

PDM

VCM PROCESS ANALYSIS

Process Safety

There are three major hazards in the VCM area:

1. Acetylene design and operation of the acetylene handling facilities in the VCM area are conservative to assure minimum detonation hazard. Research plans to investigate the deflagration characteristics of the mixed HCl-acetylene stream. It is certainly safer than pure acetylene, but just how much more is unknown. Present operation is conservative.
2. Chlorine facilities - no good way apparently exists to combat a major chlorine spill. Engineering has suggested a number of ways to minimize this hazard (L. B. Bullock to Operating Committee, Study of Hazards of Chlorine Handling Facilities - Interim Report, 6/5/61). Research intends to investigate better ways to fight a spill than the present best method (soda lime).
3. Mercury hazard - Technical Service and Research have as a continuing problem the job of preventing toxic pollution due to the use of mercuric chloride catalyst.

Process Weaknesses

1. Raw Materials *quality*

Acetylene and ethylene are both upgraded raw materials. We are ~~basic in acetylene and will be basic in ethylene when the Chocolate Bayou project is completed.~~ We have good Sales contracts on chlorine. ~~This makes us competitive with other major producers but doesn't give us any unique position in raw~~

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materials. Basic know-how in the oxidative chlorination of ethylene, gained through operation of a full-sized reactor (Department 26), allows maximum technological flexibility should the basic economics of the two hydrocarbons change, e.g., if the use of incremental ethylene from Chocolate Bayou should become more profitable to Monsanto than the use of incremental acetylene from Department 18.

2. Catalyst Usage

Catalyst life has never been satisfactory. Pilot Plant work indicated a catalyst yield of about 475 lbs. VCM/lb. catalyst. Plant yield was about 240 lbs. VCM/lb. catalyst before the use of series reactors and about 330 lbs. VCM/lb. catalyst after. The primary reason for this low life is thought to be the impurities present in our Sachsse acetylene. ^{SICE}~~Siedison~~ reports a catalyst yield of 715 lbs. VCM/lb. catalyst using carbide-based acetylene. We feel 1,000 lbs. VCM/lb. catalyst is attainable using pure acetylene with our superior cerous chloride-containing catalyst.

Technical Service has a continuing program to improve catalyst yield through testing in the plant and in their small test reactors. Research has ^{completed a literature survey of the acetylene-HCl} on their agenda a review of the catalyst problem in order to define research work needed.

mention in notes and files a research program in this area

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Product Quality

The reactivity of Monsanto VCM, as measured by dilatometer polyrates, is the highest in the industry. There has been a great improvement in our VCM quality since the last area analysis was made in 1959.

Main factors leading to this improvement were:

3. Use of series reactor which allowed longer catalyst life while maintaining acetylene impurities in the reactor effluent at low levels.
2. The new VCM fractionator, 22D14, which has resulted in virtual elimination of heavy-ends from our VCM.
1. Chlorination of crude reaction VCM which has allowed reduction of butadiene and butene content to less than the 1 ppm level.

All competitors are marketing extremely pure VCM. Our VCM compares well except for unusually "large" amounts of the saturated C₄ hydrocarbons. n-Butane normally is running at 20-50 ppm and isobutane at 10-30 ppm. Springfield feels that the butanes are chain transfer agents and desire a reduction. Additionally, VCM purchasers are extremely critical on quality. We feel that sensitive chromatography will become a sales tool, and on a chromatogram our butane peaks stick out like sore thumbs. Escambia has already questioned us about trace impurities in our VCM. Technical Service is now trying to locate the source of the butanes in our process in order to determine the cost of removing them.

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We are presently fighting an acidity problem which does not allow operation of the plant as ^{desired} envisioned in the expansion ("Split System Operation") with the chlorination facilities in operation. Solution of this problem is a top-priority project with at least stop-gap solution predicted for July or August. *Dona*

In summary, our VCM is, as far as we can tell, over 99.99% pure, with further improvement necessary before we can make the claim "as good or better than any VCM available".

Competition

All competition use the same processes for VCM that we use. Dow has oxidative chlorination know-how but we do not know whether they are using it for EDC manufacture. A listing of VCM producers is given below:

<u>Producer</u>	<u>Capacity (MM lb.)</u>	<u>Raw Material</u>
Allied Chemical Moundsville, W. Va.	100	Acetylene
American Chemical Watson, Calif.	25	Ethylene
Cumberland Chemical Calvert City, Ky.	50	Acetylene
Diamond Alkali Houston, Tex.	50	Acetylene
Dow Chemical Freeport, Tex.	100	Combined
Plaquemine, La.	60	Ethylene
	160	

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Ethyl Corporation Baton Rouge, La. Houston, Tex.	150 50 <u>200</u>	Ethylene "
General Tire Ashtabula, Ohio	30	Acetylene
B. F. Goodrich Calvert City, Ky. Louisville, Ky. Niagara Falls, N. Y.	100 100 40 <u>240</u>	Combined Acetylene Acetylene
Goodyear Tire Niagara Falls, N. Y.	50	Acetylene
Monsanto Chemical Texas City, Tex.	150	Combined
Union Carbide Texas City, Tex. S. Charleston, W. Va.	100 150 <u>250</u>	Combined Combined
U. S. Rubber Painesville, Ohio	60	Acetylene
	<u>1365</u>	

Dow's capacity at Plaquemine is expected to be 100 MM lbs./year in 1962. Plans for three other large plants have been announced. Monochem (U. S. Rubber - Borden) is scheduled for 150 MM lbs. per year at Geismar, La. by 1962; U. S. Rubber's plant at Painesville, Ohio would presumably be shut down. Tenneco (Tennessee Gas) has recently announced plans for a 200 MM lbs. per year VCM plant in Houston. Diamond plans to have a 90 MM lbs. per year expansion on stream in Houston in January 1962. The impact of the drastic 1960-1961 VCM price drop on these projects is unknown.

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Monsanto, Diamond, and Carbide (Texas City) now use hydrocarbon acetylene with its associated impurity problems. Diamond, Tenneco, and Monochem all plan integrated plants using acetylene produced by partial combustion of methane.

Alternate Processes

Monsanto has technology ^{for} in making VCM by cracking of EDC, by reaction of acetylene and HCl and by oxidative chlorination of ethylene (to EDC). Exploratory work has been done by Research on ^{oxidative} chlorination and high temperature chlorination of ethane. The former gives ethyl chloride as product. The high temperature chlorination (so-called sudden chlorination) of ethane can be modified to give a wide variety of products preferentially, including vinyl chloride, vinylidene chloride and 1,1-dichloroethane. Sudden chlorination is new technology using a raw material which has not been upgraded; the technique suffers in that large quantities of HCl (3 mols HCl/mol VCM) are made as by-product. Economics are attractive only if HCl can be moved at a chlorine value.

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Areas for Improvement of Present Process

1. Increased catalyst life and decreased catalyst cost. Purified acetylene is the major improvement foreseeable here. *Handwritten: a large amount of purified acetylene is required*
2. Elimination of equipment or process steps. Examples are elimination of the caustic washing and azeotropic drying step in EDC manufacture, or decreased number of crackers in operation if 3" cracker tubes are satisfactory. *Handwritten: Res (unwashed)*

Handwritten: 3 improve catalyst life - R & D this is a major area of research

4. Better plant control by instrumentation. Installation of chromatographs on the cracker absorber (22D5) overhead, on reactor effluent and on product column (22D14) overhead are examples of such installations accomplished or planned. *Water* *when?*

5. Preparation of a mathematical model of the VCM plant for optimizing yield and utility costs. This includes work required to develop information to prepare such a model. Reduction of losses is a part of yield improvement. *Concentration*

6. Increased product purity. *Butanes, HCl*

7. *Cl₂ spills*

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