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Sauget, Illinois

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TENTATIVE AMENDMENT "C"

TITLE

Tentative Amendment "C" to the Standard Manufacturing Process Description for Refined 2,4-Dichlorophenol, dated March, 1974, Dept. 237.

OBJECTIVE

To increase distillation capacity by 42%. The capacity for distilling chlorinated phenol to 97% 2,4-dichlorophenol will increase from 6.7 to 9.5M pounds per year. Distillation of chlorinated crude orthochlorophenol to 93% and 97% dichlorophenol will also become possible at reasonable capacities.

PRESENT PRACTICE

Present operations in Dept. 237 are limited by still capacity. Although sales forecasts can be met with existing capacities, by-product fractions generation can be profitably reduced with greater distillation capacity allowing more efficient component separation and the chlorinated crude orthochlorophenol route to 93% and 97% dichlorophenol.

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PRESENT PRACTICE (Continued)

The distillation column was designed in 1967 for greater boilup provided by an external reboiler heat exchanger. Due to severe plugging and corrosion problems, this heat exchanger was removed in the early 1970's. Operations were changed to compensate for less heat input by lowering column pressures. However, significant capacity improvement is possible before flooding becomes a problem in the distillation column.

Currently, 200 psig steam (198°C. saturation temperature) is used on the still pot coils to provide heat input to the column. Maximum vacuum is used to reduce component boiling points and maximize boilup through the column. Pressure is 20 - 40 mm Hg absolute at the top of the column and 90 - 120 mm Hg absolute at the bottom. Present operating procedure for 97% 2,4 dichlorophenol (2,4-DCP) is:

Charge: The 8,900 gallons (89,000 pounds) batch is charged to the still pot by using the neutralizer circulating pump and column vacuum. Steam is turned on the still pot coils to heat the material during charge. The reboiler pump is started to improve heat transfer. The column is kept on total reflux. A sharp loss of vacuum denotes end of charge due to sucking in air from the charge tank as it empties.

Wet Fractions: After charging, the reflux ratio is changed to 45/5. The steam (200 psig) valve is fully opened, resulting in steam flow at 3,000 pounds/hour. As the wet fractions are removed from the system, the No. 6 point (vapors to condenser) temperature levels out, the column pressure drops, and the column pressure differential increases. Forty-five minutes after the 6 point has lined out, a sample is taken to the laboratory for water analysis. The batch is considered dry if there is less than 0.25% water. The still pot temperature is about 147°C. at the end of this cut.

The wet fractions, mainly orthochlorophenol, phenol, and water, are collected for several batches and then reworked to remove the water. The phenolics are sold as "crude orthochlorophenol" to pentachlorophenol manufacturers, or is used as a raw material to produce 2,4-dichlorophenol. During the rework of wet fractions, the water cut is run to an oil-water separator. The water layer flows directly to the waste water storage tank. The oil layer is returned to the wet fractions storage tank.

Low Boilers: The forward flow is diverted to a dry fractions receiver. The reflux ratio remains at 45/5 until the crystallizing point of the forward flow rises to 41.5°C. This cut is minimized by thorough chlorination of the crude feedstock. The still pot temperature is about 148°C. at the end of this cut.

Product Cut: The forward flow is diverted to a product receiver. The reflux ratio is gradually cut from 45/5 to 25/5 as the crystallizing point is kept at or above 41.5°C. As the dichlorophenol in the still pot is removed, the reflux ratio must be raised again to maintain the crystallizing point at or above 41.5°C. The still pot temperature is about 156°C. at the end of this cut.

Highboiler Cut: When a 41.5°C crystallizing point cannot be held at a 45/5 reflux ratio, the forward flow is switched to a fractions receiver. Reflux is changed to all forward and the still is run dry. The still is considered dry when the steam flow drops below 1,200 pounds/hour.

To produce 93% 2,4-DCP, the crystallizing point is maintained above 39.0°C., otherwise, the operating procedure is the same.

The above procedure is also the same for varying feedstocks. Chlorinated phenol should contain 85 - 90% 2,4-DCP, while chlorinated orthochlorophenol crude should contain 75 - 80% 2,4-DCP.

SUGGESTED CHANGE

To increase the available heat input to the still pot, 600 psig steam (254°C. saturation temperature) will be used on the existing monel coils. These coils were designed for 600 psig steam and improved heat transfer.

The coils will be provided with emergency cooling water, after the steam is shut off, in case an emergency situation related to temperature dictates an immediate cooling for the still pot. The circulating pump will be left running to promote rapid cooling. High temperature and pressure alarms, interlocked with the steam flow, will also be added.

The vacuum on the column will be controlled by a new pressure control loop. For better separations, the pressure at the top of the column may be varied during each cut. Also, the pressure drop through the column will increase due to the greater boilup provided by 600 psig steam. Top of column pressure as high as 250 mm Hg absolute may be used, as long as still pot temperatures do not exceed 185°C. Means to break column vacuum with nitrogen will be added. Related to this, an interlock will prevent emptying the cone neutralizer when charging the still pot to prevent sucking air into the still.

A specific gravity meter will be installed on the chlorinator to help insure more consistent still charges with more reproducible chlorinator batches. A new GC on the distillation column will be installed to eliminate operating with the present one. The old GLC presents a problems in obtaining parts. It also can't be used for refining 2,4-DCP because it doesn't detect 2,6-DCP or trichlorophenol. The new GC will detect these components and water. The GC's output will be given to a programmable controller to control the batch. More consistent batches are expected.

Also, the reflux ratios at the beginning of the product cut will be lowered to at least 25/5 at the beginning. It makes no sense to keep the reflux ratio high at the beginning of this cut; the low boilers will get into the product regardless.

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SUGGESTED CHANGE (Continued)

By changing the operating pressures, and therefore the temperatures, different operating procedures will be required to make better use of the changes. Startup experience will determine final operating conditions. A computer simulation indicates the approximate conditions will be:

Charge: The charge will remain the same, except the charge tank will not be pumped out until air is sucked into the still pot. This air creates a potentially flammable situation. A heel will be left in the charge tank to prevent drawing in air.

Wet Fractions: This is assumed to remain the same. Water and chlorophenols are a non-ideal system and were not simulated. Improvement may be made by trial, on startup. The endpoint for this step will be detected by the new GC rather than by samples and analysis.

Low Boilers: Operating pressures will be 65 mm Hg absolute at the top of the column and 170 mm Hg absolute in the still pot. The still pot temperature at the end of the cut will be about 163°C. Output from the new GC will determine the end of the cut, rather than crystallizing points. Otherwise, the cut will remain about the same.

Product Cut: Operating pressures will be 65 mm Hg absolute at the top of the column and 170 mm Hg absolute in the still pot. The still pot temperature at the end of the cut will be about 172°C. Again, the new GC will determine the control, and ending, of the cut. Reflux ratio will start at 25/5, then be increased to 45/5 to prevent high boilers from contaminating the product. When the level in the still pot gets down to the top of the steam coil, 600 psig steam will be shut off automatically and 200 psig steam used to complete the batch.

Highboiler Cut: This will remain the same.

JUSTIFICATION (*)

1. Savings of \$100,000 in 1980 and 1981 based on the production of less fractions by more efficient modes of operation. The savings are achievable on a continuing basis with the projected product split.
2. The existing 93% 2,4-DCP market is expected to shift to 97% based on needs for higher assay 2,4-dichlorophenoxyacetic acid (2,4-D). Capacity for meeting these sales will be marginal in 1981 without 600 psig steam, even when operating in the highest cost mode.

(*) From memo 12/20/78, D. B. Edwards to D. E. Munie and R. G. Potter, "PCP Rehabilitation Variance."

DISCUSSION

The original design conditions for the distillation column, with Linde sieve trays, were made assuming an external reboiler on the column. The reboiler was a horizontal two-pass exchange rated for 5M BTU/hour. The reboiler was an operation nightmare due to constant tube pluggage and corrosion, and was removed. Heating the still pot was then solely provided by the still pot coil. This change lowered the available heat input, which affected rates. The column was operated at the maximum vacuum achievable to maintain column boilup. The results were reduced column efficiency and throughput.

By using 600 psig steam instead of 200 psig steam, and by increasing operating pressures, the column conditions can be improved to the original design conditions. A higher column efficiency and throughput will result. The increased capacity may range from 25 to 60%.

YIELDS

An analysis of chlorophenol test samples (see Appendix for details of tests and calculations) subjected to heat for extended periods of time showed about 0.35% residue formed per day. Based on DTA tests, shorter batch times for the proposed change, and assuming half of a full batch held at a maximum temperature of about 260°C., there would be a 30% increase in residue formed. This would be an additional 150 pounds per batch, or 0.4 pound/cwt. These numbers may be assumed to be worst case since everything in the pot was considered to be at the steam temperature for the calculation. Rates of residue formation are calculated to be 0.0073 pound residue/pound pot composition/day at 260°C., or 0.00427 pound residue/pound pot composition/day at 200°C. The additional residue formed is not felt to be significant.

SAFETY

From DTA data (see Appendix), no significant exotherm or decomposition reaction is found. The operating temperature of the proposed change of increasing pot pressure to a maximum of 250 mm Hg absolute has a maximum of about 185°C. These pressures and temperatures are in accordance with the column's original recommended operating conditions.

In the past, there have been instances of sudden vacuum loss with the steam on, and the temperature of the still pot suddenly rose to 180 - 190°C. There is no record of any adverse effects from these incidents.

However, a number of interlocks will be added to protect the safety of this process:

1. Low pressure (140 psig) in the steam lines to the vacuum jets will flood the column and still pot with nitrogen. The process line to the vacuum jets will also automatically be valved off.
2. High level in the still pot closes the valve in the charge line and shuts off the charge pump.

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SAFETY (Continued)

3. Low level in the cone neutralizer pump closes the valve in the charge line and shuts off the charge pump.
4. High temperature ($190^{\circ}\text{C}.$) in the still pot causes all steam supply to the still pot to be shut off.
5. Extreme high temperature ($200^{\circ}\text{C}.$) in the still pot or button pushed by operator causes the following to occur simultaneously:
 - a. All steam supply is cut off to the still pot.
 - b. The water supply valve to the still pot coil is opened gradually.
 - c. The coil vent valve is opened.
 - d. The coil condensate valve is closed.
6. The 200 psig and 600 psig steam supply lines are protected by a double-block-and-bleed valving arrangement. An interlock prevents both supplies from being open simultaneously.
7. The valve between the process and vacuum jets closes on high pressure in the still. This interlock can be by-passed for startup.
8. Low level in the still pot closes the 600 psig steam supply system and opens the 200 psig steam supply system. This prevents using 600 psig steam when the still pot level is below the coils.
9. High pressure in the still pot alarms at 4 psig.
10. Higher pressure (12 psig) in the still pot causes the following to occur simultaneously:
 - a. All steam supply is cut off to the still pot.
 - b. The water supply valve to the still pot coil is opened gradually.
 - c. The coil vent valve is opened.
 - d. The coil condensate valve is closed.

A rupture disc on the still pot will relieve at 15 psig into a new emergency vent tank. This pressure corresponds to about $235^{\circ}\text{C}.$ on the low boiler cuts and $255^{\circ}\text{C}.$ during the product cut.

A nitrogen vacuum break will be provided on the column to break vacuum as needed, as well as to automatically guard against potentially flammable mixtures in the event vacuum is lost.

The end of the batch during the high boiler cut is run at lower pressures and with 200 psig steam. This is when the level in the still pot is lowest, and flashing from the higher coil skin temperature of 600 psig steam would result in increased residue formation. This cut is a straight takeover distillation not sensitive to column efficiency.

Follow-up DTA data will also be run on residue made by the T.P.A. This will confirm the effect, if any, on decomposition reactions as well as the predicted levels of dioxins and furans.

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QUALITY

Crude Parachlorophenol test samples, containing 3 - 5% 2,4-Dichlorophenol, were analyzed for chlorinated dibenzodioxins and dibenzofurans (see Appendix). There were no detectable tetra-chlorodibenzodioxins (TCDD), which are the most toxic of possible by-products. The analysis made no distinction between the various possible tetra isomers, but from the chemistry, it is highly improbable that we can produce the severely toxic isomers. The severely toxic isomers require laterally substituted chlorines. The present process does not experience chlorination in the meta position which results in lateral positions on the dioxins. The estimated residue would contain the following levels of dioxins and furans up through the tetra-chlorinated compounds.

Mono-chlorodibenzodioxin	8 ppm
Di-chlorodibenzodioxin	0.3 ppm
Tri-chlorodibenzodioxin	0.4 ppm
Tetra-chlorodibenzodioxin	0
Mono-chlorodibenzofuran	3000
Di-chlorodibenzofuran	370
Tri-chlorodibenzofuran	16
Tetra-chlorodibenzofuran	0.4

Concentrations of the higher chlorinated dioxin and furan compounds are expected to be well below 1 ppm either in normal operation or prior to potential rupture release. (See memo attached to B. W. Ely from J. P. Miere dated September 1, 1977, and titled "WGK Chlorophenol Process Amendment.")

These estimated levels will be confirmed by analysis once the T.P.A. is implemented. These estimated levels are not considered significant enough to be of concern. The following information on relative toxicity shows that the desired product material is in the same range of toxicity as the by-products formed.

RELATIVE TOXICITY OF CHEMICALS *

	(1)		
2,3,7,8 Tetrachlorodibenzo dioxin	LD50	Rat Oral	0.01 Mg/Kg
Penta Chlorophenol	LD50	Rat Oral	27 Mg/Kg
Hexachlorodibenzodioxin	LDLO	Rat Oral	100 Mg/Kg
Tetrachlorophenol	LD50	Rat Oral	140 Mg/Kg
Dichlorodibenzofuran	LDLO	Rat Oral	250 Mg/Kg
Phenol	LD50	Rat Oral	414 Mg/Kg
Parachlorophenol	LD50	Rat Oral	500 Mg/Kg
2,4 Dichlorophenol	LD50	Rat Oral	560 Mg/Kg
Orthochlorophenol	LD50	Rat Oral	670 Mg/Kg
2,4,6 Trichlorophenol	LD50	Rat Oral	820 Mg/Kg
2,6 Dichlorophenol	LD50	Rat Oral	2940 Mg/Kg

Comparison of Toxicity of Chlorinated di-benzofurans (DBF) **

Dichloro DBF = Tetrachloro DBF > Trichloro DBF > Octachloro DBF

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- (1) LD50 Lethal Dose 50% Kill
(2) LDLO Lowest published lethal dose.

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QUALITY (Continued)

* From registry of toxic effects of chemical substances 1975 NIOSH.

** Memo to C. C. Sisler from J. F. Pysz, 10/15/77.

(1) Presence of these chemicals has not in all cases been confirmed.

EXTENT OF DEMONSTRATION

Start up and finalization of operating conditions and procedures will require one month. Demonstration of project claims will run two weeks at full rates.

CRITERIA FOR ACCEPTANCE

1. No unexpected safety problems of unacceptable nature develop.
2. Less than 2.5#/cwt increase in residue is formed.
3. Less than 10,000 ppm monochlorodibenzofuran or equivalent scale up of other species.
4. No detectable formation of 2,3,7,8 tetrachlorodibenzodioxin (< 0.1 ppm).
5. Expected capacity increase can be achieved.

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