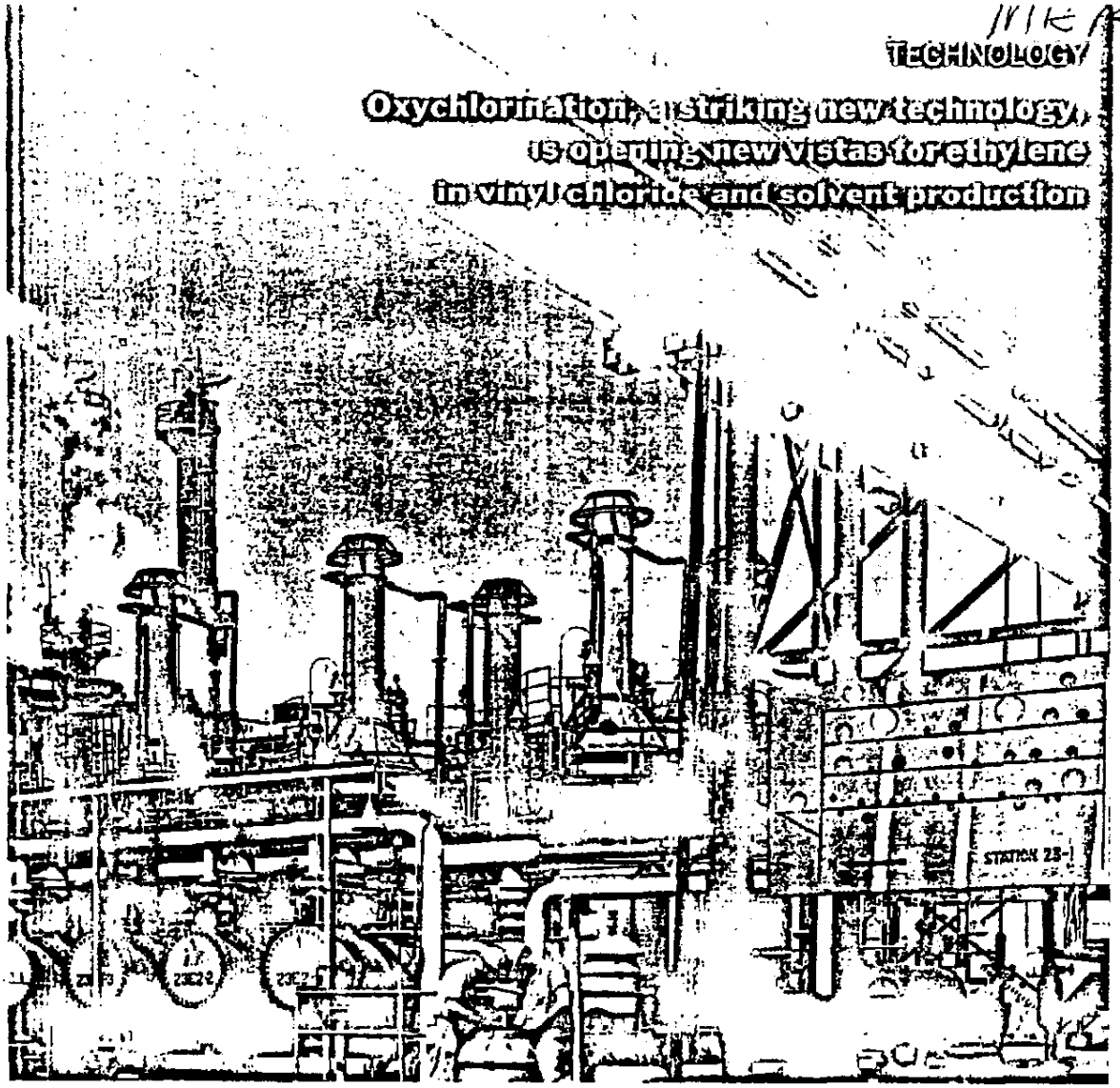
Oxychlorination, a striking new technology, is opening new vistas for ethylene in vinyl chloride and solvent production



Monsanto's Texas City vinyl plant is pioneering commercial applications of oxychlorination.

OXYCHLORINATION

Donald P. Burke and Ryle Miller

What this country needs is a good 5¢/lb. vinyl chloride monomer. And that is exactly what it can get from oxychlorination, declare some ardent boosters of the process. Others say oxychlorination is simply a tool that gives more flexibility to some operations. Wherever the truth lies—and it's probably somewhere between the two extremes—oxychlorination is generating more interest among chemical processors than anything since the development of stereopolymerization.

The reason for the interest in cheaper vinyl chloride is straightforward. It costs 3¢/lb. to convert the monomer into polyvinyl chloride. With the monomer selling for 5¢/lb., it means the polymer could sell for 8¢/lb. And at that price, it would be able to compete handily with a number of conventional structural materials on a straight cost-strength basis. If it should prove capable of competing with metals, brick, glass, or wood, it could capture a significant share of the building market. And it would quickly zoom into the No. 1 spot among plastics. Oxychlorination is anything but a new

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idea, of course. In concept, in fact, it's simply a variation on the ancient Deacon theme of making chlorine by the oxidation of hydrogen chloride. Actually, some of the current interest in making vinyl chloride centers on use of Deacon process improvements to generate chlorine in a separate unit.

The term, oxychlorination, however, more properly describes an *in situ* Deacon process. In a single reactor, hydrogen chloride is oxidized to chlorine, which reacts with an organic compound to form a chlorinated derivative.

Even that is not new; it's the basis for the classic Raschig phenol process. What is new is its application to aliphatics, and particularly to ethylene. The immediate focus is on making ethylene dichloride (EDC) for vinyl chloride production. But the long-range ramifications extend into the whole field of chlorinated solvents. Take trichloroethylene, for instance: 90% of U.S. capacity is acetylene-based. Successful oxychlorination processes could mean that future capacity would be based on ethylene-derived EDC.

Who's Doing It: Four firms in this country now are using oxychlorination commercially (for products other than phenol). Three of them are oxychlorinating ethylene to make EDC, while the fourth—Du Pont—is oxychlorinating methane at Orange, Tex., to make chlorinated hydrocarbons. Dow is employing oxychlorination to make EDC at Freeport, Tex., and Plaquemine, La.; Monsanto, at Texas City; and Goodrich Chemicals at its new plant at Calvert City, Ky. Far and away the biggest oxychlorination project yet revealed is the French Solvay 330-million-lbs./year vinyl chloride venture (*CW Technology Newsletter, June 13*). Using know-how purchased from Ethyl Corp., this company will put up the world's largest vinyl chloride plant. It will employ oxychlorination for its entire production of intermediate EDC.

Indications are, moreover, that the project may turn out to be even bigger. The 330 million lbs./year, it is felt, may represent only French Solvay's share of a plant in which others are participating. Total capacity might hit 500 millions lbs./year.

A number of other oxychlorination ventures are close to commercialization or in advanced stages of development.

(1) Pittsburgh Plate Glass has done a lot of work on oxychlorination. It is not saying much right now and, despite widely circulated reports to the contrary, it's a safe assumption that the company is not yet oxychlorinating on a commercial scale. This is probably only moments away, however.

(2) Frontier Chemical also has done much solid development work on oxychlorination, and has been talking to contractors about know-how arrangements. Any manufacturing project, however, would probably take the form of a joint venture.

(3) Hooker has carried a process through the pilot plant. Oxychlorination is bound to be a serious contender for its new chlorinated hydrocarbon venture in Louisiana.

(4) Stauffer is believed to have an oxychlorination process in an advanced stage but will not discuss the subject.

(5) Allied, which makes vinyl chloride from its own HCl and purchased acetylene (from Carbide), may have an oxychlorination trick up its sleeve for Geismar, La. Like Stauffer, it will not talk.

Engineering firms are active in the field. Lummus is offering modified Deacon as well as oxychlorination processes. Scientific Design can be expected to have an announcement soon. Pullman, in its annual report said that subsidiary M. W. Kellogg in conjunction with a major (unnamed) oil company is investigating improved vinyl processing. It's a safe bet that this means oxychlorination. (Continental Oil, when asked if it were Kellogg's partner, had no comment.)

Technical Enterprises, which has rights to Air Reduction's modified Deacon process (*CW, July 6, '57, p. 74*) is offering that method as well as oxychlorination. It says, however, that while it is prepared to offer a complete Deacon package, a firm interested in oxychlorination would have to do some development work of its own. Fluor Corp. has talked to at least one firm with know-how for sale.

Chemical consultants, too, are hip deep in oxychlorination projects. If you toss a stone at a group of consultants, the odds are good that you'll hit a man involved in an oxychlorination study.

Market Impact: At the Chemical Market Research Assn. meeting in New York last spring, Dow investigators gave a paper on uses of HCl. A little-more-than-incidental mention of oxychlorination generated a lot of heat and a fair amount of light.

In the question-and-answer session following the paper, Dow's J. M. Henske estimated that HCl now is being substituted for 455 tons/day of chlorine. Most of this is being done by Monsanto, Dow and Goodrich, all of whom use the HCl to make EDC. It means that upward of 360 million lbs. of EDC are being made by oxychlorination. Monsanto's oxychlorination capacity is 30 million lbs./year. Dow probably accounts for the larger share of the remainder—it's one way the company has quietly raised its EDC capacity to a whopping 800 million lbs./year (*table, p. 102*). Substitution of HCl for chlorine, incidentally, means that the market is being spared 500 tons/day of caustic.

Fourth Round in Japan: Throughout the rest of the industrialized world, interest in oxychlorination is running high. In Japan, for instance, oxychlorination is getting serious consideration as a key process in the country's next round of vinyl chloride expansion. The third round, just about completed, is expected to raise capacity to 615,000 tons/year. At the moment, however, production is running behind demand; the shortage for fiscal '64 is expected to be 77,000 tons.

Industry is pressuring MITI (Ministry of International Trade and Industry) to start considering a fourth round. MITI, however, will probably not reach a decision for another year at least.

Meanwhile, Toyo Soda, which will complete a 61,000-tons/year vinyl plant this September, would like to put in a 33,000-tons/year plant using its own oxychlorination process. Asahi Glass is tied up with Pittsburgh Plate Glass in an oxychlorination venture. An Asahi spokesman, however, says it has not submitted a proposal to

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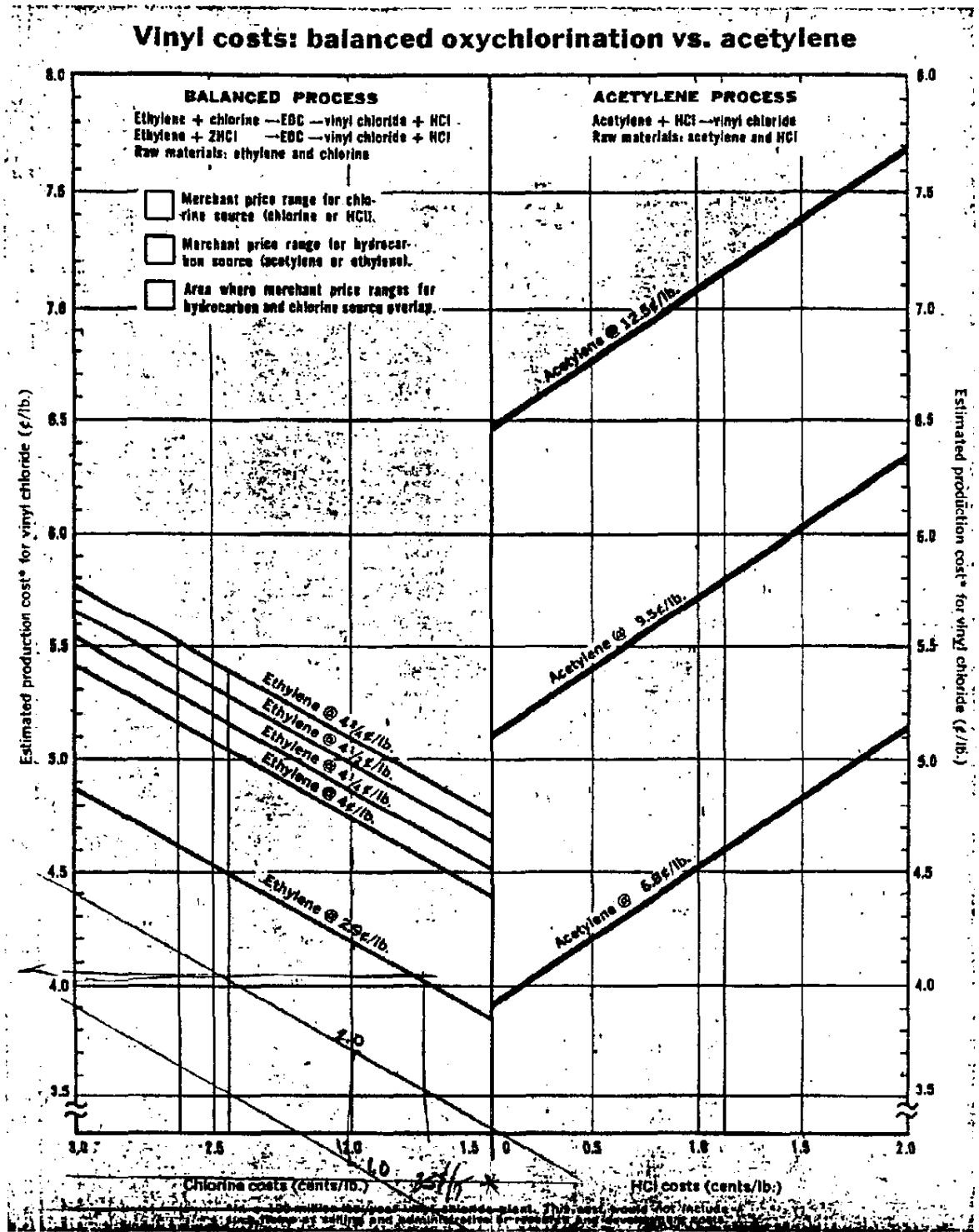
Vinyl costs: balanced oxychlorination vs. acetylene



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MITI for a plant. Similarly, Mitsubishi Chemical is experimenting with oxychlorination but has no firm plans to use it in its Mizushima project now under construction. Toyo Koatsu has been researching oxychlorination intensively for some time. It plans a petrochemical center in Sakai, near Osaka, in cooperation with Mitsui. But chances of government approval in the immediate future are not bright. By the time the project is approved, oxychlorination is bound to play an important role in production of vinyl chloride monomer. Nissan Chemical also has hopes for making vinyl chloride via oxychlorination. It would import technology from Continental Oil.

COSTS ARE THE ATTRACTION

Oxychlorination's popularity hinges on attractions of cheap ethylene, which would replace acetylene, as a starting material. The availability of cheap by-product HCl is another important consideration and one that could bring more producers into the fold. Here's why:

The big oil and chemical companies that are getting into production of linear alkylates for the new soft detergents appear to have settled on processes that will generate large quantities of HCl. One approach is to chlorinate a paraffin, then dehydrochlorinate to form an olefin and two moles of HCl. The other involves reaction of the chlorinated paraffin directly with benzene. In this case, the HCl is taken off in the alyklation step. In either case, ½ lb. of HCl is formed for each pound of linear alkylate. Proposed capacity of 600 million lbs. of linear alkylate means a potential of 200 million lbs. of HCl. The combination of available HCl, cheap ethylene and oxychlorination know-how could well be enough to encourage new vinyl capacity.

The New Balance: Historically, vinyl chloride has been made mainly in two ways: (1) Ethylene and chlorine react to form EDC, which is cracked to vinyl chloride and HCl. Or (2) acetylene and HCl react to form vinyl chloride directly. The second process has much to commend it. It's a straightforward high-yield reaction with no by-product problems. Capital investment for a plant is modest and operating costs are small.

The ethylene-based process, on the other hand, calls for a higher capital investment. It is a two-step process. And 0.58 lb. of HCl is produced for each pound of vinyl. What the ethylene process has that the acetylene process lacks is low-cost starting materials.

In the past, several big vinyl chloride producers operated "balanced" vinyl plants. That is, both ethylene and acetylene are used in two operations. By-product HCl from the cracking of EDC is fed to the second plant, where it reacts with acetylene to make more vinyl. The percentage of total vinyl chloride made from ethylene and acetylene differs from year to year but it has not varied much from 50-50. Some of the newer producers (Monochem, Tenneco) favor acetylene. But Dow has stuck to ethylene. Monsanto and Carbide employ balanced production. And Goodrich, the No. 1 producer, which has historically favored acetylene for its U.S. production, started buying EDC several years ago in a move toward a balanced operation. (Last year, it probably bought 55 million lbs. of EDC from Pittsburgh Plate Glass for vinyl production.) In its new Calvert City operations, Goodrich is employing oxychlorination in a new type of balanced plant based entirely on ethylene. And Monsanto has been using oxychlorination to supplement its acetylene-HCl production.

Setting the Parameters: An examination of raw-material requirements reveals the reasons for the trend away from acetylene as a vinyl chloride raw material. It takes 0.45 lb. of acetylene and 0.62 lb. of HCl to make a pound of vinyl. If acetylene is charged in at 9¢/lb. (a low figure), and HCl at 2¢ lb., it means that raw-material costs are 5.2¢/lb. To that must be added 0.9-1¢/lb. for other charges* to give a manufacturing cost of 6.2¢/lb. And that still does not include any administrative or selling charges, research and development costs or profits. Vinyl chloride is officially quoted at 8¢/lb., freight equalized. But it's moving for as little as 6¼¢/lb. (*CW Market Newsletter, July 18*).

*In a 100-million-lbs./year plant. These costs would include charges for utilities, depreciation, insurance, etc., that, when added to raw-material costs, would produce a "factory" or "mill" cost for making vinyl chloride.

On the other hand, an operation using ethylene to make vinyl chloride and employing oxychlorination to make more EDC would have a net requirement of 0.5 lb. of ethylene and 0.67 lb. of chlorine per pound of vinyl. Other costs would be slightly higher than in the ethylene process —1.3-1.4¢/lb.—but the difference between ethylene and acetylene could easily compensate for them.

The subject is not one that lends itself to simple generalities. A study based on official quotes can easily go astray because of special cases, where products move below lists. Sometimes, the special cases far outnumber the normal. Here, however, are the price parameters for the four key materials: acetylene, ethylene, chlorine, and HCl:

Acetylene: Companies buying acetylene to make vinyl chloride are probably paying 9.5-12.5¢/lb. In the past, the rock-bottom for acetylene prices has been considered to be 8-10¢/lb.

However, captive producers, operating partial-oxidation plants, can probably charge acetylene into a process at a shade under 7¢/lb., possibly 6.8¢/lb. As a survival matter, merchants of carbide-based acetylene could probably set a lower price on the output of amortized plants; 7¢/lb. is conceivable.

Ethylene: The current price of merchant ethylene on the Gulf Coast is 4.75¢/lb. with downward escalation depending on volume. The average price to large users is probably 4.25-4.50¢/lb. Just what charge high captive producer places on his ethylene depends on a number of factors: size and efficiency of the plant, and importantly, the return he is taking on the ethylene unit. Some large users are undoubtedly charging ethylene at less than 4¢/lb. In some of the big new plants now contemplated or completed, ethylene could be charged at less than 3¢/lb., say 2.9¢/lb. This could, of course, exert a pressure on merchant prices, bringing them well under 4¢/lb.

Chlorine: Quoted price for chlorine (gas) is $65/ton. But a large user should have no trouble getting over-the-fence chlorine at $55/ton. It's possible that, under favorable conditions, this could fall to $48/ton, Really $35 ft?

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THE CASE FOR WULFF VS. OXYCHLORINATION

As a vinyl chloride raw material acetylene seems to show off to best advantage when it is the product of a plant making ethylene and acetylene (as in the Wulff process). In this scheme, naphtha or other light hydrocarbons would be fed to the Wulff furnace; vinyl would be produced in a balanced operation. Compare this with a vinyl plant based entirely on ethylene. Here, by-product HCl from the cracking of ethylene dichloride (EDC) intermediate would be oxidized to chlorine and returned to help form more EDC. The figures (below) for this comparison were prepared for CW in association with The Lummus Co., which offers the Wulff process, various oxychlorination processes, and Deacon modifications. A choice between oxychlorination and a modified Deacon depends upon a number of variables. Alec Redniss of Technical Enterprises (New York) thinks the Deacon is slightly more expensive but gives more flexibility. On the other hand, Shell has come up with some techniques (e.g., feeding a dilute HCl stream to the chlorination step) that are potential cost cutters. In any case, there does not seem to be a significant difference between the yields of oxychlorination and Deacon processes. And their utility requirements are not much different. The ranges (per pound of vinyl chloride): steam, 1.8-3.3 lbs.; cooling water, 27-51 gal.; process water, 0-0.61 gal.; power, 0.19-0.21 kwh. Fuel requirements are 1,500 Btu./lb. for either approach.

THE ECONOMICS

	Unit	Unit Price	Wulff Complex: Units Needed	Wulff Complex: Cost per pound of vinyl	Ethylene Complex (modified Deacon): Units Needed	Ethylene Complex (modified Deacon): Cost per pound of vinyl
Raw Materials						
Naphtha	lbs.	1.0¢	1.05	1.05¢		
Ethylene	lbs.	4.5			0.5	2.25¢
Chlorine	lbs.	3.0	0.625	1.88	0.67	2.00
Catalysts and chemicals				0.14		0.07
Caustic soda	lbs.	3.0	0.001	0.003	0.0036	0.258
Phenol	lbs.	10.0	0.0005	0.005	0.001	0.01
Utilities						
Steam	lbs.	0.06	5.25	0.315	3.29	0.197
Cooling water	gal.	0.002	26.1	0.052	47.52	0.095
Process water	gal.	0.015	0.325	0.005	0.18	0.003
Power	kwh.	0.6	0.324	0.195	0.19	0.114
Fuel	1,000 Btu.	0.015	−4,350*	−0.065*	1,500	0.023
Labor						
	men shift	$32,000 year (three shifts)	7	0.15	6	0.128
Fixed Charges						
Depreciation, maintenance, interest, taxes, G&A, overhead)				1.175		0.588
Total				4.905¢		5.504¢

Basis: 150 million lbs./year of vinyl chloride.
Capital: $4-4.5 million for ethylene complex using modified Deacon; $8 million for complex making vinyl by a balanced operation using ethylene and acetylene from a Wulff process plant, and including the cost of the Wulff plant. * Credit.

THE CONCLUSION

The Wulff project for vinyl chloride comes off very well under the conditions chosen. For an incremental investment of $4 million, the differential cost of production (0.599¢/lb.) yields an additional $900,000 in pretax profits. Taking additional depreciation of $400,000/year, it means the $4 million generates $1.3 million/year cash flow. It should be remembered, however, that different conditions could change results drastically. If ethylene were charged in at 3.2¢/lb., for example, the differential would be wiped out. By the same token, it would probably be fairar to compare 3.2¢/lb. ethylene with ethane (rather than with naphtha) as the Wulff feed, and in this case the differential might reappear. In short, these figures are useful mainly as a general formula into which variables can be inserted to give an answer for a given set of circumstances. It should be remembered, too, that the capital costs are for a contractor's battery-limits plant. The operating company would have to count on a higher investment for such things as working capital and land; off-site facilities could add 30%.

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2.4¢/lb. How captive users charge their material is complicated by the fact that 1.1 lbs. of caustic is generated per pound of chlorine. So the value of chlorine depends on the market for the rest of the "package." A company like Dow, the world's biggest producer—and user—of chlorine can probably charge chlorine into a process at slightly less than $30/ton. 1.5¢/lb. However, that figure, is probably a safe minimum for normal operation—and only under favorable caustic market conditions.

HCl: The price of HCl is probably $35-40/ton. Monochem, for instance, is thought to be paying close to $38/ton for HCl (from Morton Salt). The price, moreover, is for HCl in solution, so that Monochem must add costs of distillation. Under more favorable conditions, HCl might be purchased for $25/ton. In the case of a producer charging his own by-product HCl to a process, the range is wide open. If it presents a disposal problem, the HCl could carry a negative charge, –0.1¢/lb. Cases of negative, or even no raw-material charges in chemical processing, however, almost always prove illusory.

Dow has made an economic evaluation on the subject of HCl. It concludes that it should be worth no more than 70% of the value of chlorine. That would mean, for example, that the top price should be $35/ton, if chlorine is valued at $50/ton. The bottom price, it feels, is $12/ton. This is set by sulfuric acid and is equivalent —on an acidity basis—to the cheapest sulfuric that can be purchased.

Most companies seem to be transferring HCl at prices in the middle of that range. Pittsburgh Plate Glass, for example, is thought to be charging $25/ton for HCl into an oxychlorination unit. One engineering company is basing its estimates on $30/ton.

Stating the Case: By placing raw-material requirements against a backdrop of price ranges for key materials, it is possible to compare the costs of vinyl chloride made from acetylene and from ethylene using oxychlorination to balance the production (*chart, p. 95*). It can be seen that a firm buying HCl and acetylene (even at the lower end of the cost range) would have a difficult time competing with one using purchased ethylene and over-the-fence chlorine. One buying acetylene at the upper end of the range would not be able to meet the 6.2¢/lb. vinyl price, even with free HCl and with no allowance for administrative or selling costs. At the postulated low prices for both ethylene and acetylene, the difference is less dramatic. It should be remembered, though, that small differences take on more significance at the lower cost.

Many Roads to Vinyl: There are now five processes and combinations of processes for vinyl chloride manufacture: (1) ethylene and chlorine; (2) acetylene and HCl; (3) balanced operation using acetylene and ethylene; (4) straight oxychlorination of ethylene; (5) a balanced operation using oxychlorination.

The straight ethylene process forming EDC and HCl has a number of attractions. Capital requirements are only slightly higher than those of a comparable acetylene-HCl plant. And manufacturing costs are attractive if adequate credit for HCl is made.

Companies like Dow and American Chemical can probably show good costs for vinyl chloride. Dow has a variety of uses for HCl and oxychlorination skills too. American Chemical's HCl is used to react with more ethylene to make tetraethyl lead.

Ethyl Corp., is in a particularly enviable spot. It has large HCl requirements for its tetraethyl lead production (i.e., in the reaction of ethylene and HCl to make ethyl chloride). At one time, in fact, Ethyl operated a Mannheim furnace to make HCl (with salt cake by-product). By going into vinyl chloride, it found a highly attractive alternate.

The firm also built a plant to make ethyl chloride by the direct chlorination of ethane. This, too, yields HCl as a by-product. And with two new sources of HCl, it was able to close down its Mannheim furnaces. (Morton nicely filled the void with a Hargreaves operation producing both salt cake and HCl). Ethyl does not always operate its direct chlorination process; it's used to regulate needs for HCl and ethyl chloride.

What Ethyl charges for its vinyl chloride, then, depends in good measure on what costs it places on the HCl used in making ethyl chloride. By taking a hefty credit for it, it could show vinyl costs that would be difficult to match. Lending weight to the industry belief that Ethyl costs its vinyl at between 4-5¢/lb. (and probably closer to the lower figure) is the probability that the company will use vinyl chloride as a starting material for making its chlorinated solvents (vinylidene chloride, methyl chloroform, trichloroethylene).

Regarding HCl, few companies are as well situated as Ethyl. But even Ethyl has done a lot of work on oxychlorination processing, as evidenced by its sale of know-how to French Solvay. Long-term planning could be behind Ethyl's interest in oxychlorination. Vinyl chloride and chlorinated hydrocarbons in general are growing faster than tetraethyl lead is.

NEW HOPE FOR ACETYLENE

In the early '50s, it was popular to talk of the coming battle between acetylene and ethylene as materials for petrochemical manufacture. As technology settled down, however, each found its niche. But in the past few years, ethylene has been quietly picking away at acetylene's markets; today many observers see nothing but a grim future for acetylene. Principal reasons: acetylene is inherently more expensive than ethylene and improved technology has found ways of utilizing ethylene for more processes. Carbide-based acetylene is proved technology but power costs bulk large in this scheme and impose geographic restrictions. Hydrocarbon acetylene has also been "proved" to the extent that plants have been built and operated. But running these plants has not always been easy and unexpected maintenance difficulties have added as much as 1¢/lb. to operating costs. The soot problem has been a particularly knotty one.

A plant manager of one of the pioneering complexes using the BASF hydrocarbon acetylene process was recently asked his opinion of the eventual answer.

"There is no one solution," he says. "You do everything you can and then you learn to get along with it." More recently, Diamond has installed Montecatini's acetylene process, and Tenneco has put in the SBA (Société Belge de L'Azote) process. But thus far at least, neither has proved a smash-

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How oxychlorination saves steps in vinyl synthesis

THREE-STEP PROCESS

1. Modified Deacon yields chlorine

$2HCl+\frac{1}{2}O_2 \rightarrow Cl_2+H_2O$

A chlorine-from-hydrogen chloride plant is being designed by Shell. HCl-oxidation patents: U.S. 85,370; 141,333; 165,802 (Deacon). U.S. 2,204,172; 2,204,733; 2,312,952; 2,271,056; 2,447,834 (Air Reduction). U.S. 2,577,808; 2,547,928 (Dow). U.S. 2,746,844 and South Africa 63/1650 (Shell).

2 . . . which is used to make EDC

$Cl_2+C_2H_4 \rightarrow C_2H_4Cl_2$

The direct addition of chlorine to ethylene is well established in large commercial vinyl plants. The key patents: U.S. 2,099,231; 2,284,479 (Shell). British 553,959 (Distillers Ltd.). U.S. 2,601,322 (Jefferson Chemical). U.S. 2,929,852 (Union Carbide). British 781,414 (Celanese).

3. Pyrolysis of EDC yields vinyl chloride

$C_2H_4Cl_2 \rightarrow C_2H_3Cl+HCl$

Most of today's vinyl chloride production involves pyrolysis of ethylene dichloride, and the newer oxychlorination-based processes also depend on this reaction. Important patents: U.S. 2,474,206; 2,569,923 (Shell). British 569,291 (Distillers). And U.S. 2,412,308 (Mathieson) on by-produced HCl.

TWO-STEP PROCESS

Oxychlorination combines 1 and 2

$2HCl+\frac{1}{2}O_2+Cl_2+2C_2H_4 \rightarrow 2C_2H_4Cl_2+H_2O$

This process appears to be nearing widespread utilization. By feeding on a mixture of chlorine and hydrogen chloride it absorbs the hydrogen chloride from the pyrolysis of ethylene dichloride; thus it offers a balanced route for vinyl production. Patents on this approach are numerous. Some of the more recent and more significant: U.S. 2,636,864; 2,752,401; 2,752,402; 2,866,830 (Dow). U.S. 2,644,846; French 1,352,657; Belgian 630,738; British 907,435 (Shell). French 1,304,711; 1,323,939; 1,341,711 (Pittsburgh Plate Glass). Belgian 636,856; British 932,130; French 1,321,708 (Distillers Ltd.). French 1,304,911; Belgian 608,678 (Dynamit Nobel AG.). French 1,359,016; Belgian 632,044 (Imperial Chemical Industries). Belgian 643,262;643,263 (Vulcan).

ONE-STEP PROCESS

Oxychlorination and pyrolysis

$\frac{1}{2}O_2+Cl_2+2C_2H_4 \rightarrow 2C_2H_3Cl+H_2O$

This general route is on the frontier of oxychlorination technology. Some of these processes start with ethane, instead of ethylene. In these cases it appears that the ethane is cracked to ethylene, which is oxychlorinated to ethylene dichloride; the latter is simultaneously cracked to vinyl chloride. Such processes are outgrowths of chlorinated solvent production, and they usually direct the reaction by recycling undesired chlorine compounds. Critics of these processes question the availability of ethane for large-scale production. Other processes introduce new technology. Case in point: a limited direct chlorination over a Deacon-type catalyst supplemented with palladious chloride and directive agents (e.g., esters and ethers). Distillers Ltd. has a patent (see below) on this method. Key patents issued thus far: French 1,360,896; 1,355,870; 1,355,886; 1,341,711. British 916,137; 913,040; 934,329. Belgian 631,155; 631,725 (all Pittsburgh Plate Glass). British 918,062 (Distillers Ltd.). Belgian 637,537 (Toyo Koatsu). Belgian 614,467 (Imperial Chemical Industries). Belgian 636,443 (Vulcan Materials).

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Processes employed by U.S. vinyl producers

	Capacity†	Process
Goodrich Chemical*		
Niagara Falls, N.Y.	335 (total)	acetylene
Louisville, Ky.		acetylene
Calvert City, Ky.		ethylene
Union Carbide		
So. Charleston, W. Va.	280 (total)	balanced
Texas City, Tex.		
Ethyl Corp.		
Baton Rouge, La.	160	ethylene
Houston	80	
Dow Chemical		
Freeport, Tex.	200 (total)	ethylene
Plaquemine, La.		
Tenneco Chemical		
Houston	170	acetylene
Allied Chemical		
Moundsville, W. Va.	150	acetylene
Monochem**		
Geismar, La.	150	acetylene
Monsanto		balanced with
Texas City, Tex.	350	acetylene and oxychlorination
Air Reduction (Cumberland Chemical)		
Calvert City, Ky.	60	acetylene
Diamond Alkali		
Deer Park, Tex.	90	balanced
Goodyear		
Niagara Falls, N.Y.	45	acetylene
General Tire		
Ashtabula, O.	30	acetylene
American Chemical		
Long Beach, Calif.	40	ethylene
Total	1,960	

†Estimated in million pounds/year.
*Goodrich's big switch to a balanced operation with oxychlorination at Calvert City makes it difficult to pin down its present operations. Last year it made probably 280 million lbs. of vinyl at its three plants. Historically, it has been based on acetylene. But it started to purchase EDC several years ago. Its new operations at Calvert City will probably set the pattern for the firm's future production.
**Borden and U.S. Rubber.

ing success; both Diamond and Tenneco have started suits because of what they regard as unsatisfactory operations.

Du Pont has developed a modified-arc process it is proud of. But even Du Pont is working both sides of the street, using an acrylonitrile process based on propylene as well as one based on acetylene.

The best bet, some acetylene boosters believe, is a plant making both acetylene and ethylene. This might prove particularly attractive for vinyl chloride manufacture. In any event, processes such as the perenially promising Wulff, are getting a lot of serious study. It's possible to show attractive costs for making vinyl chloride in a balanced operation using ethylene and acetylene from a Wulff furnace (*chart, p. 97*).

It has never been publicized, but Union Carbide has been operating a Wulff plant at Institute, W. Va., since '62. This unit can make up to 12 million lbs./year of acetylene. Carbide says it started up in '62, met performance guarantees in the same year. And Lummus, which offers the Wulff process, reports a lot of interest, primarily overseas, in the Wulff process. (Fluor also offers a Wulff process plant.)

In Japan, Kureha has developed a process for making vinyl chloride from a gaseous mixture of acetylene and ethylene and this, too, is getting a close look. Kureha built the process into a $10.5-million plant to make 66 million lbs./year of vinyl at Nishiki. The process, it says, cut construction costs by 20%. Figuring on naphtha at 1¢/lb., chlorine, at 3¢/lb., and oxygen at 1½¢/lb., Kureha says the process can cut selling price of vinyl chloride to 6¢/lb. This it expects to achieve when production reaches 110 million lbs./year "in the near future." In Japan, at least, one company which has made an oxychlorination arrangement with a U.S. company, is having serious second thoughts. It is now thought to be leaning toward the Kureha process.

The idea of using the dilute gas (ethylene and acetylene) from the pyrolysis of hydrocarbons has been advocated by SBA (*CW, April 11, p. 71*). In fact, SBA says that it obtained the first patents on the process in '59. It feels the patents are basic, emphasizes that it intends to do its utmost to see that they are enforced.

OXYCHLORINATION KEYS

None of the companies now working on oxychlorination or employing it commercially is saying much about its process. Dow probably has had more commercial experience than any other firm, both from the standpoint of time and quantity of material processed. It regards oxychlorination as a "flywheel" operation, to balance its requirements for EDC and vinyl chloride against the supply of chlorine and HCl.

Dow's work is an outgrowth of studies on modified Deacon processing and is covered by three patents (U.S. 2,636,864; 2,752,402; 2,866,830). Dow's oxychlorination process is not looked on as a primary method

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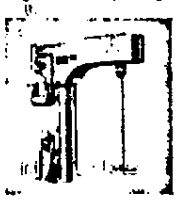

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for making EDC. Although it represents an achievement of no small stature, the process probably is not one that many others would find overwhelmingly attractive.

Monsanto also has been operating an oxychlorination unit at Texas City. The unit was shut down during '61 and '62 because acrylonitrile demand was down and the firm had excess acetylene. As the acrylonitrile market improved, the oxychlorination unit was reactivated and has been operating for 18 months. The plant is a fluidized-bed unit employing oxygen, rather than air.

The oxygen poses no problems for Monsanto; it has a plant at the site for its acetylene production. Oxygen requirements, are modest: stoichiometrically, 0.13 lb. is needed per pound of vinyl and prices of tonnage oxygen are less than ½¢/lb.

PPG's approach is also thought to call for oxygen, rather than air. Frontier, on the other hand, uses air in a fixed-bed process. It apparently does not attain complete conversion of HCl. About 5% of the total HCl fed to the unit appears as 20% acid in a by-product stream. This, of course, can be credited to the process or cleaned up for recycle. Frontier Chemical has a number of patents on oxychlorination. Its key ones, however, are just starting to appear (Belgian patents 643,262; 643,263. The Frontier patents are appearing in tandem. One relates to oxychlorination of aliphatics; the other, aromatics).

Shell's oxychlorination wrinkle is a three-step method in which chlorine is produced from HCl in a separate unit. One of Shell's contributions: feeding a dilute chlorine gas into an adjoining unit for chlorination. Result: reduced purification costs. The Shell group is planning a 30,000-ton/-year plant employing the chlorine-from-HCl process in the Netherlands, and Shell has been seeking customers for the process. It utilizes a fluidized bed and features a catalyst consisting of a mixture of copper and other chlorides. The reaction temperature is 630-800 F, considerably below the 850-1220 F typical of the Deacon. The lower temperature, as Shell points out, favors conversion of HCl into chlorine, also reduces corrosion problems. The process employs either oxygen or air; Shell suggests oxygen only if it is available at an attractive price. The content of the effluent depends upon the feed HCl. But one set of conditions produces a 48% chlorine stream that can be used, says Shell, "in various industrial processes."

Ethylene dichloride makers

Company Location	Capacity*
American Chemical	
Watson, Calif.	40
Diamond Alkali	
Deer Park, Tex.	110
Dow	
Freeport, Tex.	500
Plaquemine, La.	300
Ethyl Corp.	
Baton Rouge, La.	300
Houston, Tex.	140
Monsanto	
Texas City, Tex.	210
Olin Mathieson	
Brandenburg, Ky.	100
Pittsburgh Plate Glass	
Lake Charles, La.	120
Union Carbide	
South Charleston, W. Va.	200
Texas City, Tex.	240
Total	2,260

*Estimated in million pounds/year

Deacon's Descendants: Air Reduction's process, being offered by Technical Enterprises, can trace its lineage to the Deacon process, as in fact can all the straight oxychlorination processes now at work or under development. In the Deacon process, hydrogen chloride is oxidized with air over a hot copper catalyst to produce chlorine and water. The reactions proceed in two steps—hydrogen chloride oxidation at about 1000 F, followed by catalyst regeneration at about 550 F—but all modern processes conduct these reactions in one step. Furthermore, all of the patent innovations deal either with improving the selectivity of the complex reaction, or with catalyst volatilization, a problem inherent in the Deacon process.

Catalyst volatilization can be partly suppressed by adding alkali metal chlorides (U.S. 2,206,399). Copper chloride, however, will sublime and concentrate in places in a motionless bed of catalyst. Result: hot spots, which are the main drawback of fixed-bed reactors. These hot spots make it difficult to remove the heat of the mildly exothermic Deacon reac-

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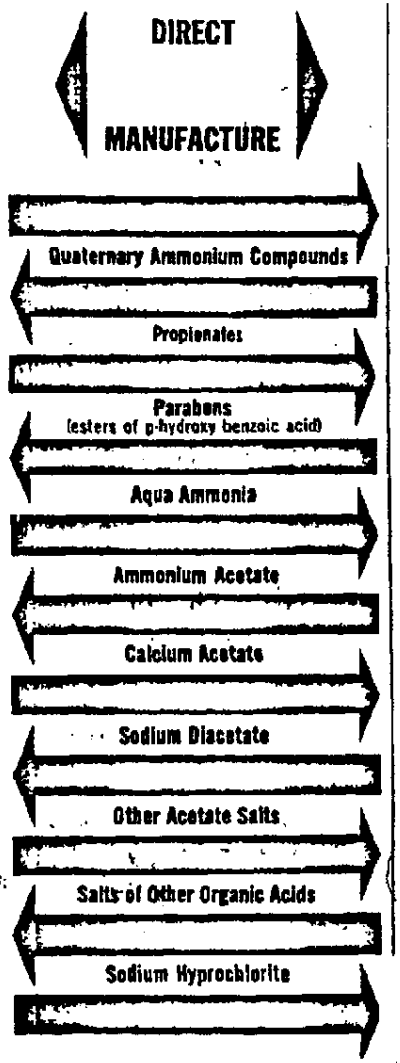

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ions, thus complicate temperature ontrol.

Hot spots can be overcome by witching to fluidized-bed reactors, ith the particle-buoying reaction ases passing upward instead of downward, through the catalyst bed. However, these fluidized-bed reactors present three additional problems: (1) the alkali metal salts, which suppress copper chloride volatility by forming a low-melting eutectic, cause the catalyst particles to become sticky and agglomerate in the fluidized bed; (2) the catalyst particles are gradually pulverized in the fluid bed, so that dust collectors must be installed in the highly corrosive gases leaving the reactor; and (3) the combined reactions and uniform temperatures of the fluidized bed are less favorable to the production of chlorine.

Chlorine Acceptors: Oxychlorination is a big step forward in improving the equilibrium limitations of the Deacon process. The hydrocarbon present serves as a "chlorine acceptor" and in effect moves the equilibrium in the desired direction. This, of course, is the foundation of the Raschig process.

In oxychlorination, however, HCl is burned in the presence of a hydrocarbon, and the trick is to keep the hydrocarbon from burning. In the Raschig process the hydrocarbon is benzene, which is stable because of its resonating* structure. Paraffins and branched-chain compounds present a different set of problems. Branched-chain hydrocarbons, in particular, prove difficult subjects for oxychlorination. Ethylene is in the intermediate class; it's tougher to process than benzene, easier than ethane.

Even in the case of ethylene, however, some oxygenated products are bound to form, and their presence could conceivably raise havoc. There's a belief that trace quantities can cause difficulties when the monomer is polymerized. Monsanto, however, says that it has experienced no such problems with its process.

Catalytic Keys: Although most of the companies involved will not give details of their processes, the patent literature is enlightening. Over a dozen innovations in oxychlorination technology have shown up in patents. Among the contributors: Distillers, Du Pont, Esso, Frontier, Imperial Chemical Industries, Pechiney, Pittsburgh Plate Glass, Shell, Toyo Koatsu.

The patents indicate that catalysts are a key subject for research and development. Distillers, which is not now offering an oxychlorination process, has a series of patents that could be significant (Belgian patents 630,963 and 636,856; British patent 932,130 and French patent, 1,321,708). Yields of ethylene chloride, based on ethylene, are pegged as high as 96.5% in these patents. Only some 1.4% of the ethylene feed is oxidized to carbon dioxide. And yields over 90%, based on hydrogen chloride, are reported.

The Distillers catalyst makes some radical departures from conventional oxychlorination catalysts. It uses a support (for the copper chloride) of activated alumina—rather than diatomaceous earth, silica gel, pumice, broken fire brick, etc., which are the conventional supports. Also, the Distillers catalyst includes 0.2-10.0% rare earth metals, such as cerium, lanthanum, and neodymium, which have atomic numbers between 57 and 71.

Only one other oxychlorination catalyst appears to use rare earths. And this catalyst, patented by Shell (British 907,435) states that conversion of ethylene into dichloroethane is practically quantitative, while the examples cited in the patent state that more than 90% of the hydrogen chloride is converted. Otherwise, this Shell catalyst uses a silica-gel support having an unusually large surface area (200 sq. meters/gram).

To suppress volatilization of the copper chloride, both the Distillers catalyst and the Shell catalyst employ about one part alkali metal salt (KCl) to one part copper chloride. Both catalysts are made by impregnating the baked or calcined support material with a solution of copper chloride and then evaporating to dryness.

In this impregnation technique, the rare earth catalysts appear to differ from other oxychlorination catalyst preparations. The support for the rare earth catalysts is soaked in copper chloride solution and then dried, whereas some other processes emphasize spraying or dropping a copper chloride solution onto a hot catalyst support, so that the solution is vaporized before it has a chance to sink

*Naphthalene, which also resonates, can be oxychlorinated. Methylnaphthalene and toluene tend to degrade under oxychlorination conditions.

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		25 g.	15.60
6648	4-Hydroxy-3-methoxybenzoic Acid MP 213-214° $HOC_6H_3OCH_3COOH$... MW 168.15	10 g.	5.60
		25 g.	12.50
8916	2-Iodothiophene BP 65-66°/10 mm. $SCH_2CHCH:CI$... MW 210.04	25 g.	6.75
		100 g.	24.35
9035	Palmitic Acid Sodium Salt $CH_3(CH_2)_{14}COONa$... MW 278.41	5 g.	2.35
		25 g.	7.00
811	Pentyl Ether BP 183-185° $[CH_3(CH_2)_4]_2O$... MW 158.29	25 g.	2.70
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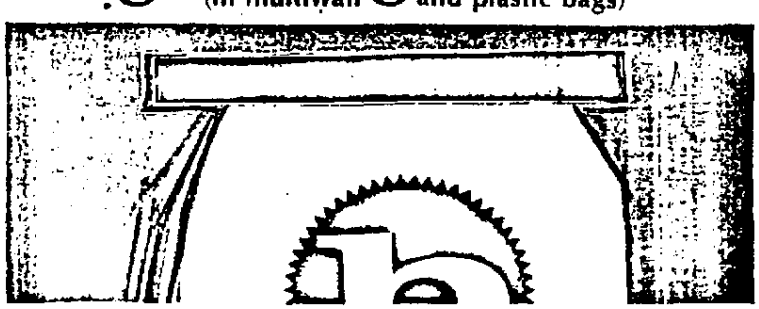

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in. In fact, an early Dow chlorine-from-hydrogen chloride process (U.S. 2,547,928) features a technique for recovering volatilized copper chloride by continuously absorbing the vapors in condensed hydrochloric acid and returning this solution to the reactor, where it is sprayed over the hot fluidized bed of catalyst.

A recent British patent (941,353) to Du Pont stresses the measled, or spotted, appearance of the desired catalyst, which has the copper chlorides irregularly distributed over the surface of the catalyst support material (calcined diatomaceous earth). However, the Du Pont patent points out that copper chloride salts remain on the surface of the support material, even though the support material is immersed in the copper chloride solution.

Another feature cited for the Shell catalyst is an unusually low reaction temperature: 485 F for oxychlorinating ethylene to EDC. This low temperature is purported to virtually eliminate corrosion and copper chloride volatilization. Thus, this catalyst appears to have licked the problems of the fixed-bed oxychlorination reactor; and if it doesn't agglomerate or pulverize in a fluid bed, it may have licked the problems of the fluid-bed reactor, as well.

Selectivity by Control: The importance of close operating control for high yields is pointed up in a voluminous group of recent patents* to Pittsburgh Plate Glass. These, plus some issued to Vulcan Materials Co. (Frontier Chemical), illustrate the pivotal position of EDC in the production of a wide range of chlorinated hydrocarbons, including vinyl chloride, vinilidene chloride, ethyl chloride, perchloroethylene, trichloroethylene, etc.

Besides serving as feed for the conventional pyrolysis vinyl chloride process, EDC can be further chlorinated in oxychlorination reactions. The usual copper chloride catalyst stabilized with potassium chloride is employed. EDC may also be used as a diluent to direct further chlorination reactions, as shown in Belgian patent 636,443 to Frontier.

In the PPG process the EDC conversion is carried out in two steps

*French: 1,285,024, 1,304,911, 1,323,939, 1,326,717, 1,341,711, 1,355,870, 1,355,886 and 1,357,451. British: 913,040, 916,137, 931,211 and 934,329. Belgian: 607,673, 631,155, 631,451 and 631,725, etc.

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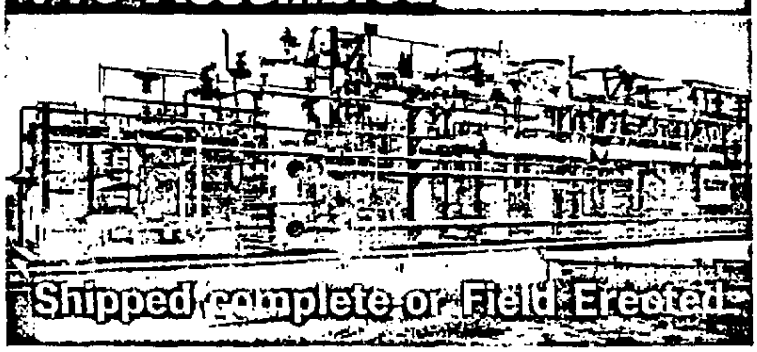

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(British 913,040): (1) chlorination, in which hydrogen chloride is a by-product; and (2), oxychlorination, in which by-product hydrogen chloride is used as the chlorinating agent. Yields of chlorinated hydrocarbons appear to be about 80%, while chlorine utilization is said to be as high as 82%. PPG is said to be using a version of this process to make chlorinated compounds in pilot quantities.

However, a more striking variation of oxychlorination is described in several PPG patents that cite ethane as the starting material. In a combined cracking and oxychlorination reaction (French 1,341,711), approximately 30% of the ethane is converted into vinyl chloride and 50% cracked to ethylene, while some 20% of the ethane is burned. And in French patent 1,355,870, the vinyl chloride alone is recovered by distillation, while the ethylene and chlorinated hydrocarbons are recycled to be converted into vinyl chloride. PPG is currently offering vinyl chloride from a proposed plant that is believed to incorporate these techniques.

Selectivity by Separation: PPG's patents also bring out the critical role of EDC in the newer oxychlorination routes to vinyl chloride. The question here, is when to crack. Three answers are proposed: (1) crack EDC as a pure component, (2) crack it in a recycle stream with selected other chlorinated components, or (3) crack it *in situ*.

The first approach is the one now used commercially in the U.S. The second, where EDC is recycled with other chlorinated hydrocarbons after the vinyl is removed, is described in the PPG patents and a Belgian patent (637,537) to Toyo Koatsu. And the third is described in Belgian patent 614,467 to ICI, as well as in British patent 956,657 to S. Tsutsumi, a professor of Osaka University (Japan).

The critical operating variable in these different approaches is temperature. Ethylene can be oxychlorinated to EDC over conventional catalysts at about 570 F, whereas EDC is not cracked until the temperature reaches 850-950 F. The proponents of the two-step route say that, while an extra step is required to crack EDC separately, this extra step is justified by the increased yields resulting from the lower operating temperatures.

Osaka University's Tsutsumi appears to get around this problem by

employing vacuum (460 millimeters of mercury or less) and ultraviolet light. Temperatures are thus reduced. His patent says that vinyl chloride yields of 85-90% based on ethylene are obtained when the pressure is 360 millimeters—over 95% when the pressure is under 260 millimeters.

Otherwise some of the recent oxychlorination patents show that researchers are still looking for new solutions of the old problems of copper chloride volatility, hot spots in fixed beds, etc. Belgian patent 632,044 to ICI describes a process for passing the feed to the oxychlorination reactor through a bath of molten copper chloride; so that the feed vapors will contain enough copper chloride vapors to suppress its volatilization from the catalyst. This process appears to permit the use of fixed-bed reactors, since it eliminates hot spots.

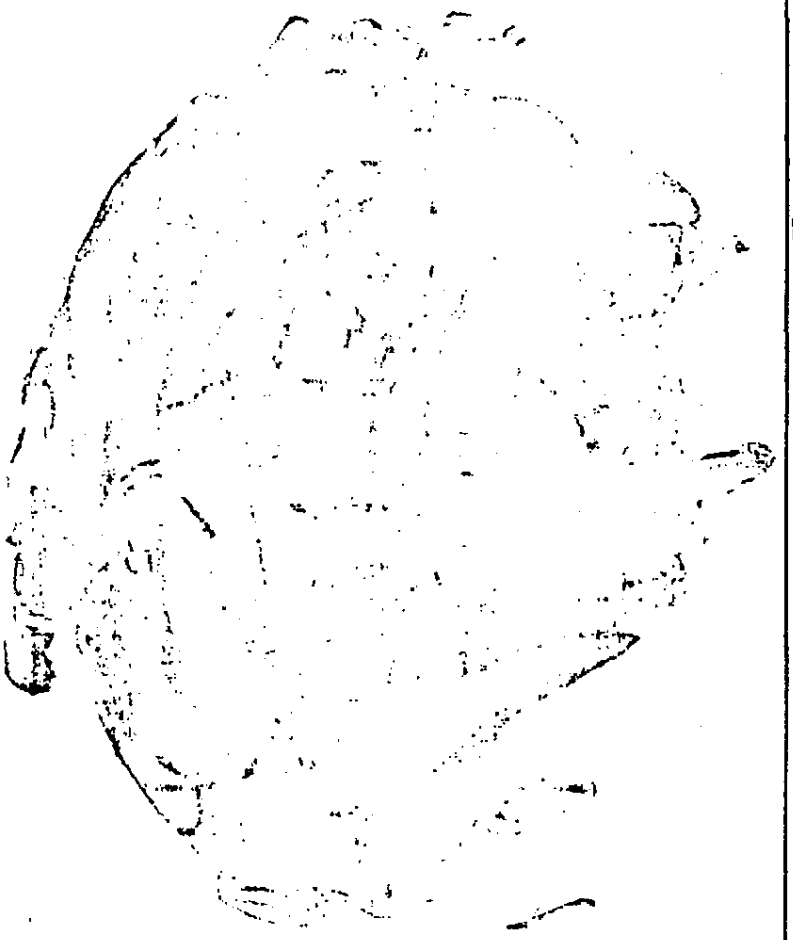
And Pechiney appears to have developed a dual-reactor process (French patents 1,286,839 and 1,304,072) combining benefits of both the fixed and fluid beds, while avoiding the difficulties of both. According to these patents, the largest part of the heat of reaction is liberated during the early parts of the oxychlorination reaction, and the products of this early reaction can subsequently act as diluents to hold down the temperature.

So Pechiney has proposed a fluidized-bed reactor to be immediately followed by a fixed-bed reactor. Heat exchange, residence time and feed materials to the fluid-bed reactor are controlled to limit the temperature and keep conversion below 80%. The fluid-bed effluent passes immediately over and down through a fixed-bed reactor, which collects any fines that result from catalyst attrition. Hot spots are said to be eliminated. And yields of EDC from ethylene are said to be well over 95%.

Weighing Up: Such high yields appear to be the rule rather than the exception in oxychlorination processes.

The importance of yield should not be underestimated. However, judging from the work that has been done, it does not seem likely that significant differences can be expected on this score.

Other factors are significant in weighing the merits of the various processes: whether oxygen or air is



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used, the life of the catalyst, and the materials used against corrosion. Whether a fluid-bed or fixed-bed process represents the best approach is a matter of some dispute. Some feel that a fluid-bed process is inherently more expensive but that it is justifiable on the basis of superior performance.

A company considering licensing might find the overbearing consideration to be the amount of development work that has been done on the process and the size of the royalty payments.

Acetylene's Future: Regardless of the merits of the individual oxychlorination processes, it seems certain that the new technology will have a heavy impact on the future of acetylene.

And acetylene can hardly afford to lose many more markets. Some time ago, it lost out in this country as a raw material for acetaldehyde. And Shawinigan Chemicals, which has been looked on as an operation to "upgrade hydropower" through acetylene chemicals, switched to ethylene for its acetaldehyde expansion (*CW, July 6, '63, p. 28*).

Acetylene captured the acrylonitrile market from ethylene oxide (except in the case of Union Carbide, which has an unusually favorable position in oxide); but it is now losing out there to propylene. ICI and Celanese are switching to ethylene for their one-step vinyl acetate processes (*CW Technology Newsletter, June 6*). And some think it is only a matter of time before Du Pont does the same.

Oxychlorination has already cut into acetylene's vinyl chloride outlets. Future inroads could reflect the success of such operations as Kureha's, the Wulff process and other new hydrocarbon processes. And oxychlorination could help elbow acetylene right out of the manufacture of chlorinated solvents, trichloroethylene, in particular. It could leave chloroprene as the only important chemical derived exclusively from acetylene.

The companies that would be most immediately affected would be the big carbide-based acetylene merchants —Union Carbide and Air Reduction. If oxychlorination processes are successful, acetylene prices would have to drop drastically for acetylene to remain competitive. And at the very best that would be felt in acetylene profits.

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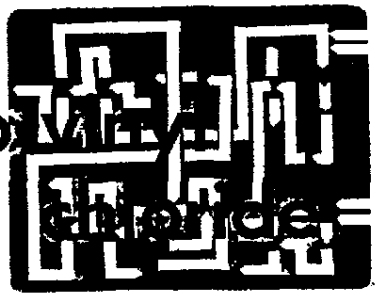
New route to vinyl chloride



Oxychlorination offers a new solution to old problem; vinyl chloride from ethylene can be produced without finding a high-value outlet for by-product HCl

EDWIN F. EDWARDS
and THEODORE WEAVER
The Fluor Corp., Ltd.
Los Angeles

VINYL CHLORIDE IS MADE today on a commercial scale from either of two raw materials, acetylene or ethylene. With acetylene feed, the synthesis is accomplished by the simple addition of hydrochloric acid:

$$C_2H_2 + HCl \rightarrow C_2H_3Cl \quad (1)$$

With ethylene feed a two-step synthesis is involved. First, chlorine is added to ethylene to produce 1,2-dichloroethane (commonly called ethylene dichloride or EDC). Then, the dichloroethane is dehydrochlorinated, usually by thermal treatment, to produce the vinyl chloride product and by-product hydrochloric acid:

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 \quad (2)$$

$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl \quad (3)$$

For both of these routes, the fixed charges against capital per pound of product are low. Thus, the final economic choice between these two alternate hydrocarbon feed materials depends very heavily on their relative costs, and on the value of the by-product hydrochloric acid.

Ethylene is usually cheaper than acetylene; therefore, one tends to be attracted to the ethylene route. However, the conventional ethylene-based synthesis as described above degrades one pound of chlorine to HCl for every pound of chlorine that appears in the vinyl chloride produced. In a really large plant it is often very difficult to find a high value use for such a large quantity of HCl.

Several producers have sought a solution to this by combining the ethylene and acetylene routes into a single facility, producing essentially equal amounts of vinyl chloride from each hydrocarbon raw material, and using the waste HCl from the ethylene operation as the chlorine source for the acetylene-based section of the plant. But, this too, has its drawbacks. First, the average cost of hydrocarbon raw material is increased by the higher price paid for acetylene. Second, one is forced to employ two smaller units in lieu of a single, larger one, with the attendant increase in unit capital cost and operating labor. Today, a new, potentially attractive solution to this problem is available through the use of an oxychlorination reaction.

Oxychlorination is a general term referring to reaction in which a mixture of oxygen and HCl is employed to bring about a chlorination reaction. As applied in the present instance, oxychlorination means a combination of by-product HCl from reaction (3) with oxygen (usually in the form of air) to bring about the chlorination of ethylene to produce 1,2-dichloroethane:

$$C_2H_4 + \tfrac{1}{2}O_2 + 2\ HCl \rightarrow C_2H_4Cl_2 + H_2O \quad (4)$$

The dichloroethane thus produced is then dehydrochlorinated conventionally to make vinyl chloride.

Oxychlorination thus provides the possibility of making vinyl chloride from ethylene

AP00034150

without significant degradation of chlorine. The requirement for fresh chlorine for the ethylene based route is thus cut in half, and essentially all of the chlorine feed appears in the final product vinyl chloride. This now makes the choice between the acetylene- and ethylene-based processes essentially a question of the relative cost of the two hydrocarbons.

What's been happening

A review of the literature shows that oxychlorination of hydrocarbons was conceived as early as 1922. In the intervening years there has been sporadic interest, building more recently to a high level of activity.

The technical literature on oxychlorination processes is confined largely to the information contained in issued patents; however, a review of these brings out a number of interesting and important features:

1. The reactions are generally catalyzed by metallic chlorides, the one most commonly mentioned being cupric chloride.
2. For any given chlorination reaction there is an optimum temperature, and temperature control is critical. If the temperature drops too far below the optimum, the reaction is difficult to initiate. On the other hand, too high a temperature level will cause the formation of compounds with a higher chlorine content than desired.
3. Catalytic reactors employed in oxychlorination tend to form hot spots, which in turn cause poor temperature control, and may cause the catalyst to vaporize and migrate through the bed.

A number of interesting solutions have been proposed to overcome the temperature control and hot spot problems. One solution is to conduct the reaction in a fluidized bed of catalyst, another is to use inert filler materials such as silicon carbide, in a fixed bed of catalyst. Today, several different processes have been successfully demonstrated on a pilot plant and commercial scale. Specific process details are treated as proprietary and confidential. Thus, only the over-all results may be described.

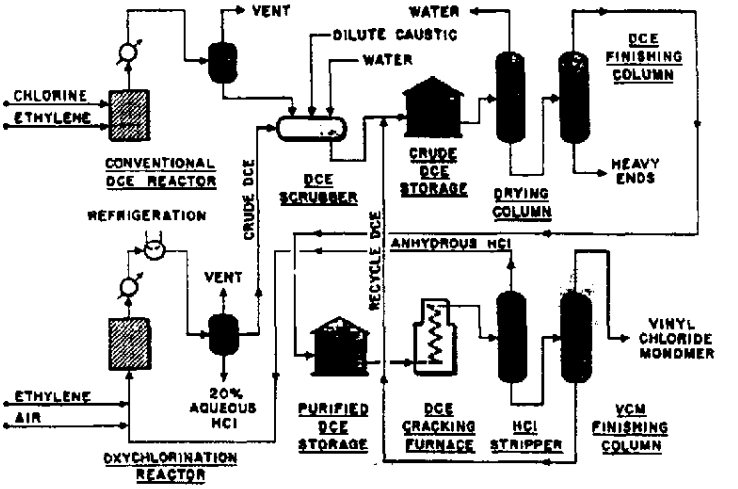


Figure 1. Vinyl chloride from ethylene with oxychlorination.

How the process works

The oxychlorination process discussed in this article has been commercialized by a substantial chemical company whose primary business is the production of chlorinated organic chemicals. The process has been fully tested in a pilot plant, and a commercial plant is now under construction.

In the oxychlorination process, ethylene and hydrogen chloride are reacted over a cupric chloride catalyst at a moderate pressure and temperature. The cupric chloride catalyst is supported on a fixed bed of inert material:

$$2\ CuCl_2 + C_2H_4 \rightarrow C_2H_4Cl_2 + Cu_2Cl_2$$

$$Cu_2Cl_2 + \tfrac{1}{2}\ O_2 \rightarrow CuO{\cdot}CuCl_2$$

$$CuO{\cdot}CuCl_2 + 2\ HCl \rightarrow 2\ CuCl_2 + H_2O$$

The exothermic heat of reaction is removed by generating steam (at about 150 lb./sq. in. gage) and special provisions are made for maintaining uniform temperature throughout the reactor.

The reactor effluent is cooled with cooling water and refrigerant to separate dichloroethane and water from nitrogen and unreacted oxygen. A small amount of unreacted HCl leaves the system with the water as a 20% aqueous solution.

Vinyl chloride monomer

Figure 1 illustrates how the oxychlorination process can be used in a complete vinyl chloride plant. In this plant two reactors are used to produce the dichloroethane (DCE) which is dehydrochlorinated to yield vinyl chloride. One employs the oxychlorination process described above and the other a conventional process for making DCE. About half of the DCE intermediate is produced in the oxychlorination reactor from ethylene and the HCl resulting from the thermal dehydrochlorination of DCE. The rest of the DCE is produced in the conventional

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reactor from chlorine and ethylene. Thus, in such a plant chlorine requirements are about one half those for a conventional vinyl chloride plant based on ethylene, and there is no co-product HCl. The oxychlorination section of the plant has already been described.

In the conventional reactor section of the plant the chlorine and ethylene are reacted in a circulating stream of DCE. A small amount of an inexpensive catalyst is added to the DCE to insure completion of the reaction. Noncondensables are separated from the reactor effluent and the effluent is washed free of impurities.

DCE from the conventional and oxychlorination sections of the plant are combined, dried, and purified in the DCE purification section. Drying is carried out by azeotropic distillation and the remaining purification steps by ordinary distillation. The latter yield a highly purified DCE, plus light and heavy ends cuts. Purified DCE is dehydrochlorinated in a pyrolysis furnace in the vinyl chloride monomer section. The furnace outlet is cooled and fed to a distillation train. In the distillation train anhydrous HCl, unreacted impure DCE, and vinyl chloride are separated from each other. HCl is fed to the oxychlorination reactor and unreacted DCE recycled to the DCE purification section. Inhibitor is added to the vinyl chloride monomer (VCM) and the monomer is sent to product storage.

The conventional process for manufacturing vinyl chloride from ethylene and chlorine employs all the process steps described above except the oxychlorination step. It thus has HCl as a co-product which must be disposed of. Plans for any new venture using the conventional ethylene route must of necessity include the marketing or captive use of about 0.6 ton HCl/ton VCM. Operating requirements for the two ethylene based processes and the classical acetylene process are given in Table 1.

In the classical acetylene, based process vinyl chloride is produced by reacting HCl and acetylene in the presence of a catalyst, usually mercuric chloride supported on carbon, in a tubular reactor. The reaction is carried out at about atmospheric pressure and around 200°C. Heat of reaction is removed by a coolant which circulates through the reactor. Reactor

[redacted]

	Units/short ton vinyl chloride		
	Ethylene route		Acetylene route
	Oxychlor.	Conv.	
Raw materials			
Ethylene 99%, tons	0.484	0.476	—
Chlorine 99%, tons	0.674	1.205	—
HCl produced, tons	—	0.590	—
Acetylene 99.8%, tons	—	—	0.424
HCl 99.8%, tons	—	—	0.596
Utilities, catalysts & chem.			
Power, kwh	214	154	156
Steam 150 lb./sq. in. gage, tons	0.46	1.05	0.51
Steam 50 lb./sq. in. gage, tons	1.07	1.07	—
Cooling water 80°F, tons	257	236	80
Fuel gas, mmBtu	3.5	3.5	—
Catalysts, chem. & supplies, $	1.25	1.10	0.91
Operating labor			
Supervisor	1/day	1/day	1/day
Operators	5/shift	4/shift	3/shift

[redacted]

	Ethylene route		Acetylene route
	Oxychlor.	Conv.	
Battery limits plant	$4,700,000	$3,700,000	$3,400,000
Off-sites	1,200,000	1,200,000	800,000
Working capital	300,000	380,000	240,000
Startup expenses	200,000	180,000	150,000
Land, negligible			
Royalty—not included			
Total	$6,400,000	$5,460,000	$4,590,000

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effluent gas is cooled and the vinyl chloride recovered and purified by distillation.

What does it cost?

To illustrate the economics of oxychlorination in vinyl chloride manufacture, we have developed costs for producing 200,000,000 lbs./year of vinyl chloride by the three process routes described above—ethylene with oxychlorination, conventional ethylene, and acetylene. Comparative manufacturing costs for the various routes are presented in the form of calculated minimum profitable selling prices for vinyl chloride. Since raw material prices and the value of by-product HCl vary from situation to situation, profitable selling prices are presented as a function of these important variables. Likewise, since fixed charges, royalty, and profit will vary from company to company, these elements of manufacturing costs are presented in such a manner that the reader may adjust them to fit his own particular situation. However, reasonable changes in the allowance made for fixed charges, royalty, and profit do not alter the relative economics of the various routes.

Capital cost estimates which are shown in Table 2, include all equipment, materials, construction labor, engineering and construction fees for erection of the plants in ready-to-operate condition in a Gulf Coast location. The estimates are predicated on building the plants at sites where the necessary utilities would be supplied from central utility producers. Utility costs used in the economic analysis allow for all direct and indirect charges and profit associated with producing the utilities; thus no capital need be added for the utility producers.

Although offsite capital costs will vary from site to site, it is our experience that the estimates made for Table 2 are reasonably good averages for the type sites envisioned. They include the cost of product storage and loading facilities and storage for heavy chlorinated organics and other minor products. In the case of the ethylene route plants, the offsite estimates include chloride unloading and storage. The gaseous raw materials—ethylene, acetylene, and HCl—are assumed to be delivered from adjacent plants by pipeline.

To illustrate the differences in the three process routes and to show the magnitude of the various components of manufacturing costs, typical manufacturing cost and profitability calculations are shown in Table 3, for two typical Gulf Coast situations:

Case 1. Ethylene is available from a large ethylene plant by pipeline at 4.5¢/lb. There is an "across the fence mar-

[redacted]

	Dollars/short ton		
	Case 1		Case 2
	Ethylene route		Acetylene route
	Oxychlor.	Conv.	
Raw materials			
Ethylene at 4½¢/lb.	43.56	42.84	
Chlorine at $50/ton	33.70	60.25	
By-product HCl at $25/ton	——	(14.75)	
Acetylene at 8¢/lb.	——	——	67.84
HCl at $50/ton	——	——	29.80
Total raw materials	77.26	88.34	97.64
Direct conversion costs			
Labor and supervision	1.79	1.46	1.12
Chemicals, catalysts & supplies	1.25	1.10	0.91
Utilities	4.35	4.04	1.63
Maintenance	2.35	1.85	1.70
Plant general expense	2.47	1.97	1.62
Total conversion cost	12.21	10.42	6.98
Estimated selling and corporate administrative costs	1.50	1.50	1.50
Estimated to be required for depreciation, taxes, insurance, royalty, and profit	26.00	22.00	18.00
Minimum profitable selling price $/ton	116.97	122.26	124.12
¢/lb.	5.8	6.1	6.2

$\frac{117-26}{117} \times 5.8 = 4.5¢/lb$ prod cost

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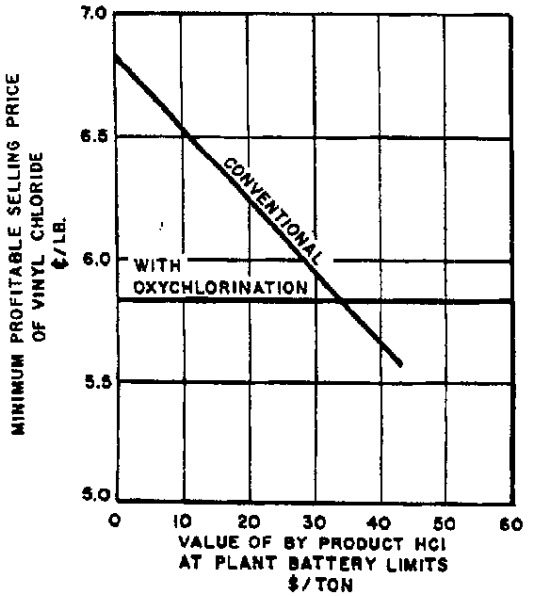

Figure 2. Effect of HCl value on the cost of making vinyl chloride from ethylene and chlorine.

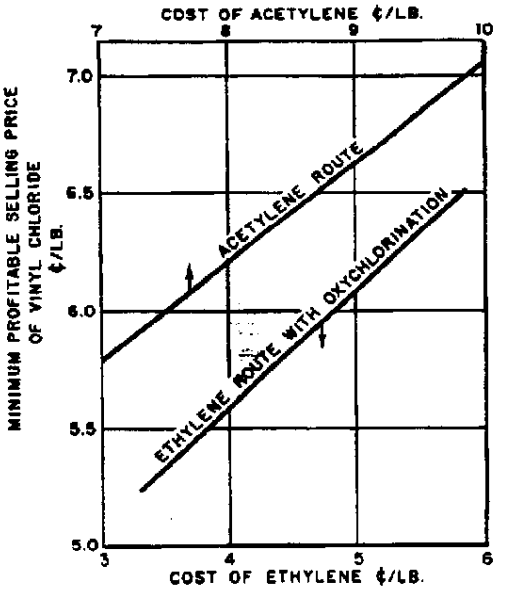

Figure 3. Comparison of ethylene and acetylene processes for making vinyl chloride.

ket" for 118,000,000 lb./year of by-product HCl at a value of $25/ton at the vinyl chloride plant battery limits.

Case 2. Acetylene is available from a large acetylene plant by pipeline at 8¢/lb. HCl is purchased "across the fence" from a chlorine plant manufacturing the HCl by reacting chlorine and hydrogen. Cost of the HCl is assumed to be the same as that for purchased liquid chlorine, as the cost of "burning" hydrogen and chlorine is small, and chlorine cell gas would be used rather than liquid chlorine.

The unit costs and indirect charges used in the calculations are given in Table 4.

How the routes compare

The importance of the oxychlorination process depends on the fact that markets for by-product HCl are limited in many cases. In the United States there are many areas of local surplus of HCl, and in many cases HCl

1. Labor	$3.20/hr. plus 20% for vacation, holiday, sick leave and other benefits.
2. Direct supervision	$11,500/yr.
3. Chemicals, catalysts and supplies	At prices prevailing on U. S. Gulf Coast
4. Utilities	
Electric power	0.6¢/kw.h.
Steam 150 lb./sq. in. gage	45¢/1000 lb.
50 lb./sq. in. gage	40¢/1000 lb.
Cooling water	2¢/1000 gal. circulated
Fuel gas	25¢/mmbtu
5. Maintenance	5% of Battery limits capital cost /year
6. Plant general	80% of maintenance and operating labor to cover local plant administration, accounting, personnel, purchasing, and analytical laboratory labor.
7. Selling & corporate administrative cost	Allowance of $150,000/year.
8. Depreciation, taxes, insurance, royalty, and profit	Assumed at 40% total capital shown in Table 2/year.

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is being neutralized and disposed of as a waste. In such areas the conventional ethylene route suffers a severe competitive disadvantage because of the need to dispose of sizeable quantities of HCl. By employing the oxychlorination process it is possible to produce vinyl chloride from ethylene and chlorine without also producing HCl. The marketing of anhydrous HCl from a conventional plant is complicated by the fact that the HCl by-product from the pyrolysis of DCE is not a normal item of commerce. It can be disposed of by pipeline to an adjoining facility, absorbed in water and shipped as aqueous HCl, or shipped in special pressurized tank cylinders. The first method is often the only economic way of disposing of the large quantity of HCl produced in a conventional ethylene-based vinyl chloride plant. In the second method, the value of the HCl is reduced and shipping costs are increased due to the need for transporting water. In the third, shipping costs can be prohibitive due to the need to ship the anhydrous gas in expensive, high-pressure, tank cylinders. Thus, the value of by-product HCl may vary considerably, depending upon the availability of the market and its proximity to the vinyl chloride plant.

Using the same basis as for Case 1, Table 3, the minimum profitable selling price has been determined for vinyl chloride manufactured by the conventional ethylene route at several different values for the by-product HCl produced by this process. These are plotted in Figure 2. The corresponding minimum profitable selling price for the oxychlorination route is also plotted in Figure 2 to show the advantage of the oxychlorination route at various values for by-product HCl. Note that the value shown for HCl is the value of this material as a gas at the plant battery limits after taking account of expenses associated with collecting, delivering, and selling it to the ultimate customer.

Figure 2 illustrates that in plants of the size studied in this paper, the additional capital cost and operating requirements of the oxychlorination route are usually justified when the spread between the value of chlorine and the value of by-product HCl is more than about $15 per ton.

A word of caution is in order. This "break-even spread" varies with plant size. For smaller plants a distinctly larger value may be found.

Ethylene vs. acetylene

Most vinyl chloride producers in this country are operating plants using the conventional ethylene route or a combination of the conventional ethylene and acetylene routes. However, some producers have found the classical acetylene route more economical and have selected it for their plants. Since their choice was made before the commercialization of the oxychlorination process, it is now appropriate to make a new comparison of the ethylene and acetylene synthesis routes.

To permit the rapid evaluation of the relative merits of the ethylene and acetylene routes for other particular situations, we have developed a picture of the minimum profitable vinyl chloride selling prices as a function of these raw material costs. This picture is presented in Figure 3. The minimum profitable selling prices shown were calculated using the same conversion and indirect costs as in the earlier analysis given in Table 3. Again, it was assumed that HCl would be produced in a chlorine plant, as explained in a the description of Case 2. Thus the chlorine cost is the same for both the synthesis routes shown.

Figure 3 illustrates that for new large plants in most, if not all, U. S. locations the ethylene route with oxychlorination is more economic than the acetylene route. On the Gulf Coast, for instance, where one may picture large quantities of ethylene selling on long-term contracts for 4 to 4½¢/lb. and acetylene for 7½ to 9¢/lb., the ethylene route with oxychlorination is the clear-cut choice.

This does not automatically foreclose the future of acetylene as a raw material for vinyl chloride, in other circumstances. For example, where existing process units are now on hand, the economic comparison between the alternate raw materials may change. Even more important may be changes in the relative cost of ethylene and acetylene that will occur in foreign situations, particularly where ethylene must be made on a small scale from a naphtha feedstock. In some of those cases the acetylene route may indeed be the better choice.

The oxychlorination process permits economic manufacture of ethylene-based vinyl chloride in areas where low cost ethylene is available and there is a poor market for anhydrous HCl. When the spread between the values of chlorine and by-product HCl is more than about $15 /ton (taking HCl as a gas at the plant battery limits) vinyl chloride can be produced at a lower cost in a large plant using the oxychlorination process than in a similar size plant using the conventional ethylene-based process.

In the U. S., except for unusual acetylene and ethylene cost relationships, the ethylene route should prove more economic than the acetylene route for new vinyl chloride plants.

Edwards

Weaver

AP00034155

Purpose

To develope a process for the oxychlorination of methane to produce chlorinated methanes. Operate miniplant to develope accurate analysis in order to obtain good material balances.

Procedure

The operation of the miniplant is described in the accompanying flow sheet. The reactants were cylinder methane, air and hydrochloric acid.

Data

Twelve runs of four-hour duration were made. The results of 10 runs were inconsistent necessitating minor changes in the product recovery system and analysis.

Hydrochloric acid (HCl), carbon dioxide (CO_2) and chlorine (Cl_2) are measured by volumetric titrations. The remaining components except water (H_2O) are measured by gas chromatographic methods. H_2O is measured by weight difference.

The data obtained for the last two runs (No. 16 and 17) is listed below.

A. Reactant Flows (Moles/Hour)

	CH_4	O_2	N_2	HCl
Run No. 16	0.370	0.517	2.168	1.044
Run No. 17	0.370	0.577	2.169	1.200

B. Reactor Temperature Points (°C)

	2	3	4	5	6	7	8
Run No. 16	389	334	395	397	396	393	[illegible]
Run No. 17	398	393	[illegible]	395	395	[illegible]	[illegible]

C. Exit Products (Moles/Hour)

	CH_2Cl_2	$CHCl_3$	CCl_4	CO	CO_2	CH_4
Run No. 16	0.0050	0.0385	0.0910	0.0495	0.0217	0.0816	0.0206
Run No. 17	0.0275	0.0574	[illegible]	0.0371	0.0276	0.0870	0.0227

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Interpretation of Data

A complete carbon analysis was obtained on runs 16 and 17; however, the numbers for methyl chloride are estimated. Some of this material vaporized when the collection traps were allowed to warm to room temperature. A separate procedure will be used to measure methyl chloride yields.

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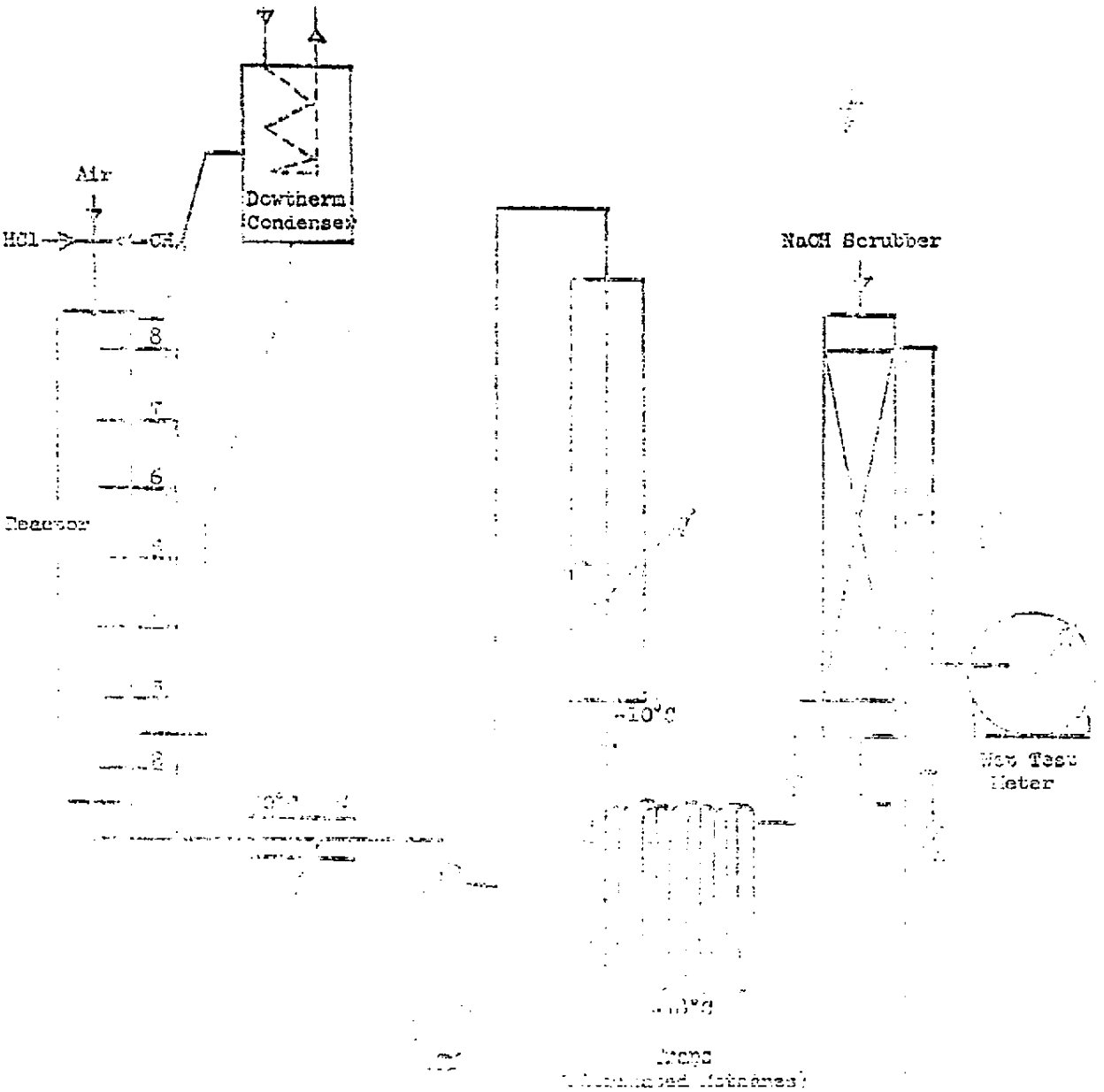
Reactor (nickel) - Packed with 1/4"
Celite 22 pellets burdened with
5% Cu^{+} as $CuCl_2 \cdot 2H_2O$
5% Na^{+} as NaCl



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