

892

TECHNOLOGY RISK EVALUATION REVIEW

CEA 3306

PARACHLOROPHENOL REHABILITATION

W. G. KRUMMRICH PLANT

SAUGET, ILLINOIS

MARCH 14, 1978

COMPANY CONFIDENTIAL

BY R. A. YEO

632748

I. INTRODUCTION

On May 5, 1977 a Safety Audit was completed of the chlorophenol processes at the W. G. Krumrich plant. It had been ten years since the last major process improvements had been made to this area. Further, the Italian dioxin incident triggered a concern at many levels of Monsanto management since dioxins could be produced in this area.

The Audit identified twelve areas where corrective action was needed. Six were directly related to the production of Pentachlorophenol (Penta), the process where dioxin formation is a potential hazard. These were resolved by the decision of MICC's Detergents & Phosphate Division to go out of this business.

The remaining six findings in the Audit are related to operations in the parachlorophenol (PCP) production area. The largest use for PCP is as the raw material in Santophen-1 manufacture, also at the Krumrich plant. These findings are summarized below:

1. TWA limits for exposure to chlorophenol vapors have been exceeded on occasion.
2. Leakage of water into the process greatly accelerates corrosion.
3. Badly corroded equipment jeopardizes personnel safety.
4. Leaks and spills of chlorophenols cause excessive sewer loadings.
5. The emergency notification procedure after a spill was too cumbersome.
6. Work practices and the working environment permit excessive contact with chlorophenols.

Following the Audit, a number of changes to work practices and revisions to plant procedures were made by supervision in the PCP production area. The plant initiated a number of capital projects aimed at correcting those problems requiring immediate attention. At the same time, a \$48 capital project was initiated in CED under CEA 3306 to rehabilitate the entire PCP area. The CED project is targeted for July, 1978 approval.

The objectives of the rehabilitation project are to produce PCP at minimum cost, in a safe worker environment, and with adequate control over spills. Because of uncertainties related to marketing and our intent to provide new technology, the rehabilitation is to extend the useful life of the PCP area six years, through 1983.

With this as background, the project objective includes four major thrust areas.

1. Extend the useful life of the PCP area six years, through 1983. Included is replacement of corroded facilities and prevention of corrosion caused by water leakage.
2. Make the adjustments necessitated by the shutdown of the Penta area.
3. Minimize worker exposure. Concerns for meeting TWA limits and improving the working environment are included.
4. Reduce environmental impact due to spills.

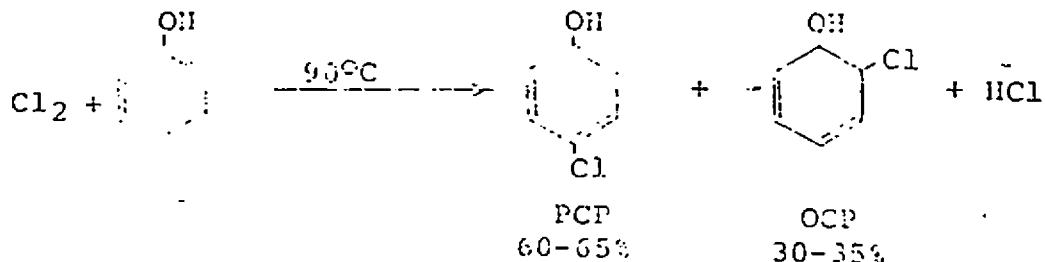
II. DISCUSSION

Synopsis of the Process

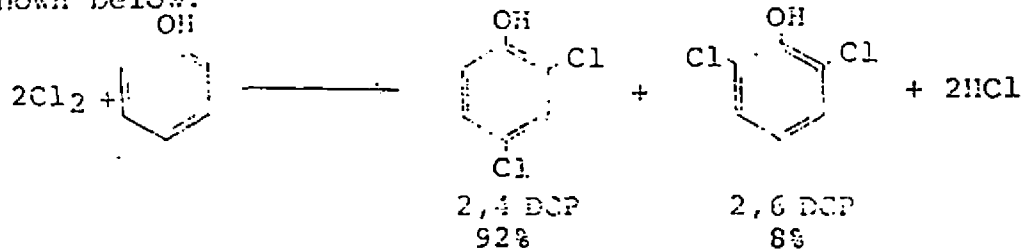
Parachlorophenol (PCP) is produced by chlorinating phenol and then refining the crude product. Both steps are batch processes. The batch refining process produces a number of cuts besides PCP. One, the para-rich cut, chlorinates directly to 2,4 dichlorophenol (2,4 DCP). A second cut, orthochlorophenol (OCP) may be refined for sale or used to produce 2,4 DCP. Those cuts not required for the production of PCP or 2,4 DCP are used to make OCP Crude, which is sold to manufacturers to make Penta or incinerated.

Chemistry

Phenol and chlorine react as follows to form monochlorophenols:



Additional chlorine will produce di-chlorophenols as shown below:



Since PCP chlorinates directly to 2,4 DCP, a high purity 2,4 DCP can be produced from the mono-chlorinated crude after the bulk of the PCP has been removed. Production of 2,4 DCP from OCP, however, gives a product which contains only about 8% 2,4 DCP. Refining is necessary to separate out the undesirable 2,6 DCP.

Manufacturing Processes

The manufacturing processes for parachlorophenol and 2,4 dichlorophenol are illustrated on Figures 1 and 2. PCP can be produced with or without phenol recycle. The former reduces OCP Crude production; the latter increases PCP production rates. Referring to Figure 1, 2,4 DCP is normally made from the para-rich cut which already contains some of this product. Additional 2,4 DCP can be made from either the ortho crude or from the phenol/para-rich/para cut illustrated in Figure 2.

Other products are OCP Crude and refined OCP. In order to meet specifications for Penta production, OCP Crude must contain a minimum of 70% equivalent phenol. It may be necessary to dilute OCP Crude with Phenol to meet this specification. Refined OCP will be made from OCP Crude as needed to meet sales.

Waste Treatment

Since phenols and chlorophenols increase COD in waste streams, and adversely affect the taste of fish and drinking water, the department wastes are treated before being released to the WGR plant sewer system. The waste treatment process is illustrated in Figure 3.

Chlorophenols are removed from the by-product HCl gas stream by contacting the gas with sulfuric acid. Caustic scrubbing is used to remove chlorophenols from the vent fumes. Chlorophenols in waste water and in spent caustic are removed in the acidifier. Here, spent sulfuric acid is used to acidify the waste streams, and the chlorophenols

are extracted by absorption into Santophen residue. The oil layer from the acidifier must be neutralized before it is incinerated, and the water layer is sewerred. Overall, about 65% of the chlorophenols in the waste streams are removed and incinerated.

Changes to the Manufacturing Area by CEA 3306

Upgrading the PCP facilities will be accomplished by replacing structural steel, equipment, piping, and electrical systems which have deteriorated. Corrosion will be minimized by using electrical tapes rather than steam to heat tanks and by segregating the different process materials.

Adjustments due to the Penta shutdown include relocation of the 2,4 DCP chlorinator to the PCP area and the installation of mixing equipment for OCP Crude storage tanks. Improvements will be made to the still to increase capacity. As a result, more PCP can be made with phenol recycle, decreasing OCP Crude production and our dependence on Penta manufacturers to consume this product.

Several improvements are being made to the operator's environment. Overflows and ruptures will be contained in new tanks. Organic residues will be handled in new pipelines. Instruments will be provided to monitor tank levels. A new drumming area, control room and eating room are being provided.

Spill controls will be provided through a system of curbs or dikes for all organic tanks. A pad and a sump will be built under the tank truck loading area. All materials collected in these areas will pass through a monitoring station before they are released into the sewers, and waste water high in chlorophenols will be diverted for treatment.

Changes to the Waste Treatment Area by CEA 3306

Relatively few changes are being made to the waste treatment facilities. There will be fewer open vents. HCl will continue to be drowned. Waste water in the sumps will be collected and monitored in a central sump, a first step towards treatment of these streams. There will be improved handling systems for the organic waste streams.

III. TECHNICAL UNCERTAINTIES AND RISKS

The following is intended as an outline of the risks. There will be a detailed assessment of them during the review.

A. Related to Operation through 1983

The rehabilitation project will replace most of the PCP facilities with the exception of the majority of the tanks and pumps. Recently, some tanks not included in the project have leaked, and been repaired. The risk that some of these tanks may require replacement before 1983 is a known risk assumed by the Business Group.

A greater concern is that the WGR plant program for reducing chlorophenol discharges to the river may not satisfy state and federal requirements. The State of Illinois specifies that chlorophenols should not exceed 0.3 mg/liter in the discharge to the river. Presently, the Village of Sauget, which processes Monsanto's waste water, is operating under a variance permitting 19 mg/liter based on a 30 day average. It is expected that this variance will be extended until the new secondary treatment plant goes on stream (1982). Risks in this area are as follows:

1. That an extension may not be granted.
2. That chlorophenols may prove difficult to treat.
3. That federal action on the Priority Pollutants list may require chlorophenol reduction before the treatment plant is ready.

B. Related to Adjustments from the Penta Shutdown

With the shutdown of the Penta area, there is no longer an easy, assured method to dispose of the OCP Crude. Presently, two Penta manufacturers have expressed an interest in purchasing OCP Crude. To guard against cutbacks in sales, the project has provided flexibility to minimize production of OCP Crude. Should other measures not prove adequate, the surplus OCP Crude would be shipped to Rollins Environmental Services, Inc. at New Orleans and incinerated.

The risk is that the PCP production area may not be able to dispose of the OCP Crude product. One cause might be that the new project facilities do not achieve the desired reduction in OCP Crude production. A second cause might be the inability of the incinerator contractor to dispose of the OCP Crude.

C. Related to Improvement of Worker Safety

A survey was taken to determine the eight hour average exposure level by operators to phenols and chlorophenols in the PCP production area. Phenol exposure was not shown to be a problem. The average exposure to chlorophenols was estimated at 3.2 mg/cu m (TWA), slightly above the limit of 3.0 mg/cu m (TWA). The survey also pinpointed certain operator activities as major contributors to this level. This project will take positive action to reduce operator exposure in each of the problem areas.

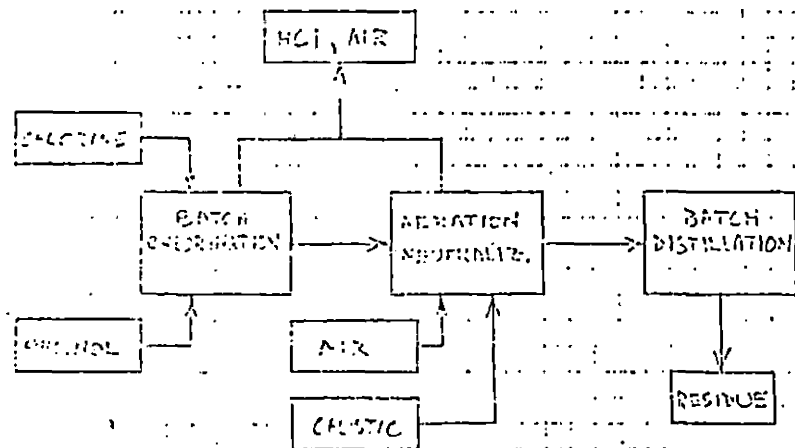
The risk is that the new facilities may not give adequate operator protection in the event of an unforeseen incident. The situation would be complicated should hazardous dioxins be present. Fortunately, conditions necessary to form these hazardous dioxins are very unlikely to occur during PCP or 2,4 DCP production. In order to produce these dioxins, 2,4,5 trichlorophenol must first be made. Considerable production experience has demonstrated that the meta chlorinated phenol is rarely found in the product, making it highly unlikely that hazardous dioxins could be made.

D. Related to Reduction of Spills

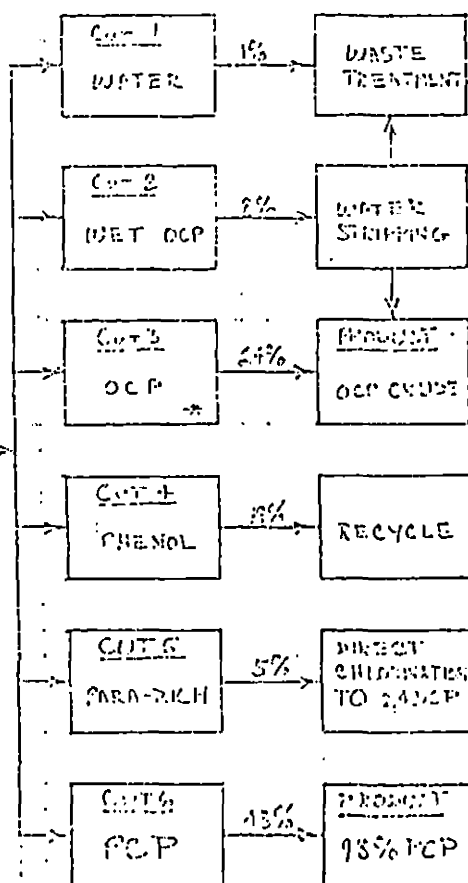
The project will provide dikes, curbs, and pads to contain spills and prevent them from reaching the plant sewer system. All organic storage and handling operations will be protected except for tank car loading and unloading.

The risk is that a tank car may be overfilled, creating a large spill which would not be contained. Instrumentation and plant operating procedures will be used to control this problem.

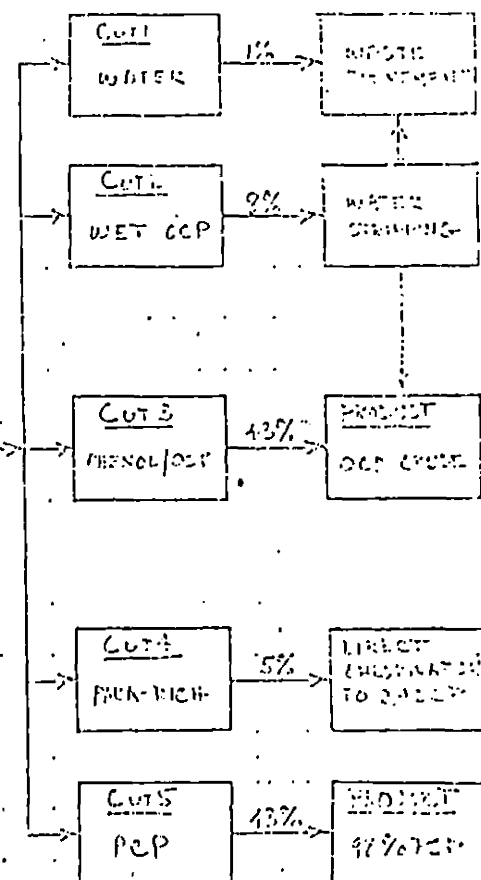
FIGURE 1
PCP PRODUCTION



BRACKET III PRODUCTION
WITH PHENOL RECYCLE



BRACKET II PRODUCTION
NO PHENOL RECYCLE



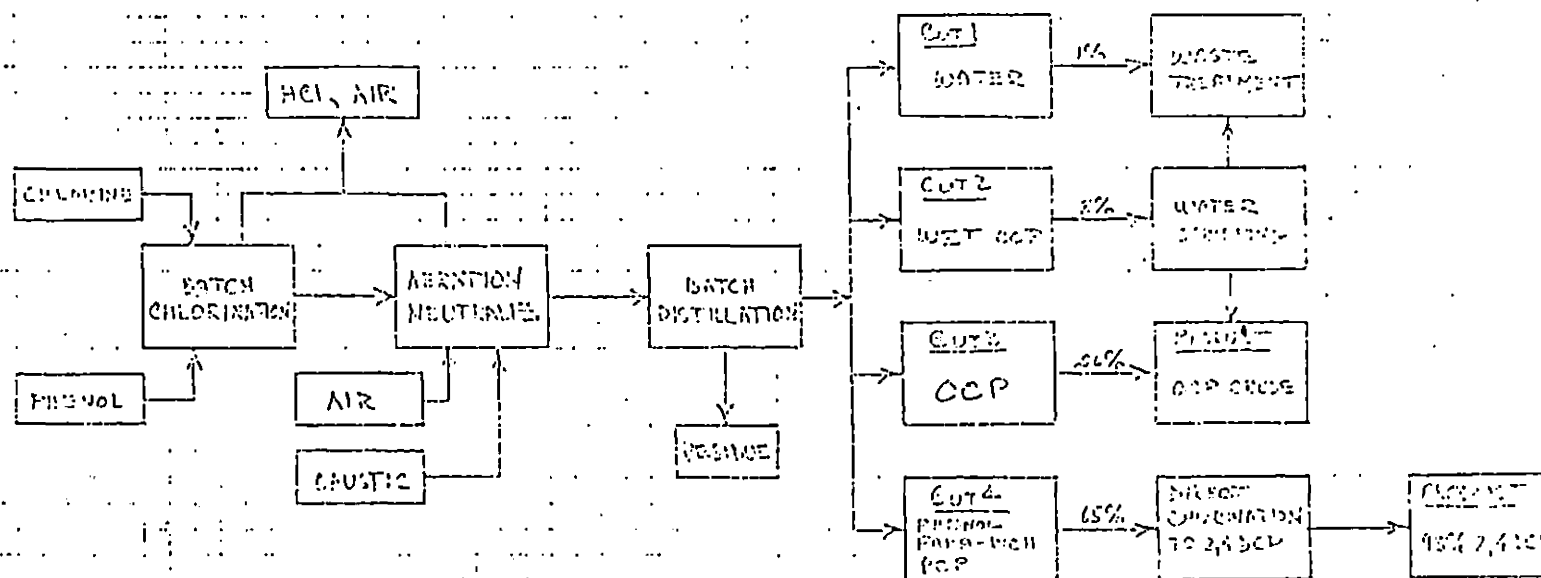
AFTER PROJECT RATE: 730 K lbs/mo.

AFTER PROJECT RATE: 965 K lbs/mo

A PORTION OF THIS CUT MAY BE CHLORINATED TO 2,4,6-CP

FIGURE 2

2,4 DCP PRODUCTION FROM PCP CRUDE



AFTER PRODUCT RATE : 2200 K lbs/mo.

FIGURE 3

WASTE TREATMENT PROCESS

