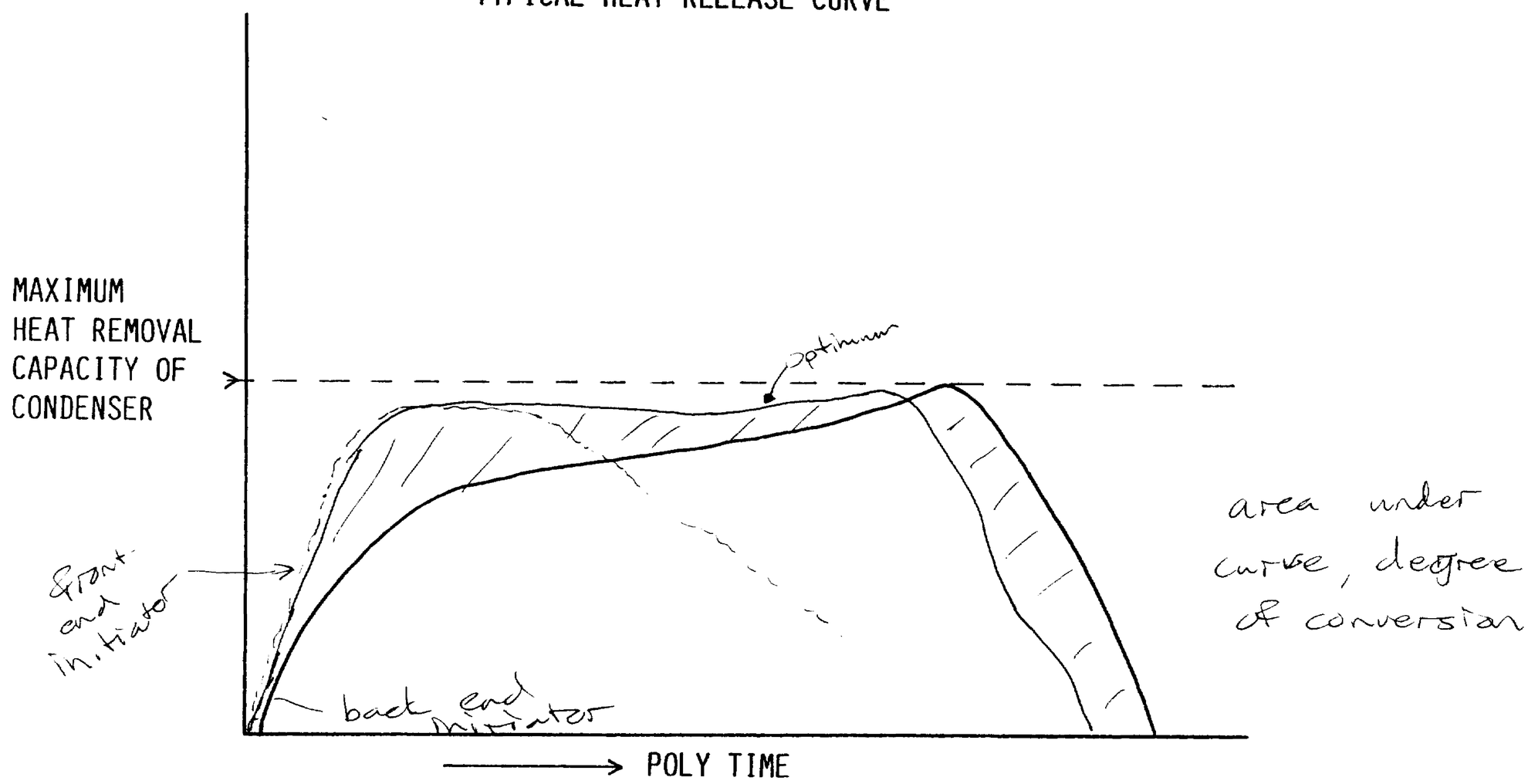
TYPICAL HEAT RELEASE CURVE



Typical of S385 w/ L-223 initiator

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VISTA RESIN GRADES

(MOLECULAR WEIGHTS)

Grade	Monomer Units	Poly Temp (F)	Inherent Viscosity	Molecular Weight
5265	700	150	0.66	40,000
5305	950	150	0.74	59,375
5385	1200	134	0.92	75,000
5415	1325	127	1.04	82,800
5465	1475	119	1.10	92,200

PVC RESIN APPLICATIONS

5465

Automotive Wire
Vinyl Car Tops
Toys

5385

Pipe
Seat Covers (Calendering)
General Flexible Applications
Siding
Garden Hose
Shoes (Flexible Molding)
Profile Molding

5265

Pipe Fittings

5425

Building Wire
Communication Wire
General Purpose Calendering
Vinyl Car Tops
Flexible Automotive Molded Parts

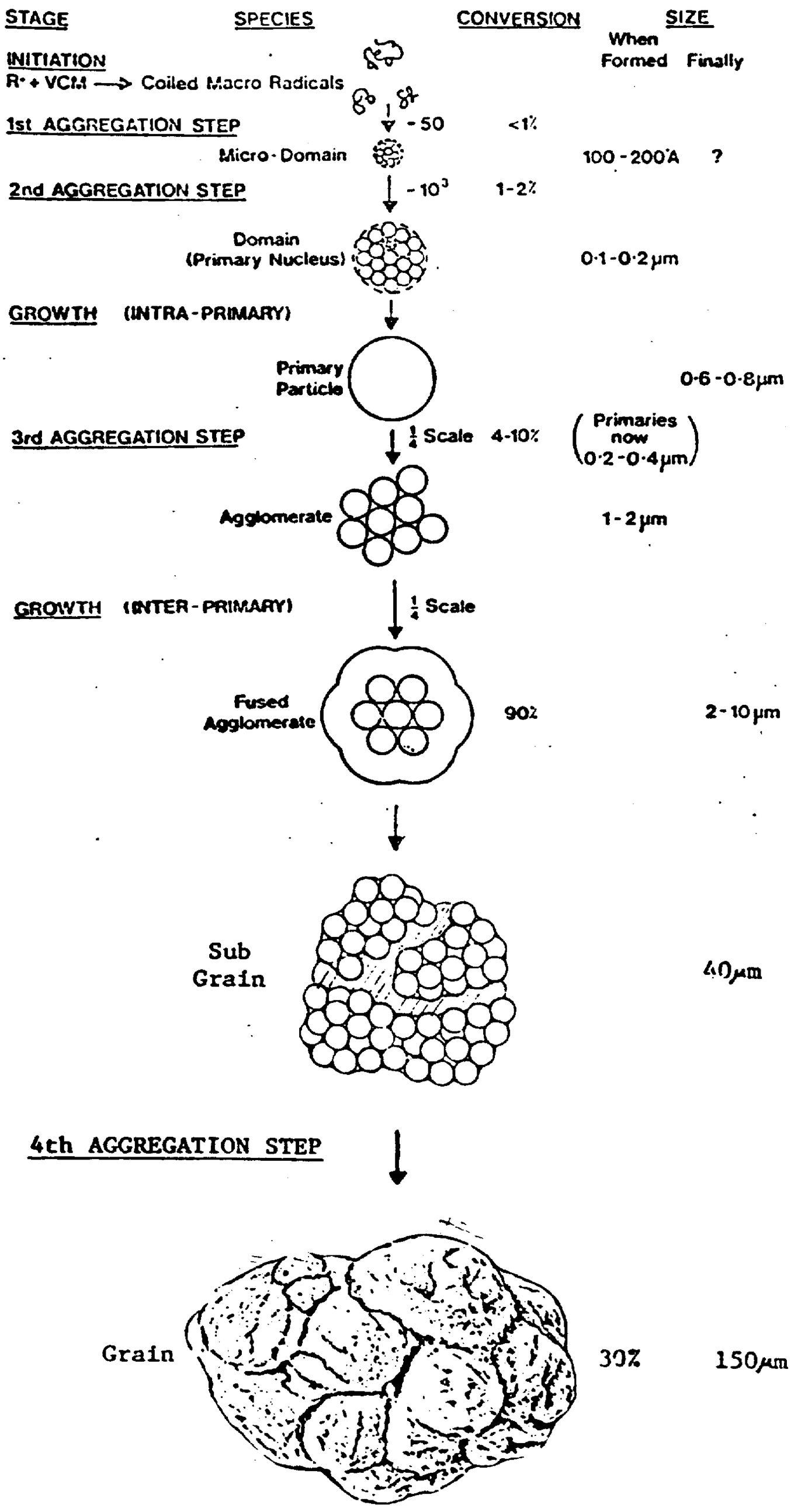
5305

Rigid Pipe Fittings
Semi-Rigid Calendering

Resin Morphology -- Shape

IMPORTANT MORPHOLOGICAL FEATURES

- GRAIN SIZE
- GRAIN SHAPE
- DEBRIS
- AGGLOMERATE SIZE
- POROSITY



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EFFECT OF PROCESS VARIABLES ON RESIN PROPERTIES

PROPERTY	PROCESS VARIABLE
A. MOLECULAR WEIGHT (INHERENT VISCOSITY)	1. POLYMERIZATION TEMPERATURE 2. CHAIN TRANSFER AGENTS 3. CHAIN COUPLING AGENTS
B. PARTICLE SIZE DISTRIBUTION	1. SUSPENDING AGENT CONCENTRATION 2. AGITATION
C. BULK DENSITY	1. STATIC 2. RESIN PARTICLE SHAPE 3. ADDITIVES
D. POROSITY (BRABENDER DRY TIME, COLD PLASTICIZER ABSORPTION, RESIDUAL VCM)	1. DEGREE OF CONVERSION OF VCM TO PVC 2. POLYMERIZATION TEMPERATURE 3. ADDITIVES
E. GELS	1. CLEANLINESS OF REACTOR 2. AGITATION 3. ADDITIVES
F. RESIN COLOR	1. HEAT HISTORY 2. ANTIOXIDANT
G. HEAT STABILITY	1. HEAT HISTORY 2. KILLING AGENT 3. ANTIOXIDANT
H. MOISTURE	1. DRYING EFFICIENCY
I. ELECTRICAL PROPERTIES	1. TYPE INITIATOR 2. ADDITIVES 3. TYPE POLY WATER

PVC PROPERTIES--REACTOR RELATED

Resin Property	Process Variable	Process Change
Molecular Weight (MW) (Inherent Viscosity)	• Polymerization Temperature • Chain Transfer Agent (CTA)	• Higher Temperature; Lower MW • Lower Polymerization Temp with Increased Amounts of CTA
Particle Size Distribution (Average Particle Size [μ] and Coefficient of Variation)	• Suspending Agent (SA) (Methocel^{R})	• More SA; Finer the Resins
Bulk Density (gms/cc)	• Conversion	• Kill Polymerization After Pressure Drop
Plasticizer Absorption (Brabender Dry Time [min])	• Conversion • Additives	• Higher Kill Pressure; Faster Dry Time • Addition of OMS
Gels (Fish Eyes)	• Clean Reactor • Charging and Killing Procedures	• Adequate Cleaning and Rinsing of Reactor • Proper Charge Sequence and Initiator Addition Along with Proper Killing

PVC PROPERTIES--DRYER RELATED

Resin Property		
• Moisture	• Dryer	• Better Control of Dryer
• Contamination	• Dryer • Chem Wash	• Clean Dryer • Clean Chem Wash Filter/Tank
• Static Flow	• Dryer	• Add Additional CaSt
• Residual VCM	• Steam Stripping	• Proper Steam Stripping Procedure
• Gardner "b" Color and Heat Stability (Static Oven, Dynamic Mill, and Brabender)	• Dryer • Steam Stripping • Antioxidant	• Proper Dryer Conditions • Proper Steam Stripping Procedure • Increase Level

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Q.C. TESTING

Q.C. Test	ABD Routine	ABD Spot	OKC Routine	OKC Spot
1. Inherent viscosity		every day		X
2. Moisture	once/hr.		X	
3. Contamination	every 2 hrs.		X	
4. Bulk density	every batch		X	
5. Screen	every batch		X	
6. Gels	every batch		---	---
7. Dry time	every batch			3/week
8. Gardner "b" color	every batch			X
9. RVCM	every batch		every shipment	
10. Heat stability (oven)		3/week		2/week
11. Static flow	every shipment		every shipment	

Plasticizer Absorption / VCM Removal

1. Plasticizer Absorption

want even absorption of plasticizer

want rapid absorption of plasticizer

2. VCM Removal

want complete removal of VCM

want rapid removal of VCM

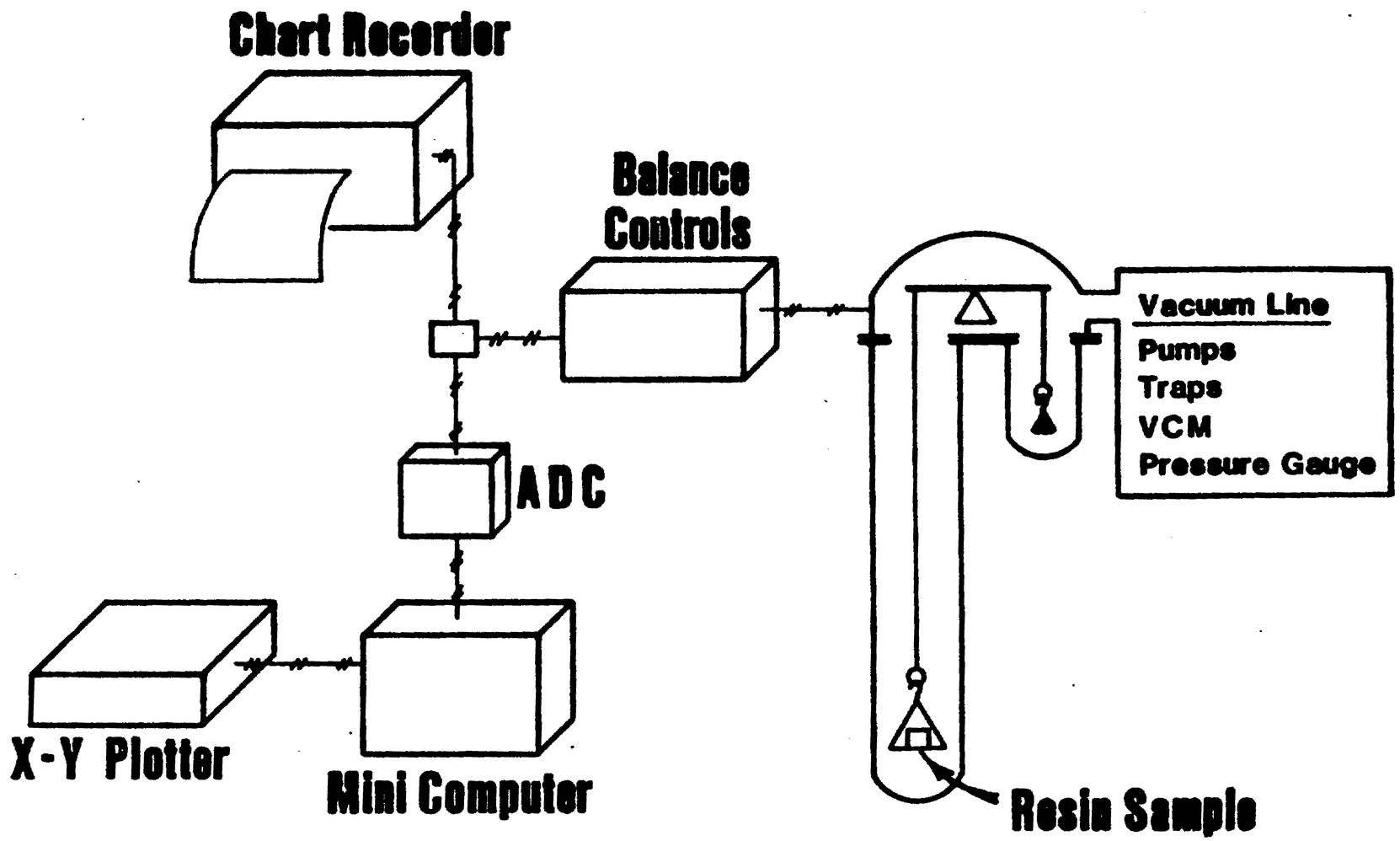

Figure 1. Diagram of Gravimetric Sorption Apparatus

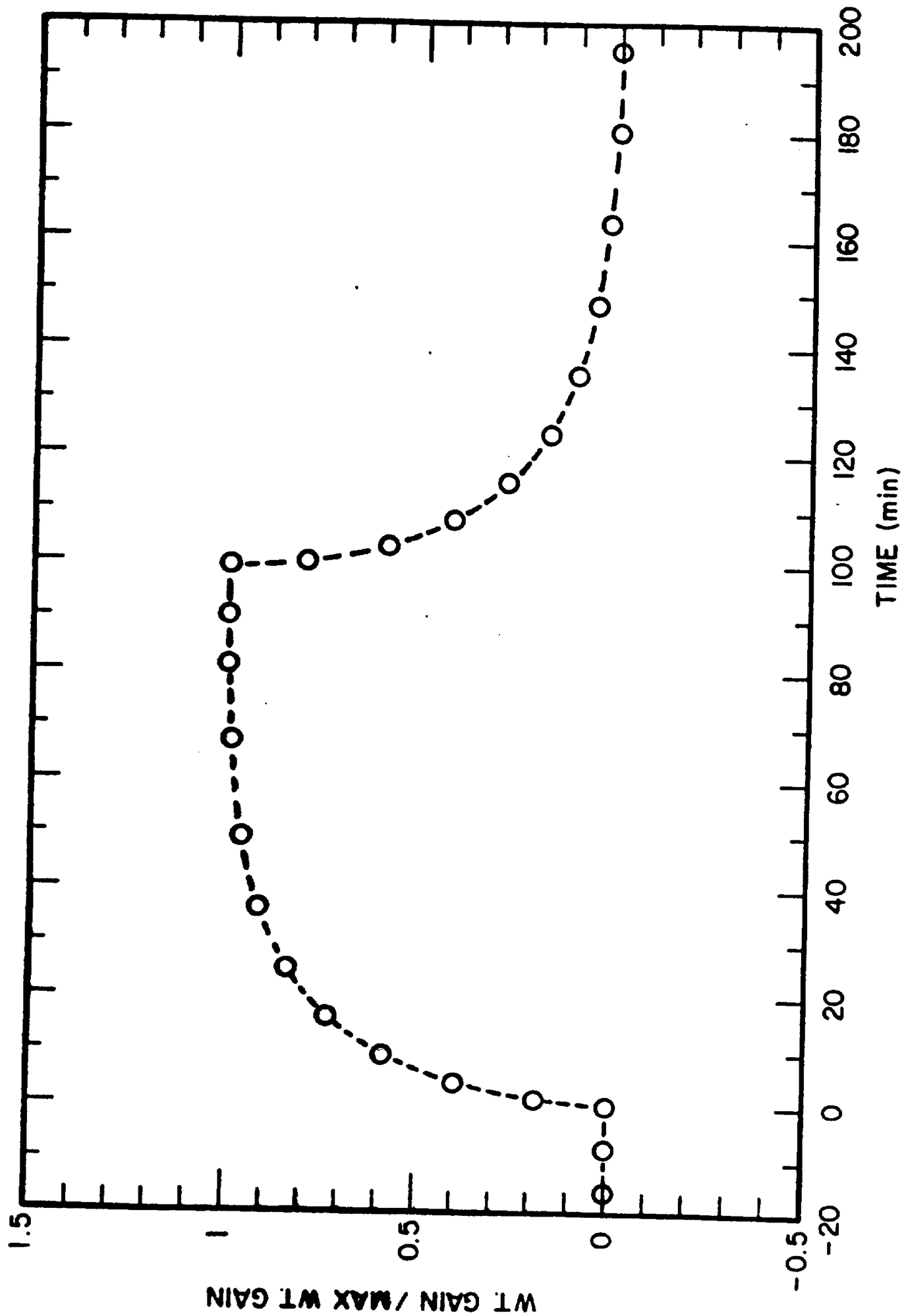

Figure 2. VCM Sorption Data

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CRANK'S SOLUTION TO FICK'S LAW FOR SPHERES

$$1-\frac{C_T}{C_\infty} = \frac{6}{\pi^2} \sum_{N=1}^{\infty} \frac{1}{N^2} \text{ EXP} \left(\frac{-4N^2\pi^2 DT}{d^2}\right)$$

C = VCM CONCENTRATION

T = TIME

D = VCM DIFFUSION COEFFICIENT

d = PRIMARY PARTICLE AGGLOMERATE DIAMETER

REARRANGE TO

$$\text{LN}\left[1-\frac{C_T}{C_\infty}\right] \cong \text{LN}\,\frac{6}{\pi^2} - \left[\frac{4\pi^2 D}{\bar{d}^2}\right] T$$

AND

$$\bar{d} = \left(-\frac{4\pi^2 D}{\text{SLOPE}}\right)^{1/2}$$

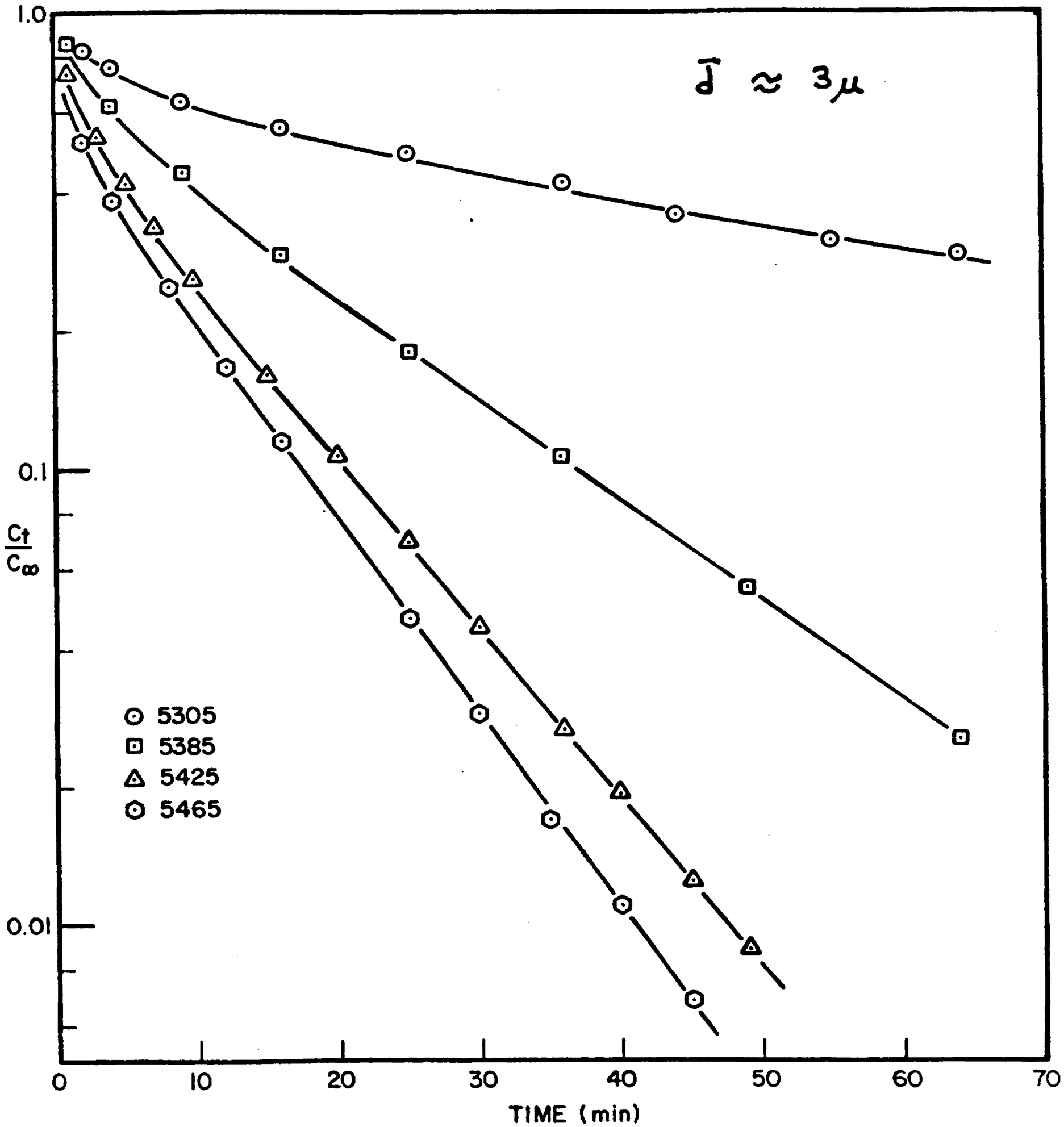


Figure 11. Diffusion Curves for Conoco Resins

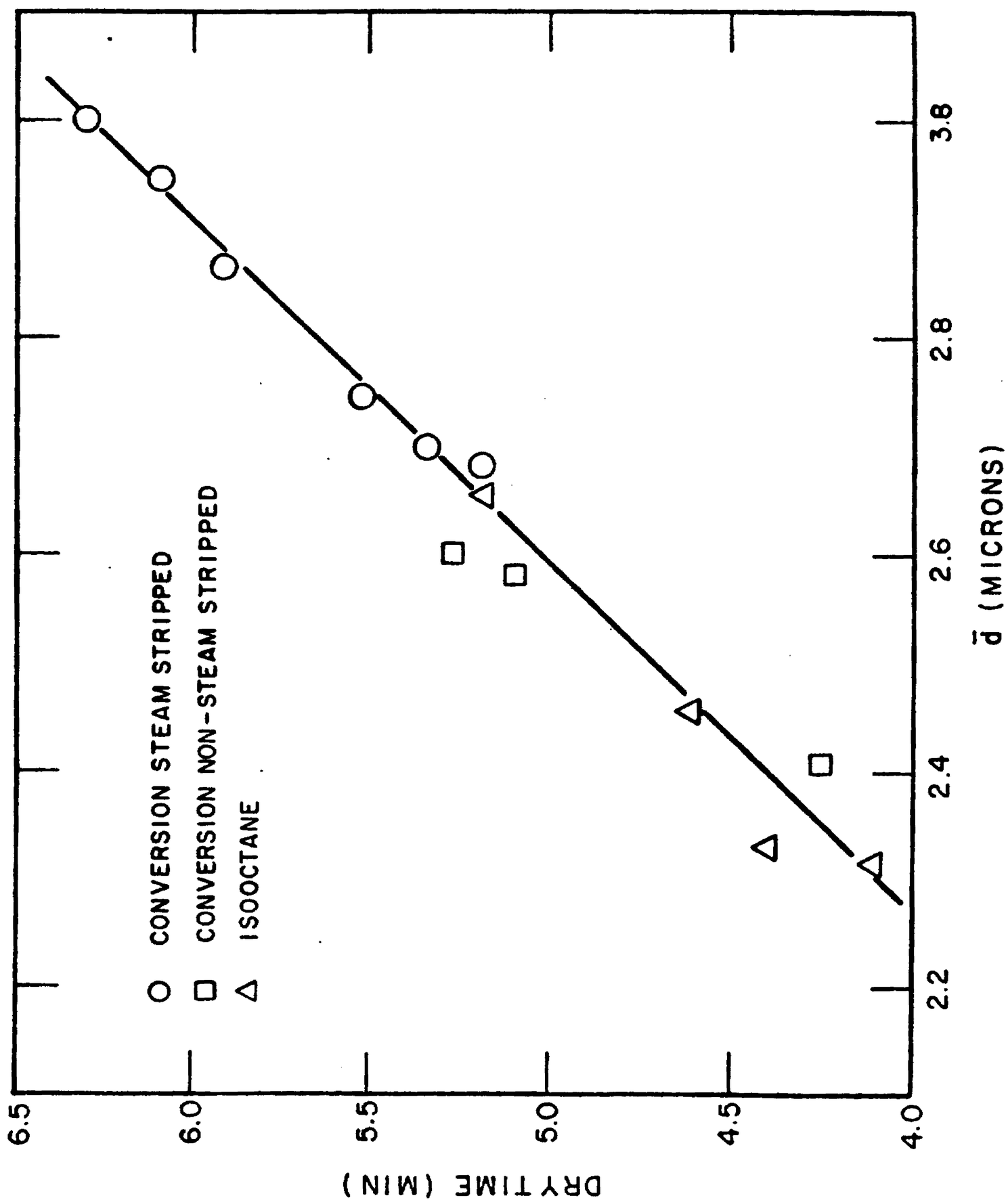


Figure 7. The Effect of Primary Particle Agglomerate Diameter on Brabender Dry Time

CONCLUSION

PRIMARY PARTICLE AGGLOMERATE DIAMETER CONTROLS VCM ABSORPTION AND BRABENDER DRY TIME.

PVC HARD PARTICLES

SYMPTOMS--SURFACE BUMPS OR IRREGULARITIES
ON FLEXIBLE PRODUCTS

CAUSES

NON-RESIN RELATED

POORLY DISPERSED
FILLERS, CLAYS,
PROCESSING AIDS,
OR PIGMENTS.

RESIN-RELATED

A. RESIN GRAINS WITH
ANOMOLOUS MORPHOLOGY

B. MIXTURE OF
MOLECULAR WEIGHTS

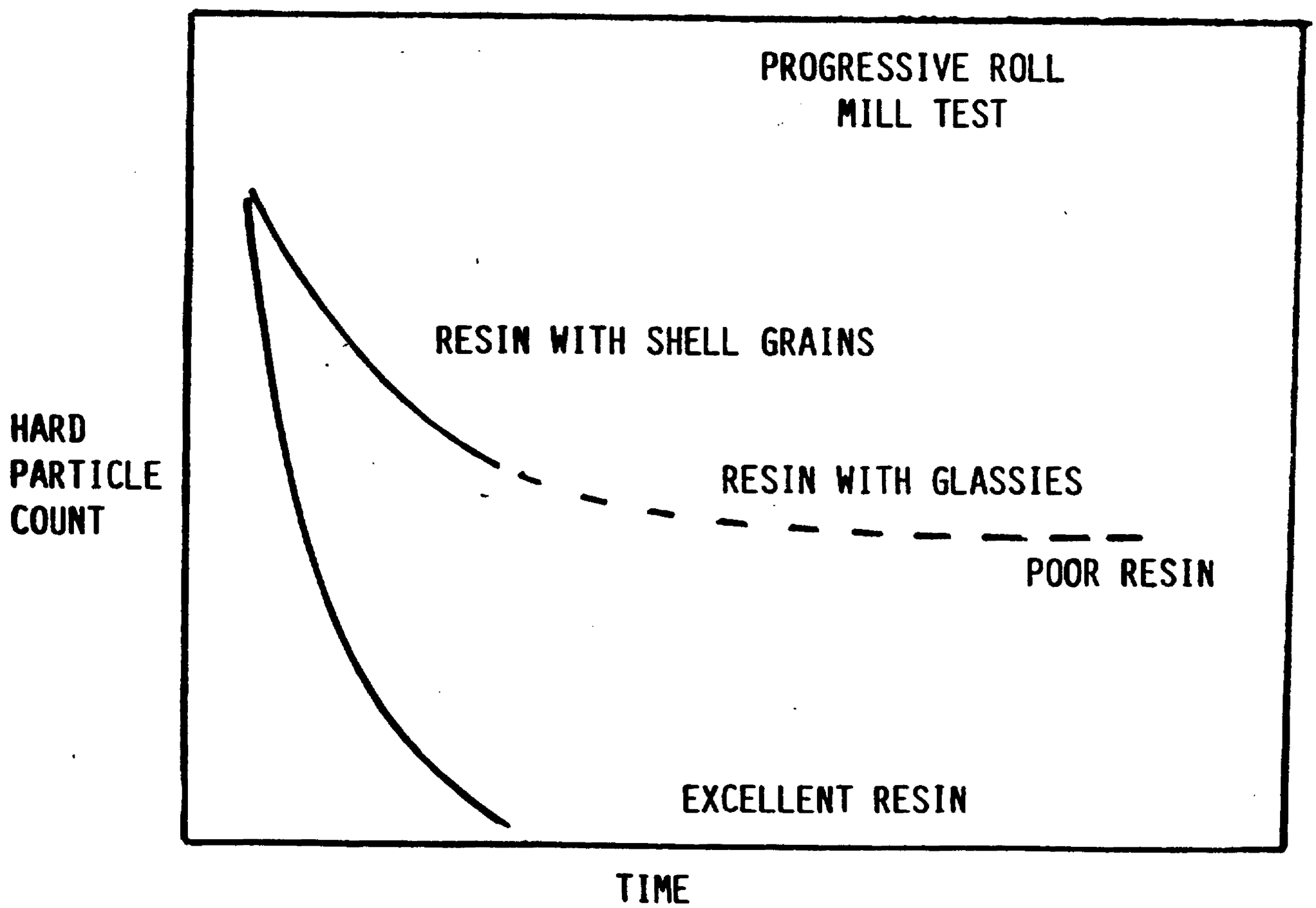
GENERALLY, NO RELATIONSHIP BETWEEN HARD PARTICLES AND GELS.
THAT IS, A TYPE 1 RESIN MAY HAVE HIGH HARD PARTICLES AND A
TYPE 3 RESIN MAY HAVE LOW HARD PARTICLES.

A

RESIN-RELATED

1. GLASSIES, FISHEYES - NON-POROUS TRANSLUCENT PVC GRAINS. VERY DIFFICULT TO REMOVE BY EXTRA COMPOUNDING OR WORKING.

2. SHELL GRAINS - SIMILAR TO GLASSIES, ONLY SLIGHTLY MORE POROUS. ABSORB PLASTICIZER VERY SLOWLY. CAN BE COMPOUNDED OUT.



A

CHAIN TRANSFER AGENTS

FUNCTION: TERMINATE MACRORADICAL CHAIN AND INITIATE NEW CHAIN.

EFFECT: TERMINATE CHAINS AT SHORTER LENGTH THAN NORMAL FOR A GIVEN TEMPERATURE.

PURPOSE: ALLOWS PRODUCTION OF LOW MOLECULAR WEIGHT PVC AT LOWER TEMPERATURE (AND PRESSURES).

CHAIN TRANSFER AGENTS

CONOCO PVC Grade	Monomer Units	Reactor Conditions Without CTA	Reactor Conditions With 2-EH	Reactor Conditions With 2-ME
5305	900	152°F	150°F	150°F
		170 psia	164 psia	164 psia
			0.05 phm	0.002 phm
5265	700	160°F	150°F	150°F
		190 psia	164 psia	164 psia
			0.40 phm	0.02 phm

2-ETHYLHEXANAL

- PRESENT CTA
- ADVANTAGES
  - * LIQUID
  - * NO ODOR
  - * COMPATIBLE
  - * SAFE
  - * USES OPEN CHARGING METHODS
  - * CHEAP ($0.37/LB)
- DISADVANTAGES
  - * RECOVERED WITH RVCM
  - * VOLATILE FROM RESIN
  - * LOW ACTIVITY (0.4 PHM)
  - * CONDENSER FOULING

REQUIRED CHARACTERISTICS OF CTAs

MUST BE

- Highly Active
- Liquid
- Compatible with Reactor Additives
  - * Initiators
  - * Suspending Agent
  - * Kill Agent
- Compatible with Dryblend Additives
  - * Stabilizers (Pb, Ba-Cd-Zn)
  - * Pigments
- Commercially Available

MUST NOT

- Foul Reactor/Condenser
- Contaminate RVCM
- Contaminate PVC
- Harm PVC Heat Stability
- Harm PVC Morphology
- Be Expensive

A

CLASSES OF CTAs SCREENED

- MERCAPTANS
- PHOSPHITES
- ALDEHYDES
- RING STRUCTURES

A

CHAIN TRANSFER AGENTS TESTED

CTA	Relative Activity (2-EH=1)
methyl-3-mercaptopropionate	31.0
mercaptoacetic acid	26.0
2-mercaptoethanol	23.0
pentaerythritol tetra-3-mercaptopropionate	18.0
ethylene-bis-mercaptoacetate	16.0
n-butyl-3-mercaptopropionate	16.0
triphenylantimony	15.0
trimethylolpropane tri-3-mercaptopropionate	15.0
hydroxyethyl mercaptopropionate	14.0
3-mercaptopropionic acid	14.0
2-mercaptopropionic acid	4.5
ethyl-2-mercaptoacetate	2.0
tetralin	1.6
decanal	1.2
2-ethylhexanal	1.0
dimethylmalonate	0.5
ethylcyanoacetate	no activity
isooctyl-3-mercaptopropionate	no activity
tri-n-butyl phosphite	no activity

PROPOSED CTA: 2-MERCAPTOETHANOL

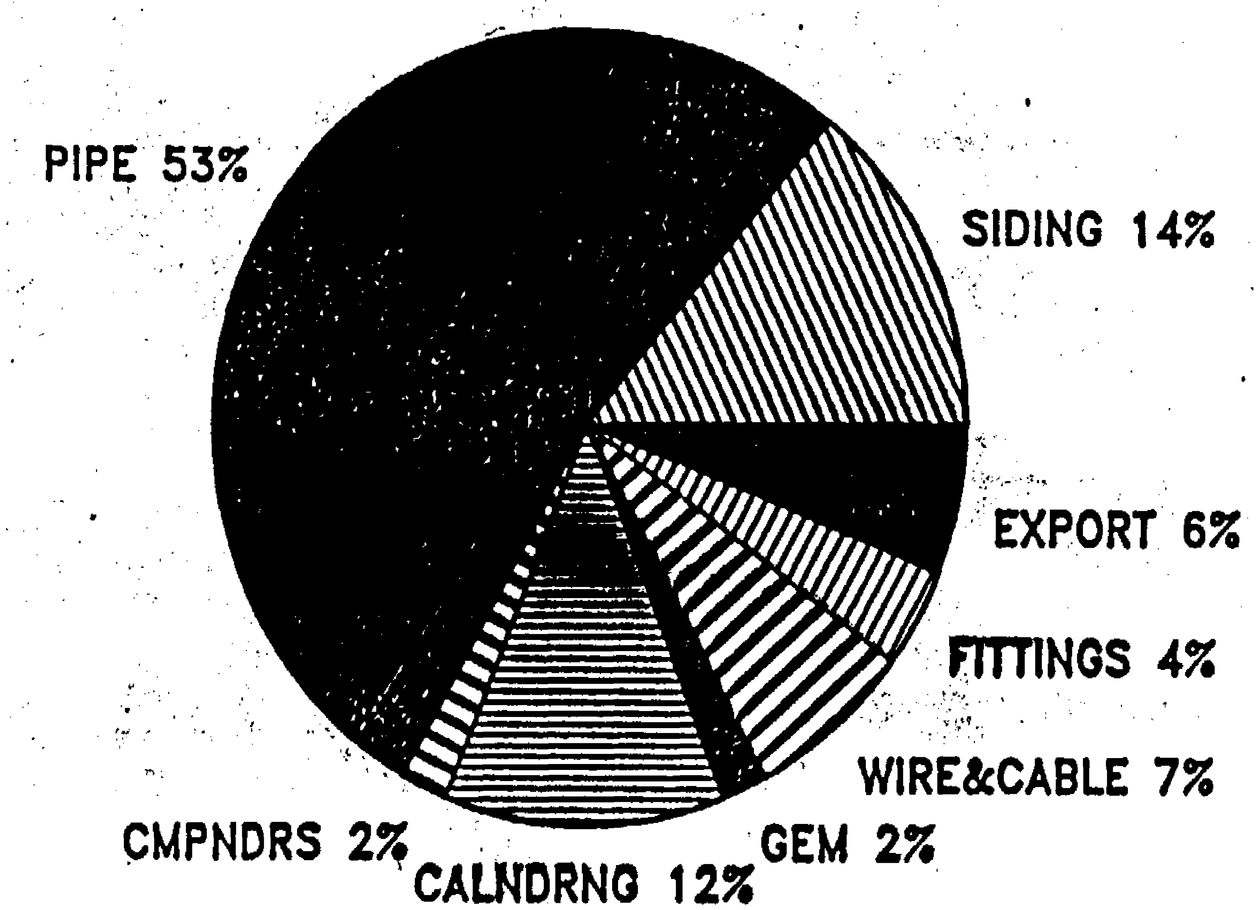
ADVANTAGES

- VERY ACTIVE
  - * LOW USE LEVEL (0.02 PHM)
  - * LOW COST ($0.93/LB.)
- NO CONDENSER FOULING
- EXPENDED DURING POLYMERIZATION
  - * NO RVCM CONTAMINATION
  - * NO COMPATIBILITY PROBLEM
  - * NO RESIN ODOR
- NO PATENT PROBLEM
- IMPROVES PVC HEAT STABILITY/COLOR
- LOWERS W/M RATIO
- ALLOWS USE OF RVCM
- DECREASES POLY TIME

DISADVANTAGES

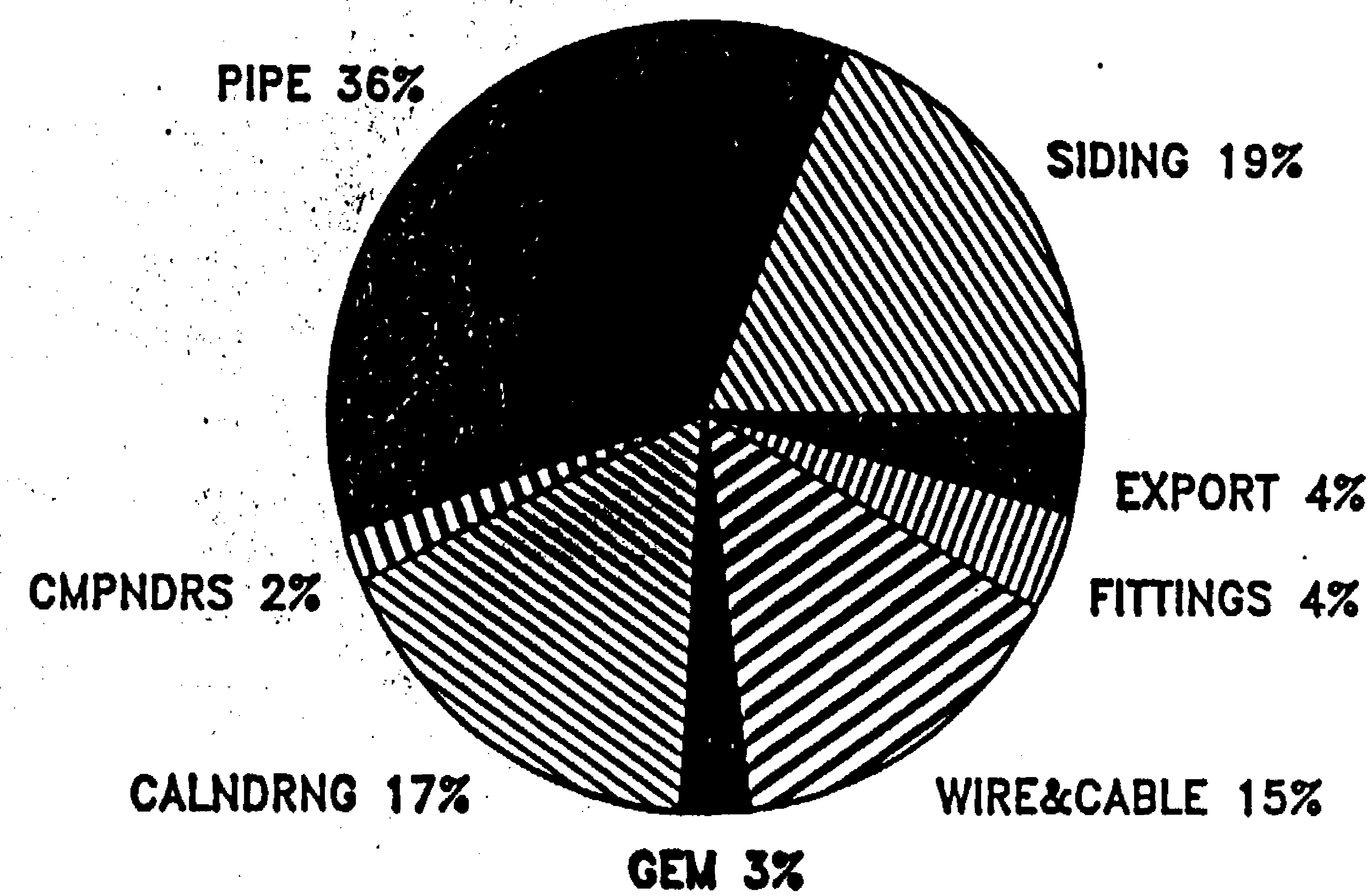
- STRONG ODOR
- TOXIC
- CLOSED ADDITION SYSTEM
- DECREASES RESIN POROSITY

VISTA POLYMERS
RESIN SALES
1986 VS 1988



1986 ACTUAL

588 MM LBS



1988 BUDGET

614 MM LBS

TOTAL SALES

8/87

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IR ACTIVITY TEAM
TASKS

DETERMINE & RECOMMEND

- HOW GOOD DO WE NEED TO BE?
- HOW GOOD CAN WE GET?
- HOW DO WE GET THERE?
- HOW MUCH WILL IT COST?
- WHO'S GOING TO DO IT?
- HOW LONG WILL IT TAKE?

WHAT AFFECTS IR?

ANTISTATS

Bright Boss

- GLYCERINE
- LUBRICAL 48N
- DRY CaSt
- GMS Atmer 129

SODIUM

- BATCH WATER
- CLEAN WALL
- STEAM
- OTHER

OTHER

- DRYERS
- ANTIOXIDANTS
- POROSITY ENHANCERS

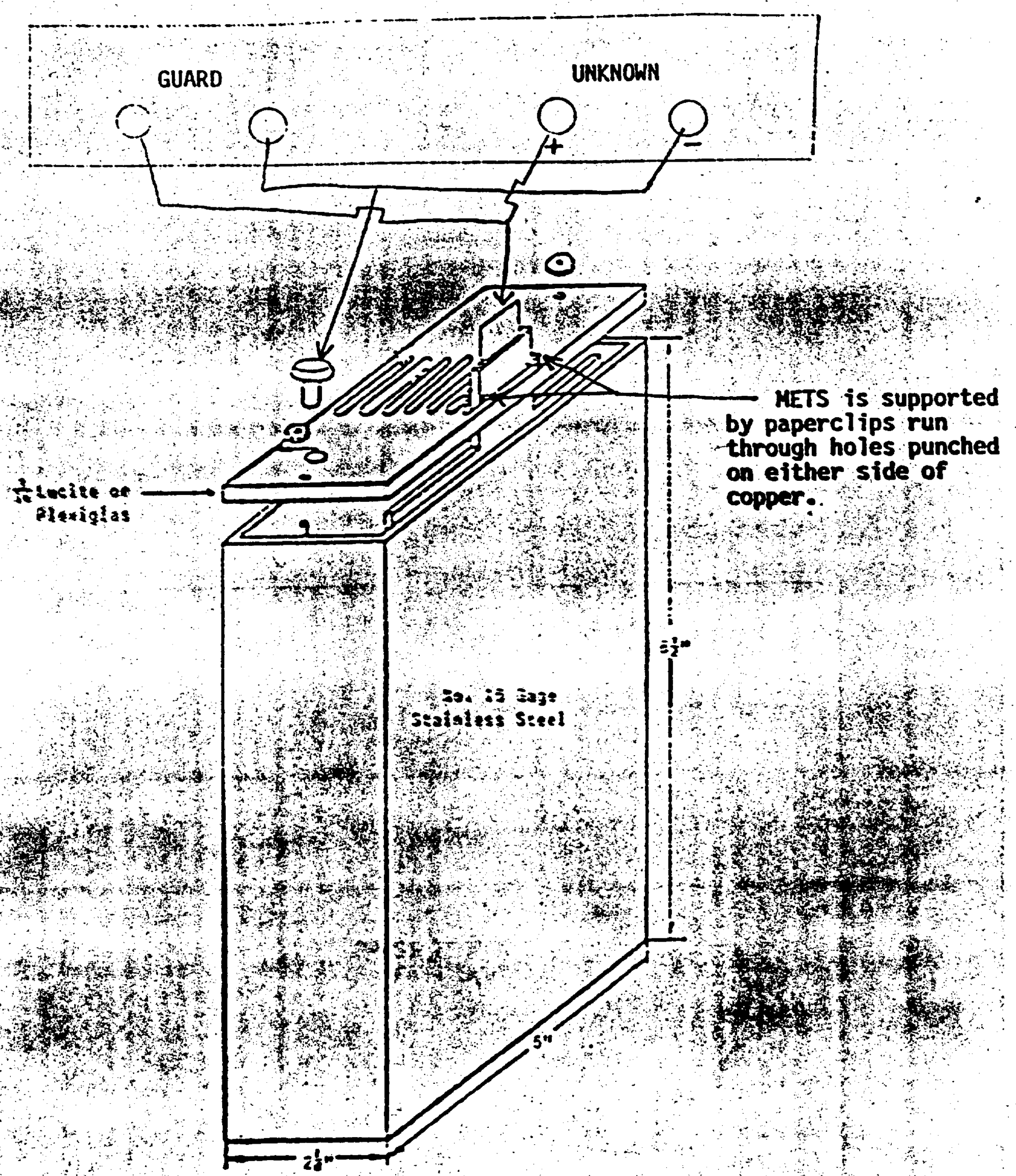
PARAMETERS

RESINS

- 5415
- 5465
- 5385

PLANTS

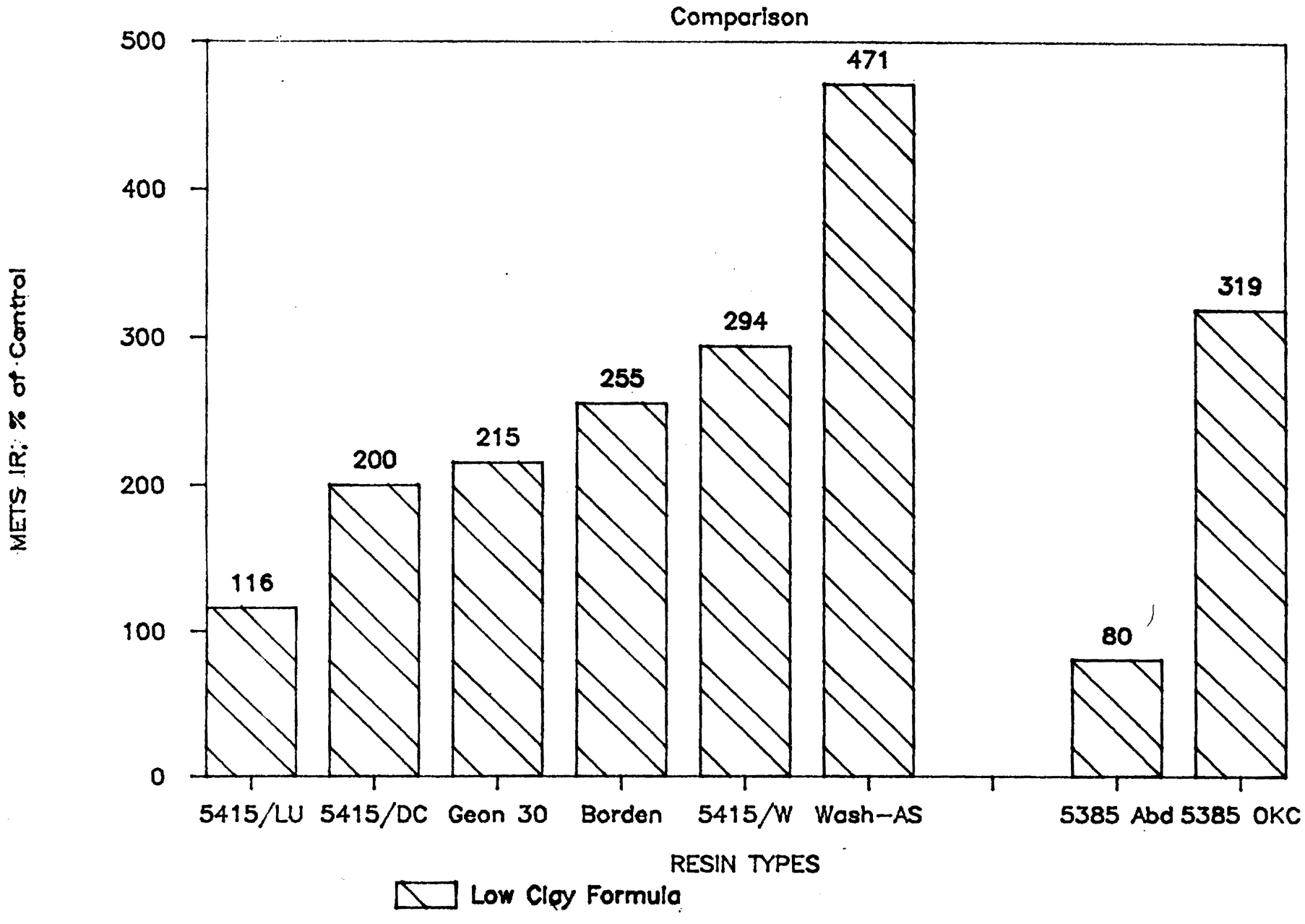
- ABERDEEN OLD MODULE
- ABERDEEN NEW MODULE



Water Immersion Vessel

RRH

Resin METS–IR Values



Rod Hammonds

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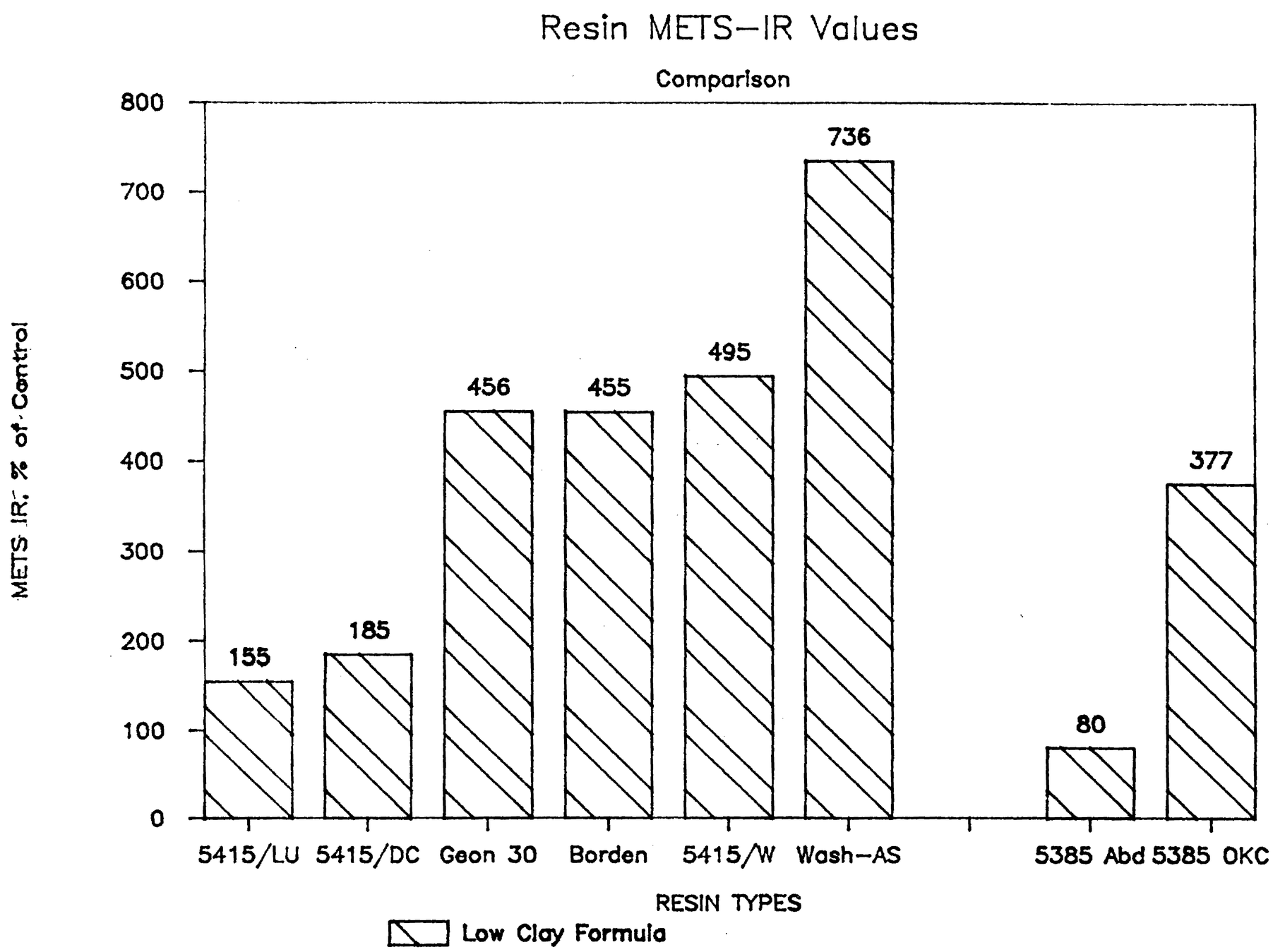
LGC



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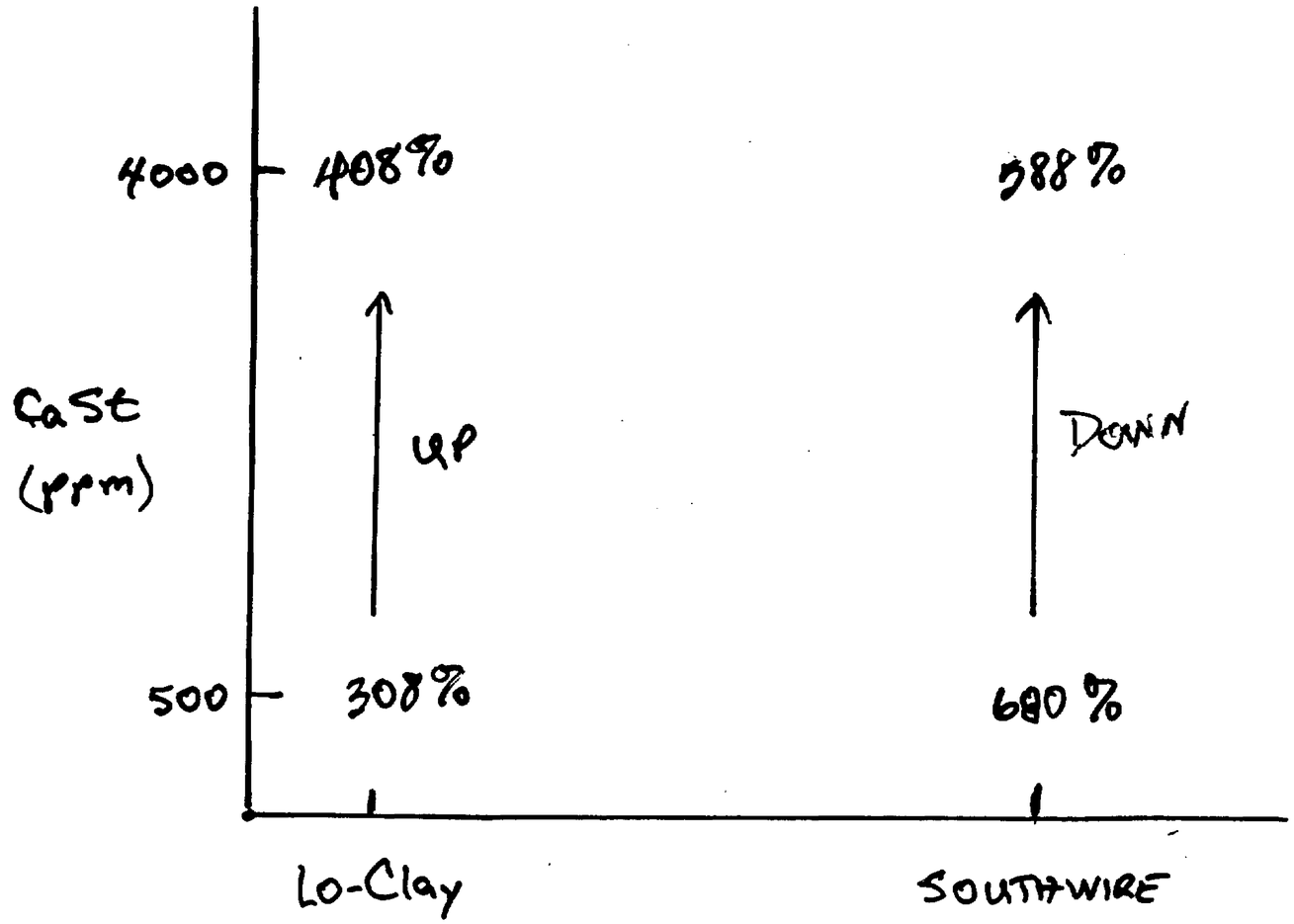
LGC

RESIN SENSITIVITY TO LEAD IN THE METS IR TEST

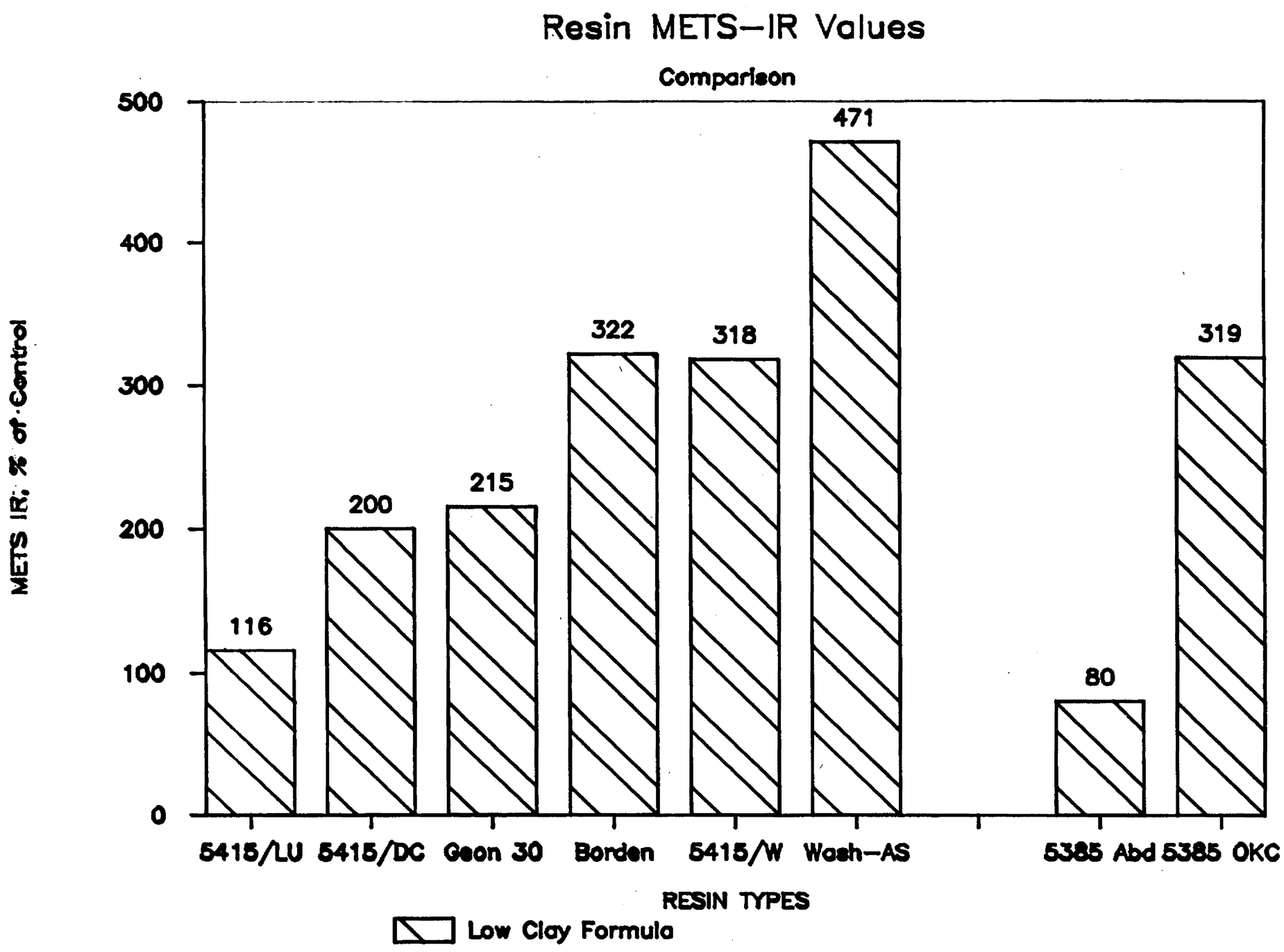
RESIN	ROD'S LEAD (%)	LYNDOL'S LEAD (%)
OKC	400	300
Competitive resin	230	640
Competitive Resins		
5385 Equiv	230	460
5415 Equiv	260	430
5465 Equiv	290	560
Vista Resins		
5415 No Antistat	330	326
5415 BPA/Lubrical	109	137
5415 Dry CaSt	266	271
Washed Vista Resins		
5415 No Antistat	471	736
5415 BPA/Lubrical	248	469
5415 Dry CaSt	397	495
Sodium levels	14 ppm	5 ppm

FORMULATION EFFECT ON METS-IR RESPONSE TO CaSt LEVEL



TEST RESIN WAS 5415 W. NO A/S (NUMBERS ARE % OF Lo-clay standard)

METS-IR FORMULATION



Washing Borden resin does not increase IR
They probably wash w/ DI water

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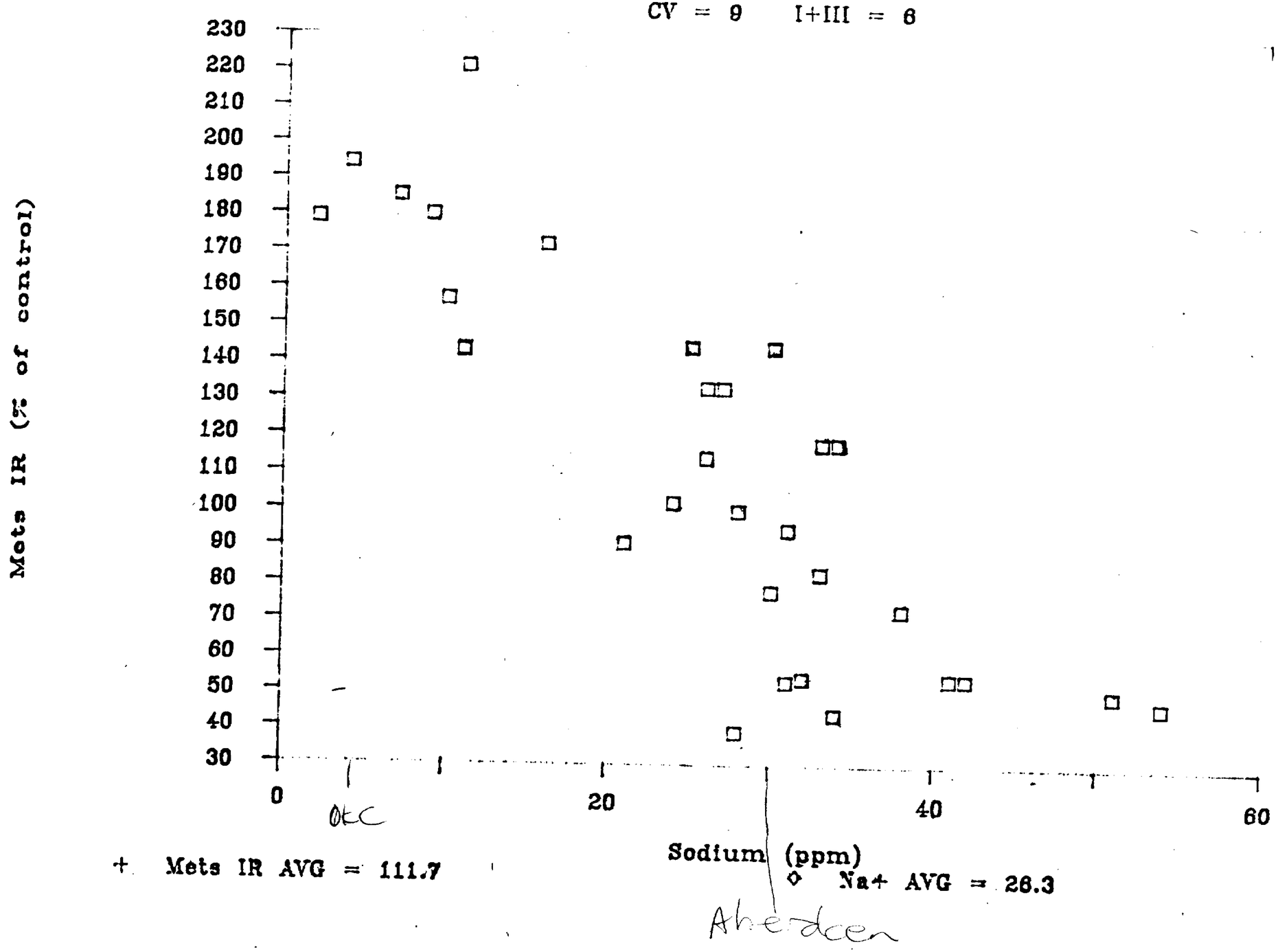
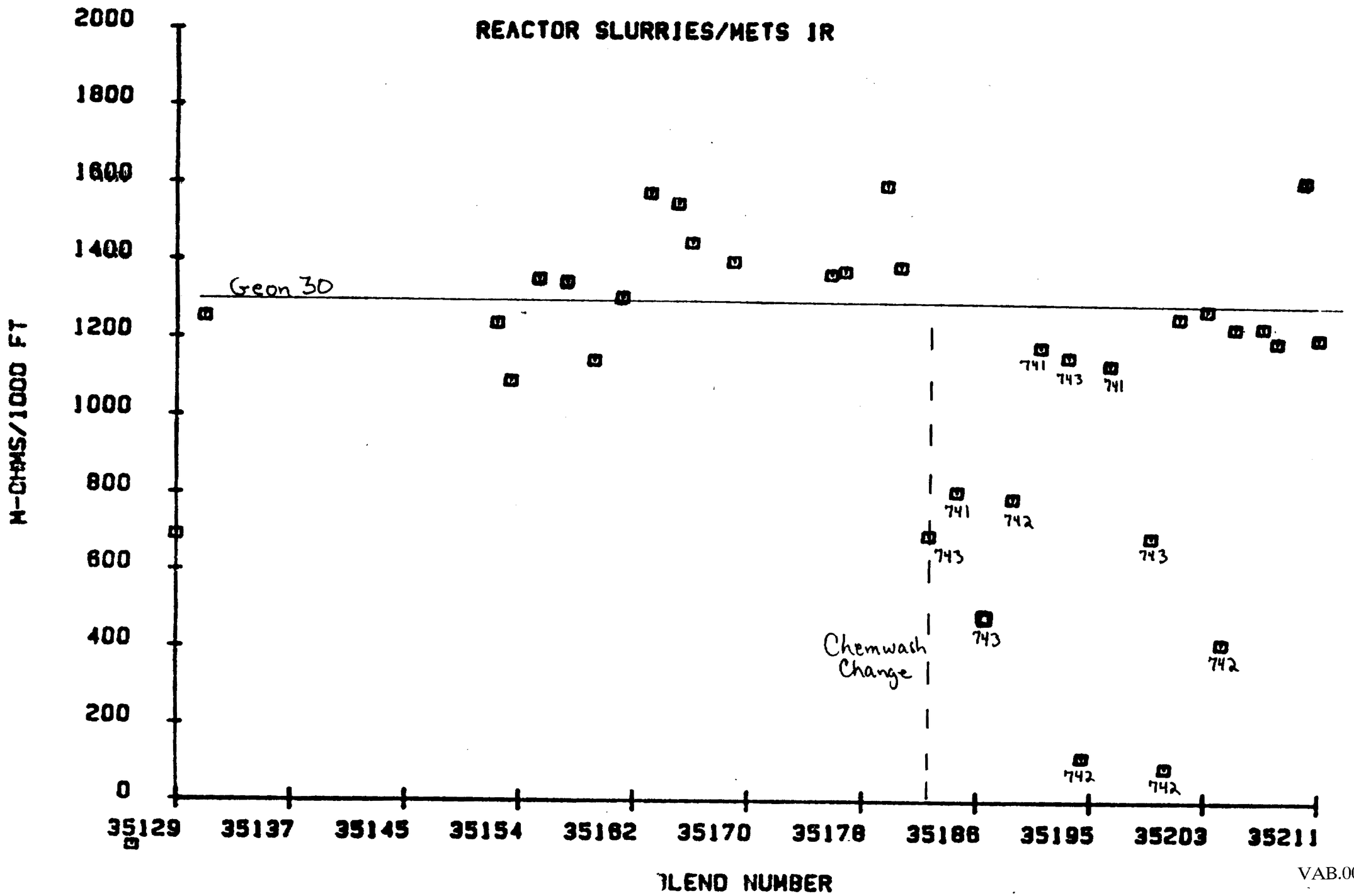
Mets IR vs Sodium

CV = 9 I+III = 6



+ Mets IR AVG = 111.7

◇ Na+ AVG = 26.3



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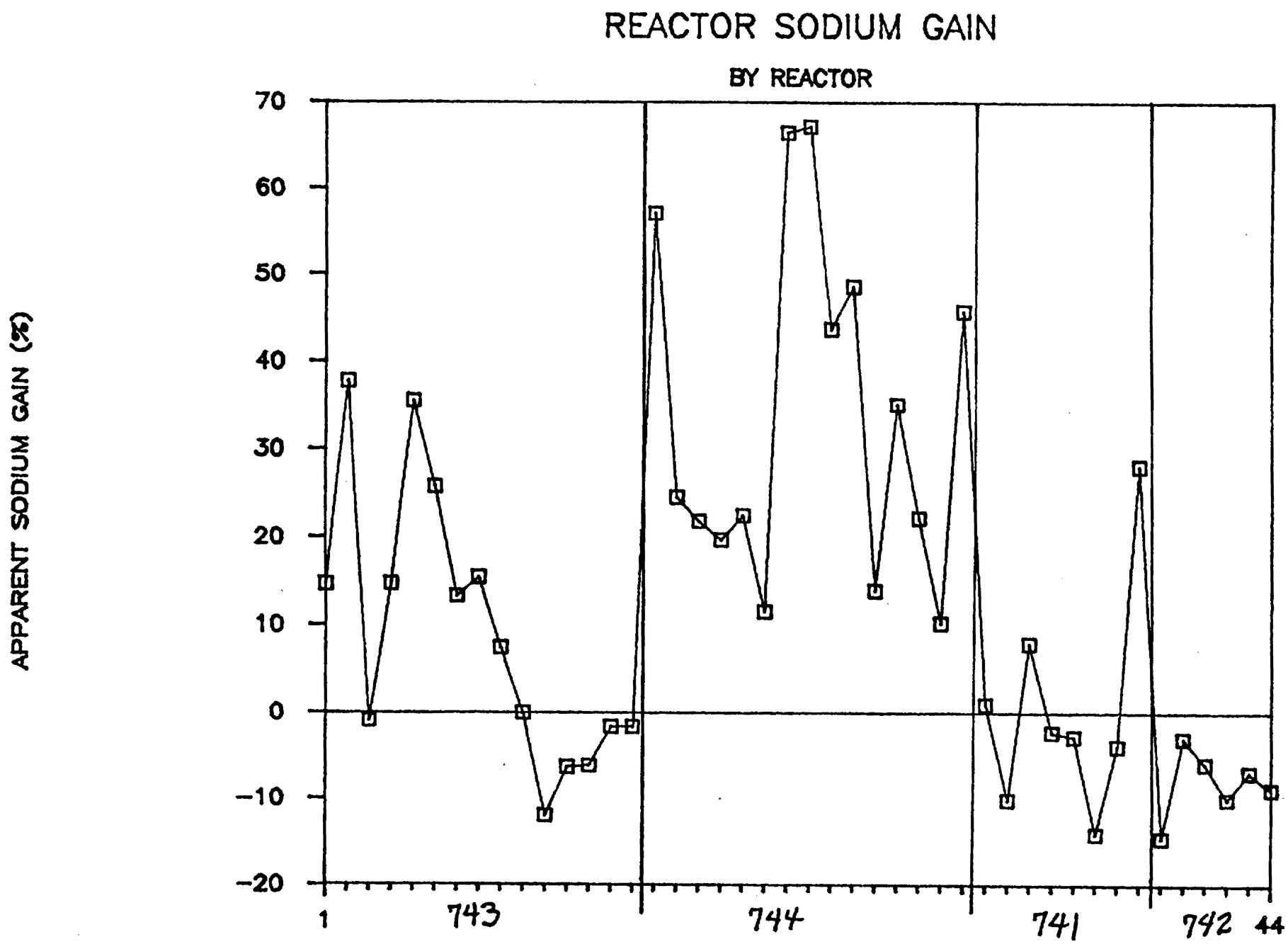

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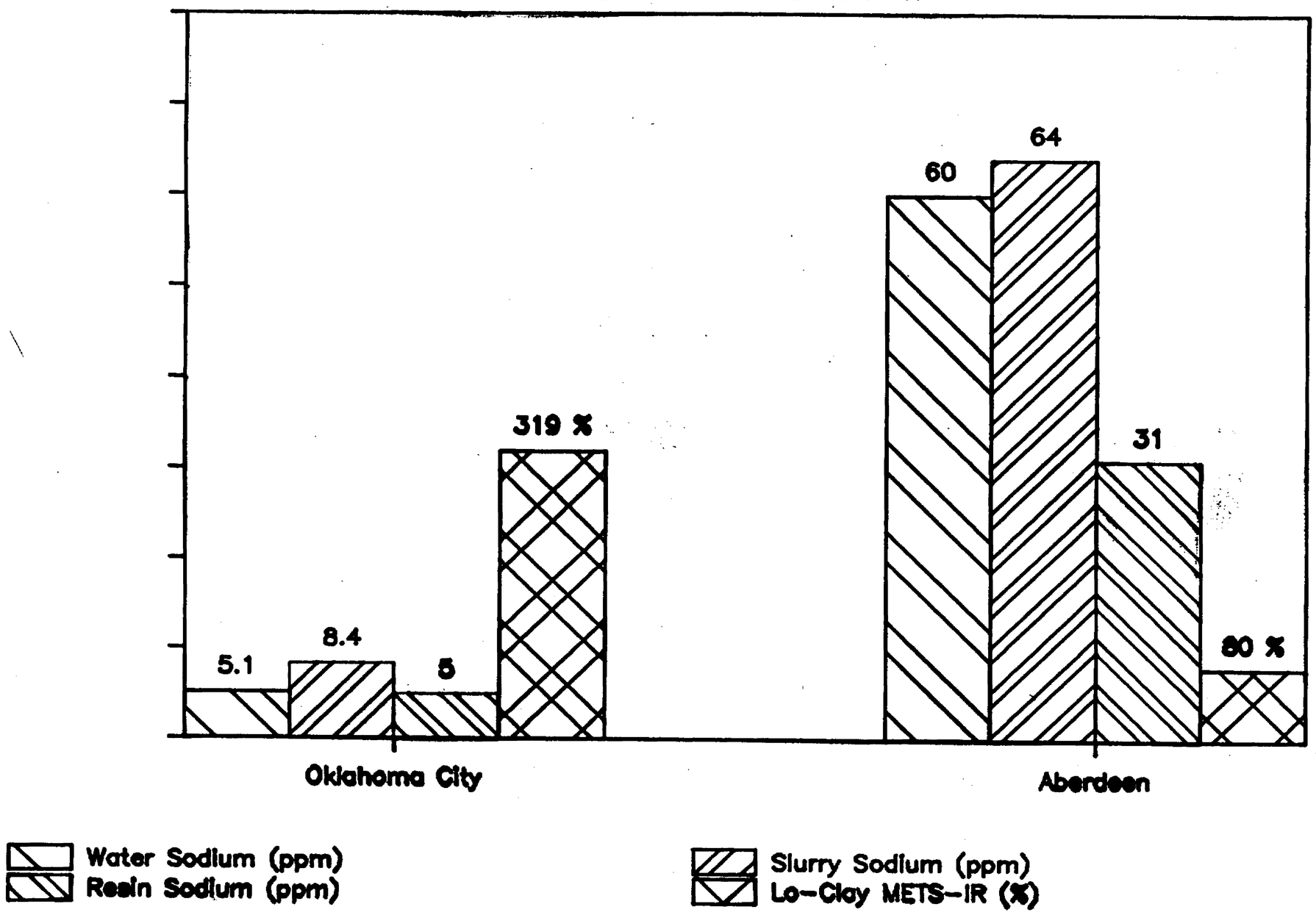
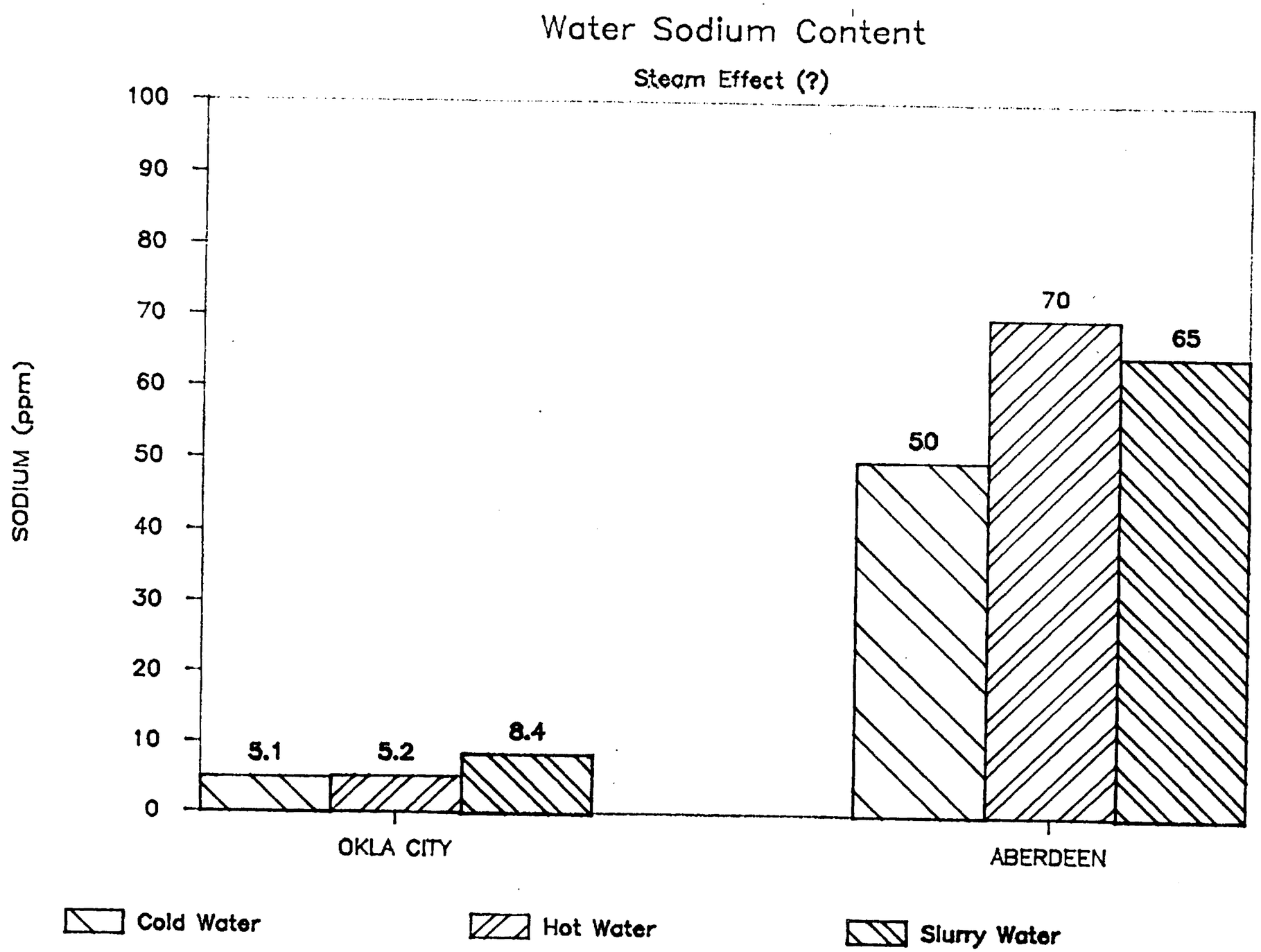
Plant Comparison

Water Sodium and METS–IR




Water Sodium Content
Steam Effect (?)
SODIUM (ppm)
100
90
80
70
60
50
40
30
20
10
0
5.1
5.2
8.4
50
70
65
OKLA CITY
ABERDEEN
Cold Water
Hot Water
Slurry Water

WATER SOURCES

SOURCE	WATER			SLURRY	BUFFER
	Na+	HCO3−	pH	pH	
OKC	5	0	10	6.5	NONE
EUTAW	60	157	7.8	8.5	NONE
GORDO	5	36	6.4	LOW	?
BUFFER	120?				STP

GORDO WATER CHARGE TRIAL

TRIAL OPTIONS

- RAW GORDO WATER
- RAW WATER WITH MANGANESE GREENSAND IRON REMOVAL
  (pH RAISED FROM 7.5 TO 8.0)
- SAME WITH NON-SODIUM BUFFER
- SAME WITH SODIUM BUFFER
- WEST POINT TREATED WATER
  (CaO, ALUM, Cl)

PROJECT STEPS

- BUFFER AND RECIPE
- WATER HANDLING EQUIPMENT
- HOOKUPS AND CHARGE PROCEDURE
- SAMPLES AND ANALYSIS
- RESIN DISPOSITION
- FUNDING

DRAFT PROPOSAL FOR PLANT TRIAL TO BE READY BY OCTOBER 22

TABLE A

Data according to Procedure B

BLEND NUMBER	SODIUM CONCENTRATION BEFORE DI WASHING	SODIUM CONCENTRATION AFTER DI WASHING
46449	25	11
46472	21	10
46481	33	2
46489	31	4
46506	41	7
46501	38	9
46511	24	16
46477	34	2
AVERAGE	30.9	7.6

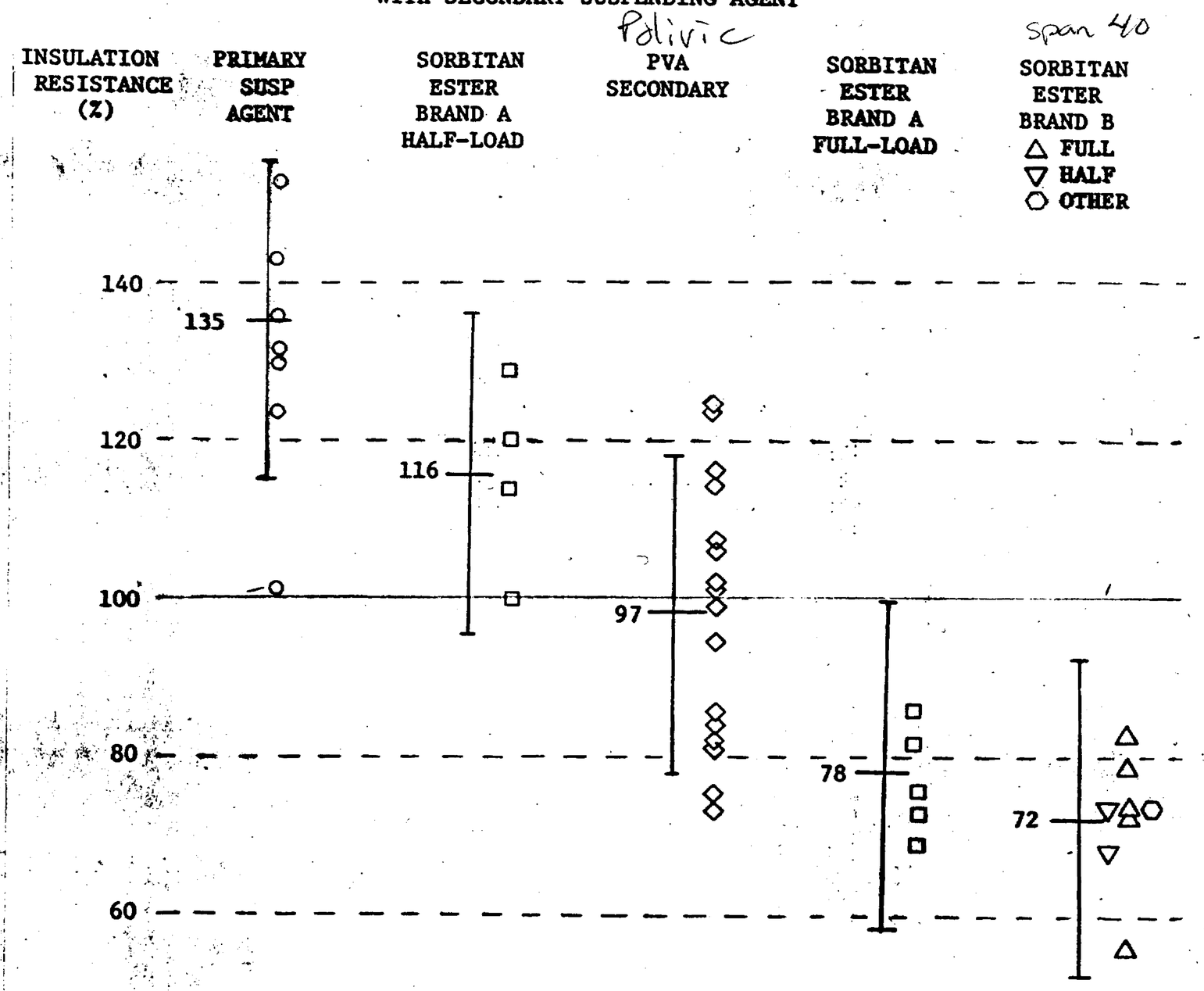
75%

(~~206~~ decrease in sodium concentration)

BLEND NUMBER	METS IR BEFORE WASHING	METS IR AFTER WASHING
46449	144	221
46472	91	157
46481	118	179
46485	83	185
46489	95	190
46497	44	157
46501	73	180
46511	102	172
46527	99	156
46536	63	167
46531	39	183
46543	114	187
46553	88	193
46569	54	140
46573	61	144
46477	67	158
AVERAGE	83.4	172.1

(106.4% increase in METS IR value)

VARIATION OF INSULATION RESISTANCE
WITH SECONDARY SUSPENDING AGENT



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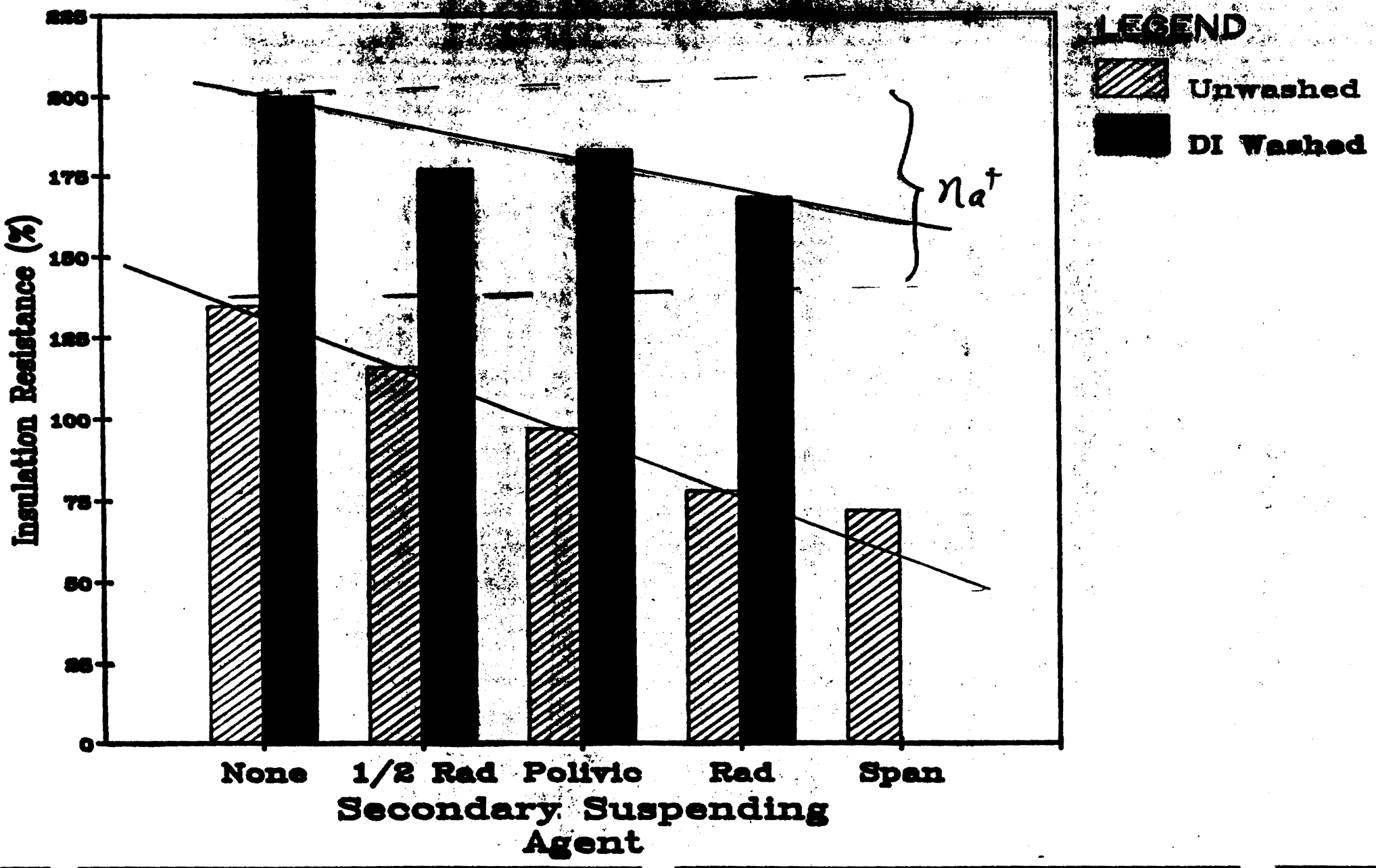
High Porosity 5415
Insulation Resistance



RIGID PVC

RIGID PVC TRAINING MANUAL

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FORMULATING RIGID PVC

With many thermoplastic polymers, it is necessary to add only small amounts of a few additives to obtain satisfactory properties for fabrication and physical properties. PVC, on the other hand, requires significant portions of additives. Without these additives, the properties of the PVC resin would be unsuitable for fabrication operations, such as extrusion; and the end-use properties of a fabricated article would also be unsatisfactory. This has resulted in a significant amount of technology on PVC additives and a substantial industry to supply this market. A benefit of PVC, with regard to additives, is the wide variation in properties that can be obtained depending on the type and amount of additives used. The stiffness of the PVC can be varied from very rigid items like PVC pipe to very flexible items like weather stripping or gasketing. Similarly, other properties can be widely varied with the same basic PVC resin by changing the additive package employed.

In flexible PVC compounds, the major consideration in selecting additives is their effect on the physical properties of the fabricated article, such as hardness. With rigid PVC, on the other hand, more consideration must be given to the effect of additives on the processing of the compound. This is due to the high melt viscosity of rigid PVC relative to flexible PVC, and the resultant greater tendency for thermal degradation and poor melt flow. Typical rigid PVC formulations will contain from 93% to 75% PVC resin, with the remainder being additives. A typical rigid PVC formulation might contain seven (7) ingredients in addition to the PVC resin. Based on their function, these additives can be classified into various categories which we will discuss below.

Stabilizers

Without the addition of heat stabilizers to PVC, subsequent processing and fabrication operations would be virtually impossible. PVC is much more heat sensitive than most thermoplastics. Exposure of PVC to heat causes decomposition of the polymer. This involves both chain scission (breaking) and cross-linking between polymer chains. This thermal degradation can occur even at relatively low temperatures, such as in the intensive mixing step of dryblend preparation. Thus, it is necessary to add thermal stabilizers to PVC before any mixing or fabrication operations are carried out.

In addition to decomposition of PVC due to thermal energy, ultraviolet (uv) light exposure causes PVC degradation in a similar

fashion. Stabilizers also play an important role in minimizing ultraviolet light degradation of PVC. Even with the use of the best additives, neither thermal degradation nor uv degradation can be totally prevented; but the amount of degradation can be minimized to the extent that the useful properties of the polymer are maintained.

The decomposition of PVC due to either thermal or light degradation results in several changes in the properties of a PVC compound. These changes include an increase in the melt viscosity with resultant changes in the processing characteristics; changes in physical properties such as increased stiffness, increased brittleness, and generally lower strength characteristics; and discoloration. The change in color is the symptom of thermal degradation that is generally noticed first by a PVC processor. This color change initially is a yellowing of clear or light-colored PVC, becoming progressively brown or greenish-gray as degradation continues. Eventually, the polymer will turn black. This color change is accompanied by an increased tendency of the PVC compound to stick to the metal surfaces of the processing equipment. This combination of changes can result in a somewhat catastrophic situation when degradation problems occur during processing operations. Once a PVC compound begins to degrade, the auto-catalytic degradation is accompanied by evolution of hydrochloric acid which is irritating to the equipment operators and can result in corrosion of processing equipment. A typical result of severe degradation is etching or chrome removal from processing tooling due to HCl evolution. The sticking tendency of degraded PVC contributes to the problem because it is more difficult to remove the degrading PVC from the metal tooling surface. Since the HCl evolution of degrading PVC further catalyzes the degradation process, a small area of degradation in an extrusion die, for example, can rapidly lead to degradation throughout the die with potential economic losses due to damage to the metal surface. Thus, it is apparent that adequate stabilization of rigid PVC compounds is important. However, the tin compounds which are commonly used as stabilizers in the United States are relatively expensive compared to other PVC additives. Thus, the formulator must strike a balance between adequate stabilization and minimal stabilizer costs.

Various test methods are used in the laboratory to intentionally cause thermal degradation of a compound for purposes of stabilizer evaluation and a determination of the appropriate degree of heat stability required. Generally, these tests can be classified in two categories. Since the color change of degrading PVC is the symptom most obvious to a PVC customer, a common type of stability test is to measure the color change of a test compound on exposure to heat for varying time periods. Another common test involves measurement of the rheology changes that occur with degradation of PVC. This is most commonly done with a torque rheometer and is the method Vista uses for quality control of thermal stability for our dryblend products.

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A

In selecting a stablizer type and amount for a rigid PVC formulation, various factors must be considered. Thermal stability and cost are most important. The fabrication process and end-use often determine whether a color stability test or a torque rheometer stability test is best suited. Stabilizers in liquid form can decrease the maximum end-use temperature of the PVC compound, since liquids have a plasticizing effect in rigid PVC formulations. Most stabilizers also have some weak lubricant action, and the lubricity contribution of the stabilizer must be considered to insure adequate processing. In applications requiring outdoor weathering of the fabricated article, the light stability characteristics of the stabilizer must be considered. The toxicity of the stabilizer must be considered, primarily with respect to extraction of PVC compound ingredients in food contact or potable water applications, but also with respect to worker exposure to dusts from PVC dryblend which may contain heavy metals. In some applications, such as food packaging, the odor characteristics of the stabilizer should be considered, particularly since most stabilizers used for rigid PVC in the United States have disagreeable sulfur odors. Each of these characteristics should be considered when selecting a stabilizer for a rigid PVC formulation.

The vast majority of stabilizers used in rigid PVC in the United States are tin mercaptides (organo tin compounds containing sulfur). In Europe, it is customary in many applications to use barium cadmium compounds or lead compounds to stabilize rigid PVC. However, these two stabilizer types are not often used for rigid PVC in the United States, primarily due to toxicity concerns with such heavy metals. In a few applications, other stabilizer types are used in the United States such as calcium zinc compounds in food applications where tin mercaptides result in odor problems, or non-sulfur tin compounds (carboxylates) where weathering properties are particularly important. In general, though, the vast majority of rigid PVC compounds contain tin mercaptide stabilizers in the United States. These stabilizers typically range in price from $2.00 to $4.00 per pound and are used at concentrations of 0.3 to 2.5 weight percent. Nearly all tin mercaptide stabilizers are liquid; these are often the only liquid components used in rigid PVC formulations in the United States. The major U.S. suppliers of tin stabilizers are M & T Chemicals, Argus, and Carstab. Also available are "package stabilizers" which are combinations of tin mercaptide stabilizer plus various lubricants. The advantage of these additives is a reduced number of ingredients which the compounder must add to his PVC resin.

Antimony mercaptides have taken some share of the PVC pipe stabilizer market from tin stabilizers due to lower cost. Performance is similar to low-strength tin stabilizers except for lubricity characteristics. The major supplier of antimony stabilizers is Synthetic Products (Synpro).

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Processing Aids

Processing aids are additives which assist in the fabrication of PVC by processes such as extrusion or injection molding. Processing aids generally have no direct effect on the physical properties of the finished compound, such as impact strength, but can have an indirect effect on physical properties by assisting processing, such as through more complete fusion. Processing aids perform several functions to assist fabrication. A primary benefit is that processing aids promote fusion of PVC resin.

Other beneficial functions include reducing plate-out, increasing the "hot strength" of the PVC melt, improved thermoforming characteristics, and improving surface appearance of injection-molded articles. Without processing aids in injection-molded rigid PVC, appearance defects known as splay and blush are likely to occur.

As a result of these beneficial characteristics, processing aids are used in most rigid PVC applications in the United States. The major exception to this is PVC pipe. Due to the importance of low formulation costs for PVC pipe, processing aids are generally not used on twin-screw extruders. This makes processing more difficult; but, with care, good results are obtained.

The processing aids most often used are acrylic co-polymers. These are high molecular weight powdered polymers. The more common grades cost approximately $1.20 per pound and are commonly used at 0.5 to 3% concentration. The major U.S. supplier of acrylic processing aids is Rohm & Haas Company, with M & T Chemicals and Kaneka as minor suppliers.

Impact Modifiers

Impact modifiers are rubbery polymers which are compatible with PVC. Addition of these rubbery polymers increases the impact strength of rigid PVC and causes breakage to be more ductile in nature. This improved "toughness" is critical in some applications for rigid PVC but is unnecessary in other applications. A major market where impact modifiers are not needed is in PVC pipe. Most other rigid PVC applications use impact modifiers to some degree to increase impact resistance. The improvement in impact strength of the rigid PVC as a result of impact modifiers is particularly pronounced at low temperatures.

Due to the high amounts of impact modifiers required in some circumstances, and the relatively high cost of such modifiers, the rigid PVC formulator must use only the minimum quantity of impact modifier required. An additional reason for minimizing use-levels is the generally detrimental effect of impact modifiers on processing characteristics. Impact modifiers generally increase

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