MAY 1965

SUMMARY

Operating limits for heat treated catalyst preparation have been defined and a Tentative Process Report is being written. All equipment for the pilot plant catalyst manufacturing unit is on order with start-up scheduled for August.

Flammability limit studies have shown allowable oxygen concentrations for 100% safe operation of oxidative chlorination units to be so low that a different feed system will be necessary. Work on redesign, to give separate injection of oxygen and ethylene in the catalyst bed, has been started in the lab. The redesigned system is expected to give better economics in CEV as well as reduce operating hazards.

EDC cracking to 99% conversion in the presence of cracking inhibitors has been achieved using garnet as a catalyst. A detailed economic evaluation is being made.

The cause of high HCl content in VCM tank cars at Springfield has been found to be stratified layers in the rundown tanks, spheres, and tank cars. Multi-level samples are being taken from tank cars for quality control and mixing studies are in progress.

Springfield reports that the cause of the paste resin coagulation problem is concentration of unknown impurities in a free water-phase which collected in their storage tanks during May. Study of the impurities present in the water at Springfield and the water at Texas City are in progress.

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to simulate a spectrum of impurities and determine if there is one present that might give problems in the cracking step. To date, no impurity has been found that inhibits reaction appreciably. This includes an extensive amount of chloroprene - one of the better inhibitors. Estimates would indicate that in our present chlorine catalyzed crackers, a maximum of 5-10% conversion would be achieved with the 2-1/2% chloroprene in the feed. Using the garnet catalyst, 100% conversion was realized. Attempts were made to make a very accurate material balance around the cracker and a 98% closure was obtained. Work has been suspended on this cracking operation until a detailed economic evaluation is completed. Future work will depend on results of this evaluation.

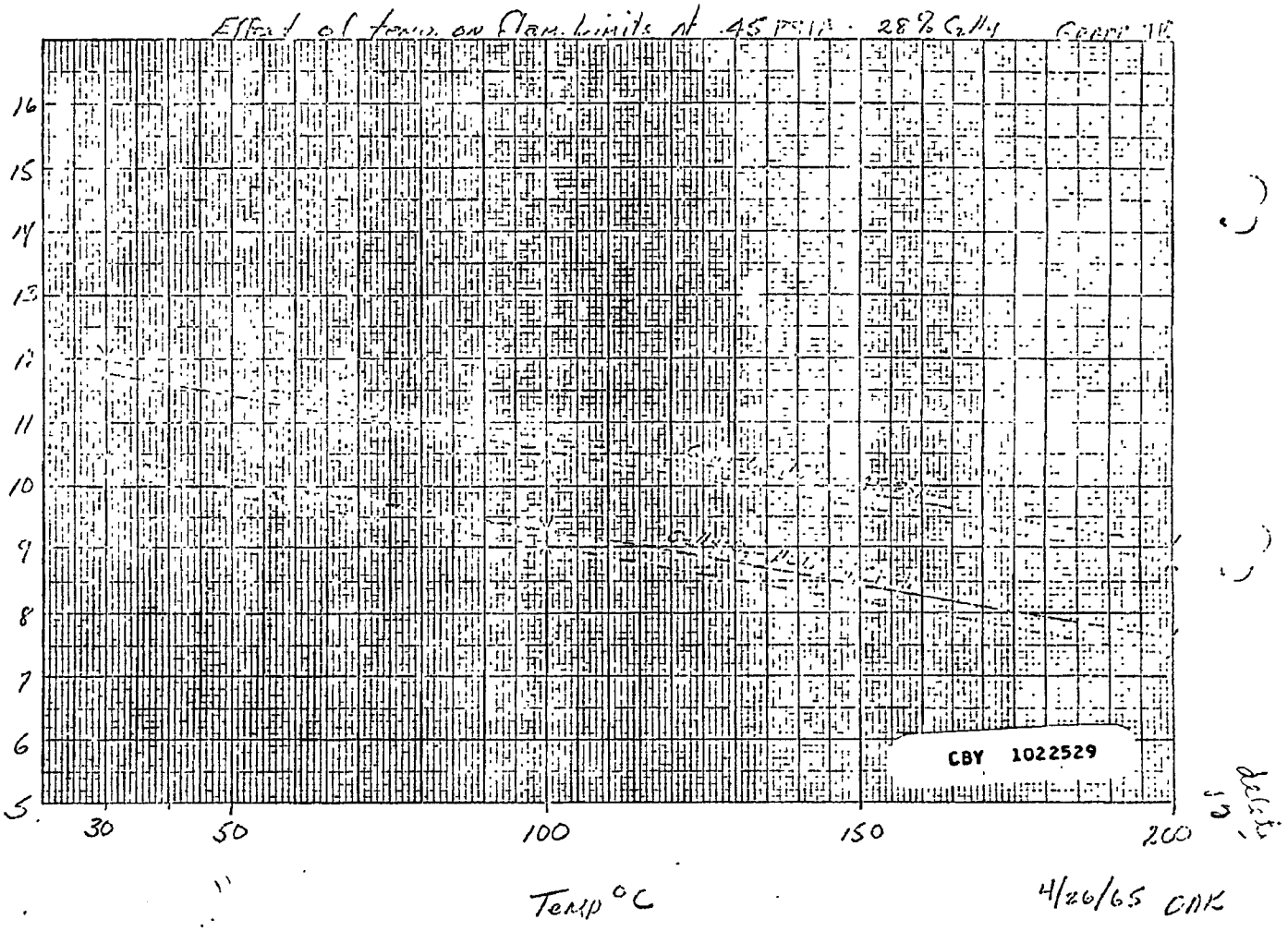
Flammability Studies

Flammability data obtained at Texas City were reviewed with Fenwal in an attempt to determine why the major differences between Texas City and Fenwal data exists. The only obvious difference was in the ignitors used. Pictures of ignitor voltage drop taken from an oscilloscope indicated the Fenwal ignitor takes about ten times as long to discharge as does our ignitor, approximately 600 microseconds vs. 70 microseconds. Fenwal will do additional work to check their ignitor reproducibility. In any case, no reason for not accepting our data could be found, it is much more reproducible than Fenwal data and must be used.

Additional work has been done to determine the effect of temperature and pressure on flammability limits for the systems ethylene-HCl-O_2 and ethylene-N_2-O_2. An increase in either temperature or pressure decreases the allowable oxygen concentration. Results are shown in Graph IV and V. Extension of the study of these systems at 45 psia and 200°C has shown a deflection in the allowable oxygen concentration between 10% and 19% ethylene when nitrogen is used as a diluent. These data are shown on Graph IX. Mixtures of HCl and N_2 as diluents have also been studied with results shown on Graph VI.

Flammability studies have been extended to include three of the impurities normally found in oxidative chlorination feeds, methane, ethane, and CO. Data are shown in Graphs VII, VIII and X. Graphs I, II, and III were in last months report. Two surprising things were found:

1. Methane and ethane have very close to the same allowable oxygen concentrations. Both have much higher allowable oxygen concentrations than ethylene.



4/26/65 CNK

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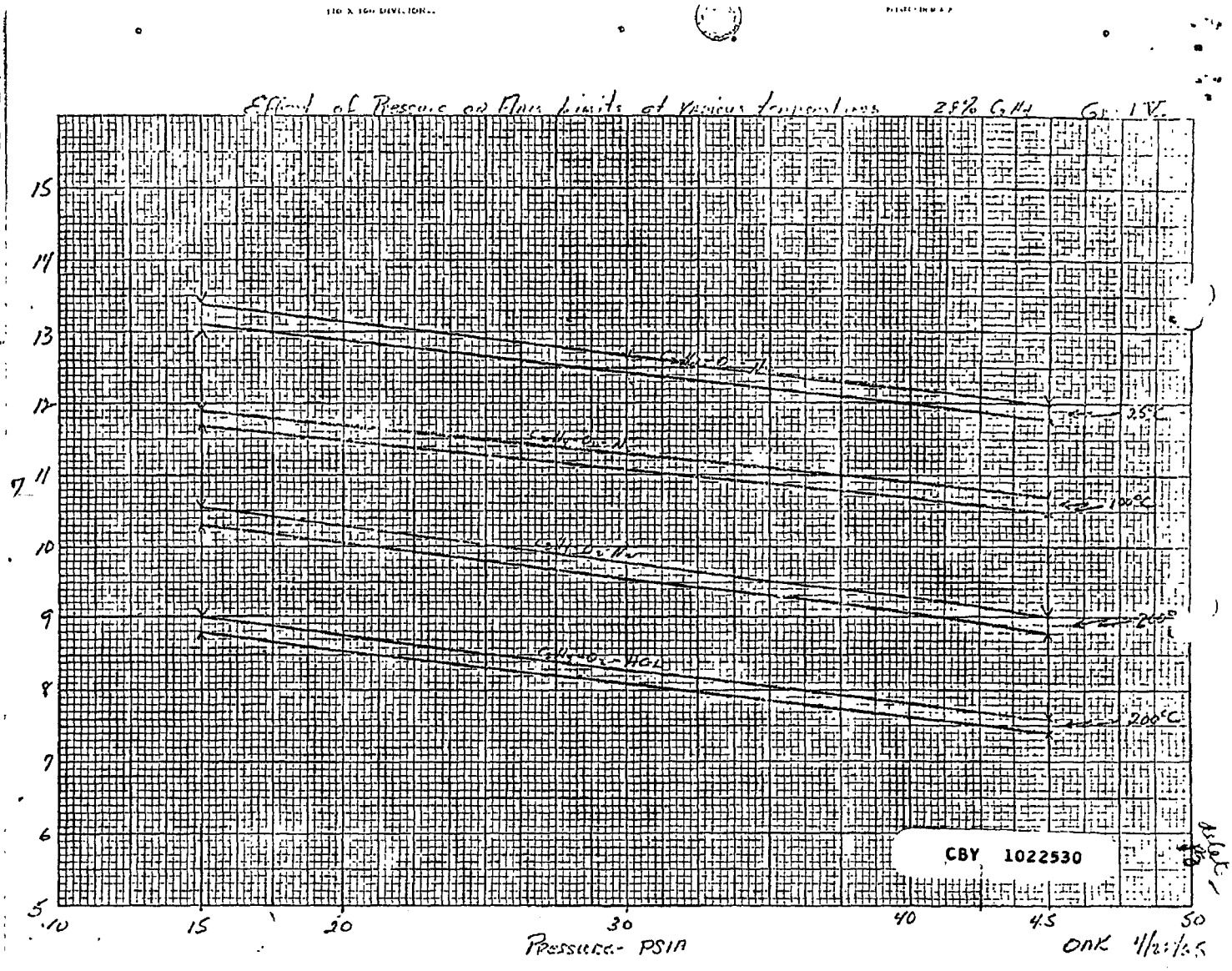
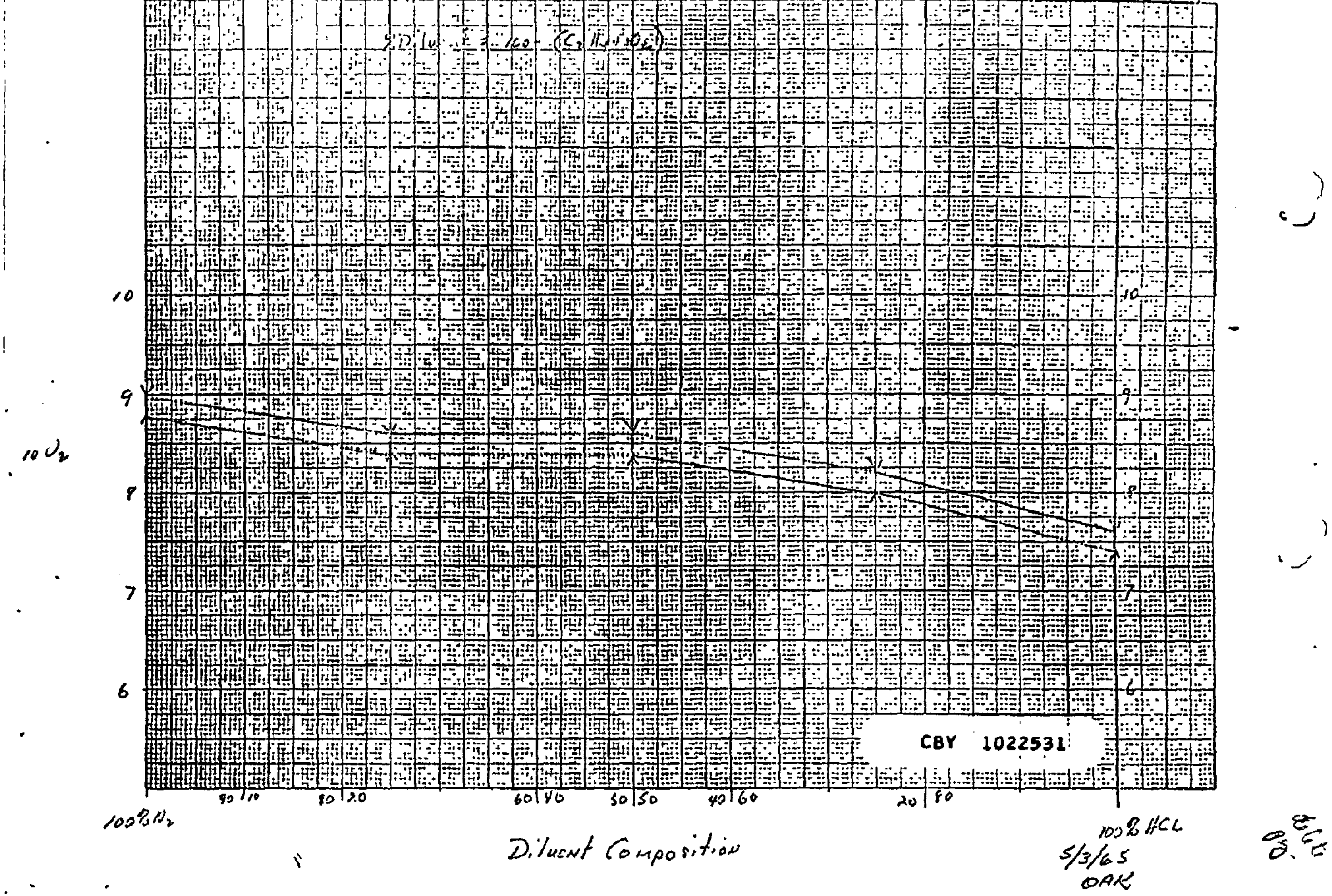

Effect of Pressure on flam limits at various temperatures 25% CH4 Gr. IV
15
14
13
12
11
10
9
8
7
6
5
25°C
100°C
200°C
CBY 1022530
.10
15
20
30
40
45
50
Pressure- PSIA
ONK 4/2/65

RSV0032357

Effect of diluent Composition on Flam Limits for 28% C_2H_4 at 200°C and 45 PSIA



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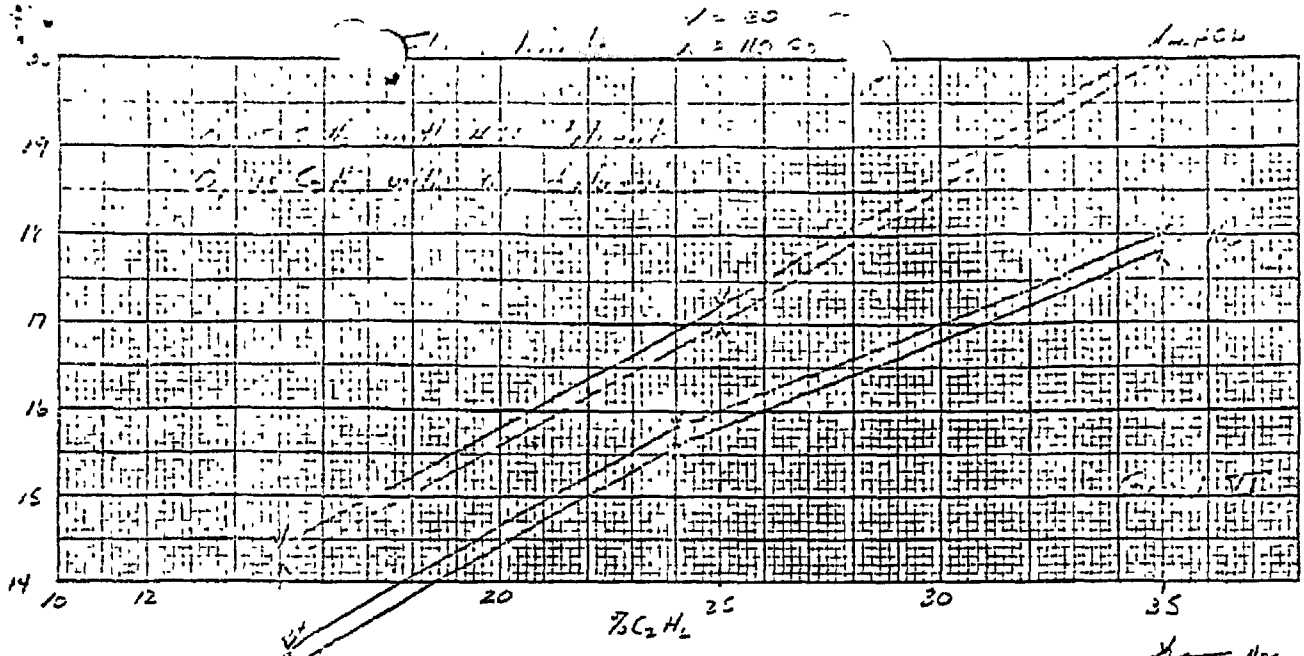

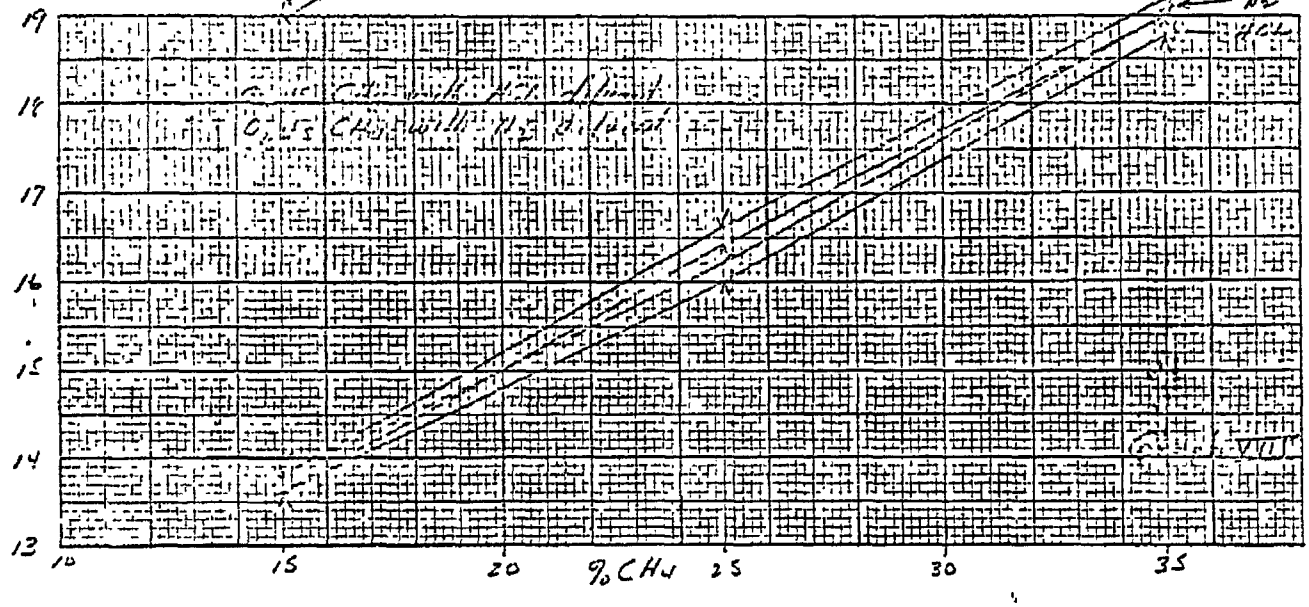

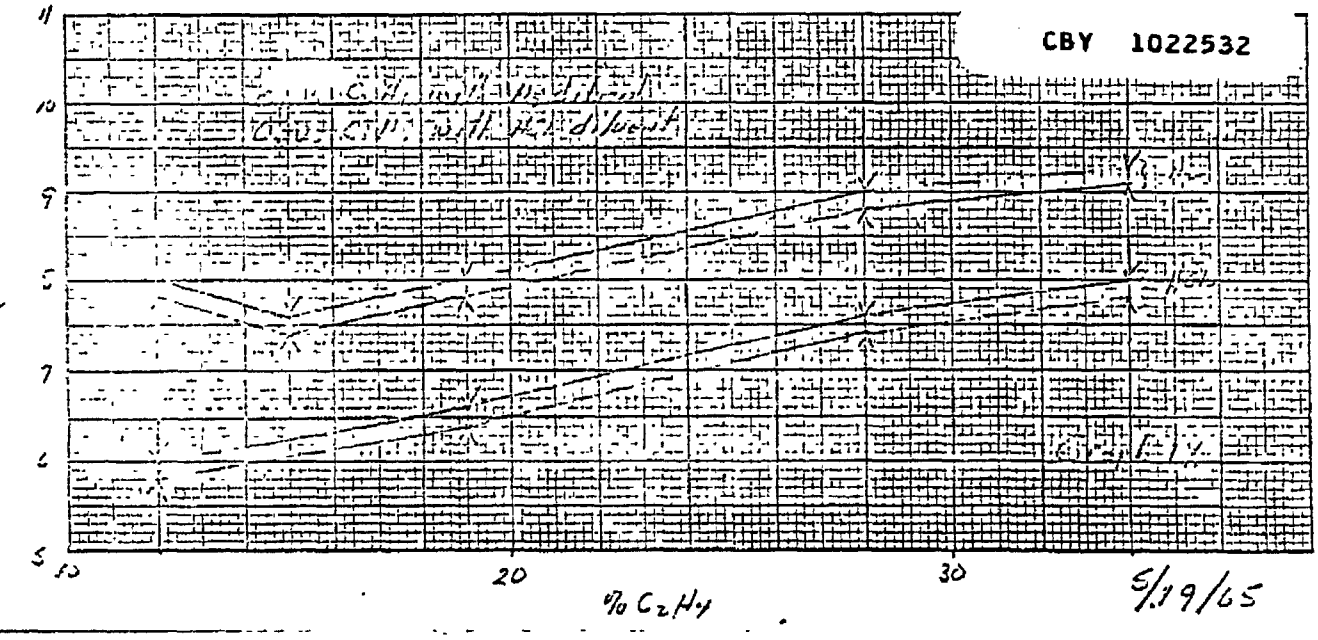

CBY 1022532

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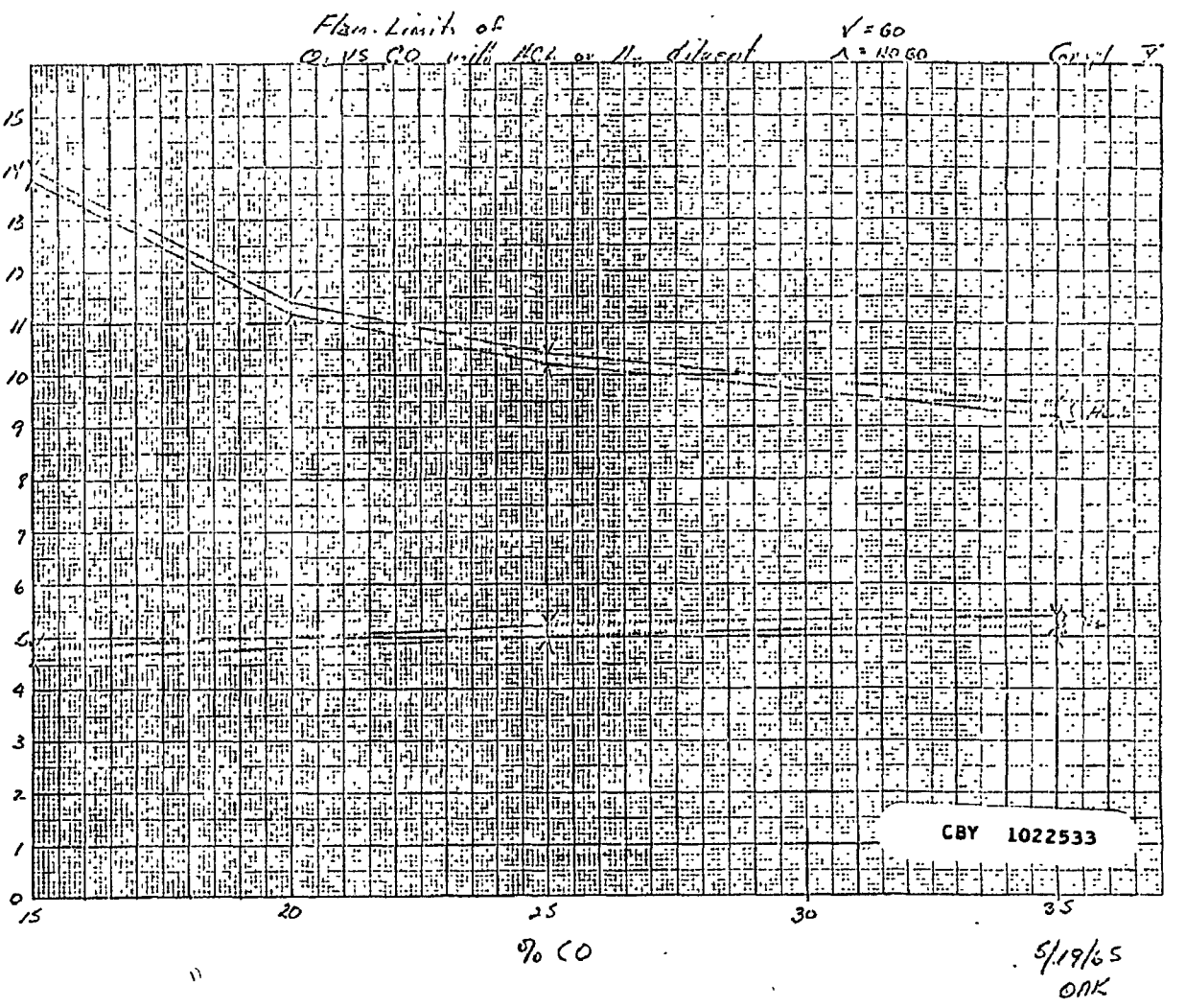

5/19/65
OAK

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2. The relative effects of HCl and N_2 are not the same for each material tested. HCl is the best diluent with ethane and CO, N_2 the best with ethylene, and there is little difference with methane. This suggests that reactions other than oxidation are taking place in the high temperature arc. Analytical data will be required to pin this down.

Possible ways of modifying the oxidative feed system to allow operation with feeds which would be flammable are being considered. Engineering is designing a feed manifold for the EIF plant as one method. Data on pressure developed, with various feed compositions, when feeds are ignited are being obtained for use in design of this system. Means of separate injection of feeds are being tested in the lab and will be tested on a six-inch glass unit. This system is being considered for Dept. 26.

Project 1043 - Oxidative Chlorination Catalyst Improvement

Lab work to define operating ranges for preparation of heat-treated catalyst continues. Tests to define limits of time and temperature necessary to prepare active catalyst have shown a temperature of 450°C to 550°C to be satisfactory with reaction time of 5-8 hours. Temperature as low as 400°C is acceptable but requires longer reaction time. Longer time at temperature is not detrimental, at least up to 21 hours tested.

Commercial copper chloride has been tested (two sources) and found to be satisfactory. However, grinding to a finer particle size than commercial samples available was necessary. An attempt is now being made to obtain commercial material which passes through a 100-mesh screen (about 10% of present material is larger than 100 mesh).

A Tentative Process Report for catalyst preparation is being written. Major equipment is on order and design work is almost complete. The reactor should be fabricated and installed during June for testing in July. Long delivery items are scheduled for July, which would allow August start-up.

Project 1044 - VCM Quality, Cost, Capacity Improvement

Quality Improvement

Further HCl sampling and analysis technique studies have shown stratification in rundown tanks, storage tanks, and tank cars to be the cause for failure to consistently detect presence of HCl in the VCM. Samples of VCM in rundown tanks were taken by PTE from April 25 to May 2 in addition to the normal production samples. No

significant difference between Production and PTE samples were found (Table 1). Samples were taken by PTE from three levels of VCM in tank cars between May 5 and May 14th. The HCl concentration was found to vary significantly between top and bottom VCM levels in some tank cars, Table 2. Production reported that sampling frequently during a rundown tank transfer showed significant differences to exist in HCl content of VCM throughout the tank. Piping modifications were made 5/15 to increase mixing in the rundown tanks by using the 300 GPM transfer pump as well as the 70 GPM circulation pump. This change was an improvement but did not completely mix a tank in 13 hours as shown by production samples and tank car (3 level) samples. Studies of equipment needed for complete mixing in rundown tanks are in progress by PTE and Plant Engineering with a proposal expected by June 1. A recommendation was made that Material Handling sample each tank car at three levels for HCl analysis (Done since 5/15).

Springfield Research studies on the paste resin coagulation problem show the cause to be impurities concentrated in a free-water phase which appeared in their storage tanks. It was reported that a small amount of this water added to a "coke-bottle" test gave laboratory duplication of plant coagulations. Further test work is planned to identify compounds present in the water and to determine which ones cause the paste problem. The VCM processed just prior to the finding of the free-water was a test car (MCPX 21014) made during a period of water surge in the VCM product column while the VCM drier was being by-passed. Examination of an apparent polymer in one of the tank cars returned from Springfield turned out to be a frozen water emulsion. This was taken from the middle of a tank car, so we are evidently obtaining a material that is intermediate in density to water and VCM. Degassing of this ice through liquid EDC has resulted in the appearance of three or four unidentified peaks on the chromatograph that has been developed for light-ends analysis. If these compounds can be concentrated, then identification will be attempted by MS-GC.

Plant Engineering is preparing a cost estimate for a second VCM drier which would eliminate the once per week surge of water in product VCM. The control laboratory was requested to reactivate the equipment and to demonstrate ability for water analysis on product VCM samples.

TABLE I

Tank No.	Date, 1965	Time, Hrs.	HCl, ppm
455	4/28	1515	<.1
456	4/28	1600	<.1
T4-3	4/28	1600	<.1
457	4/28	0625	<.1
457	4/28	0730	<.1
458	4/29	1430	<.1
458	4/29	1620	<.1
459	4/29	0600	<.1
460	4/30	1545	<.1

CBY 1022536

TABLE II

PTE Samples From Tank Cars

Car No.	Date, 1965	Gauge-Rod Positions (Normal) ppm HCl	Gauge-Rod Positions (Lowest) ppm HCl	Test Tube (Car Bottom) ppm HCl
MCPX 21002	5/5	<.1	<.1	<.1
MCPX 21000	5/5	0.3	<.1	<.1
MCPX 21005	5/6	1.0	1.0	* No Sample
MCPX 33002	5/6	<.1	0.3	<.1
MCPX 21007	5/7	<.1	<.1	2.5
MCPX 33004	5/7	<.1	<.1	<.1
MCPX 33016	5/10	<.1	1.0	<.1
MCPX 33024	5/10	<.1	<.1	<.1
MCPX 33015	5/10	<.1	<.1	<.1
MCPX 33005	5/11	<.1	<.1	0.5
MCPX 33025	5/12	<.1	<.1	<.1
MONX 14954	5/13	<.1	<.1	* No Sample
MONX 14961	5/13	<.1	<.1	* No Sample
MCPX 33010	5/14	<.1	<.1	<.1
MCPX 33003	5/14	<.1	<.1	<.1
MCPX 33006	5/17	<.1	<.1	<.1

All samples were clear and colorless with no suspended matter except MCPX 33025 (5/12) which showed a small amount of suspended matter similar to cigarette ash in the sample taken at the normal gauge-rod position.

* Unable to take samples due to leaking fittings.

CBY 1022537

Product VCM Column Stability

An 8 point Sanborn recorder is now operating to monitor temperature profile and pressure drop across the lower part of the column. Occasional partial or complete flooding at the 40th tray or below has been detected. Temperature records show a cycle of about 20 minute duration occurs most of the time but at varying amplitudes with the flooding incidents being more frequent when the cycle amplitude is large. The pressure drop record does not show the 20 minute duration cycle at all but often shows a more rapid cycle of about 3 minute duration prior to onset of flooding incidents. No connection between flooding incidents and control of HCl in product has been found. Collection and observation of the data will continue but little progress in analyzing it is expected until after completion of work on HCl control.

Optimization of Acetylene Purification

The review of the safety of handling acetylene at high temperatures indicated that it would be safe to drop the required water concentration in the acetylene to 30% instead of the 42% previously specified. This relieves the reactor from highly corrosive conditions and will allow more leeway in keeping out of the corrosive range.

The acetylene purification system was brought on stream on May 9th. However, on May 14th a tripout occurred with indications of a tube failure. Operating data for this five day period is being reviewed for other possible inter-related causes for the tripout.

Dept. 23 Caustic Automation

The system continues to operate satisfactorily. Report to be completed in June. Project was closed out.

Cracking VCM Column Control (22D7)

A PAFE covering the installation of the 22D7 feed forward control system is circulating for approval.

Improve Raw Material Accounting and Weight Recovery

A brief discussion with the Yield Department revealed that the C_2H_2 in the acetylene purification recycle gas is not being included in the acetylene distribution balance due to lack of data. A

A set of samples was taken in Dept. 26 for material balance calculations in mid-May. Calculations will be complete by end of month. Two more material balances will be made in June to determine reproducibility and stream compositions at current "standard" operating conditions.

Work will begin in June on a computer program to make material balance calculations in Dept. 26. Target date for completion of program is July 15.

In view of the flammability report of last month, a recommendation has been made that the operating department reduce the allowable oxygen concentration to 9%, which is about 1% below the allowable limit as defined in last month's report. Operation has been smooth at this lower oxygen concentration.

Oxidative Chlorination Optimization

Collection of operating data has begun. Data correlation will begin in June and completed by July 31.

Minor Approved Capital Projects

Job No. 12805 - 22H1, EDC Cracking Furnace Controls

An extensive study of the automatic Cl_2 control system costs is complete. A letter is being prepared describing the history of the project from its initial concept to the present, showing the effect of changes of the control system design on the project costs. It has been reported that approval of the PAFE supplement is imminent. Work will resume as soon as official approval is received with installation complete by August 31 and the project complete by September 30.

Tar make, although slightly higher in April, is being held in 5 lbs tar/100 lbs of cracked VCM range by manual Cl_2 control. See Figure I for the tar make history in VCM plant.

Job No. 14858 - Pilot Plant Catalyst Manufacturing Unit

Equipment is on order with electric heater and off-gas scrubber scheduled for delivery in early July. The reactor will be shop fabricated. Dismantling has been completed. Start-up is scheduled for August.

Next Job on Agenda

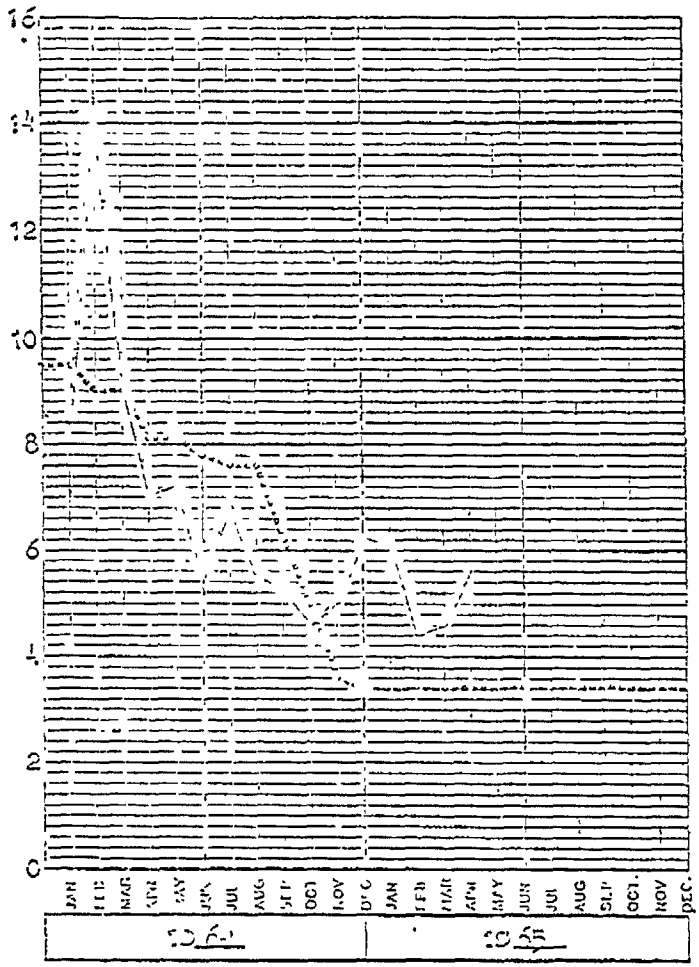
Vinyl chloride from ethane pilot plant design.

Figure 1

CROSS BAR MIXE

Departments 22, 23, & 26

1964-1965



lbs Tar
100 lbs Cracked VCM

CBY 1022540

RSV0032367

II. MISCELLANEOUS

T. P. Li presented a paper at the Monsanto Catalyst Conference on May 24.

J. C. Parks, T. E. Shirley and W. D. Staten attended the Southwest Area Conference on Industrial Relations in Houston on May 13 and 14.

W. R. Johnson and O. A. Koskela visited Fenwal, Inc. on May 6th to discuss differences in flammability data.

Our work on oxidative chlorination of C_2 hydrocarbons was discussed with two visitors from Societa Edison (Cavallo and Renaldi). This is part of our contract for exchange of information. A trip to discuss their work on oxidative chlorination of methane is tentatively scheduled for September.

Personnel

Group 13

Technical	Lab Technicians
S. B. Walker	G. L. Biggs
T. P. Li	R. J. Armstrong
O. A. Koskela	

Group 15

E. H. Cause	P. E. Lutes
R. L. Harmett	R. D. McGrew
J. C. Holland	C. G. Standard
C. J. Lamonte	
H. S. Leach	
G. Mayorga	
J. C. Parks	
J. L. Price	
T. E. Shirley	
J. D. Shoemaker	
T. C. Singleton	
W. D Staten	

III. CHART 2

CBY 1022541

Attached

W. R. Johnson

J. W. Kongable

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SUMMARY OF MAJOR PROJECTS APPROVED - May 31, 1965

VINYL CHLORIDE

Request No.	Title	Authorized Appropriation	Estimated Expenditures	Target Date of Plant Start-up	Predicted Plant Start-up	Comments
26	Reactivated Oxidative Chlorination Facilities	$ 230,000	$ 234,153	January, '63	In operation	Catalyst level indicator was ordered in May. This will complete installation of facilities for this project. An overrun of no more than 5% is expected.
	TOTAL - VINYL CHLORIDE	230,000	234,153			

SUMMARY OF PAPE'S APPROVED - May 31, 1965

PAPE No.	VINYL CHLORIDE					
12805	22H1 Chlorine Controls	42,000	42,104	Sept. 1964	3rd qtr. '65	Supplement for $13,900 circulating now.
14858	Pilot Plant Catalyst Manufacturing Unit	30,000	4,000	Aug. 1965	Aug. 1965	Equipment ordered. Major items scheduled for early July delivery.

CBY 1022542