Trends in suspension PVC manufacture

With dynamic technology, large reactors, optimization, clean wall systems, and VCM containment, PVC should hold its position as a leading thermoplastic

J.B. Cameron, Conoco Chemicals Co., Houston;
A.J. Lundeen and **J.H. McCulley, Jr.,** Conoco, Inc., Ponca City, Okla.

USES OF PVC are divided into the broad areas of flexible (or plasticized) and rigid (non-plasticized) applications. Historically, flexible applications appeared first. Initially, plasticized PVC found use as wire insulation. Soon after, calendered PVC, introduced as a leather replacement, became widely known as "vinyl" to the public. Flexible PVC was initially processed on equipment used in the rubber industry. Now, however, specialized equipment has been developed for flexible PVC.

Rigid PVC, used in pipe, fittings and building profiles, has grown rapidly in the past decade (Fig. 1). Improved resin quality, stabilizer systems, extrusion equipment and high demand for these products all contributed to this spectacular growth.

PVC resins produced in the U.S. span the inherent viscosity range from 0.65 to 1.16. Other resin properties of importance in most applications are porosity, fusion rate, heat stability and bulk density. High volume resistivity is needed in electrical applications and a low gel content is required for certain flexible and rigid products. Resin properties required for different applications are given in Table 2.

Three types of processes are used for PVC homopolymer manufacture. These are suspension, emulsion and mass (or bulk) processes. The proportion of PVC made by each process is now reasonably stable and should remain so in the next few years.[1] About 80 percent of all PVC is produced by suspension processes. This review is limited to a discussion of PVC suspension processes.

The chemistry of vinyl chloride polymerization. Vinyl chloride monomer (VCM) is polymerized efficiently in the presence of a free radical source. The general reaction scheme and initial kinetics are typical of a free radical chain reaction.

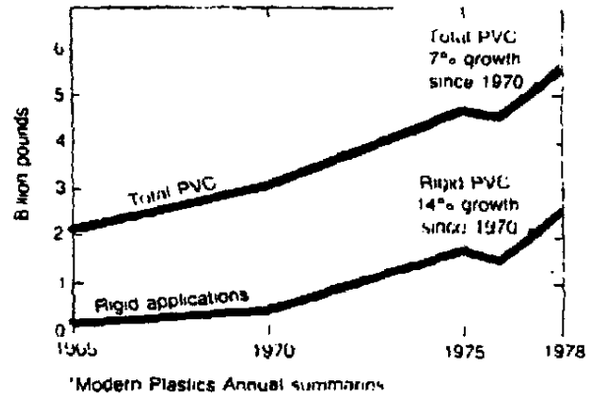


Fig. 1—Growth of the PVC industry.

Initiation	$\text{Initiator} \xrightarrow{K_i} 2I\cdot$
Polymerization	$I\cdot + M \xrightarrow{K_p} R\cdot$ $R\cdot + M \xrightarrow{K_p} R'$
Chain transfer to monomer	$R\cdot + M \xrightarrow{K_1} \text{PVC} + R\cdot$
Other chain transfer agent (CTA)	$R\cdot + \text{CTA} \xrightarrow{K_t} \text{PVC} + R\cdot$
Termination	$2R\cdot \xrightarrow{K_t} \text{PVC}$

Overall, polymerization rate is influenced by the initiator (or initiators) used. Vinyl chloride polymerization is inhibited by oxygen, nitrous oxide and other free radical inhibitors. Complex kinetics arise because of different polymerization rates in the monomer and polymer phase. Termination reactions (K_t) are retarded because of reduced radical mobility in the polymer phase. Consequently, the overall rate generally increases with the amount of polymer formed (Trommsdorf effect) as shown in Fig. 2. Some companies have developed initiator combinations to provide for more uniform reaction rate throughout polymerization.[8,9]

The molecular weight of PVC decreases with increasing polymerization temperature, i.e., K_t increases more rapidly than K_p. The relationship of polymerization temperature to a measure of molecular weight (inherent viscosity) is shown in Fig. 3.

Polymer molecular weight is nearly independent of

TABLE 1—Listing of PVC producer capacity, third quarter 1979
(Approximate name plate capacity, MM lbs)

NORTH AMERICA	
Canada	
Diamond Shamrock - Alberta Gas	220
ESSO Chemical Canada	85
B. F. Goodrich (2 locations)	347
Total	~650
Mexico	
Industrias Resistol (2 locations)	88
Plasticos Omega	7
Policyd (2 locations)	230
Polimeros de Mexico	66
Promociones Industriales Mexicanas	66
Total	~450
United States	
Air Products and Chemicals (2 locations)	330
Borden (2 locations)	530
Certain-Teed	220
Conoco Chemicals (2 locations)	550
Diamond Shamrock (2 locations)	570
Ethyl	180
Firestone (2 locations)	420
General Tire and Rubber (2 locations)	175
Georgia-Pacific	550
B. F. Goodrich (6 locations),	1,400
Goodyear Tire and Rubber	75
Great American Chemical	75
Hooker Chemicals and Plastics (2 locations)	180
International Materials	50
Keysor-Century	50
Panasote (2 locations)	120
Rico Chemicals	160
Shintech	330
Stauffer Chemical (3 locations)	420
Tenneco Chemicals (3 locations)	665
Union Carbide	150
Total	~7,200
CENTRAL AMERICA	
Nicaragua	
Polycasa	55
SOUTH AMERICA	
Argentina	
Electroclor SACI	65
Indupa	40
Viplastic	15
Total	~120
Brazil	
Brasivil Resinas Vinilicas	100
C.P.C. - Petroquimica	300
S.A. Gaso do Brasil	90
Industrias Quimicas Electro Cloro	165
Total	650
Chile	
Petroquimica - Dow	30
Colombia	
Colombiana de Carburo y Derivados	17
Petroquimica Colombiana	80
Peru	
Sociedad Paramonga	
Venezuela	
Plasticos Petroquimica	
WESTERN EUROPE	
EEC	
Belgium	
Badiphit	
Solvic	
Total	
France	
Societe Artesienne de Vinyl	
CdF Chimie	
ATO Chimie	
Produits Chimiques Ugine Kuhlmann	
Rhone - Poulenc (3 locations)	
Shell Chimie	
Solvic	
Total	~2,5
West Germany	
BASF	
Chemische Werke Huels	
ICI	
Solvay	
Hoechst (2 locations)	
Lonza	
Wacker - Chemie (2 locations)	
Total	~2,4
Italy	
Societa Chimica Ravenna	
Liquiquimica Ferrandina	
Montedison (3 locations)	1,
Rumianca Sud	
Societa Italiana Resine	
Solvic	
Total	~2,4
Netherlands	
DSM	
Shell	
United Kingdom	
BP (2 locations)	
British Industrial Plastics	
ICI	
Vinatex	
Total	1,
OTHER WESTERN EUROPE	
Austria	
Halvic Kunststoffwerke	
Finland	
Petenia Oy	
Greece	
ESSO Pappas Chemical	
Northern Greece Chemical Industry	
Norway	
Norsk Hydro	

initiator type but is somewhat dependent on initiator concentration.[10] However, in addition to the temperature dependence, molecular weight can be reduced by a chain transfer agent (CTA). A chain transfer agent reacts with the growing polymer chains (R·) more rapidly than monomer ($K_x >>> K_y$) terminating that chain and initiating a new chain. Common chain transfer agents are thioglycolates[11], halogenated hydrocarbons[12] and aliphatic aldehydes.[13]

Initiators used in suspension PVC processes are generally peresters, peroxydicarbonates, peroxides or azo compounds. Initiators are chosen to have decomposition rates that produce polymerization rates to match reactor heat removal capabilities. Other consid-

	Portugal	
17	Companhia Industrial de Resinas Sinteticas	80
	Spain	
120	Energia y Industrias Aragonesas	5
	Hispavic Industrial (2 locations)	230
	Monsanto Iberica (2 locations)	190
	Rio Rodano (2 locations)	150
	Total	575
165	**Sweden**	
375	Kemanord (2 locations)	300
~540		
	Switzerland	
	Lonza	65
300	**EASTERN EUROPE**	
220		
220	**Bulgaria**	
230	State Industry (2 locations)	350
700		
300	**Czechoslovakia**	
550	State Industry (2 locations)	230
~2,520		
	East Germany	
	VEB Chemische Werke	220
350		
560	**Hungary**	
250	State Industry (2 locations)	450
450		
600	**Poland**	
55	State Industry (4 locations)	800
700		
~2,485	**Romania**	
	State Industry (4 locations)	500
	USSR	
300	State Industry (5 locations)	1,100
115		
1,300	**Yugoslavia**	
220	Hemijska Ind. (2 locations)	175
300	Jugovinil	55
220	Organsko Hemijska Ind.	25
	Polychem	125
~2,456	Vinyl Plastika	45
	MIDDLE EAST	
330		
400	**Israel**	
	Electrochemical Industries	200
	Turkey	
575	Petkim (2 locations)	335
200		
~750	**FAR EAST**	
125		
1,650	**India**	
	Ahmedabad Manufacturing	45
	Chemicals and Plastics India	45
	IMOCIL	45
	Plastics Resins and Chemicals	30
130	Rajasthan Vinyl	60
	Indonesia	
110	P. T. Eastern Polymer	35
	P. T. Standard Toyo Polymer	50
100	**Japan**	
130	Asahi Glass	50
	Central Chemical	50
	Chisso (2 locations)	200
165	Chisso Petrochemical	100
	DENKA (3 locations)	375
	Kanegafuchi Chemical (3 locations)	450
	Kawasaki Organic Chemicals	80
	Kureha Chemical	265
	Mitsubishi Monsanto	240
	Mitsui Toatsu	260
	Nippon Zeon	425
	Nissan Petrochemicals	50
	Ryo - Nichi	250
	Shin - Etsu Chemical (2 locations)	480
	Sumitomo Chemical (2 locations)	220
	Sun Arrow Chemical	130
	Toagosei Chemical	100
	Tokuyama Seidsui	100
	Toyo Soda	200
	Total	~4,000
	North Korea	
	State Industry	50
	South Korea	
	KPIC (6 locations)	380
	Lucky	100
	Malaysia	
	Malayan Electo Chemical	25
	Synthetic Resin	25
	Pakistan	
	Arokay	10
	Philippines	
	Mabuhay Vinyl	85
	Philippine Vinyl Consortium	45
	Singapore	
	Singapore Polymer	35
	Taiwan	
	Cathay Plastics	80
	China Gulf Plastics	80
	Formosa Plastics	650
	Ocean Plastics	40
	Thailand	
	Thai Plastic and Chemical	40
	OCEANIA	
	Australia	
	B. F. Goodrich	135
	ICI	230
	AFRICA	
	Algeria	
	Sonatrach	60
	Libya	
	National Organization for Industrialization	130
	Morocco	
	SNEP	55
	South Africa	
	AE & CI (2 locations)	100
	AE & CI and Sentrachem	220

Sources:
1. World-wide HPI Construction Seasons, Gulf Publishing Company
2. World Petrochemicals—Chemical Information Service, SRI International Inc.

rocar-

s are
des or
ecom-
tes to
onsid-

erations are effect on polymer heat stability, safety and convenience of use.

Suspension polymerization requires that vinyl chloride droplets of 100-150μ average diameter be dispersed in a water-continuous phase by use of suspending agents and suitable agitation. Typical suspending agents (often called protective colloids) for use in PVC manufacture are water-soluble polymers such as a modified cellulose or a partially hydrolyzed polyvinyl acetate.

The suspending agent concentrates in the vinyl chloride-water interface and prevents (or minimizes) droplet coalesence. The nature and quantity of suspending agent and the agitation employed are major

TABLE 2—PVC applications—Resin requirements

Process	Applications	RESIN REQUIREMENTS: Inherent Viscosity	Special Properties
1. Extrusion			
Rigid (non-plasticized)	Pipe	0.88-0.95	High Heat Stability
	Profile	0.88-1.12	High Heat Stability
	Sheet	0.74-0.96	High Heat Stability, High Clarity, Good Early Color, Low Gels
	Film	0.74-0.82	High Heat Stability, High Clarity, Good Early Color, Low Gels.
Flexible (plasticized)	Wire and Cable	1.00-1.12	Good Electrical Properties, Low Gels, High Plasticizer Absorption
	Profiles	0.90-1.12	Low Gels, High Plasticizer Absorption.
	Sheet	0.90-1.04	Low Gels, High Clarity, Good Early Color
	Film	0.90-0.98	Low Gels, High Clarity, Good Early Color.
2. Injection Molding			
	Rigid	0.60-0.82	High Heat Stability
	Flexible	0.90-1.04	High Plasticizer Absorption
3. Blow Molding	Bottles	0.60-0.82	High Heat Stability, High Clarity, Good Early Color, Low Gels
4. Calendering	Flexible Sheet	0.72-1.04	High Plasticizer Absorption, Low Gels, Good Early Color

factors in determining resin properties such as particle size, particle size distribution, porosity and bulk density.* Effects of agitation in the suspension polymerization of vinyl chloride have recently been correlated with resin properties by use of Weber number.[14]

Other variables of importance in suspension polymerization of vinyl chloride are impurities present, order of addition of reaction materials and rate of mixing as well as rate of heating to reaction temperature. A typical procedure would call for removal of oxygen from the reactor by evacuation, addition of water, vinyl chloride and suspending agent and finally addition of initiator. Polymerization begins as the system is brought to reaction temperature.

Consistent batch-to-batch results in PVC manufacture require control of essentially all variables. These include impurities (oxygen, butadiene, etc.), rates and temperatures of additions, thoroughness of mixing

*Bulk density and porosity are also dependent on the extent of conversion.

Successful PVC manufacture depends upon closed systems with reactor internals being cleaned without opening any vessels and complete removal of any remaining VCM.

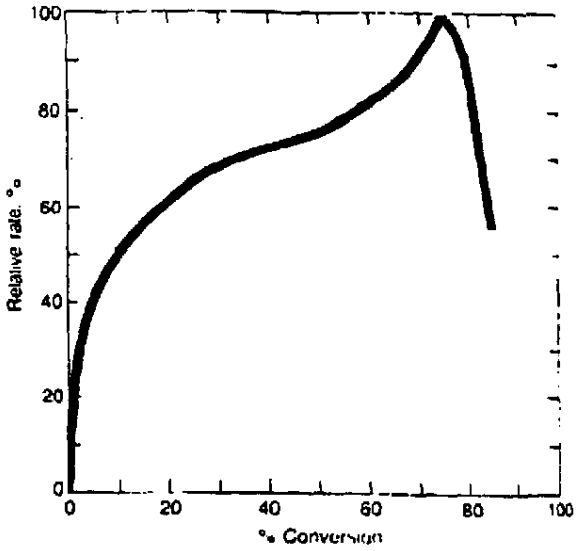


Fig. 2—Reaction rate versus conversion.

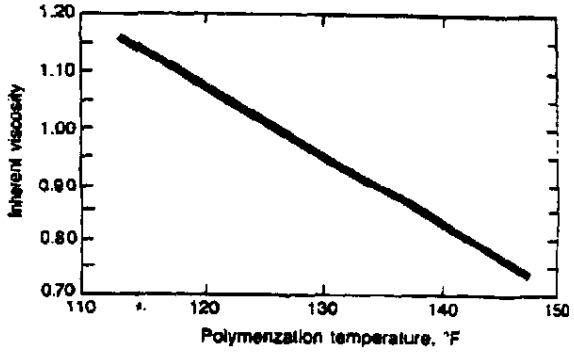


Fig. 3—PVC inherent viscosity versus polymerization temperature.

and rate of heating to reaction temperature. A complete description of a polymerization procedure including polymer isolation is given in a subsequent section.

Interactions between polymerizing monomer droplets and also interactions between growing primary polymer particles lead to differences in the structure of PVC. PVC morphology is affected by the suspension system, agitation, polymerization temperature, non-reactive additives, conversion and other factors. Differences in PVC morphology are illustrated by the photomicrographs in Fig. 4. A uniformly porous resin (4A) is desired for ease of VCM removal and processing. Large gel regions, shown in 4B will release VCM relatively slowly making the stripping process less effective and may cause non-uniformity in the final product.

Commercial processes. Polyvinylchloride plants in the 50s and 60s contained many small batch reactors grouped in one or more reactor modules. A typical

A. Uniformly porous resin

B. Resin containing a large gel

4—Scanning electron micrographs of PVC resin cross section (500X).

all reactor module contained twenty 2,300-gallon actors. Polymerization began with addition of water, spending agent and initiator to an open reactor at bient conditions. The reactor was then closed, evacuated to remove oxygen, vinyl chloride added and the ture agitated and heated to polymerization temrature. Constant temperature was maintained until 90 percent of the monomer had been converted to lymer. Unreacted vinyl chloride was removed by acuation and the polymer recovered from the water rry by centrifuging and drying. Reactors were ened and cleaned manually after each cycle. The al cycle took approximately 12 hours.

Processes using larger reactors[15,16,17] were developed the late 60s. The larger reactors offer increased oductivity, lower plant costs and improved product iformity. Although continuous PVC processes have en patented,[18,19] none have been commercialized to te.

With the discovery of the link between VCM expore and angiosarcoma of the liver, OSHA quickly ued regulations in 1974 limiting employe exposure. oducers implemented many process refinements marily aimed at reducing or containing VCM emisns. Reactor cleaning emissions were reduced by veloping water-lancing equipment that would oper- in a closed reactor and chemical treatment to duce reactor fouling.[20]

In 1975, the EPA declared VCM to be a hazardous pollutant and issued an emission standard in 1976, ting the VCM concentration in the resin slurry, actor opening emissions and other plant VCM emisns. Producers began developing stripping processes lower the VCM emissions and fugitive losses. Rapid ylchloride removal by steam stripping required that e resin be highly porous.[21] Therefore, dense nonrous resins previously popular for rigid applications ve been phased out in favor of porous, more easily pped resins.

To control VCM exposure in downstream fabrica- shops, the industry established a 10 ppm VCM

HISTORICAL

Although polyvinylchloride (PVC) was first made in the laboratory about 100 years ago, commercial production of the homopolymer did not begin until the late 1930s.[1] A major reason for the long delay between discovery and commercialization was that unmodified PVC is not a useful material. Progress in PVC technology has involved a complex interaction between resin development, effects of additives and equipment design as well as market demands. In the past decade, a major new requirement has appeared—that of meeting EPA and OSHA regulations.

To appreciate the latest developments in PVC technology, it is useful to briefly review past milestones in PVC progress. Foundations of the modern PVC industry were established by a series of discoveries extending back about 50 years.

Initial commercialization of PVC homopolymer was made possible by discovery of the plasticizing effect produced by esters, such as tricresyl phosphate or phthalates.[2] World War II stimulated interest in replacement of rubber by plasticized PVC. Use of plasticized PVC as wire and cable insulation was common within the decade as was use of calendered PVC as a leather replacement. By 1957, the fledgling PVC industry had sales of over 600 MM pounds,[3] mostly in flexible applications.

In the early 1960s, advances in heat stabilizers and extruder design contributed to the rapid growth of rigid PVC. Growth of rigid PVC (pipe, fittings, construction profiles) from 1965 to the present has been spectacular (Fig. 1).

The discovery in 1973 that exposure to vinyl chloride resulted in increased incidence of a form of liver cancer (angiosarcoma) resulted in fundamental changes in the PVC industry. A result of compliance with EPA and OSHA vinyl chloride emissions standards has been loss of capacity, estimated to be about 20 percent[4] which contributed to PVC shortages in 1978 and 1979. However, technology to control emissions now has been developed, and a new round of plant expansions has been announced.[5] In 1979, U.S. companies will have about 7 billion lbs of PVC capacity (Table 1) with world capacity about 30 billion lbs.

Supporting the rapid rise in PVC production has been improving technology for vinyl chloride production. This has recently been reviewed and will not be discussed here.[6]

Reactor design is important in resin quality control, along with agitation, speed of agitator, baffle location and ability to move baffles from outside the reactor.

concentration limit in dried PVC resin and arranged for surveying and enforcement by the Plastic Pipe Institute.

Typical suspension PVC process. A PVC process can be divided into polymerization, monomer stripping and resin drying sections. The process flow of a typical large reactor plant is outlined in Fig. 5.

The process begins with the charging of process water, fresh VCM, recycle VCM, and suspending agent to an air-free reactor. Charge quantities of each must be accurately controlled to avoid changes in the resin particle size and other quality parameters. The charge is controlled by flow measurements, loss of weight measurements, or a combination of both. Water to monomer ratios of 1.1 to 2.0 are normally used depending on the quality of the local water and the polymerization technology used.

Monomer soluble initiator(s) is added to start the reaction. The heat of reaction is removed through a water jacket around the reactor. Initially, hot water is circulated through the jacket to help bring the rea contents to the desired polymerization temperat Cooling water is then used to control the rea temperature.

As the reaction proceeds, a stable suspension VCM in water is formed by agitation of water, V and the suspending agent. The product particle and distribution is generally believed to be establis early in the reaction.

At a conversion of around 70 percent, reactor p sure (and reaction rate) begins to drop due to reacted monomer being absorbed by the PVC parti (Fig. 2). The reaction is usually terminated at a spe conversion measured as a specific drop from rea run pressure or at a final reactor pressure. The t monomer to polymer conversion ranges from 7 percent, depending on product quality requireme

Unreacted monomer is recovered from the l product by depressurizing the reactor to a reco system containing slurry disentrainment equipm vacuum pumps and compressors. The vacuum pu and compressors are usually water-sealed.

The reactor is rinsed with water before rechar to remove residual resin which, if left in the rea would degrade the quality of the resin produced in next batch. Hydroblasting may be used to remove s that has formed. The reactor surfaces also may rinsed or sprayed with chemicals which help pre polymer scale formation on the reactor internals.

EPA standards specify that the residual mono content of the resin be reduced to 400 ppmw m mum by additional monomer recovery in a strip process. There the slurry is heated and stripped contact with steam in a trayed tower. The strip

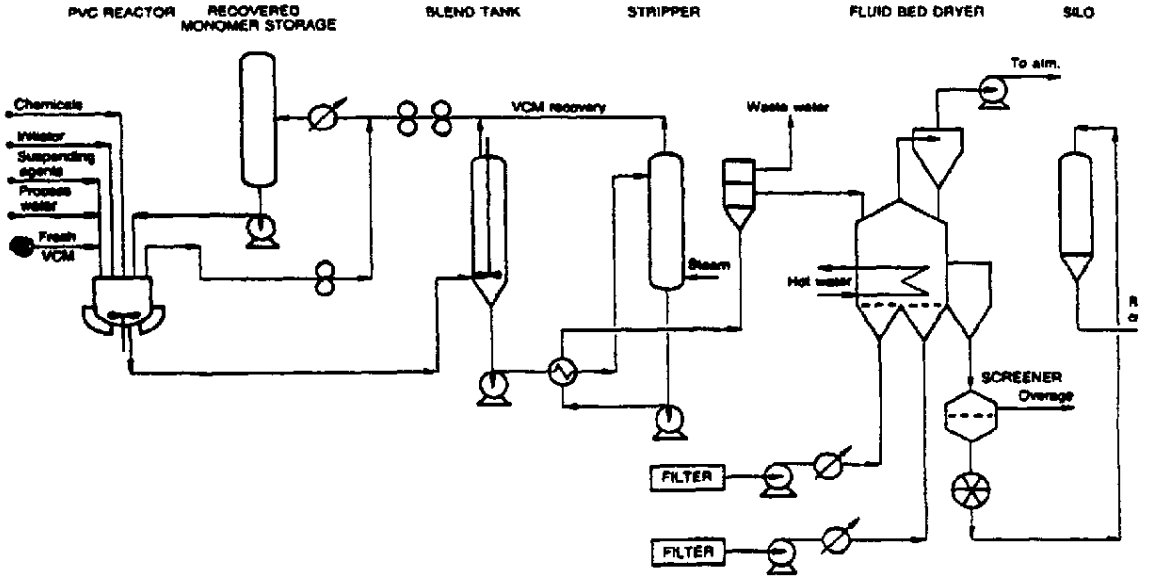


Fig. 5—Typical PVC process flow diagram.

process must be designed to minimize the heat exposure of the resin to avoid heat stability (resin degradation) problems in customer processing equipment.

In the drying section, the polymer slurry is centrifuged to produce a wetcake having a water content of 18-25 percent wt. water. The range is due to variation in the intra-particle resin pore volume. A two-stage fluid bed is used to dry the resin to below 0.3 percent wt. water content. The first stage is backmixed and operates in the constant rate-drying section of the drying curve (Fig. 6). Approximately 90 percent of wetcake water content is removed there by the fluidization air. Water at 190-220°F is circulated through heat exchangers in the backmixed section of the fluid bed to provide 80 percent of the evaporative heat requirement with the fluidization air, at a comparable temperature, providing the remainder.

The second stage of the dryer operates in the falling-rate region of the drying curve and is designed to approach plug flow of the resin. Heated fluidization air, again between 190-220°F, provides the heat input. An air cooling section may be added if the resin is particularly sensitive to heat. Normally, there is little, if any, degradation in the heat stability of a resin across a fluid bed dryer even though the resin residence time is 60-120 minutes. Evaporative cooling balances the heat transfer in the backmixed section of the dryer. Resin temperature does not approach the drying air temperature until the outlet of the plug flow section.

The product resin is usually shipped by rail in hopper cars, but some is shipped in bulk by truck or in bags or gaylords. The rail cars are epoxy-clad to prevent resin contamination with rust. All parts of the process contacting the resin are either stainless steel, aluminum or epoxy-clad carbon steel for this reason. Some processes use glasslined reactors.

Reactor design. Reactor design is governed by resin quality and reactor productivity requirements and plant production considerations.

The polymerization recipe determines many aspects of resin quality. However, recipe changes cannot always correct for deficiencies in reactor design. Agitation is the primary design variable affecting product quality. The mixing blades are usually either retreat curve or turbine types that pump the slurry from the bottom of the reactor upwards around the sides of the reactor. Reactors are usually baffled. Agitators may be single or variable-speed and the reactor baffles may be externally adjustable.

Quality can also be affected by reactor size and configuration. The variation in product quality from batch to batch can be reduced by using large reactors since it is easier to control several large reactors than many small reactors. However, it is necessary that the process be well controlled since many more pounds of off-grade resin are produced by a bad batch in a large reactor than in a small reactor.

Productivity is maximized by initiator choice and reactor heat removal but may be limited by quality considerations. Typically, reaction cycle times range between seven and ten hours. Of this, reaction requires 70-80 percent with charging, degassing, dumping and

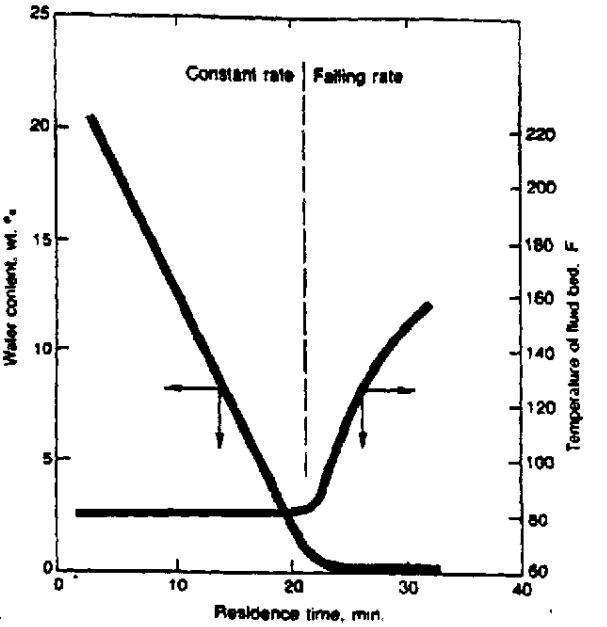


Fig. 6—Batch fluid drying curve.

turnaround taking the remainder. Obviously, the largest potential for improved productivity is in minimizing polymerization time. Polymerization time is limited by the reactor's heat removal capabilities and by the polymerization heat release curve (Fig. 2). Different initiators can be chosen to produce a heat release curve that best matches the reactor's heat removal capabilities.

The heat released during polymerization is commonly removed from the reactor by circulating chilled water through a reactor jacket. Specially-designed cooling baffles may also be used. The slurry side jacket heat transfer coefficient decreases rapidly as the monomer conversion approaches 60 percent (Fig. 7). The decrease is dependent on the slurry concentration. Since the wall thickness of large reactors approaches one inch, the thermal conductivity of the reactor wall is an important consideration. In this regard stainless steel-lined carbon steel has an advantage over a solid stainless steel or glasslined reactor.[22,23]

A few producers have developed reflux condenser technology to improve the reactor's heat removal capability. VCM vaporized from the reacting slurry is condensed in a vertical condenser mounted externally to the reactor. Condensed VCM is returned to the reacting slurry. Since the condensing heat transfer coefficient may be higher than the jacket coefficient and the condenser area is not limited by reactor dimensions, plant cooling water can be used instead of chilled water. Initiators that give nearly uniform heat release throughout the reaction are used since reaction heat removal is not heavily dependent on slurry jacket transfer coefficient. Reactors with condensers may have productivities of 2,500 lbs/yr/gal reactor volume

With the trend to larger reactors, there has been a corresponding trend to remote or automatic valves with many safety interlocks.

or more. Reactors without condensers usually have productivities under 2,000 lbs/yr/gal.

Plant production considerations can also affect reactor design. To minimize plant capital investment, the reactor size and number of reactors in a module should be balanced with the size of the recovery system

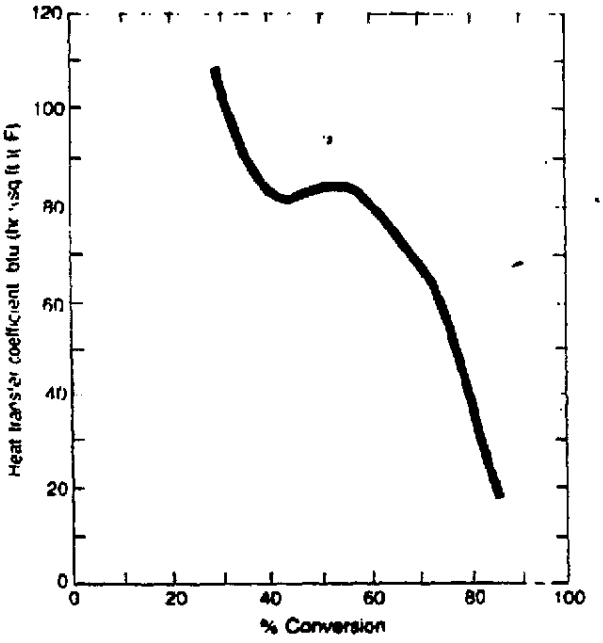


Fig. 7—Jacket inside heat transfer coefficient versus conversion.

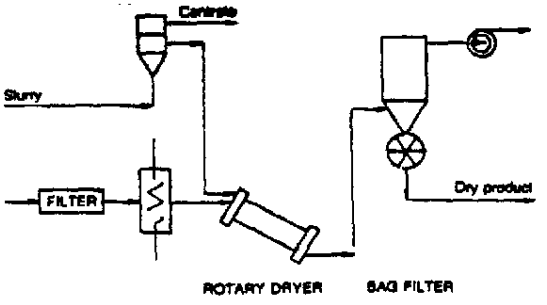


Fig. 8—Typical rotary dryer arrangement.

and other support systems. The support systems are used more efficiently when they approach continuous usage without bottlenecking the reactors.

Stripping options. The process selection for stripping residual VCM (RVCM) from the resin slurry is dependent on the resin characteristics, quality requirements, and the final RVCM concentration required. The resin VCM/PVC equilibrium relationship is important in stripping. Heat stability specifications limit the heat history of the resin and may limit the number of options that can be considered.

In every case, the resin stripping depends on a combination of time, temperature and purge gas (water or nitrogen) to remove VCM from the resin. Most processes use steam to provide the heat input and remove VCM. Processors have developed new recipes and additives to make resins easier to strip and to prevent resin degradation.

Of the stripping options in use, the most common are batch and continuous stripping of slurry. Steam is injected directly into the slurry. In batch stripping the slurry temperature profile is adjusted to control the RVCM of the product slurry. Continuous stripping may be done in a trayed-stripping tower, again using steam to heat and strip the slurry. The continuous process may have advantages in providing more consistently low product RVCM. Also, plant production can be increased by eliminating an in-reactor stripping time requirement. Both batch and continuous stripping are generally conducted in a way to minimize exposure of the slurry to high temperatures. With a continuous process, this can be done by heat exchanging against the feed slurry.

Other schemes using inert gas stripping of the slurry or of the centrifuge wetcake have been proposed and may be in use.

Drying options. In addition to the two-stage fluid bed dryer discussed in the typical process section, rotary and flash-fluid bed dryers are used. The type of dryer selected depends upon the dryer size, product properties, quality requirements and fuel availability and costs.

Rotary dryers (Fig. 8) utilize co-current flow of wetcake and the drying air. The dryers are designed with internal-lifting flights and baffles to promote contact between the resin and the drying air. Thermal efficiency of a rotary dryer can approach that of a fluid bed but only when high temperature drying air is used. The air heating can be done either by direct-fired natural gas in an inlet burner or by indirect means through heat exchange with steam or hot oil. Direct oil firing is questionable because combustion products might downgrade product quality. Rotary dryers can have initial cost advantage in the smaller sizes. The disadvantages of the rotary dryer are that its high inlet temperature can burn resin and its thermal efficiency is lower than that of a fluid bed dryer.

A flash-fluid bed dryer (Fig. 9) is a two-stage dryer that uses a high temperature air stream to entrain the wetcake in a duct and dry it through the constant rate section of the drying curve. The resin is recovered in a cyclone and the drying completed in a plug-flow

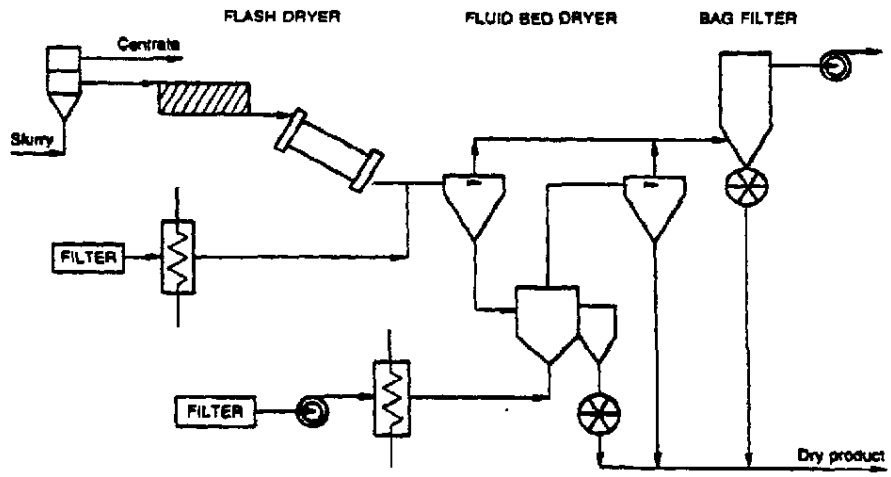


Fig. 9—Typical flash/fluid bed dryer arrangement.

fluidized bed. While the fluid bed section should produce a more uniformly dried product than a rotary dryer, the flash section has the same potential resin burning disadvantage as the rotary dryer. Depending on the drying air temperatures, the thermal efficiency of the flash-fluid bed dryer should be comparable to or better than a rotary dryer.

The two-stage fluid bed dryer has the advantage of never exposing the resin to high temperatures. Also its thermal efficiency is the highest of the three types of dryers and its heat input can be provided by steam. Since its higher thermal efficiency results in higher humidity exhaust air, care must be taken with dryer insulation, heat tracing and in the dryer operation to prevent condensation in the exhaust cyclones or baghouses.

Safety aspects. There are several aspects of a PVC plant and its operation that merit special attention from a safety standpoint. First, being a batch process, there are many reactor startup and shutdowns occurring everyday. This increases the risk of a mistake that could endanger lives and equipment. With the trend toward larger reactors, there has been a corresponding trend to remote or automatic-operated valves. Producers have added many safety interlocks to these automatic valves to prevent them from being opened or closed at the wrong part of the batch cycle.

Also, provision must be made for controlling the polymerization in an emergency situation such as a power failure. All producers have chemical injection wstems that will chemically stop the polymerization in an emergency. Some producers provide diesel or steam turbine-driven cooling water pumps to provide for reactor cooling during a power failure. Those having reactor condensers can benefit from cooling even without agitation. Some producers elect to provide back-up power for the reactor agitators and the cooling system. The important point is that the plant must have a reliable and effective system to control polymerization in an emergency.

Of course, reactor pressure relief systems must be designed to control pressure in the event that a runaway reaction did occur. The design of the relief valve discharge piping must carefully consider the flowing characteristics of the different multiphase flows that could be relieved at different points in the polymerization. Several articles[24,25] discuss reactor relief system requirements.

Initiators used in PVC manufacture are generally unstable at room temperature and must be stored at low temperatures. Suppliers have specific recommendations in this area.[26,27] Operating procedures are important in insuring that the initiator is kept refrigerated when being transported from the storage freezer to their process area.

The recovery and initiator injection systems must be designed to prevent initiator carryover into the recovered monomer system or initiator injection into a monomer line or vessel.

Vinyl polyperoxides can sometimes be found in the recovered monomer system. Since these compounds can self-detonate under certain conditions, care must be taken to avoid concentration when clearing equipment of VCM. Recovered monomer can be caustic-treated to destroy polyperoxides.

PVC dust can be ignited by a very high energy discharge. It becomes more flammable if mixed with combustible additives, such as plasticizers.

Because VCM is a flammable gas, the reactor area in most plants is equipped with a water deluge system designed to help dissipate a VCM vapor cloud and to cool equipment in a fire. The deluge system is automatically activated by combustible hydrocarbon analyzers and by heat actuated devices. The VCM storage tanks are also protected by a water-deluge system. Reference 28 provides detailed recommendations in

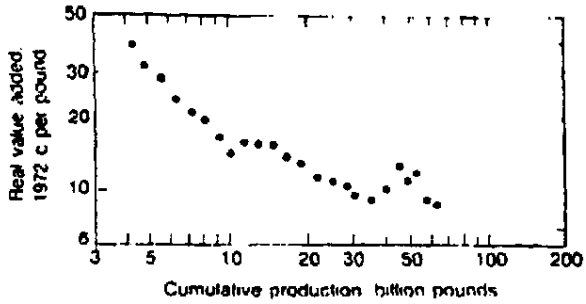


Fig. 10—Value added manufacturing experience curve for PVC in the U.S.A., 1953-1978.

these and a number of other safety areas in PVC plants.

VCM regulations. In addition to air emission and water discharge regulations in general, PVC producers must also comply with the OSHA-employe VCM-exposure standard[28] and the EPA VCM-emission standard.[29]

The OSHA standard established a permissible employe VCM-exposure limit of 0.5 ppm and a maximum exposure of 1.0 ppm over an eight-hour period without regard to the use of respirators. Employe-exposure monitoring, training, and medical surveillance must be provided. Also, the producer is required to implement feasible engineering and administrative controls to reduce exposure to or below the permissible level. The standard does not specify what controls are to be used.

Producers have attained compliance with the OSHA standard by modifying equipment clearing and operating procedures and by eliminating VCM emissions or collecting them in vent headers. Ventilation of buildings and equipment is also used.

The EPA VCM standard limits the average VCM content of the stripped resin at 400 ppmw and the reactor opening loss at 20 lbs per million lbs of resin produced. Other equipment opening losses are also controlled. VCM emissions from vent and water streams upstream of the stripping step are limited to a concentration of 10 ppm. The standard also requires that there be no manual or relief device discharges to the atmosphere from equipment in VCM service with the exception of an emergency relief.

As previously discussed, VCM-stripping procedures and equipment have been installed to control the VCM content of the resin slurry, and purging procedures used or process changes made to comply with the reactor opening loss limit. The VCM content of water streams is controlled by steam stripping. Incinerators, carbon adsorption or solvent absorption systems are used to control vent emissions.

The EPA standard differs from the OSHA standard in that it requires specific controls be used to control fugitive emissions. Pumps and compressors in VCM service must have double mechanical seals or be sealless. Agitators must also have double mechanical seals. Rupture discs must be installed under VCM relief valves that discharge to the atmosphere. Equivalent controls may be used with EPA approval.

The industry has found that the cost of compliance with the EPA standard, measured both in capital and in lost production, is significantly greater than that of the OSHA standard.

TABLE 3—Polyvinyl chloride price and production history 1953 - 1978

Year	U.S. production: Annual (million lbs)	U.S. production: Commulative (million lbs)	Raw material cost (1972 ¢/lb)	Value added (1972 ¢/lb)	PVC price (1972 ¢/lb)	PVC price (Current ¢/lb)
Prior	N.A.	3,000	N.A.	N.A.	N.A.	N.A.
1953	435	3,435	N.A.	N.A.	65.9	38.8
1954	397	3,832	N.A.	N.A.	63.0	37.6
1955	527	4,359	17.0	36.8	55.6	34.0
1956	637	4,996	17.2	31.4	48.6	30.6
1957	689	5,686	16.8	28.1	44.9	29.2
1958	657	6,342	16.8	23.3	40.1	26.5
1959	905	7,247	16.1	20.9	37.0	25.0
1960	936	8,183	14.8	19.0	33.8	23.2
1961	977	9,160	11.7	16.2	27.9	19.3
1962	1,218	10,378	10.6	14.3	24.9	17.6
1963	1,388	11,761	9.8	15.5	25.3	18.1
1964	1,637	13,398	8.7	15.4	24.1	17.5
1965	1,837	15,235	8.2	15.1	23.3	17.3
1966	2,164	17,399	7.7	13.9	21.6	16.6
1967	2,142	19,541	6.7	13.2	19.9	15.7
1968	2,635	22,176	5.6	11.4	17.0	14.0
1969	3,032	25,208	5.1	10.7	15.8	13.7
1970	3,115	28,323	4.5	10.5	14.8	13.5
1971	3,437	31,760	4.4	9.8	14.0	13.4
1972	4,322	36,082	4.0	9.0	13.0	13.0
1973	4,594	40,676	4.0	10.2	14.2	15.8
1974	4,744	45,420	7.1	12.7	19.8	23.0
1975	3,965	49,385	7.8	11.1	18.9	24.1
1976	4,545	53,930	7.5	11.8	19.3	25.9
1977	5,267	59,147	8.7	10.0	18.7	26.5
1978	5,878	65,075	8.4	8.6	17.0	25.8
1979 (est)	6,050					

Basis of raw materials cost: Theoretical raw material content of 1 lb of vinyl chloride monomer per pound of PVC

Manufacturing efficiency. Fig. 10 shows a value added manufacturing experience curve for PVC production in the U.S.A. between 1953 and 1978. This curve expresses a relationship between cumulative PVC production (experience) and the "value added," or PVC price less the VCM price, with both adjusted to a constant dollar basis. The entries are plotted on both coordinate axes as logarithmic values. This graph, prepared by Townsend et al[31] plots historical price and production information (listed in Table 3) gathered by the U.S. International Trade Commission. The observed yearly prices are adjusted to a 1972 basis by the GNP deflator.

The "value added" over and above the raw material cost in constant dollars is a measure of the efficiency of the manufacturing step. The raw material expense is taken as the cost of 1.0 lbs of VCM per pound of PVC resin produced. As manufacturing expense is decreased with experience, as for example by increasing the scale of operations to dilute fixed costs per pound of output, the "value added" declines.

The experience curve covers a 25-year history of PVC production, and the steadily declining value added is indicative of the improvements made in the

manufacturing techniques during this period. The discontinuity occurring between 1974 and 1976 is believed to be due to increased energy costs and government regulations.

If producers are to continue increasing the efficiency of PVC manufacturing, further process improvements will be necessary. It is likely that contributions in this area will include: (a) replacement of small inefficient process plants as they become obsolete by larger scale equipment to reduce fixed costs; (b) further improvements in raw material and energy efficiencies; and (c) more productive equipment utilizing faster reactions, improved process control and more sophisticated means of dissipating the heat released by polymerization.

Manufacturing cost. Table 4 gives an illustration of the cost structure for suspension PVC manufacture. The cost shown is for a hypothetical 200 MM lbs/yr name plate (175 MM actual) plant beginning operation in the conditions existing during the third quarter of 1979. The plant is assumed to be located in the U.S. Gulf Coast area. The plant capital cost is estimated as 50 million dollars. Several companies who license their suspension PVC technology provided non-confidential information about their process before this article was prepared.[32] The raw material and energy use and manpower requirements, although not patterned after anyone's specific process, represent an approximate average of the information supplied by the licensors. The hypothetical plant is assumed to produce a typical suspension resin slate. This size plant would utilize four reactors about 22,000 gallons each in capacity, use steam stripping for monomer recovery and include recycle of unreacted vinyl monomer. The plant would meet all applicable environmental and worker protection regulations.

The overheads, sales expense and miscellaneous costs are typical of published figures and are probably fairly realistic for an operation of this size. Total plant employment would be approximately 100, with 75 hourly and 25 salaried employes. The staffing level could probably be reduced by approximately 10 percent if the plant were to be located as part of a large established manufacturing complex.

The computed product value for PVC manufactured in this plant with third quarter 1979 conditions is 31.26 cents per pound, which is approximately the market price at the time. This PVC price includes a pretax return on the investors capital of 10 percent which is relatively low. The returns on new PVC capacity must be adequate to encourage investors to install new production facilities if a capacity squeeze is to be avoided.[33] Hopefully, several factors will help to improve rates of return on investment for new facilities (1) larger scale plants can be installed; (2) companies already producing a large-base load PVC volume can incur less burdensome fixed costs in their new facilities as a result of further distribution of overheads, sales and management expense, and the like; (3) continuing improvements in techniques will lead to cost savings in spite of the general inflationary bias; and (4) as newer facilities become a more prominent share of total supply, margins will increase to reflect the higher capital burden of the industry as a whole.

TABLE 4—Typical suspension PVC manufacturing expense new 200 MM lb/yr large reactor plant Gulf Coast U.S.A. Third Quarter 1979 conditions

Product: PVC Powder
Process: Batch suspension in four 22,000-gallon reactors
Steam stripping and recycle of recovered monomer
Nameplate capacity: 200 MM lbs
Capacity utilization: 87.5 percent
Actual capacity: 175 MM lbs
Capital investment: $50 MM

Raw materials	Unit cost ¢/unit	Consumption/lb	Cost $M/yr	¢/lb PVC
1. Vinyl chloride	17.2 ¢/lb	1.025	30,853	17.63
2. Byproducts	15.0 ¢/lb	(0.015)	(394)	(0.23)
Subtotal			30,459	17.40
Other variable costs				
1. Catalysts and chemicals			1,050	0.60
2. Royalties and licenses			875	0.50
3. Operating supplies			175	0.10
Subtotal			2,100	1.20
Utilities				
1. Electricity	2.65 ¢/KWH	0.17	788	0.45
2. Steam	5.00 $/M lbs	1.2	1,050	0.60
3. Process and cooling water			350	0.20
Subtotal			2,188	1.25
VARIABLE MANUFACTURING COST AT 87.5% OF CAPACITY			34,747	19.85
Hourly labor and supervision (8 operating jobs per shift)			1,600	0.91
Maintenance materials and supplies (2.5% of capital)			1,250	0.72
Operating Supplies			50	0.03
Subtotal			2,900	1.66
Total of direct costs			37,647	21.51
Interest on working capital (12% of $5 MM)			600	0.34
Plant overheads (100% of labor costs)			1,600	0.91
Taxes and insurance (1.5% of capital)			750	0.43
Depreciation (10% of capital)			5,000	2.86
Subtotal			7,950	4.54
Cost at plant gate			45,597	26.06
Sales expense, R&D and general administrative (7.5% of sales price)			4,100	2.34
Profit and income tax (10% of fixed capital)			5,000	2.86
Product value at cost plus 10% ROI			54,697	31.26

Future trends. PVC technology has evolved at a rapid pace during the past decade. An indication of the dynamic nature of this technology is given by the number of announced technology improvements, plant expansions and license agreements. It is often difficult to determine the exact nature of the technology change reported because details are carefully guarded. However, the impression of a dynamic industry created by this activity, we believe, is accurate.

As production facilities at existing installations which utilize numerous small-sized reactors become obsolete

and in need of replacement, they will be replaced by a small number of much larger reactors. The capital cost associated with these new reactors will be partially offset by the savings in fixed cost that the large reactors provide. Gains in product consistency and quality, improvements in controllability and improved plant safety will be side effects of more widespread use of large-scale reactors.

The evolution to even larger reactors will encounter mechanical and logistical constraints. An optimum range in which benefits of large reactor technology are obtained but operational problems are avoided will be established.

Suspension and initiator systems will be improved to achieve optimum results from large reactors. This will allow most grades of resin to be made by large reactor technology. Clean wall systems, VCM containment procedures and emergency kill systems will continue to be improved. Improvements in efficiency from the best presently available large reactor technology over the next decade will probably be modest. However, in the highly competitive PVC industry, advantages presented by advanced large reactor technology over small reactors or first generation large reactor technology will be significant.

PVC licensors. A listing of companies who have licensed some phase of their PVC production techniques is shown in Table 5. The list is probably not complete as it merely represents those companies known by the authors to have shown some activity in licensing in the PVC field.

TABLE 5—Companies with PVC licensing activity

North America	Western Europe	Far East
Conoco Chemicals	ATO Chimie	Kureha Chemical
Diamond Shamrock	Rhone-Poulenc	Mitsui Toatsu
B. F. Goodrich	Chemische Werke Huels	Shin-Etsu Chemical
Stauffer Chemical	Hoechst	Sumitomo Chemical
Union Carbide	Lonza	
	Wacker-Chemie	
	Montedison	
	ICI	
	Solvay	

The tabulation also includes companies licensing stripping methods for removal of unreacted monomer from the polymer product and licensing methods to inhibit the formation of scale on the surfaces inside the polymerization reactor. These two areas have been of the highest research priority since the discovery of the health hazard posed by the vinyl chloride monomer and the need to reduce human exposure to very low levels.

There are many patents concerning PVC production, primarily grouped in the areas of polymerization chemistry, reactor design, resin stripping and control of reactor fouling. While most licensors will have patent protection in one or more of the processing steps, process and operating know-how is usually the most important part of a licensor's package.

About the authors

Jack B. Cameron is a project supervisor, Conoco Chemicals, Houston. His duties include process evaluation and economics of chemicals manufacture. Cameron received his B.S. in chemical engineering from the University of Missouri. Before joining Conoco he was with DOP.

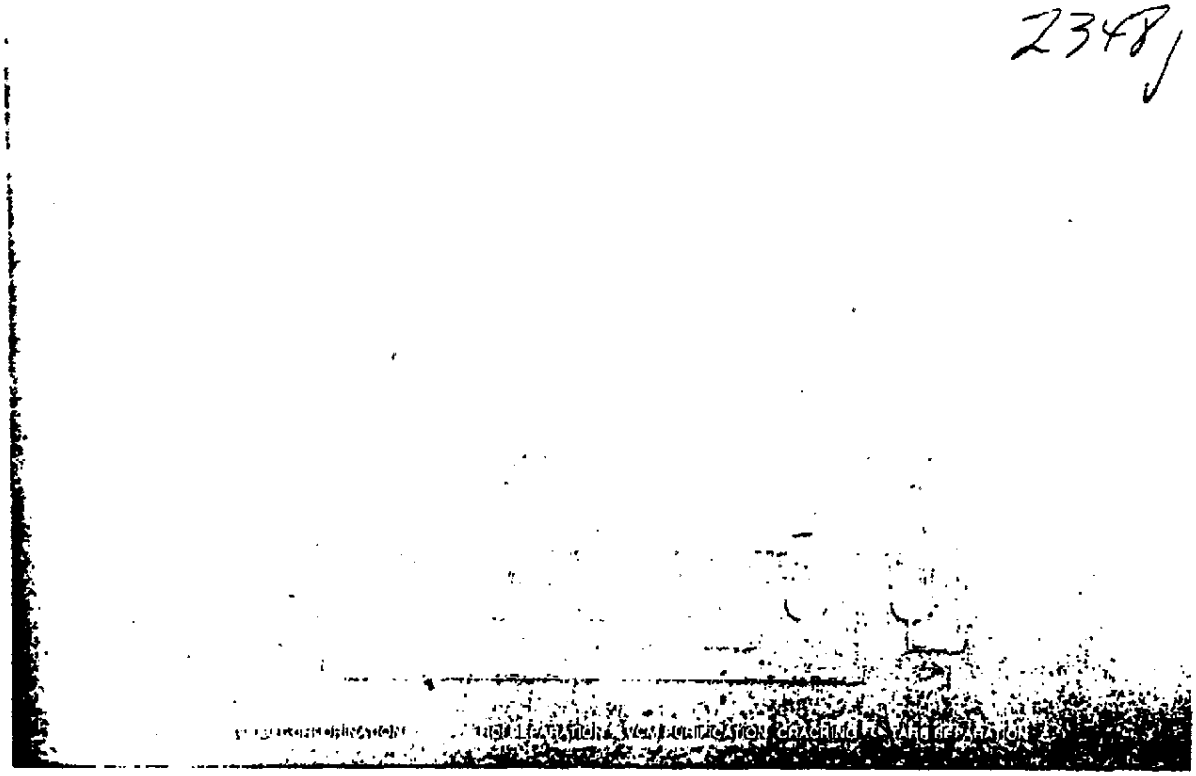
Allan J. Lundeen is director, Plastics Research, Conoco Inc., Ponca City, Okla. Dr. Lundeen has worked in exploratory research and as a research chemist for Conoco, Inc. He received his Ph. D. in organic chemistry from Rice University and his B.S. in chemistry and mathematics from Southwestern College (Kansas).

James H. McCulley, Jr. is a supervising process engineer with Conoco, Inc., Ponca City, Okla. He is responsible for supervision of the PVC process design and plant maintenance. Mr. McCulley received his B.S. in chemical engineering from Rice University.

REFERENCES

1. Mathews, George, Vinyl and Allied Polymers, Vol. 2, page 2 (1972)
2. Berman, W. L., U.S. Patent 1,929,453 (1933); 2,188,396 (1941).
3. *Modern Plastics*, Jan. 1967, p. 139.
4. *Modern Plastics*, March 1970, p. 49.
5. *Plastics World*, Dec. 1970, p. 72.
6. McPherson, R. W., Starks, C. M., and Fryar, G. J., *Hydrocarbon Processing*, March 1970, p. 75.
7. Burgess, R. H., in "Developments in PVC Production and Processing," Whelan, A. and Craft, J., ed. London 1977, pp. 89-92.
8. U.S. Patent 3,709,512 (1973).
9. U.S. Patent 3,703,128 (1973).
10. Langsam, M., J. Applied Polymer Science, 23, p. 987 (1979).
11. German Patent 2,214,501 (1972).
12. Staudabach, J. R., SPE Tech Paper, 25, p. 868 (1977).
13. Ryska, M., Reichrtek, M. and Lim, D., J. Polymer Sci., 55, p. 537 (1971); U.S. Patent 4,039,477 (1977).
14. Johnson, G. R., "The Effect of a Modified Water Soluble on Resin Properties During VCM Suspension Polymerization," AIChE 71st Annual Meeting.
15. German Patent 2,038,365 (1972) Ibid. Beckmann, Gunter, Chem. Tech., pp. 304-310 (1933).
16. Burgess, R. H., *Applied Science*, 19, (1977).
17. U.S. Patent 3,980,628 (1976).
18. Lanthier, R., U.S. Patent 3,551,398 (1970).
19. Gavernale, L. C. and Lavigne, J. A., U.S. Patent 2,972,492 (1961).
20. U.S. Patent 1,105,840 (1978), U.S. Patent 1,107,841 (1978), U.S. Patent 1,058,582 (1978).
21. Herrero, A. R., *Food Technology*, 1, 8 (1979).
22. Albright, L. F. and Volland, J., Purdue University, "Design and Operation of Heat Transfer Surfaces for Batch Reactors."
23. Markham, R. L., "Improve Heat Transfer with Electrodeposited Coil Reactors," *Hydrocarbon Processing*, Aug. 1975.
24. "Venting of Chemical Plant Equipment," Industrial Risk Insurers (formerly HAL) Bulletin No. 55.
25. "Comparative Simulations of Polymerizer Pressure Relief with Two-Phase Flow in Relief Systems," Huff, J. E., Paper No. 37(d), 69th Annual AIChE Meeting, Nov. 27-30, 1972, New York City.
26. "Fire and Explosion Hazards of Organic Peroxides," Research Report No. 11, American Insurance Association, 1968.
27. "Storage of Peroxides," Private communication from G. J. Kraus, Enfield Division, Pennwalt Corp.
28. "Polyvinyl Chloride Manufacturing Plants," Industrial Risk Insurers (formerly HAL) Fire Edition, Aug. 1, 1970.
29. Federal Register, Vol. 39, No. 191, Friday, Oct. 1, 1974.
30. Federal Register, Vol. 41, No. 250, Thursday, Oct. 1976.
31. "The Impact of Energy Costs, Technological Change and Capital Equipment Cost Trends, Raw Materials Competitions 1978-1988," Springborn Laboratories Inc. and Phillips Townsend Assoc. Inc.
32. Mitsui Toatsu Chemicals, Inc., c/o T. Iwama, P. O. Box 83, Kasumigaseki Building, Tokyo 100, Japan; Tonen Ltd., c/o M. Ikeno, Mitsubishi Corporation, Ote Center Building, Sumitomo Chemical Co., Ltd., c/o S. Tanaka, 15 Kitahama, Higashi-ku, Osaka, Japan; Rhone-Poulenc, 47, rue de Villiers, F-92 527 Neuilly-sur-Seine Cedex GmbH, Deggendorferstrasse 10-12, P. O. Box 262, 4600 Dortmund 1, Germany; Montedison S.p.A., C/o Francesco Bissa, Largo Donegani 2, 20121 Milan, Italy; ATO Chimie, Tour Aquitaine Cedex No. 4, 92080 Paris la Defense, France.
33. Sears, T. L., "What's Ahead for PVC and VCM," *Chemical Engineering Progress*, Vol. 75, No. 10, pp. 13-18.

2348



Vinyl chloride — STAUFFER CHEMICAL CO.

Application: A process to produce vinyl chloride monomer and 1, 2-ethylene dichloride (EDC) from ethylene, chlorine and oxygen or air.

Description: Ethylene dichloride is produced in both the addition chlorination and oxychlorination sections of the process. In addition chlorination, ethylene and chlorine are reacted in the liquid phase to produce EDC:

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 + \text{Heat}$$

The heat of reaction is used to distill the EDC produced in direct chlorination and oxychlorination sections of the plant, and recycle EDC from the cracking section. This saves as much as 0.8 ton of steam per ton of VCM over conventional processes. Additional savings are realized by an equivalent cooling water reduction.

In the oxychlorination section, ethylene, oxygen and HCl are reacted to produce EDC:

$$C_2H_4 + 2\ HCl + \tfrac{1}{2}\ O_2 \rightarrow C_2H_4Cl_2 + H_2O$$

This is a catalytic vapor phase reaction with the reaction heat used to generate high pressure steam. Using oxygen rather than air reduces vent gas quantity by 95% and reduces energy and capital cost requirements.

Vinyl chloride monomer (VCM) is produced by cracking purified EDC in a pyrolysis furnace:

$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl$$

After quenching, the products are separated into HCl, which is recycled to oxychlorination, high purity VCM, and unreacted EDC which is recycled.

Light and heavy ends from the process are incinerated to HCl which is recovered. Alternatively, light and heavy ends can also be used as feedstocks for other chlorination processes.

The aqueous effluent from the VCM plant is steam stripped and can be treated biologically.

The VCM process can be "balanced" so that only VCM is produced, or the plant can be operated to produce HCl and/or EDC or to use "imported" EDC or HCl as raw materials.

The process is automated for stable, safe operation with wide turn-down capability. In addition, the process is designed for easy startup and shutdown. Manpower, capital, operating and maintenance costs are low.

Commercial installations: There are 33 major units in operation or in construction with combined capacity of 8 billion pounds per year of VCM and 19 billion pounds per year of EDC. Plant capacities range from 15 million to 1 billion lbs/yr. of VCM.

Vinyl chloride monomer... What you should know

This survey of the VCM (vinyl chloride monomer) industry, commercial developments, chemistry, commercial processes and new developments indicates that VCM can remain competitive with rising crude costs

I. W. McPherson, C. M. Starks and **G. J. Fryar,**
Continental Oil Co., Ponca City, Okla.

DEVELOPMENT OF THE VINYL chloride monomer (VCM) industry has been closely interrelated with the polyvinyl chloride (PVC) industry. Effectively 96 percent of the VCM production goes into the manufacture of PVC. Therefore, technological advances in one area have significant impacts upon the other, producing a domino effect. This, in conjunction with increasingly tighter environmental regulations, has insured a continuing evolution of VCM technology. It is timely to review the state of the art.

INDUSTRY PROFILE

The commercial significance of vinyl chloride monomer (VCM) can be highlighted by the statistical ranking of the 19th largest chemical commodity in the United States. Turning our view upstream, we realize the significance VCM plays in wedding the petrochemical and chloro-alkali industries. Fig. 1 schematically depicts the U.S. market integration surrounding VCM. Pondering the posture individual companies present to the market (Table 1), one can muse as to the motivational forces behind their respective business strategies.

It holds that, if 96 percent of the VCM demand in this country is derived from PVC, then VCM's future is inescapably tied to that of PVC's. Within the scope of known-unknowns, one basic fact attests to its longevity. On an energy-equivalent basis, PVC is one of the most energy-efficient construction materials available (Table 2). This follows even after weighing the socioeconomics of health and environment.

Looking at the two principal components of the PVC

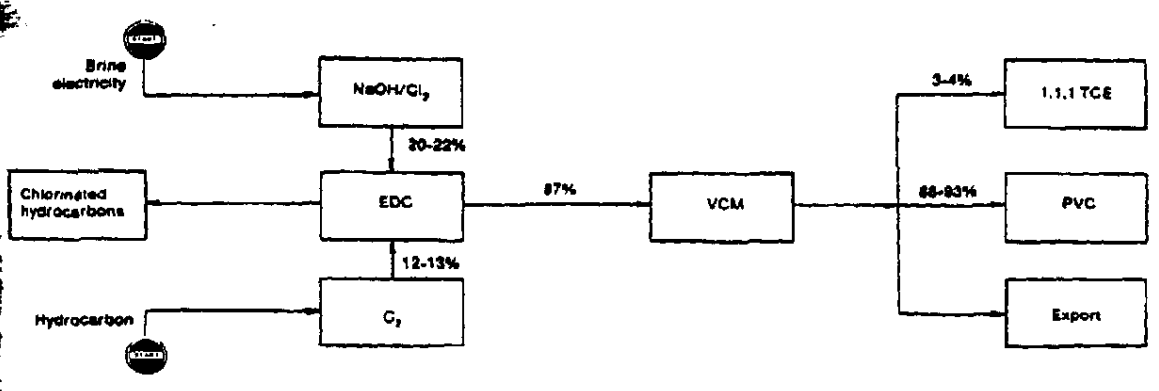


Fig. 1—Shows the U.S. market integration surrounding vinyl chloride industry.

market, flexible or plasticized products, of which fabric for automobile interiors and electrical wiring insulation are examples, and rigid products, including sewer and water pipes, electrical conduits and shoe soles, we find the rigid aggregate growing at 9 percent per year, as opposed to the flexible area which is increasing at a rate of approximately 5 percent. Within the past few years, the rigid aggregate has surpassed the size of the flexible market which can be witnessed by the creeping seasonal response the VCM industry has to construction, the major end-use outlet for rigid products.

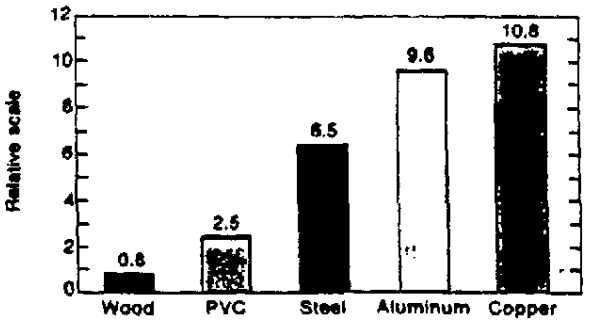


Fig. 2—Relative energy content of various construction materials.

TABLE 1—Nameplate capacities (MM pounds)

	PVC	VCM	Ethylene	Chlorine
Borden	550	300	None	None
Conoco	550	700	650	None
Diamond	None	1,000	None	2,500
Dow	None	2,250	4,800	8,400
Ethyl	175	300	None	500
B. F. Goodrich	1,100	1,100	350	250
ICI	None	300	None	300
Monochem	None	300	None	None
PPG	None	900	None	2,900
Shell	None	1,540	2,700	200
Stauffer	420	170	None	780

TABLE 2—Commercial types of VCM technology

I. High Purity Acetylene Feedstock
II. Dilute or Mixed Gas Feedstock
III. Balanced Ethylene Feedstock
A. Air-Based Oxychlorination
B. Oxygen-Based Oxychlorination

Developer/Licenser	Technology	
	Basic	Oxychlorination
Dow	III	A
Ethyl, ICI, Solvay	III	A
B. F. Goodrich	III	A,B
Kureha	II	—
Mitsui Toatsu	III	B
Monsanto	III	A,B
PPG	III	B
Rhone Poulenc	III	A
Stauffer	III	A,B
Tokuyama Soda	III	A
Toyo Soda	III	A
Hoechst	I	—
ICI	I	—

Over the course of the past ten years, VCM ha come a major item of international commerce, wit United States the architect of this business. Between and 1977, eight percent of the VCM produced carried offshore, making it third only to styrene mono and toluene in the generation of trade dollars by a ch eal commodity. This factor has tended to fill in the v in demand brought about by construction. More si cantly, it has permitted the VCM industry to consist operate near capacity levels by exporting domestic pluses into the world arena. Looking at the global V market, we view forces at work changing the dispos of trade. Beginning within the past five years, Eu as a whole has swung from a net importer to exp of VCM. With ten billion pounds of VCM cap integrated to where there is less than 15 percent chantly derived PVC demand, producers are now lenging U.S. material for a share of the remaining v exports.

Japan, whose five billion pound VCM industry built to serve the whole of the Asian-South Pacific ma first in PVC and then later in VCM, has witness major influx of U.S. and now European monomer ducers into their domain.

The present situation in the U.S. is manifested cheaper feedstocks, vis-a-vis energy, and an underva currency that together are able to offset logistical and remain competitive in the consuming mar Eventually, merging energy parity and emission cost p throughs will leave U.S. VCM no more competitive that of any other nation. We conclude, therefore, exports will continue as developing third world ma seek to establish a plastics industry in advance of pe chemicals. Conversely, the major market imbalance the past have gone by the wayside, and market gr will come from the domestic sector. Fig. 3 depicts longer term outlook for VCM. In making our projecti we assume that the growing capital commitment requ to make VCM will not force PVC to become uncomp tive with alternative products. Secondly, we foresee major technological innovation on the horizon that cr radically alter the economics of production. We do however, technological improvements of degree that rectionally level out the inflationary trend of plant c struction. Within the U.S., we project a 700 to 1, MM lb. per year grass roots plant will be required ev two years to meet demand. It is within the scope of time frame that innovation will be tested.

COMMERCIAL DEVELOPMENT

VCM was first produced commercially in the ea 1900s via reaction of HCl and acetylene derived fr calcium carbide. VCM usage in the manufacture of s thetic rubber accelerated dramatically during and af World War II. This increased demand prompted searc for more economical hydrocarbon feedstocks. Acetyl was recovered from refining steps, and new technol was developed to produce acetylene specifically fr hydrocarbon cracking.

Ethylene became plentiful in the early 1950s. Dir chlorination processes to produce 1,2-dichloroeth (EDC) from chlorine and ethylene were developed

conjunction with EDC cracking technology to yield VCM. This process yielded byproduct HCl and did not proliferate immediately, except in conjunction with acetylene-based technology which needed HCl to produce VCM.

In the U.S., ethylene production from abundant supplies of low cost LPG began to predominate. In Europe, ethylene prices also continued to drop, though not to the same degree since higher priced naphtha and gas oil were the primary feedstocks. Therefore, while European producers continued to use acetylene-based VCM technology, American companies moved rapidly to ethylene-based technology. With the startup in 1958 of the first large scale oxychlorination process to yield EDC from HCl and ethylene, a new era in VCM technology began. This "balanced" process allowed production of VCM from two commodity chemicals, chlorine and ethylene, without voluminous byproduct HCl.

VINYL CHLORIDE CHEMISTRY

Large scale production of vinyl chloride was first done by addition of hydrogen chloride to acetylene:

Hydrochlorination of acetylene

$$HCl + HC \equiv CH \xrightarrow{\text{Catalyst}} H_2C = CHCl \quad (1)$$

However, much lower costs for production of ethylene than acetylene and the discovery that 1,2-dichloroethane (EDC) thermally decomposes to vinyl chloride in excellent yield led to the following reaction sequence as the predominant manufacturing method for VCM:

Direct chlorination of ethylene

$$CH_2 = CH_2 + Cl_2 \rightarrow ClCH_2CH_2Cl$$

EDC cracking to VCM

$$ClCH_2CH_2Cl \xrightarrow{\text{Heat}} CH_2 = CHCl + HCl$$

This method was especially advantageous for those producers having a use for the HCl by product, particularly so if acetylene were available; since then, a balanced VCM process with no coproducts could be operated.

Later, the discovery that oxychlorination technology could be applied to ethylene to give 1,2-dichloroethane in high selectivity now allowed a completely balanced process based only on ethylene and chlorine as feedstocks.

Oxychlorination of ethylene

$$CH_2 = CH_2 + 2HCl + 1/2O_2 \xrightarrow{\text{Catalyst}} ClCH_2CH_2Cl + H_2O$$

At present, about 92 percent of the vinyl chloride produced in the United States is from plants that use the balanced process based on ethylene via chlorination, oxychlorination, and thermal cracking of EDC.[1] These three separate steps are described in greater detail below. Additionally, the hydrochlorination of acetylene is also discussed below since plants using this chemistry are still in operation. Moreover, some recent crude oil cracking technology may narrow the cost gap between acetylene and ethylene with consequent revival of interest in VCM from acetylene. Some chemistry on direct preparation of VCM from ethane is also briefly outlined.

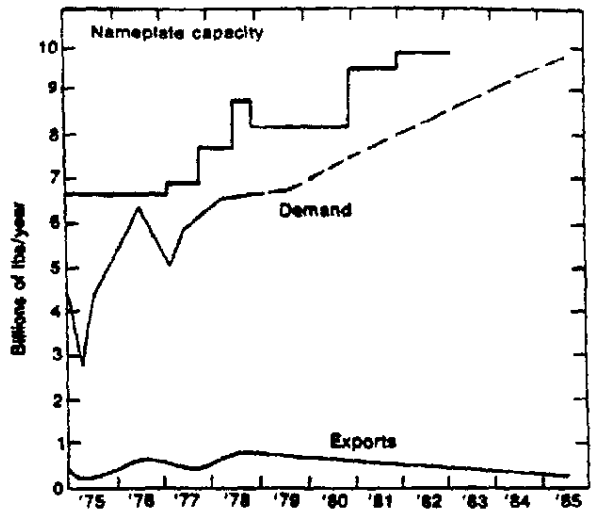


Fig. 3—U.S. vinyl chloride nameplate capacity versus demand.

Direct chlorination of ethylene. Direct chlorination of ethylene to 1,2-dichloroethane is almost always conducted in a liquid phase reactor by intimately mixing ethylene and chlorine in liquid EDC. Ferric chloride, a highly efficient and selective catalyst for this reaction, is normally used in commercial processes. Amides, such as n,n-dimethylformamide, have been reported to increase EDC selectivity.[5] Oxygen, frequently present as an impurity in chlorine, likewise increases EDC selectivity in direct chlorination of ethylene by inhibition of free radical reactions that give 1,1,2-trichloroethane.

Direct chlorination reactions may be run rich in either ethylene or chlorine, depending on the methods available to the plant for handling offgases from this reactor. Conversion of the lean component is usually 100 percent, and selectivity to EDC is greater than 99 percent.

1,2-Dichloroethane, as it comes from the direct chlorination reactor, is frequently of sufficient purity for cracking, except that it may contain ferric chloride, which would lead to rapid fouling of the cracking reactor. To avoid expensive purification of this already pure EDC, one may remove $FeCl_3$ by adsorption on activated carbon[3] or other solids.[4] Alternately, one may operate the direct chlorinator at the boiling point of EDC, taking pure EDC overhead and using the heat of reaction to supply the heat for vaporization.[5,6,7,8]

Oxychlorination of ethylene to EDC. Ethylene oxychlorination is normally conducted at temperatures of 225-325° C and at pressures of one to 15 atmospheres. Catalysts for this reaction almost always contain copper chloride and sodium or potassium chloride deposited on alumina or other suitable support. The detailed mech-

anism of the catalyst's activity is not known, but it is recognized that cupric chloride is the active chlorinating agent. The cuprous chloride produced is rapidly reconverted to $CuCl_2$ under the reaction conditions, but the presence of some cuprous chloride is thought to be advantageous because it complexes with ethylene, bringing it into contact with $CuCl_2$ for a long enough time for chlorination to occur. The sodium or potassium chloride serves to increase EDC selectivity, mostly by inhibiting formation of ethyl chloride. Other catalyst components, such as rare earth metal chlorides, sulfate salts, ferric chloride and numerous other additives, have been described in the patent literature.

Good temperature control of the highly exothermic oxy reaction is a key element in successful production of 1,2-dichloroethane. Temperatures higher than about 325°C lead to increased byproduct formation, mostly through increased dehydrochlorination of EDC to vinyl chloride followed by additional oxychlorination to give products having high levels of chlorine substitution. High temperatures also increase the amount of ethylene burned to carbon monoxide and carbon dioxide. Of equal importance, high temperatures deactivate the catalyst by highly accelerated coking and consequent powdering of the catalyst units and by increased sublimation of copper, chloride away from the catalyst.

Temperature control in fluidized bed reactors is maintained by the excellent intermixing of the catalyst particles and by use of internal cooling surfaces.[18] Temperature control in fixed bed reactors is more difficult since "hot spots" tend to develop. To keep the hot spot temperature below below 325° C, yet get maximum utilization from the reactor, it is common practice to pack the reactor tubes with active catalyst and inert diluent mixtures in proportions of each so adjusted as to have low catalyst activity at the inlet, steadily increasing to maximum activity at the outlet. This grading of the catalyst activity flattens the temperature profile, allowing for good temperature control with high productivity. For example, one patent[9] indicates the use of four zones with 93 percent, 85 percent, 40 percent, and 0 percent, respectively, of the active catalyst pellets replaced by inert graphite. As an alternate to using inert materials in the catalyst bed, catalysts, each with higher levels of $CuCl_2$ and consequently of increasing reactivity, are sometimes used.

Fluid bed oxychlorination of ethylene, operated under good control, results in 94-97 percent ethylene conversion, 95-97 percent HCl conversion, and EDC selectivities in the range of 94-96 percent. Fixed bed oxychlorinations are normally run with excess ethylene relative to HCl, resulting in 93-97 percent ethylene conversion, 94-95 percent HCl conversions, and EDC selectivities of 93-95 percent. These data do not include recovery of excess ethylene in subsequent reaction steps. Excess ethylene in vent gases from oxychlorination is normally converted to EDC by direct chlorination with chlorine,[11,13] although, if oxygen is used rather than air, the excess ethylene may be recycled directly back to oxychlorination.

Byproducts of ethylene oxychlorination are vinyl chloride, ethyl chloride, 1,1-dichloroethane, vinylidene chloride, *cis*- and *trans*-1,2-dichloroethylenes, trichloroethylene, chloroform, carbon tetrachloride, methyl chloride, methylene chloride, chloral and high boiling compounds. All of these byproducts present problems in one way or another, such that their production needs to be minimized to lower raw material costs, to lessen the difficulties of preparing pure EDC, and to prevent fouling in the cracking reactor. Chloral, in particular, needs to be removed since it polymerizes readily in strong acids to give solids which clog and foul operating lines and controls.

One must also take care to see that the feeds to oxychlorination are pure. Normally, the only problem is with low levels (0.1 to 0.5 percent) of acetylene present in the HCl from cracking of EDC. Acetylene in the feed leads to the formation of considerable highly chlorinated byproducts and tars. Selective hydrogenation of this acetylene to ethylene and ethane is practiced by many companies.[19]

Oxychlorination with oxygen instead of air. Use of oxygen instead of air for ethylene oxychlorination has received much attention.[14-17] The outstanding benefits from using oxygen are avoidance of expensive facilities to recover EDC, ethylene and other chemicals from the large nitrogen vent gas stream; a large reduction in the quantity of offgases that will probably need to be incinerated; and the ability to use ethylene as a diluent for oxychlorination, a procedure said to improve heat transfer in tubular reactors.

Purification of EDC for cracking. Great care must be taken to ensure that EDC used for cracking to vinyl chloride is of high purity, normally greater than 99.5 percent, since cracking is exceedingly susceptible to inhibition and fouling by trace amounts of impurities. Additionally, the EDC must be bone dry to prevent excessive corrosion downstream of the cracker. For these purposes, one must consider removal from EDC of byproducts from three sources: EDC from direct chlorination, EDC from oxychlorination, and EDC recovered from the cracking step (see below).

EDC from direct chlorination is usually quite pure, greater than 99.5 percent; and, except for the $FeCl_3$ present, it needs little further purification. As mentioned previously, ferric chloride may be removed by adsorption on a solid, or the EDC may be distilled away from $FeCl_3$ in a boiling reactor. Alternatively, the ferric chloride may be removed by washing with water, usually in conjunction with oxy-EDC.

1,2-Dichloroethane from oxychlorination contains a variety of impurities as listed previously. EDC from this source is usually washed with water and then with caustic solution to remove chloral and other water extractable impurities.[20] Low boiling impurities and water are taken overhead in a first (light ends) distillation column, and then pure dry EDC is taken overhead in a second (heavy ends) column.

EDC recovered from the cracking step contains an

ppreciable number of impurities, of which two, chlorobenzene and trichloroethylene, are not readily removable by distillation, necessitating the use of other treatments. Chloroprene, if not altered by chemical treatment, concentrates in the light ends column where it can polymerize to solid or rubbery materials which seriously foul and upset this column. Trichloroethylene forms an azeotrope with EDC, boiling very close to EDC. If it is not removed in some way, it accumulates in the EDC, leading to reduced cracking rates and increased fouling. Both impurities may be removed by subjecting the recycle EDC stream to chlorination prior to distillation.[23-25] Treatments with HCl[24-26] and by hydrogenation[27] have also been patented as methods for removal of chloroprene.

Cracking of 1,2-dichloroethane to vinyl chloride. At temperatures in the range of 425-550° C, and near atmospheric pressure EDC undergoes clean thermal dehydrochlorination (cracking) to yield vinyl chloride and hydrogen cloride:

$$ClCH_2CH_2Cl \xrightarrow{Heat} CH_2 = CHCl + HCl$$

The mechanism of this reaction has been extensively investigated[28] and shown to involve a sequence of free radical intermediates.

Use of pressure up to 25 to 30 atmospheres during cracking at temperatures of 500-550° C provides better heat transfer, reduced equipment size and easier separation of HCl from the product by fractional distillation. EDC conversion levels are normally maintained in the range of 50 to 60 percent at residence times of 2 to 10 seconds, with selectivities of VCM ranging from 96 to 99+ percent. Some byproducts generated during cracking act as inhibitors to the free radical sequence so that increasing severity leads to smaller and smaller increases in EDC conversion with correspondingly increasing levels of byproducts. Various materials, such as chlorine, bromine, or oxygen have been shown to be initiators for EDC cracking.[28] Recently, however, exclusion of oxygen is claimed to result in considerable reduction of fouling on the cracker tube walls.[29] A rather spectacular claim has been made that use of nitromethane as an initiator provides EDC conversion levels of up to 92.5 percent at 480° C.[30] An important processing requirement in EDC cracking is rapid cooling or quenching of the reaction mixture. If cooling is done too slowly, substantial yield losses to heavy ends and tars result.[21, 26, 31]

Byproducts from the cracking reaction include acetylene, ethylene, methyl chloride, butadiene, vinyl acetylene, benzene, chloroprene, vinylidene chloride, 1,1-dichloroethane, chloroform, carbon tetrachloride, 1,1,1-trichloroethane and other compounds. Most of these impurities remain in the unconverted EDC fraction and are removed when this stream is distilled. Ethylene and acetylene codistill with the HCl and are thus routed back to oxychlorination (after optional hydrogenation of the acetylene to ethylene). Methyl chloride and butadiene more or less codistill with the vinyl chloride, depending on the efficiency of the VCM fractional distillation system. Addition of chlorine or carbon tetrachloride to the cracker feed is claimed to suppress methyl chloride formation.[33] Removal of butadiene, a contaminant which can interfere with polymerization of VCM, has been done by treatment with chlorine,[34] anhydrous HCl,[35] or selective hydrogenation.[36]

HCl addition to acetylene. Recent development of a new crude oil cracking process[37] using very high temperature steam (2,000° C) as a heat transfer fluid produces substantial yield of acetylene along with ethylene. Under some economic and geographic conditions, the use of this cracking process may be advantageous and may, thereby, provide acetylene for vinyl chloride production.

Typical conditions of hydrogen chloride addition to acetylene are total pressures on the order of five to 15 atmospheres, temperatures of 150 to 180° C, and use of a mercuric chloride-on-carbon catalyst.[38] With stoichiometric quantities of reactants, essentially 100 percent conversion is observed with VCM selectivities on the order of 98 percent. It is notable that ethylene does not react under these conditions, thereby allowing the use of mixed ethylene-acetylene streams as feeds. Ethylene, easily recovered from the vinyl chloride product by fractional distillation, is then chlorinated to yield 1,2-dichloroethane.

Other catalysts have been shown to be effective for addition of HCl to acetylene, but $HgCl_2$ is vastly superior.[38] However, in addition to the general toxicity problems involved in working with mercury-containing substances, $HgCl_2$ has appreciable volatility under the above reaction conditions leading to a need for considerable care and control in operation of the reactor. In fixed bed operations, $HgCl_2$ vaporizes from the hot spot of the reactors, condenses at cooler locations downstream and results in continuous movement of the hot spot downstream with eventual loss of catalytic activity. This loss is minimized by periodic reversal of flow through the reactor.

Ethane-based vinyl chloride processes. A number of patents dealing with chemistry for conversion of ethane to EDC and/or VCM have been published in recent years.[39-44] Most of these reactions involve high temperature oxychlorinations, such as

$$CH_3CH_3 + HCl + O_2 \xrightarrow[350\text{-}450^\circ C]{CuCl_2\ Catalyst} CH_2 = CHCl + 2H_2O$$

However, these processes suffer from a number of disadvantages, the most important of which includes low selectivities, low conversions and difficult operating conditions such as $CuCl_2$ sublimation.

One reaction system based on ethane, called the "TRANSCAT" process, has been developed on a large pilot plant scale but is not yet in commercial practice.[45-51] The chemistry of this process is a complex series of reactions, generally involving chlorination, dehydrochlorination and oxychlorination. A mixture of ethane, ethylene, ethyl chloride, chlorine and HCl are fed to a melt of cupric oxychloride and potassium chloride, yielding vinyl chloride, water, and cuprous chloride as the main products. The cuprous chloride-potassium chloride product is taken to an oxidation reactor where the cupric oxychloride is regenerated by treatment with air. Vinyl chloride is separated from the organic product and puri-

fied by fractional distillation. Removal of about 0.4 percent butane plus butenes present in the main VCM cut represents a very difficult separation.[43] Ethyl chloride and ethylene can be recycled into the feed. Chlorine values in the chlorinated byproducts can be recovered by incineration and then feeding these gases to the cuprous chloride oxidative regenerator reactor.

Disposal of byproducts. Disposal of byproducts presents special problems for vinyl chloride manufacturing plants, since a variety of gaseous organic liquid, and acqueous streams must be handled, each with its own particular problems.

Vent gas streams from various units may contain small amounts of HCl, chlorine, ethylene, vinyl chloride, methane and carbon monoxide. These streams may sometimes be treated by scrubbing, chemical treatment, sorption, or other methods to recover some chemicals when economically justified. Otherwise, the common cleanup technique is either incineration or catalytic combustion followed by recovery of HCl from the vent gases.

Two organic byproduct streams are produced. The light ends contain mainly ethyl chloride, *cis-* and *trans-*1,2-dichloroethylene, chloroform and carbon tetrachloride. The heavy ends or "tars" contain mostly 1,1,2-trichloroethane, lesser concentrations of tetrachloroethanes, chlorinated butanes, chlorinated aromatics and a large number of other compounds present in small amounts. These streams are normally fractionated to recover useful components, the others incinerated to recover chlorine values either as aqueous or anhydrous HCl.

Process water streams are steam stripped to remove volatile organics followed by neutralization and then treatment in an activated sludge system to remove nonvolatile organics in the water.[48]

COMMERCIAL PROCESSES

Broadly speaking, there are three types of VCM processes in commercial use today. These are categorized as acetylene, ethylene, or mixed gas based on feedstock requirement. Within the "ethylene-type" plants, further classification is desirable to distinguish the type of oxychlorination technology used, i.e., oxygen versus air feedstock (see Table 2). Over 90 percent of the world's listed 35 billion lb. per year VCM capacity currently is based upon the balanced ethylene feedstock route. Of this, just under 90 percent uses air-based oxychlorination. However, of the projected worldwide plant startups for the period 1979-1981, approximately 30 percent of the 7.7 billion lbs. per year VCM will be derived from oxygen-based oxychlorination. Other existing producers will undoubtedly be evaluating the conversion of present air-based plants to the use of oxygen during this time frame.

Table 3 presents a summary of the technology sources in use today. It is thought that the technology currently licensed by ICI and Solvay is similar to the process normally attributed to Ethyl. Therefore, all are listed under Ethyl's technology. It is interesting to note that several plants exist where the oxychlorination process

TABLE 3—Current VCM technology sourc

Technology Source	Existing		Planned (1979-	
	Plants	VCM, MM Lbs./Yr.	Plants	V MM L
1. B. F. Goodrich	18	5,840	4	7
2. Hoechst/BFG*	11	4,290	2	
3. Stauffer/BFG*	5	2,360	—	—
4. Stauffer	19	6,390	2	
5. Ethyl, Solvay, ICI	14	5,000	1	
6. Dow	7	3,040	3	1
7. PPG	5	1,700	3	1
8. Rhone-Poulenc	5	1,330	1	
9. Monsanto	4	1,110	1	
10. Toyo Soda	3	400	1	
11. Tokuyama Soda	2	660	—	—
12. Mitsui Toatsu	3	610	1	
13. Kureha	2	410	—	-
14. Miscellaneous	10	2,400	1	
	107	35,540	20	7.

* Oxychlorination process provided by BFG.

of one licensor, B. F. Goodrich, has been combine direct chlorination and VCM technologies of othe Hoechst and Stauffer. Table 4 presents a tabula worldwide VCM producers. This summary was pr from scores of literature sources, some of whic contradictory. However, the authors have exercise best judgment in the absence of specific informatio the listed licensors.

The reader is referred to Leonard,[54] Gomi,[56] or for details of the acetylene and mixed gas routes to The technology discussion herein will be limited balanced ethylene feedstock route used overwhel today.

Although each of the major technology license many patents, none has complete coverage of ea of his process. As a result, the sequence and t operating steps tend to be very similar from pro process. The basic differences stem from the oxych tion technology and the types of impurities appea the crude EDC. The licensor, therefore, provides know-how primarily, as opposed to patent positio result, published literature by major licensors is standably very sparse and highly simplified, with exceptions.[36, 37, 58, 59]

TYPICAL VCM PROCESS

The typical VCM process combines direct an chlorination (oxy) processes to provide 1,2-di ethane (EDC) feedstock for the EDC pyrolysis un Fig. 4).

The direct chlorination process relative to oxy i acterized by low capital investment, low operatin and high purity product. However, HCl generate the EDC pyrolysis unit dictates the use of an ox With the current pyrolysis yield of approximatel mol VCM per mol EDC fed, and the HCl yield of per mol VCM, the oxy unit size is set at approxi 0.5 mol EDC per mol of VCM desired. This s direct chlorination unit size at approximately 0 EDC per mol VCM.

The combined EDC streams are caustic treated

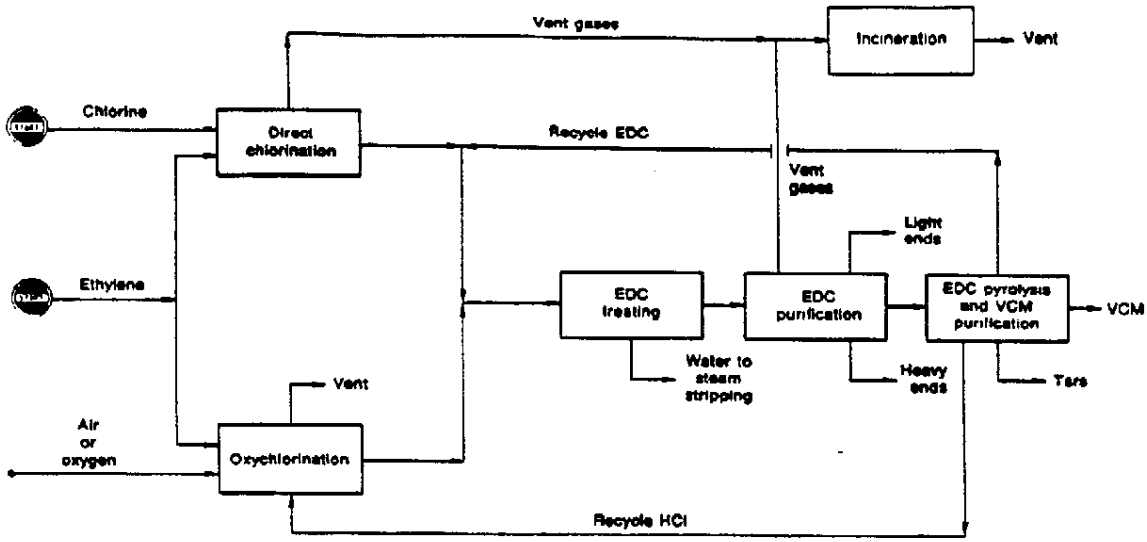


Fig. 4—Typical vinyl chloride monomer block/flow diagram.

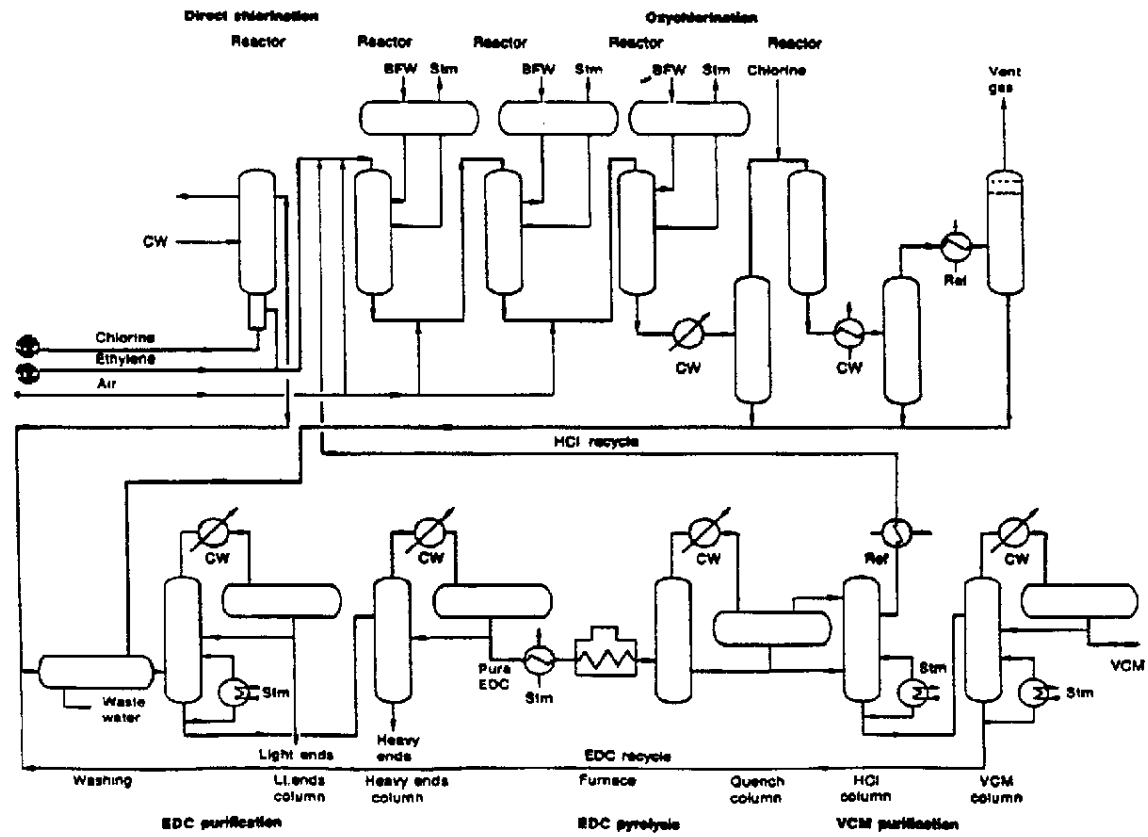


Fig. 5—Schematic of the Stauffer vinyl chloride monomer process.

TABLE 4—VCM plants—worldwide—(cont'd)

Operator	Location	Process	Startup Year**	Licensor	Engineer/ Contractor	VCM Capacity, 1000 Lbs/Yr*
Italy						
Anic	Ravenna	A/-/-	1971	Stauffer	Foster Wheeler	168
Montedison	Brindisi	M/A/D	1969	BFG		408
	Porto Marghera	M/A/D	1970	BFG		408
Rumianca Sud	Cagliari	E/-/D	1965	PPG	Opt. Setes	154
	Cagliari	F/A/D	1976	PPG	Futura	250
SARP	Termini Imerese	....	....	.....	.....	(110)
Sincat	Priolo	....	....	Ethyl	.....	298
Solvic	Rosignano	....	....	Solvay	Solvay	110
Sir Consorzio Industrie	Porto Torres	....	....	Sir	Futura	316
Japan						
Asahi Pana	Chiba	AE/-/D	1967	PPG	.....	91
Chiba VCM	Chiba	E/A/B	1971	Stauffer	Sumitomo	350
Chisso	Minimata	....	....	Toyo Soda	Hitachi	220
Denki Kagaku	Chiba	....	....	Denki Kagaku	.....	(330)
Japanese Geon	Tokuoka	M/-/D	1967	Japanese Geon	.....	267
Kanegafuchi	Takasago	E/A/B	1969	Stauffer	Sumitomo	331
Kanegafuchi	Takasago	E/A/B	1970	Stauffer	Kanegafuchi	331
Kashima VCM	Kashima	E/A/B	1970	BFG	.....	331
Kureha	Hiakiri	M/-/D	1964	Kureha	Chiyoda	220
Mitsubishi-Monsanto	Yokkaichi	AE/A/-	1976	Monsanto	.....	245
Mitsui Toatsu	Nagoya	AE/A/D	1964	Mitsui Toatsu	Toyo Engineering	330
	Osaka	E/A/B	1970	Mitsui Toatsu	Toyo Engineering	330
Nissan	Chiba	AE/A/D	1968	Toyo Soda	Hitachi	330
Nyo-Nichi Co., Ltd.	Mizushima	E/A/B	1970	BFG	.....	77
Sanyo Monomer	Mizushima	AE/A/D	1970	BFG	.....	440
Showa Petrochemicals	Tokuyama	A/-/-	....	Tokuyama Soda	.....	238
Sumitomo	Niihama	E/A/B	1963	Stauffer	.....	440
Sun Arrow Chemical	Tokuyama	E/A/D	1967	Tokuyama Soda	.....	180
Toyo Gosei	Tokushima	M/-/D	....	Toyo Gosei	.....	220
Toyo Soda	Tokuyama City	E/A/B	1966	Toyo Soda	Hitachi	88
	Yokkaichi	....	....	Toyo Soda	.....	110
						220
Korea						
Korea Pacific	Yeo-Su	....	(1979)	Dow	Fluor/Daelim	(330)
Korea Pacific	Ulsan	....	....	Dow	Procon	132
Libya						
GNOI	Abu Kammash	.....	(1980)	BFG, Hoechst	F. Uhde, Salzgitter	(136)
Mexico						
Pemex	Pajaritos	E/A/B	....	Monsanto	Lummus	155
	Pajaritos	E/A/B	1978	BFG	Rufelo	440
Morocco						
SNLP	Mohammadia	....	1976	Stauffer	Krebs	99
Norway						
Norsk Hydro	Rafnes	E/A/B	1978	BFG, Hoechst	Badger	660
Peru						
Socieded Paramonga LTDA.	Paramonga	E/A/D	....	Vulcan	.....	17
Poland						
Psimex-Cokop	Wloclawek	E/D/B	(1979)	PPG	Petrocarbon, Davy-Powergas	(450)
Portugal						
CNP	Sines	Planned	(1981)	.....	.....	(330)
Rumania						
Industrial Import	Rimnicu Vilcea	....	....	Dow	Klock	88
State Authority	Rimnicu Vilcea	E/D/B	....	Mitsui Toatsu	Toyo Engineering	350
South Africa						
Africa Explosives and Chemicals	Sasolburg	E/-/D	1968	ICI, Solvay	Humphries & Glasgow	88
	Sasolburg	A/-/-	1978	Tenneco	Crawford-Russel	440
Spain						
Monsanto	Tarragona	....	....	Monsanto	Lummus	176-330
	Tarragona	....	....	Monsanto	McKee, CTIP	(250)
	Tarragona	....	....	Monsanto	.....	530
	Tarragona	....	....	Monsanto	McKee, CTIP	220
Rio Rodano	Huelva	....	(1980)	Rhone-Progil	.....	(500)
Viniclor	Martorell	E/A/B	1970	Solvay	McKee, CTIP	265
Dow	Huelva	.....	(1981)	Dow	.....	(770)
Sweden						
Kemanobel	Stenungsund	E/A/B	1967	Stauffer	Lurgi	180
Switzerland						
Lonza	Leiden	A/-/-	....	.....	.....	44
Taiwan						
Formosa Plastic	Kaohsiung	E/A/B	1973	Stauffer	.....	530
Chung Tai (F)	Touliu	E/D/B/	....	Mitsui Toatsu	.....	(530)
Turkey						
Petkim	Yarimca Izmit	....	....	Solvay	Humphreys and Glasgow	119
Petkim	Aliaga-Izmir	E/-/D	(1981)	ICI, Solvay	CTIP	(257)
United Kingdom						
British Petroleum	Baglan Bay, Wales	AE/A/D	1971	BFG	.....	573
ICI	Wilhelmsburg	....	....	Solvay	C. F. Braun	
	Runcorn	A/-/-	....	Solvay	C. F. Braun	
USSR						
Technopromimport	Dzerzhinsk	....	....	Rhone-Progil	Speichim	66
	Gorki	E/A/B	1970	Stauffer	Speichim	77
	Gorki	....	....	Rhone-Progil	Speichim	66
	Kalush	E/A/B/	1974	BFG, Hoechst	F. Uhde	550
	Volgograd	EA/-/D	....	Kureha	Chiyoda	145
	Zima	E/A/B	(1979)	BFG, Hoechst	F. Uhde	(595)
Venezuela						
Petroplas	El Tablazo	E/A/B	1977	BFG	.....	110
Yugoslavia						
Ork. Kem. Ind.	Skopje	....	....	Rhone-Progil	.....	110
Hemijska Ind	Pancevo	E/A/B	(1979)	Stauffer	Foster Wheeler	(220)
Dow/Ina	KRK	.....	(1981)	Dow	.....	(440)

* Information tabulated from many sources. In cases (several) of contradictory reports, authors have exercised their best judgment.
** Parentheses denote that plant is thought to be in engineering and/or construction stage and has not reached an operational status.

Legend:

Hydrocarbon Feedstock	/ Oxy Basis	/ Process
(E)thylene	(A)ir	(B)alanced
(A)cetylene	(O)xygen	(O)xy
(M)ixed Gas		(D)irect

TABLE 4—VCM plants—worldwide

Operator	Location	Process	Startup Year**	Licensor	Engineer/ Contractor	VCM Capacity, MM Lbs/Yr**
United States						
ICI America	Baton Rouge, Louisiana	E/A/B	1968	BFG		360
Conoco Chemicals	Lake Charles, Louisiana	E/A/B	1968	Stauffer	R. M. Parsons	700
Dow	Freeport, Texas			Dow		200
	Oyster Creek, Texas	E/A/D	1969	Dow		700
	Plaquemine, Louisiana		1978	Dow		1,150
Ethyl Corp.	Baton Rouge, Louisiana			Ethyl		360
	Houston, Texas			Ethyl		150
B. F. Goodrich	Calvert City, Kentucky	E/A/D	1964	BFG		1,050
Monochem	Geismar, Louisiana	A/ /				360
PPG	Lake Charles, Louisiana	E/D/B	1968	PPG	Ford, Bacon & Davis	400
	Lake Charles, Louisiana	E/D/B	(1980)	PPG	R. M. Parsons	(1,000)
Shell Chemical	Guayanilla, Puerto Rico	E/D/B	1971	PPG	Fluor	500
	Deer Park, Texas	E/A/B/	1972	Stauffer	R. M. Parsons	840
Stauffer	Norco, Louisiana	E/A/B	1972	Stauffer	R. M. Parsons	700
Borden Chemical	Long Beach, California	E/A/B	1957	Stauffer	C. F. Braun	175
Georgia Pacific	Geismar, Louisiana	E/A/B		Stauffer	R. M. Parsons	330
Diamond Shamrock	Plaquemine, Louisiana	E/D/B	(1980)	PPG	Brown and Root	(1,000)
	Deer Park, Texas	E/A/B	1978	Stauffer, BFG	Lummus, Badger, Brown & Root	1,000
Algeria						
Sonatrach	Skikda	E/D/B	(1979)	Mitsui Toatsu	Toyo Engineering	(88)
Argentina						
Dow Quimica	Bahia Blanca			Dow	Chemico	110
Electrector	Capitan, Bermudez	E/A/B		ICI		73
	Bahia Blanca			BFG	Badger	287
Australia						
Ici anz	Botany	A/-/D		ICI		7
Belgium						
BASF	Anvers	E/A/B	1967	Stauffer	BASF	240
Lieuchem	Feluy			BFG		(1,100)
Limburgse (LVM)	Tessenderlo	E/A/B	1972	Hoechst, BFG	Badger	440
		E/A/B	1976	Hoechst, BFG	Badger	440
Solvic	Jemeppe-Sur	F/A/B	1968	Ethyl	Solvay	550
Brazil						
Copama	Elgin	E/A/B	1972	Solvay, ICI	McKee, CTIP	220
Monomeros Vinilicos	Bahia Blanca			BFG	Badger	(286)
Petroquim Camacari	Camacari		(1979)	BFG	Badger/Promon	(330)
Bulgaria						
Technocomplekt	Burgas Devnya	E/D/B	(1979)	PPG	Technip/TPL	(330)
Canada						
Dow	Sarnia, Ontario			Dow		7
	Fort Saskatchewan		(1979)	Dow		(660)
Shawinigan	Varennes, Quebec	F/A/B	1967	BFG	Badger	126
	Shawinigan, Quebec	A/A/D	1969	BFG		126
Chile						
Petroquimica	Concepcion				Fish Engineering	35
Dow/ENAP	Concepcion			Dow		35
China						
Technical Import Corp.	Peking	E/A/D	1978	B. F. Goodrich	F. Uhde	176
Colombia						
Petroquimica Columbiana		E/A/B	1973	Stauffer		
Czechoslovakia						
Chemopetrol	Nanstorice	E/A/B	1972	Stauffer	R. M. Parsons, Veest, Alpine	265
Chemickezavody W. Plecka	Novaky, Slovakia	M/-/D	1972	BFG, Hoechst	F. Uhde	249
Finland						
Pokama Oy	Porvoo		1971	Solvay	CTIP	88
France						
AKZO	Centrovelle					
Chemie	Le Havre					
EMC/DSM	Ottmersheim					
Daufac	Jarrie	E/A/B	1967	Stauffer, BFG, Hoechst		
Rhone-Poulenc	Lavera	M/-/D		Rhone-Progil	Rhone-Progil	440
	St. Auban	F/A/B	1970	Rhone-Progil	Rhone-Progil	795
	St. Fons		1965	Id G, Hoechst		291
Solvic	Tavaux	E/A/B		Solvay, Ethyl	Solvay	440
PCUK/Shell Chemie	FosSurMer	E/A/B	(1980)	BFG	Badger	440
East Germany						(440)
Industrie Anlagen Import	Schkopau		(1979)	Hoechst	F. Uhde	(440)
West Germany						
Airwaise	Wilhelmshaven					(660)
Huls	Marl	AE/-/D		Huls		700-770
BASF	Ludwigshaven	AE/-/D		Stauffer		160-320
Solvay	Rheinberg	E/A/B	1973	Solvay	Solvay	440
Dynamit Nobel	Leistdorf	E/A/D	1966	Stauffer, BFG	C. F. Braun	130
Hoechst	Gendorf	E/A/D	1972	BFG, Hoechst	Uhde	375
	Knapsack	E/A/B/D	1963	BFG, Hoechst	Badger, Uhde	220
Knapsack, AG	Wesseling					(440)
	Knapsack			BFG	Badger, Uhde	220
Wacker	Knapsack			BFG	Badger, Knapsack	330
	Burghausen	E/A/D	1971	Stauffer/Stauffer	R. M. Parsons	176
ICI	Burghausen	E/A/B		Wacker	R. M. Parsons	350
	Wilhelmshaven		(1980)	ICI	Fluor	(580)
Greece						
Ethyl Hellas	Thessaloniki	E/-/D		Ethyl		33
Holland						
AKZO	Botlek	E/A/B	1971	Stauffer/BFG	Comprime-Lurgi	660
	Botlek (Expansion)		(1979)		AKZO Engineering	(330)
Hoechst	Vlissingen		(1981)	Hoechst		(350)
Shell?	Pernis					
Hungary						
Chemkomplex	Borsonte			Hoechst	Uhde	79
	Borsonte	E/A/B		BFG, Hoechst	Badger	350
Beszedi Vegyi Kombinat	Kazincbarcika	T/A/B	1978	BFG, Hoechst	Badger	350
India						
C&P India	Madras	C/-/D	1967	BFG		33
National Organic Chemistry	Bombay	A/-/-		Shell, BASF		45
Iran						
Abadan Petrochemical	Abadan	E/A/B	1969	BFG	Badger, Lummus	130
Iran-Japan J.V.	Bandar	E/A/B	(1979)	Toyo Soda	Hitachi	(330)
Iraq						
State	Basra		(1980)	Stauffer	Lummus, Thyssen	145
Israel						
Electrochemical Industries	Haifa	E/A/B		Monsanto		29
	Akko		(1979)			(220)

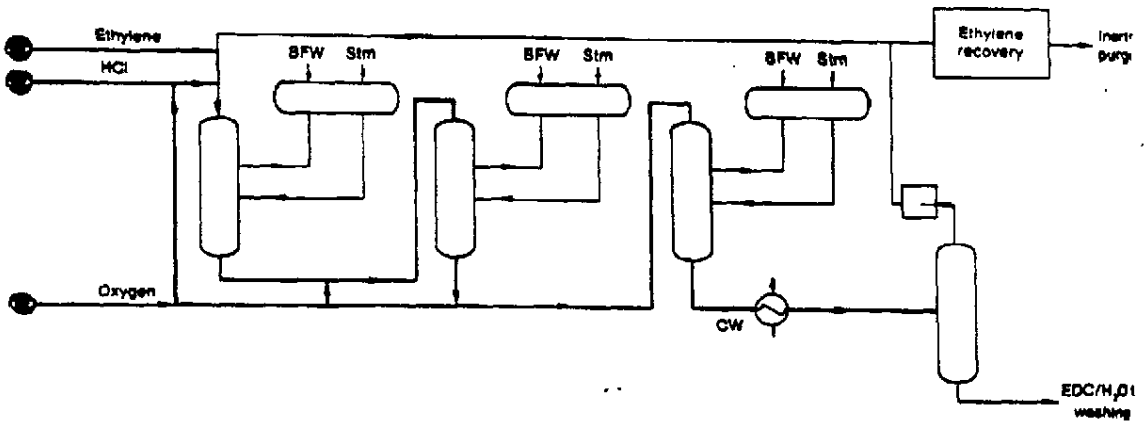


Fig. 6—Modifications used in the Stauffer oxygen-based oxychlorination process.

move HCl and certain chlorinated byproducts which otherwise would hinder fractionation or pyrolysis. The "clean" EDC is subjected to distillation steps in which water and other light components are removed, as well as heavy components typically labeled tars. The dry product EDC, generally of 99.5 percent or greater purity, is thermally cracked to yield HCl and VCM in an EDC carrier stream. Further distillation equipment separates EDC and HCl for recycle and yields product VCM for final treating.

The typical VCM plant includes VCM treating, offgas treating, light ends/tars handling and waste treating facilities. It will also include incineration units for reclaiming waste chlorinated hydrocarbons from offgas or liquid streams.[1]

Stauffer technology.[60,61] In the Stauffer direct chlorination process (see Fig. 5), ethylene and chlorine are reacted, in the liquid phase and under controlled conditions, to yield a crude product which analyzes 99.7 percent EDC. The reactor product is then combined with the crude oxy EDC, washed and distilled to remove water, light ends and heavy ends.

Pure EDC is preheated in the economizer of the pyrolysis furnace and then vaporized with steam. EDC vapor is then heated to dissociation temperature in the furnace tubes to yield a mixture of vinyl chloride and hydrogen chloride. Conditions are controlled to maintain EDC conversion at 50 to 55 percent. Following a quench and condensation step, HCl, VCM, and uncracked EDC are separated by distillation. Hydrogen chloride gas is sent to the oxy section. Unreacted EDC is recycled to purification.

The oxy section combines recycle HCl with fresh ethylene and air in tubular fixed-bed catalytic reactors. The ethylene and air are fed in excess of stoichiometric requirements to assure high HCl conversion.[61] Reaction heat is removed by generation of steam on the shell s of each reactor. The final reactor effluent is cooled condense EDC, and the offgas is contacted/reacted w chlorine to recover ethylene as additional EDC. T offgas stream is cooled versus cooling water and refr eration to further condense EDC before exiting the p cess. Residual ethylene concentration in the vent gas reportedly as low as 10 ppm.[61]

Stauffer also offers an oxygen-based oxy process (F 6) in which the main reactor offgas, following conden tion of EDC, is compressed and recycled to the first o reactor. An excess of ethylene is used to maximize H conversion and minimize byproducts. A small slipstre from the ethylene-rich recycle is purged to an ethyle recovery unit for control of inerts.

Ethyl Integrated VCM process.[62] Gaseous chlorine a ethylene are introduced into a direct chlorination reac in which they combine to form EDC. The very hi purity EDC product can be sent directly to (or, af degassing, can bypass) the EDC purification system (s Fig. 7).

Air and gaseous ethylene and HCl are introduced in an oxychlorination reactor in which EDC is produced an elevated pressure and temperature in the presence a fluidized catalyst. The reaction products are neutralis and partially condensed to recover EDC which is first se to a drying column and then to the EDC purificati system. A portion of the vent gas, consisting primari of nitrogen and carbon dioxide is recycled to the react for added safety.

The purified EDC stream which contains recycl EDC as well as the EDC from direct and oxychlorin tion is vaporized and introduced into a furnace. At le half of the EDC stream is cracked to HCl and VC The reaction products are cooled rapidly, partially co densed, and then sent to the VCM purification syste

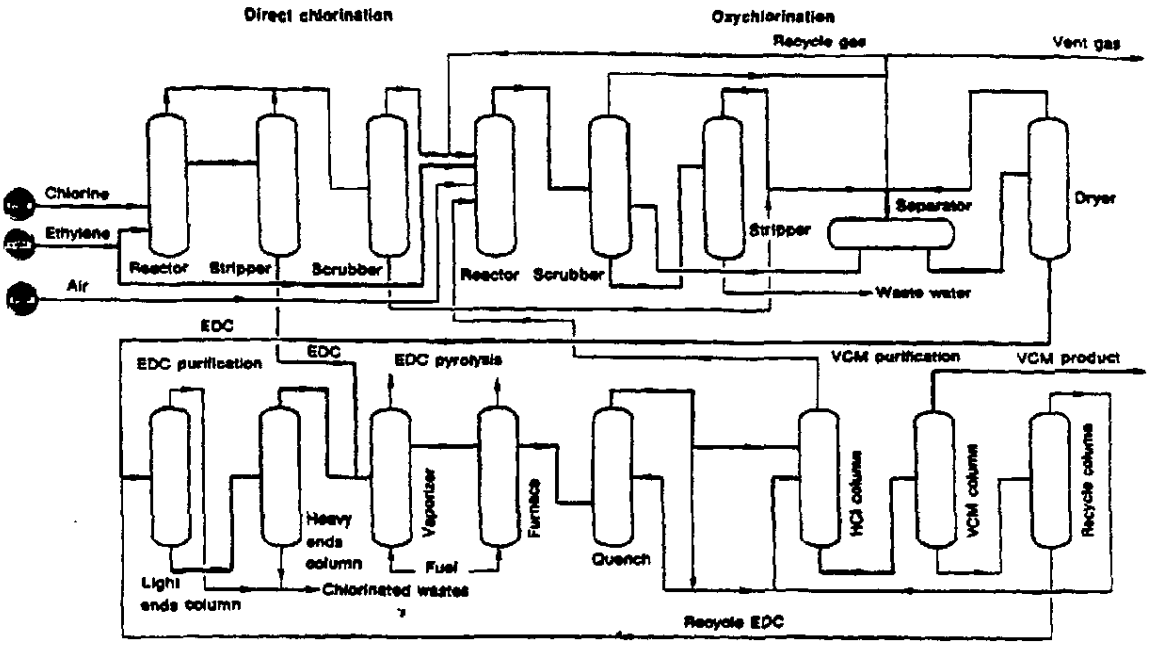


Fig. 7—Ethyl Corp.'s integrated vinyl chloride monomer process.

HCl and VCM are separated by fractional distillation from the unconverted EDC and small amounts of byproducts. The EDC, containing the byproducts, is recycled to the EDC purification system.

Mitsui Toatsu Chemicals technology.[55] The MTC technology utilizes a boiling liquid process for the direct chlorination reaction. Reaction heat is dissipated with the gaseous EDC exit stream which is condensed externally and sent to purification.

The oxychlorination process is characterized by the use of oxygen feedstock and a fluidized bed reactor. The reactor effluent gases are quench cooled with circulating EDC followed by caustic neutralization. The neutralized gas is cooled to condense EDC and water. Uncondensed gases, primarily ethylene, are recycled back to the oxy reactor. A small stream is vented from the recycle gas to allow purging of inerts. EDC liquid is phase separated from water and dehydrated before joining the EDC streams in the purification system.

A conventional EDC purification system splits crude EDC into light ends, heavy residue and pure EDC. The latter is cracked to yield VCM which is purified in a manner similar to that described in the Stauffer technology (see Fig. 8).

PPG technology.[56] The EDC production technology appears very similar to that described for Mitsui Toatsu, particularly in the use of oxygen feedstock and fluidized bed reaction for oxychlorination. However, PPG does not indicate use of a dehydrator to dry crude oxy EDC prior to purification. Also, PPG uses three rather than two towers to obtain the HCl-VCM-EDC separation.

B. F. Goodrich technology.[57,70] Goodrich direct chlorination uses conventional water-cooled technology similar to that shown for Stauffer. The air-based, fluidized bed oxychlorination technology is similar to that shown for Ethyl. Goodrich also utilizes an absorber-stripper system on the oxy vent gas stream to minimize hydrocarbon losses. Goodrich, in conjunction with Badger, Inc., offers complete technology for waste treating of VCM plant effluent streams.

Toyo Soda technology.[58,67] This technology appears very similar to that offered by Stauffer. The principal differences are in the use of an absorber-stripper on the oxy vent gas effluent (as with Goodrich) and the dehydration of crude EDC prior to purification. As with other oxychlorination processes, steam generation is used to remove reaction heat.

Phone-Poulenc technology [58,71] Rhone-Poulenc offers two processes, Chloe I and Chloe II. The former is of a special nature[67] to yield concurrently significant quantities of other chlorinated hydrocarbons such as trichloroethylene and trichloroethane. The Chloe II process is "true" VCM technology using air-based, fluidized bed oxychlorination in combination with boiling liquid direct chlorination.

Monsanto technology.[72] This process appears very similar to that offered by Stauffer.

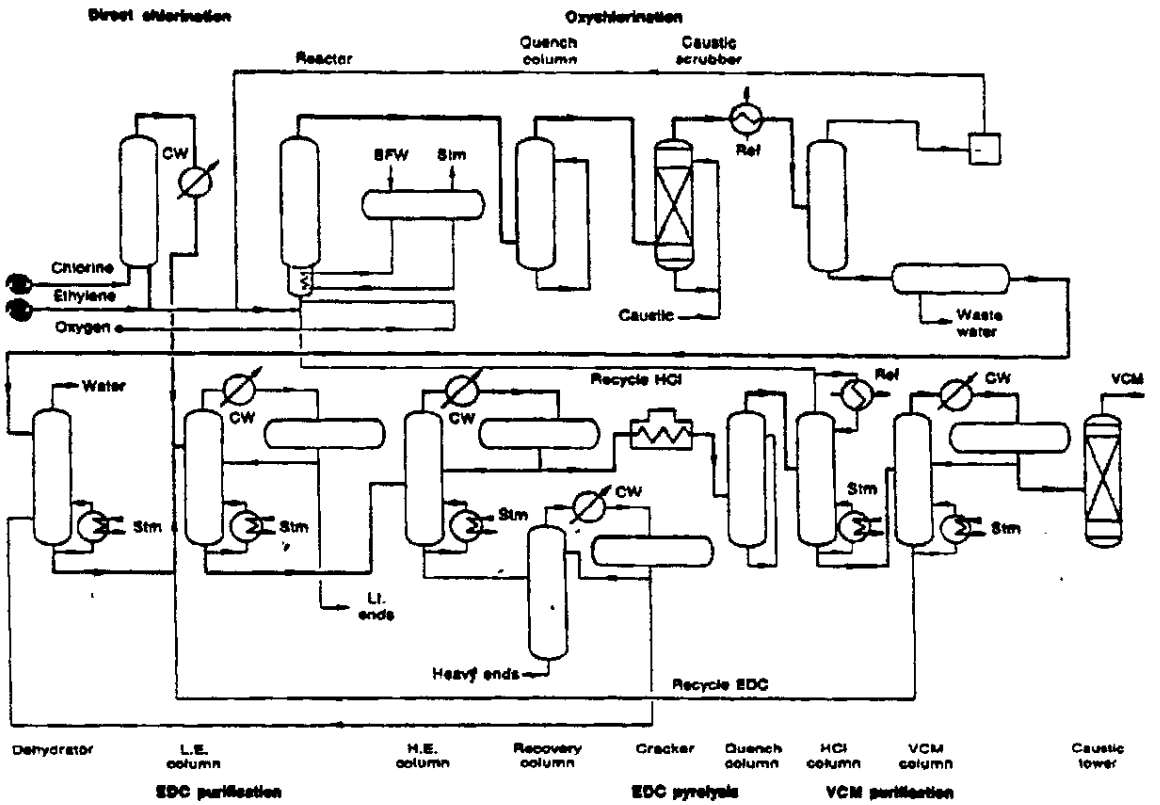


Fig. 8—Mitsui Toatsu uses these modifications in their vinyl chloride monomer process.

Dow technology. Dow's technology has not been publicized. It has been used only by Dow and its foreign affiliates.

NEW DEVELOPMENTS

Although it is believed that several VCM producers currently use boiling liquid reactors for direct chlorination, Stauffer has developed a unique application of this concept.[46] Their approach, "High Temperature Chlorination," in effect uses the reactor as a reboiler for the conventional EDC purification system (see Fig. 9) Purified EDC is withdrawn as a side stream from the tower, and any light components formed are removed overhead. Normal feed to the tower consists of treated EDC from oxy and recycle. Small amounts of the normal heavy ends or tars are purged from the base of the reactor. This application eliminates approximately 100,000 lbs. per hour of 150 psig steam consumption for a one billion lb. per year VCM plant. A similar energy savings is achieved in reduction of cooling water usage relative to a conventional reactor and light ends tower. B. F. Goodrich[73] also offers a boiling liquid process in which the heat of reaction is utilized to purify all EDC processed in the purification train.

Increased activity by EPA (U.S. Environmental Protection Agency) and state agencies in regulating hydro-

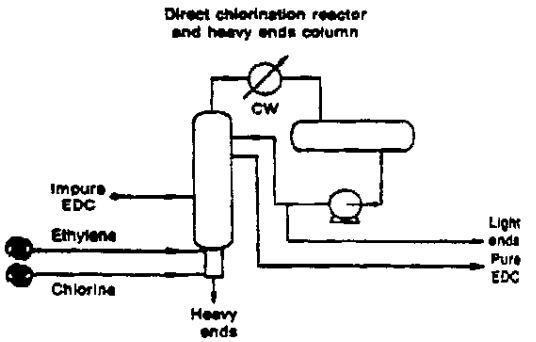


Fig. 9—Stauffer high temperature chlorination and ethylene dichloride purification schematic.

carbon emissions are likely to stimulate further new developments, particularly in oxychlorination processes. These will range from development of new oxygen-based technology to various add-on systems for cleaning up oxy vent gas. The latter may include catalytic oxidation, incineration (of oxygen-based oxy vent gas), solvent absorption, combined refrigeration and absorption techniques and/or other combinations. Several companies not active as VCM producers are involved in developing these add-on systems.

It is expected that companies will continue to devote considerable effort to the development of cracking promoters and inhibitors of side reactions in pyrolysis chemistry. Current cracking practices limit EDC conversion to 50-60 percent. Considerable energy and cost savings could be achieved through increased conversion levels without concurrent losses of EDC to undesirable side reactions.

EPA regulations. EPA's "Standard Support and Environmental Impact Statement: Emission Standard for Vinyl Chloride,"[1] presented the following regulations:

- Emissions from all point sources except oxychlorination would be reduced to 10 ppm VCM by volume
- Emissions from the oxychlorination reactor would be reduced to 0.02 lb. VCM per 100 lbs. EDC product from the oxy process
- Preventable relief valve discharges would not be permitted
- Fugitive emissions would be minimized by requiring enclosure of the emission sources and collection of the emissions.

EPA estimated typical VCM plant emissions in 1974 as follows:

Source	Lbs./VCM/ 100 Lbs. VCM
Fugitive	0.1215
EDC Finishing Column	0.05
VCM Finishing Column	0.24
Oxy Process	0.0364
Process Water	0.0007
Total	0.4479

The regulations were predicated upon reduction of such emissions by 94 percent using best available technology. Compliance testing of these installations was begun in the last quarter of 1978.

Additional EPA and state actions were initiated in mid-1977 to reduce hydrocarbon emissions from VCM plants in non-attainment regions, i.e., much of the Gulf Coast. EDC production is reported to account for 28 percent of the hydrocarbon emissions in the southern Louisiana and East Texas AQCRs.[66] These actions were directed primarily against oxychlorination vent gas from air-based units. The amount of hydrocarbon reduction sought varies from region to region. No published guidelines are currently available to reference.

The net effect of these various regulations has been to increase substantially the scope of add-on technology in VCM plants, such as:

- Installation of primary and redundant incineration facilities for VCM point (ex oxy) source and collected fugitive emissions
- Installation of HCl scrubbing and neutralization or recovery units in conjunction with the incinerators
- Installation of closed process sewers, collection systems and larger or redundant waste water strippers
- Replacement of single mechanical seals on pumps and agitators with double mechanical seals. (In some cases, conventional pumps were replaced with canned or magnetic drive pumps)
- Leak detection systems and portable monitors
- Enclosed sampling and analytical systems
- Vapor recovery systems for VCM loading/unloading and equipment clearing.

The EPA report estimated a maximum capital impact of $0.8 to $1.9 MM (1975 dollars) for a "model" 700 MM lb. per year VCM plant. Recent cost estimates indicate the true impact for these items is nearer $15 MM based on 1978 dollars. Addition of hydrocarbon compliance (proposed regulations) may add another $2-$5 MM.

EPA also has proposed further reductions in VCM emissions.[65] Under consideration at present are regulations which will reduce allowable emissions from 10 ppm to 5 ppm for all point sources, including oxy vent gas. EPA further plans to prohibit emission increases within 8 kilometers of an existing source due to construction of a new emission source. This will effectively prevent expansion of existing facilities or construction of new plants in the vicinity of existing plants. The proposed oxy vent gas regulation will also dictate substantial capital expenditures for add-on facilities and possibly the conversion of air-based to oxygen-based plants to facilitate incineration of tail gases.

ECONOMICS

Table 5 presents a 1981 manufacturing cost buildup for a typical 700 MM lb. per year grass roots VCM plant. Raw materials total 12 cents per lb. VCM or 54 percent of the required FOB plant selling price. Capital-related costs amount to 6.8 cents per lb. VCM or 32 percent. Utilities are only 6.7 percent of the total VCM cost. In perspective, the 1972-1973 reported VCM selling price[67] was only 4-5 cents per lb. By 1981, the capital-related unit costs alone will exceed this by 50 percent.

The obvious major factor in VCM pricing is raw materials cost. Although chlorine price is expected to double between 1973 and 1981, the impact of ethylene price will be even greater (three cents per lb. versus 17 cents per lb.). The real culprit, of course, is crude oil cost. During the late 1960s and early 1970s, plants using inexpensive LNG feedstocks were significant contributors to the low cost U.S. ethylene supply picture. The energy crisis rapidly reversed the low cost feedstock trend. LNG scarcity

dictated construction of naphtha and/or gas oil crackers for present and future ethylene production. This tied VCM prices irreversibly to crude oil prices through ethylene, fuel and power (particularly via its impact on chlorine).

ACKNOWLEDGMENTS

The authors gratefully acknowledge contributions by A. B. Stryker, Jr., of Stauffer and H. H. Wall of Ethyl and permission by their companies to use the information presented on their respective processes.

LITERATURE CITED

[1] U.S. Environmental Protection Agency Report No. EPA-450/2-75-009, Research Triangle Park, N.C., (1975).
[2] Leach, H. S., (to Monsanto Chemical Co.) U.S. Patent 3,338,982 (1967).
[3] B. F. Goodrich Co., British Patent 1,233,238 (1971).
[4] Campbell, R. G., (to Stauffer Chemical Co.), U.S. Patent 4,000,205 (1976).
[5] Benedict, D., (to Union Carbide), U.S. Patent 2,929,852 (1960).
[6] Di Flore, L., and Calcagno, B., (to Soc. Ital. Resine), U.S. Patent 3,911,036 (1975).
[7] Tsao, U., (to Lummus Co.), U.S. Patent 3,917,727 (1975).
[8] Kurtz, B. D., and Omellan, A., (to Allied Chemical Co.), U.S. Patent 3,941,568 (1976).
[9] Vulcan Materials, British Patent 980,985 (1965).
[10] Van Antwerp, A. E., Harpring, J. W., Sterbens, R. G., and Kang, T. L., (to B. F. Goodrich), U.S. Patent 3,488,398 (1970).
[11] Severino, P. T., (to Stauffer Chemical Co.) U.S. Patent 4,046,822 (1977).
[12] Stauffer Chemical Co., British Patent 1,230,617 (1971).
[13] B. F. Goodrich Co., Belgium Patent 681,415 (1966).
[14] Kita, H., (to Mitsui Toatsu Chemical), Japanese Patent 46-43367 (1971).
[15] Miyauhi, K., (to Mitsui Toatsu Chemical), British Patent 1, 189,815 (1970).
[16] Takahashi, T., (to Mitsui Toatsu Chemical), Japanese Patent 45-32406 (1970).
[17] Mitsui Toatsu Chemical, Japanese Patent 46-33010 (1971).
[18] PPG Industries, French Patent 2,080,666 (1971).
[19] Murn, A. P., (to PPG Industries), British Patent 1,220,394 (1971).
[20] Ahlstrom, Jr., R. C., (to Dow Chemical Co.), U.S. Patent 3,966,900 (1976).
[21] Strini, J. C., and Costes, J. R., (to Rhone-Progil), U.S. Patent 3,935,296 (1976).
[22] Smalley, E. W., Kurtz, B. E., and Bandyopadhyay, B., (to Allied Chemical Corp.), U.S. Patent 4,060,460 (1977).
[23] Knapsack Co., British Patent 1,266,676 (1972).
[24] Solvay et cie, French Patent 1,592,522 (1971).
[25] Krekeler, A., (to Knapsack Co.), U.S. Patent 3,484,493 (1969).
[26] Jacklin, A. O., (to ICI), British Patent 956,618 (1964).
[27] Froelich, W., (to Hoechst), German Patent 2,217,694 (1973).
[28] Barton, D. H. R., J. Chem. Soc., 148 (1949).
[29] Young, D. P., (to B. F. Chemicals, Ltd.), U.S. Patent 3,896,182 (1975).
[30] Mitsui Chemical Industries, Japanese Patent 42-22921 (1967).
[31] B. F. Goodrich, British Patent 938,824 (1963).
[32] Knapsack Co., U.S. Patent 3,476,797 (1969).
[33] Monsanto Chemical Co., British Patent 1,168,729 (1969).
[34] Keating, H. J., (to Monsanto Chemical Co.), U.S. Patent 3,125,603 (1964).
[35] Gause, P. M., (to Monsanto Chemical Co.), U.S. Patent 3,142,709 (1964).
[36] McDonald, D. W., (to Monsanto Chemical Co.), U.S. Patent 3,125,608 (1964).
[37] Gomi, S., Eighth World Petroleum Congress, Proceedings 4, 321 (1971).
[38] Kureha Chemical Industries, British Patent 977,578 (1964), British Patent 1,068,735 (1967).
[39] Barton, D. H., and Mugdan, M., *J. Soc. Chem. Ind.*, (London), 69, 75 (1950); Patat, F., and Weidlich, P., *Helv. Chim. Acta.*, 32, 783 (1949).
[40] Gordon, K. D., and Starks, C. M., (to Continental Oil Co.), U.S. Patent 4,046,823 (1977).
[41] Kuck, M. A., (to Stauffer Chemical Co.), U.S. Patent 3,987,118 (1976).
[42] Winstein, N. J., (to Princeton Chemical Research, Inc.), U.S. Patent 3,551,506 (1970).
[43] Kurtz, B. E., Smalley, E. W., Sommerman, W. E., and Van Atta, J. R., (to Allied Chemical Corp.), U.S. Patent 3,987,119 (1976).
[44] Gordon, T. H., and Kummerle, H. F., (to Owens-Illinois, Inc.), U.S. Patent 4,042,639 (1972).
[45] Riegel, H., (to Lummus Co.), U.S. Patent 3,796,641 (1974).
[46] Riegel, H., (to Lummus Co.), U.S. Patent 3,557,229 (1971).
[47] Riegel, H., (to Lummus Co.), U.S. Patent 3,937,744 (1976).
[48] Sze, M. C., (to Lummus Co.), U.S. Patent 3,949,010 (1976).
[49] Tsao, U., (to Lummus Co.), U.S. Patent 3,963,581 (1976).
[50] Tsao, U., (to Lummus Co.), U.S. Patent 3,992,460 (1976).
[51] Riegel, H., (to Lummus Co.), U.S. Patent 3,935,288 (1976).
[52] Tsao, U., (to Lummus Co.), U.S. Patent 3,965,816 (1976).
[53] Minot, J. D., *Chem. Eng. Progr.*, 69, (8), 71 (1973).
[54] Leonard, E. D., *Vinyl and Diene Monomers (Part 3)*, John Wiley and Sons, Inc., New York, 1971.
[55] Sittig, M., *Vinyl Chloride and PVC Manufacture*, Noyes Data Corp., 1970.
[56] Gomi, S., *"Japan's New Vinyl Chloride Process (Kureha)," Hydrocarbon Processing*, Vol. 43, No. 11, November 1964.
[57] Rosenzweig, M. D., "Vinyl Process Has Wide Range of By-Products," (Rhone-Progil), *Chemical Engineering*, Vol 78, No. 24, Oct. 18, 1971.
[58] Robert, J., and Bergier, A., "Rhone-Progil New Processes for the Manufacture of Vinyl Chloride Monomer and Chlorinated Solvents from Ethylene," 164th A.C.S. National Meeting, New York, Aug. 27-Sept. 1, 1972.
[59] Buckley, J. A., "Process Flow Sheet/Vinyl Chloride via Direct Chlorination and Oxychlorination," *Chemical Engineering*, Vol. 75, No. 24, Nov. 21, 1968.
[60] Private Communication from A. B. Stryker, Jr., Stauffer Chemical Co. Nov. 29, 1978.
[61] Reich, Peter, "Air or Oxygen for VCM?" *Hydrocarbon Processing*, March 1976, pp. 85-89.
[62] Private Communication from H. H. Wall, Ethyl Corp., Nov. 28, 1978.
[63] Vinyl Chloride, *"Hydrocarbon Processing*, Nov., 1975.
[64] EPA-450/3-73-006-C, Vol. 3, November, 1974.
[65] *Federal Register*, June 2, 1977.
[66] EPA-600/2-76-053, March, 1976.
[67] Keane, David P., et al, "Vinyl Chloride: How, Where, Who—Future," *Hydrocarbon Processing*, February, 1973.
[68] "Vinyl Chloride—Mitsui Toatsu Chemicals," *Hydrocarbon Processing*, November 1971.
[69] "Vinyl Chloride—PPG Industries, Inc.," *Hydrocarbon Processing*, November 1975.
[70] "Vinyl Chloride—B. F. Goodrich Chemical Co., *Hydrocarbon Processing*, November 1975.
[71] "Vinyl Chloride—Rhone-Poulenc S.A.," *Hydrocarbon Processing*, November 1975.
[72] "Vinyl Chloride—(Monsanto Co.)," *Hydrocarbon Processing*, November 1975.
[73] Private communications from J. S. Benson, B. F. Goodrich Chemical Co., Jan. 5, 1979.

TABLE 5—Estimated 1981 VCM manufacturing cost

	Lbs/Lb VCM	¢/Unit	Cost, ¢/Lb/ VCM	%
Raw Materials				
Chlorine	0.56	9.6	5.53	14.1
Ethylene	0.49	17.1	8.45	36.8
Catalyst and chemicals	....	....	0.39	1.8
Utilities	....	....	1.42	6.5
Total variable			13.79	63.3
Labor			1.18	5.4
Miscellaneous			0.98	4.5
Total fixed			2.16	9.9
Total manufacturing cost			15.95	73.2
Capital charges and depreciation				26.8
Selling price FOB plant			21.79	100.0

Bases:
1. 700 MM Pounds/Year Balanced VCM Plant.
2. 1981 Startup
3. Gross Fixed Investment = $140 MM.
4. Light and heavy ends incinerated; recovered HCl sold as muriatic acid to break even on incineration costs.
5. Fifteen percent DCF rate of return to cover interest charges and profit.
6. Unit values are generalized and are not specific to a particular licensor or technology.

About the authors

ROBERT W. MCPHERSON *is products manager, Continental Oil Co., Houston. He is responsible for the worldwide profit performance of Conoco's chlorinated hydrocarbons and their strategic development. Mr. McPherson received his B.S. from Cornell University.*

CHARLES M. STARKS *is director of exploratory research, Continental Oil Co., Ponca City, Okla. Dr. Starks received his B.S. from the University of Oklahoma and his Ph.D. from Massachusetts Institute of Technology.*

GARVIN J. FRYAR *is supervising process engineer with Continental Oil Co., Ponca City, Okla. He is responsible for the supervision of process designs, technical consulting and economics for chemicals processes. Mr. Fryar received his B.S. in chemical engineering from the University of New Mexico.*

picture? The firm could be sworn to secrecy on transfer price, if necessary. Authorize the auditors to present their findings to Congress and the public. Let's get profits out in the open! The alternative is a "peccable" audit by the government.

If higher gasoline prices or tax credits are required to build badly needed downstream refining capabilities, the public can be sold. And if the public is convinced, Congress will *act*. The alternative is a shortage of refined products, especially unleaded gasoline. And when gasoline is not available for Americans' love—their automobiles—politicians and oil companies alike will face their wrath.

Coming next month

Computer optimization and control, the June Special Report, is a subject teeming with potential. The reasons: greater conservation, operating flexibility and the advent of more reliable and less expensive computer control equipment.

The report begins with the concepts of, the mathematical techniques used, and places where on-line computer process optimization really pays off for a variety of HPI processes.

So existing plants can evaluate the possible benefits of computer control, the second article provides a description of how to interface computers with existing plants.

Computer optimization doesn't apply only to process areas. To exemplify this, the third article describes an optimal, energy saving, microprocessor based control system for centrifugal compressors. June's issue is one you'll definitely want to keep on file.

THE MAIL BOX

Errata

Several mistakes appeared in my article "Vinyl chloride monomer—What you should know," March 1979, pp. 75-88.

On page 77, right hand column, at the end of the twelfth line from the top, "PVC" should be "EDC."

On page 78, right hand column, second paragraph ending, the reference number "15" should be deleted.

On page 80, Table 3, line 8 should read Rhone-Poulenc.

On page 88, Table 5 appears corrected below.

Garvin J. Fryar
Ponca City, Okla.

TABLE 5—Estimated 1981 VCM manufacturing cost

	Lbs/Lb VCM	¢/Unit	Cost, ¢/Lb VCM	%
Raw Materials				
Chlorine	0.44	5.6	2.47	16.3
Ethylene	0.47	17.1	8.04	37.7
Catalyst and chemicals	....	....	0.39	1.8
Utilities	....	....	1.42	6.7
Total variable			13.32	62.5
Labor			1.18	5.5
Miscellaneous			0.98	4.6
Total fixed			2.16	10.1
Total manufacturing cost			15.48	72.6
Capital charges and depreciation			5.84	27.4
Selling price FOB plant			21.32	100.0

Bases:
1. 700 MM Pounds/Year Balanced VCM Plant
2. 1981 Startup
3. Gross Fixed Investment = $148 MM.
4. Light and heavy ends incinerated; recovered HCl sold as muriatic acid to b[illegible]ok even on incineration credit.
5. Fifteen percent DCF rate of return to cover interest charges and profit.
6. Unit values are generalized and are not specific to a particular licensor or technology.

Alloy selection for VCM plants

Data aids engineers in selecting alloys for critical equipment in direct chlorination, oxychlorination and EDC pyrolysis sections of vinyl chloride monomer plants

C. M. Schillmoller, VDM Div., The Ore & Chemical Corp., Houston

DESIGN CONDITIONS, alloy selection and operating experience are all part of the proprietary package offered by various VCM process licensors. Therefore, of necessity, this article will be limited to the three separate operating steps that all "balanced ethylene feedstock" plants have in common: direct chlorination, oxychlorination and EDC pyrolysis. We will look into the corrosive effects of chlorine and hydrogen chloride gases as well as that of hydrochloric acid. Aspects of alloy selection are based on published information of various processes, knowledge of corrosion and privileged information on actual sales of large quantities of high-nickel alloys for VCM plants in Europe, Japan and the USA. The data presented, within the limited scope of this article, are intended only for guideline purposes, without any guarantee of performance.

(Editor's note. Alloys 200, 201, 400, 600, 800 and 825 referred to in this article correspond to the VDM trade names shown in Table 1 with which the author has the most recent experience in vinyl chloride monomer plants.)

SELECTING ALLOYS

Nickel and high-nickel alloys are among the few metallic materials having useful resistance to dry chlorine, hydrogen chloride and hydrochloric acid. These alloys are not new to the chlor-alkali industry, being more or less standard selections in caustic, brine and salt processing. We will, in turn, deal with each of the three chief corrosive environments encountered in VCM processes. Table 1 provides a brief description of alloys commonly in use, their ASTM specifications and the tradenames under which they are known.

Chlorine. Gaseous chlorine at low temperatures and in the absence of moisture is not severely corrosive and is commonly handled by carbon steel. Usually a more resistant material such as Alloy 400 is specified for critical parts such as valve trim, instrumentation and orifice plates in chlorine pipe lines. In contrast, wet chlorine is extremely corrosive on steel and nickel alloys, and requires Hastelloy* C or titanium. At elevated temperatures, corrosion rates on steel increase with temperature. The upper limit of usefulness is around 400° F when the protective effects of the corrosion products disappear. Ferric chloride vaporizes at 420° F.

Fig. 1 provides a guide to the selection of various alloys in dry chlorine. The surface coating of chlorides tend to provide protection up to a temperature level

TABLE 1—Alloys commonly used in VCM plants

Materials	Reference in text	Nominal Composition, %					ASTM B number	ASME B number	VDM trade names	Comparable products
		Ni	Cr	Mo	Cu	Fe				
Nickel										
Nickel	Alloy 200	99.6					161-163	161-163	VDM-Nickel 200	Nickel 200
Low Carbon Nickel	Alloy 201	99.6					161-163	161-163	VDM-Nickel 201	Nickel 201
Nickel-copper alloys										
Nickel-Copper Alloy	Alloy 400	67			31	1.3	163-165	163-165	NICORROS 400	Monel 400
Nickel-chromium-iron alloys										
Nickel-Chromium-Iron Alloy	Alloy 600	76	15			8	163-168	163-168	NICROFER 600	Inconel 600
Nickel-Iron-Chromium Alloy	Alloy 800	32	21			46	163-407	163-407	NICROFER 800	Incoloy 800
Nickel-Iron-Chromium-Molybdenum-Copper Alloy	Alloy 825	42	21	3	2.3	30	163-423	163-423	NICROFER 825	Incoloy 825

Note: NICORROS and NICROFER are registered trademarks of Vereinigte Deutsche Metallwerke AG Germany. Monel, Inconel, Incoloy are registered trademarks of The International Nickel Co. Hastelloy is a registered trademark of Cabot-Stellite Division.

ALLOY SELECTION

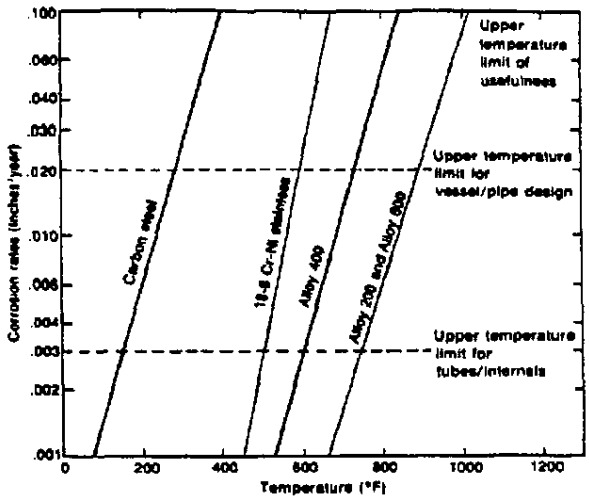


Fig. 1—Chlorine. Alloy selection guide.

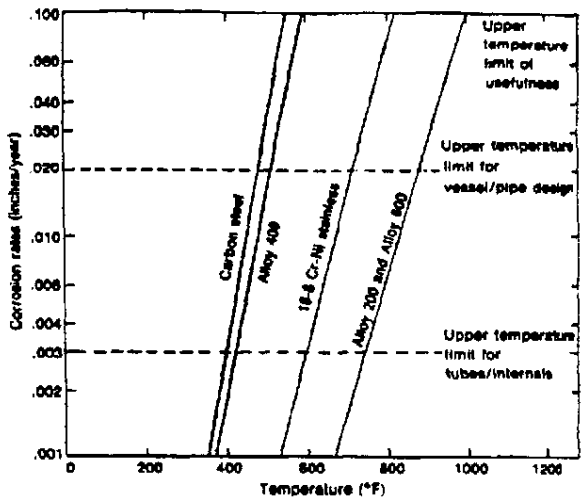


Fig. 2—Hydrogen chloride. Alloy selection guide.

at which melting, vaporization or decomposition removes such films. The corrosion rate appears proportional to the vapor pressure of the metal chlorides. The common design parameter for tubing, valve trim and internals is 0.003 in. per year (IPY) maximum corrosion rate, while for vessels and pipe an upper corrosion rate of 0.020 IPY is frequently adopted with a corrosion allowance of ⅛ to ¼ in.

Alloy 200 and Alloy 600 are the most commonly used alloys for reactors, coils and agitators in the 500 to 1000° F range.

Hydrogen chloride. Dry HCl behaves in a similar manner as chlorine, and carbon steel can suffice up to 450° F above which Alloy 200 is usually specified. Fig. 2 provides a guide to the selection of various alloys in dry HCl gas and the design parameters of 0.003 IPY and 0.020 IPY upper corrosion rates for certain components are shown. The presence of moisture does not appreciably increase corrosion rates above the dewpoint over that by dry gas.

It must be pointed out that there are many variables, and even small amounts of addition agents to control catalyst activity, may exert an influence on the tenacity and vapor pressure of the protective corrosion scales. Therefore, absolute corrosion rates for different temperatures in chlorine and HCl systems are difficult to predict. Even so it is felt that Figs. 1 and 2 are sufficiently accurate to serve as a guide. These figures should be checked against actual experience of each of the different VCM processes.

The performance of Alloy 200 in dry as well as wet hydrogen chloride gas has been consistently good. In cyclic operating conditions, particularly in the presence of air or oxygen, Alloy 600 and Alloy 825 offer good all-round resistance. It is prudent to assume that Types 304 and 316 stainless steels would be subject to chloride stress corrosion cracking conditions during shutdown in spite of various precautions that may be taken.

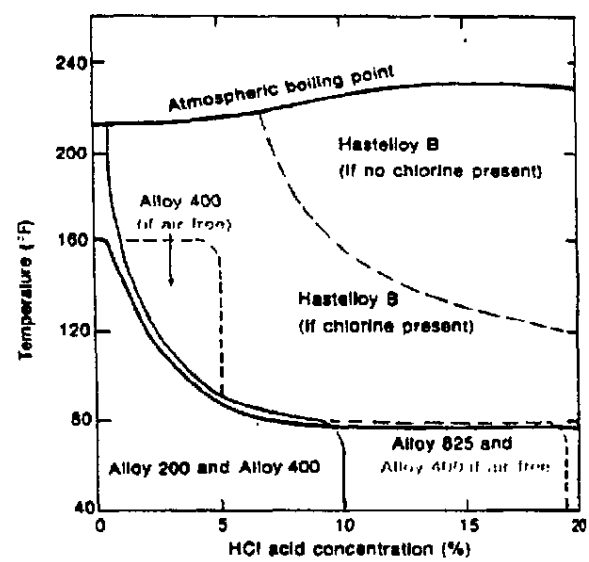


Fig. 3—Hydrochloric acid. Alloy selection guide (Basis: 0.020 IPY max. corrosion rate).

Hydrochloric acid. HCl is a typical reducing acid through its entire concentration range. Its strongly acidic character is harmful to steel. Alloy 200 and Alloy 400 behave similarly and find application at ambient temperature up to 20 percent concentration and at higher temperature below 5 percent concentration. Fig. 3 shows isocorrosion lines for 0.020 IPY which is generally considered the upper design limit of an alloy selection. The graph immediately delineates the conditions suitable for handling with Alloy 400 and those where Hastelloy B is required.

It should be noted that in most cases in which hydrochloric acid is formed as a result of hydrolysis of chlo-

rides or chlorinated hydrocarbons such as EDC, the acid concentrations are less than .5 percent and both Alloy 200 and Alloy 400 can withstand such conditions satisfactorily at temperatures up to 400° F.

Also in hydrogen chloride gaseous processes when cooling takes place near the dewpoint of HCl (that is below 260° F) it is prudent to assume that because of the hygroscopic nature of the chloride on steel that HCl might condense with resultant high corrosion rates. In applications where 18-8 Cr-Ni stainless steel is used at elevated temperatures such condensation can lead to chloride stress cracking. Alloy 800 is highly resistant to chloride stress corrosion cracking while Alloy 600 and Alloy 825 are immune to this phenomena in this application.

Even though with special precautions a system can be kept dry during operation, adequate consideration must also be given to protect equipment during shutdown and when starting up the unit. Purging with inert dry gas prior or during shutdown is helpful in sustaining a dry atmosphere. Alternately one can maintain temperatures above the dewpoint. Also, sludges present in the system absorb chlorides and must be kept dry otherwise aqueous HCl acid is formed from moisture pick-up. Alloy 400 is widely used for handling dilute HCl acid in waterwash solutions and for heat-exchanger tubes in the EDC purification.

VCM PROCESS COMPARISON

The typical VCM process combines direct chlorination and oxychlorination processes to provide ethylene dichloride (EDC) feedstock to the pyrolysis unit. Because of the large amount of hydrogen chloride generated in the cracking of EDC, plant economics dictate the need for an oxy unit. The sequence and three principal operating steps are quite similar from process to process and are shown in Fig. 4. It is not the writer's intention to make a detailed analysis of the entire alloy selection for the various licensed processes, but instead, to comment on the basis of previously provided corrosion data, on alloy considerations applicable to each of the three principal steps.

Direct chlorination. Ethylene is reacted with dry chlorine in the presence of a catalyst, to produce ethylene dichloride. The catalyst usually is a ferric chloride. Liquid EDC is used as a reaction medium to insure intimate mixing. Conventional water cooling removes the exothermic heat of reaction. Temperatures are controlled at 130° F to 150° F. The EDC produced is usually treated for removal of ferric chloride carry-over. In a number of systems lately, the reaction is carried out at the EDC boiling point (approximately 230° F) taking pure EDC overhead and using the heat required to vaporize part of the reactor content, to control the temperature. Fig. 5 shows the direct chlorination process.

It is necessary to insure a dry chlorine feedstock and to properly control the temperature by thorough mixing of the reactants to prevent hot spots and runaway temperatures. With such operating control conditions, carbon steel can be safely used for the reactor and auxiliary equipment. As can be seen from Fig. 1, a suitable corrosion allowance may need to be applied depending

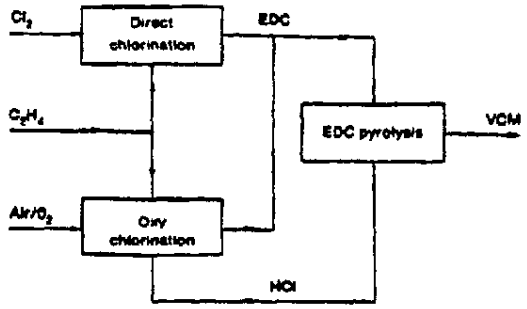


Fig. 4—Principal VCM process steps.

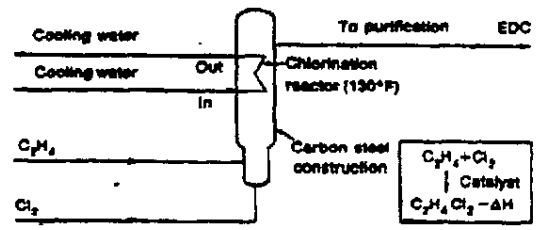


Fig. 5—Direct chlorination.

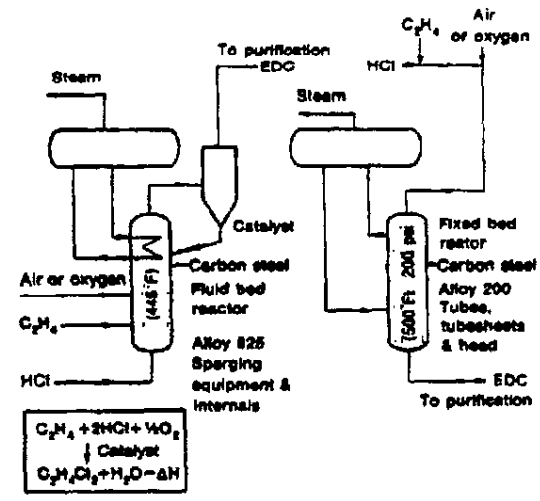


Fig. 6—Oxychlorination.

on temperature and experience. Further, proper shutdown procedures should be employed keeping the unit dry or free from chlorine to prevent attack by wet residual chlorine on the steel when the unit is not in operation.

Oxychlorination. Ethylene is reacted with dry hydrogen chloride and oxygen in the presence of a catalyst to produce EDC and water. The catalyst usually is im-

ALLOY SELECTION

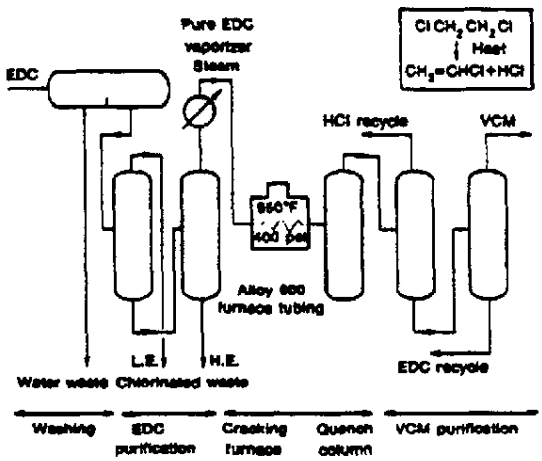


Fig. 7—EDC pyrolysis.

pregnated with copper chloride. The oxychlorination process can be carried out either in a fluid bed of catalyst or in tubular fixed bed catalytic reactors. Further, the reaction of ethylene and HCl can take place either with air or oxygen. Both process systems are shown in Fig. 6.

Fluid bed. Reaction with a fluidized catalyst generally takes place at 435° F to 450° F and atmospheric pressure. The reaction is highly exothermic and the temperature is controlled by good intermixing of reactants and catalyst and by the use of internal cooling surfaces. A carbon steel reactor can be used. Referring to Fig. 2, we can expect corrosion rates in the order of 0.010 IPY which means a corrosion allowance of ⅛ in. or 3/16 in. should be applied. For internals, where corrosion can occur on both sides of the metal, where velocity effects may interfere with protective scales or where a corrosion allowance is not practical or interferes with the rate of heat transfer, a corrosion resistant alloy is commonly specified.

Good service with Alloy 600 and Alloy 825 has been obtained when used for the sparging equipment to introduce the gases in the fluid bed, and for pipe, nozzles and fittings inside the reactor. These alloys are not susceptible to chloride stress corrosion cracking if hydrolysis takes place during shutdown. Occasionally a problem is experienced from the combined effect of corrosion and erosion by the catalyst which removes the protective corrosion products on steel. Also, accumulation of catalyst on the bottom of the reactor can cause localized attack and should be avoided. Because of the carbon steel reactor construction, it is definitely necessary to control temperatures below 500° F. Proper shutdown procedures to prevent corrosion on steel by dilute hydrochloric acid, when the unit is not in operation, is of course most desirable.

High nickel alloys are often restricted to locations in critical equipment. Less expensive materials are often selected as soon as allowed by process conditions.

Fixed bed. Reaction in a fixed-bed catalyst reactor is carried out at temperatures of 450° F to 600° F and pressures from atmospheric up to 200 psi. The catalyst is contained in a number of vertical tubes held in a tubesheet at top and bottom. Reaction heat is removed by the generation of steam on the shell side of the reactor. It is more difficult to control temperatures uniformly than in the fluidized bed, and occasional hot spots tend to develop on the tubes.

As can be seen from Fig. 2 operating conditions require corrosion-resistant alloys. Both Alloy 200 and 600 are preferred alloy selections. Usually Alloy 200 is used for the reactor tubes and has given excellent performance. The tubesheets and heads of the reactor are clad with nickel on steel. The reactor shell which is exposed to water and steam is made of carbon steel. When three or four reactors are required, nickel is also used for the interconnecting piping. Temperatures should be controlled no higher than 600° F to prevent by-product formation and deactivation of the catalyst. Also, when localized hot spots occur on the Alloy 200 tubes we have observed intergranular embrittlement on some tubes. Alloy 201, which has a low carbon level, is resistant to such intergranular attack.

Oxygen versus air. The use of oxygen instead of air in the oxychlorination process improves operating efficiency and product yield. It permits operation at a lower temperature. Even though alloy selection is not affected by this, from a metals standpoint substantially less quantity of alloy is required as the equipment tends to be more compact and smaller. Also capital savings are possible for not having to separate EDC, ethylene and other chemicals from a large nitrogen vent gas stream and burning the vent gas.

EDC pyrolysis. Ethylene dichloride is vaporized and thermally cracked to vinyl chloride yielding volumous by-product hydrogen chloride. Cracking is carried out in a fired furnace at a temperature of 900° F to 1000° F and at an elevated pressure of about 400 psi. The reaction products are cooled rapidly, partially condensed and then sent to a VCM purification system where HCl and VCM are distilled from the unreacted EDC and small amounts of by-products. The cracking process is susceptible to inhibition and fouling by trace amounts of impurities and therefore the crude EDC is purified and the light and heavy ends removed—both of which contain chlorinated waste products. Further, to prevent excessive hydrochloric acid corrosion here and

downstream of the cracker, it is necessary that the crude EDC is washed, neutralized with caustic, and dried. The pure EDC is preheated in an economizer and then vaporized in a steam heated kettle-type reboiler. See Fig. 7 for the EDC pyrolysis process system.

For alloy selection of the pyrolysis furnace tubing we are guided by the fact that hydrogen chloride is formed in the thermal decomposition of EDC, that the furnace requires periodic decoking and that during shutdown conditions hydrolysis of hydrogen chloride is likely to occur. Alloy 600 is the preferred alloy section for this application and has consistently given good reliable performance. In recent years, Alloy 800 has been used with success. It is prudent to assume that the 18-8 Cr-Ni type of stainless steels are subject to chloride stress corrosion cracking below the dew point and during shutdown. One company reported that they had used 5 Cr-½ moly steel without excessive corrosion when insuring a bone-dry feed to the unit and taking the usual special shutdown and start-up precautions of gas-blanketing and keeping the unit dry. Alloy 600 is often specified for the cooling coil where halogen corrosion is the greatest. Also Alloy 600 solid or as clad plate has been used for batch polymerizer reactors in an aqueous medium in the presence of a catalyst and suspending agents, producing PVC resin.

In the purification system, corrosion can be very severe because of the hydrolysis of hydrogen chloride and of various organic chlorides. This can occur at temperatures of 260° F and downwards forming dilute hydrochloric acid. It is extremely difficult to insure a bone-dry system, that is, zero free water and below 10 ppm of total dissolved water. Inadvertent moisture pick-up from sources such as leakage at water coolers and steam heaters and intrusion of humidity at flanges and seals is always a possibility. Also entrained water is frequently carried along in the distillation process. Carbon steel in dry systems usually corrodes less than 0.002 IPY while in the presence of water, dilute HCl acid is formed and corrosion rates are approximately 0.010 to 0.160 IPY depending on the temperature and concentration. In the presence of 2 percent hydrochloric acid, carbon steel corrosion often exceeds one inch per year.

From Fig. 3 we can see that Alloy 400, in most cases, would be the desired economical choice of alloy. It has been used in industry to resist a wide variety of chlorinated hydrocarbons and solvents. Hastelloy B finds use for critical components such as valve trim and pump impellers. Corrosion of steel equipment tends to be the greatest in reboilers, the bottom section of distillation columns, bubble caps, plates, condensers, water separators, valves, pumps and fittings.

It should be pointed out that titanium is *not* a suitable selection in dilute hydrochloric acid, because of its strong reducing nature. Where titanium is used, it has provided useful life under mild conditions with a pH above 1.5. For economic reasons, various coatings and liners are frequently considered and used as an alternate to alloy. The following applications have been reported: a gunnite lined pretreater, glass-lined vessels, polypropylene-lined steel piping, Saran and Kynar-lined pipe, glass-coated pumps, various coatings in accumulators. Even though attractive from a first-cost standpoint, special care is required to maintain such coatings and prevent damage at joints.

About the author

C. M. "DICK" SCHILLMOLLER *is responsible for the technical marketing activities for VDM in the USA. VDM is a member of Metallgesellschaft Group. He is located in Houston, Texas. Before returning to the United States in March, 1978 he had 19 years with International Nickel in the USA, Australia and Europe followed by a period of management consulting in Brussels, Belgium. Schillmoller holds a degree in chemical engineering. He is the author of over 200 technical papers dealing with corrosion and high temperature material problems in the process industries, and has lectured at Stanford and the University of California. He is well known to the petroleum/petrochemical industry and serves on a number of technical committees.*

TECHNOLOGY TRENDS

No major changes in the use of established materials of construction is foreseen. Brief mention has already been made of a trend towards higher temperature direct chlorination using the reactor as a reboiler to remove the heavy ends. Also a substantial share of new plants appears to utilize oxygen instead of air in the oxychlorination step. This approach discharges fewer chlorinated hydrocarbons with the vent gases into the atmosphere. For this reason and also to increase existing plant capacity, some VCM plant oxychlorinators are being converted from air to oxygen.

Emission control standards are getting more severe, forcing the scrubbing and neutralization of HCl, use of waste water strippers to remove volatile organics, enclosing and collecting emissions for incineration. Corrosion in parts of this equipment can be very severe and the rate of attack is not always predictable; some of the previously mentioned alloy selection guidelines do apply.

Conclusion. For economic considerations, special high-nickel alloys are often restricted to critical locations from where one downgrades to less expensive materials as soon as process conditions permit. During the final design, the limitations of each material selected must be scrutinized as well as the means used to minimize corrosion by control of process conditions. For example, what will be done to control exothermic reactions, velocity/impingement effects, moisture content, pH/acidic conditions, impurities, sludges and acid concentrations? We have the tools available to do this and particularly in chlorine and HCl processes we should not overlook proper start-up and shutdown procedures, since severe corrosive attack may take place while the unit is not in operation.

REFERENCES

1. "Vinyl Chloride," *Hydrocarbon Processing*, November, 1975, pp. 214-216.
2. Buckley, J. A., "Process Flowsheet Vinyl Chloride via Direct Chlorination and Oxychlorination," *Chemical Engineering*, November 21, 1960.
3. Reich, P., "Air or Oxygen for VCM," *Hydrocarbon Processing*, March, 1976, pp. 85-89.
4. "Resistance of Nickel and High-Nickel Alloys to Corrosion by Hydrochloric Acid, Hydrogen Chloride and Chlorine," INCO Corrosion Engineering Bulletin CEB-3, July 1975.
5. "Resistance to Corrosion," Huntington Alloys Technical Brochure, November, 1970.
6. Schillmoller, C. M., and Mason, J. F., "What to do about Corroding Isomerization Units," *Petroleum Refiner*, July, 1958.
7. Gladis, G. P., "Effects of Moisture on Corrosion in Petrochemical Environments," *Chemical Engineering Progress*, October, 1960.