PROGRESS REPORT

TECHNICAL SERVICES DEPT. – W. G. KRUMMRICH PLANT

JOB NO.	REPORT NO.	DATE
91370:3794	3	3, 20, 68

W.G. KRUMMRICH PLANT		RESEARCH	GENERAL OFFICE	OTHERS
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* TO RECEIVE DETAIL SECTION

TITLE: IMPROVE AROCLOR QUALITY

PERSONNEL: R. M. McCutchan (T. E. Greenman)

PROBLEM: Define operating conditions for improved quality Aroclor production in batch plant, both before and after start-up of continuous chlorination plant scheduled for 12/2/68.

SUMMARY

The only process change anticipated or recommended to date is to chlorinate at 195°C instead of 150°C. This insures that the 1967 quality level will be maintained during 1968 in spite of the probable increase of bromine in the chlorine supply. A small improvement in quality may result. This change will be accomplished by 4/1/68. Other work to be accomplished during 1968 pertaining to Aroclor quality in the batch plant is:

	EDC
1. Evaluate tangential separator for Still #1.	6/1/68
2. Establish re-lime and boil-down frequency.	5/1/68
3. Make nitrogen blanketing system operable.	5/1/68

With the start-up of the new plant, changes in the batch plant operations which affect quality will be:

1. Catalyst addition (if any) to the crude 1142 to be established.
2. Chlorination temperature will continue to be 195°C.
3. Still #1 will be used for 1260 only and Still #2 for boil-downs only.
4. For routine use, porocel columns will replace the Sparkler filter. The nitrogen blanketing system will be extended to include the columns and auxiliary tanks.

ACKNOWLEDGEMENTS

Appreciation is expressed for the cooperation and efforts of those directly involved in improving Aroclor quality: D. C. Armstrong, V. Brawley, B. L. Caraway, J. A. Gloeckner, C. Hamlet, and H. Ray.

DSW 296888

DETAILS

I. CHLORINATION

A. Temperature and Catalyst

1. Temperature and catalyst concentration are the two most important variables in producing high quality crude Aroclors. The process description calls for 150°C chlorination temperature and a catalyst concentration of 0.05%. PR & D work indicated that at 200°C or at 0.2% $FeCl_3$ concentration, thermal chemical chloride (TCC is a measure of stability) analysis of less than 0.15 ppm could be achieved. Analysis at normal conditions in the laboratory had a range of 0.16-0.56 ppm TCC. The effects of high temperature and high catalyst level were not additive. The corporate goal for Aroclor 1242 is 0.10 ppm TCC.

   Extensive plant testing of the PR & D findings were carried out. (For details of PR & D work and initial plant tests see reports 91370:3794-1 and 2 by J. A. Gloeckner.) The first phase of the plant tests was to analyze chlorinator "profiles" under varying conditions. A profile is one crude sample from each of five chlorinators. The crude sample is then distilled and earth treated in the laboratory before analysis. Results of this work are as follows:

No. of	Conditions		TCC Analysis	
Profiles	Temp	Catalyst	Average	Ave. Range
21	150°C	0.05%	0.62 ppm	0.54 ppm
5	195	0.05	0.29	0.10
2	195	0.20	0.36	0.16

   Plant results confirm laboratory findings, but the improvement was not as marked (<0.15 ppm TCC in the lab vs 0.29 in the plant). At 195°C, quality is more consistent as indicated by the reduction in range from 0.54 ppm TCC to 0.10 ppm. For similar TCC improvement, high temperature is favored over high catalyst because $FeCl_3$ tends to foul spargers, valves and piping.

   The second phase of plant testing was to produce a storage tank of Aroclor 1242 (15-20,000 gallons) under standard conditions, and immediately follow with a storage made under high temperature conditions. Biphenyl quality does vary, but producing storages consecutively minimized this effect.

I. CHLORINATION (Continued)

1. Cont'd

This test was carried out six times with these results:

1242 Storages, TCC ppm

Test No.	Date	Lot Nos.	150°C 0.05% $FeCl_3$	195°C 0.05%	195°C 0.20%
1	6/28-7/2	KI-447 & 448	0.53	-	0.28
2	10/9-11/67	KI-471 & 472	0.38	0.30	
3	10/23-27	KI-476 & 477	0.41	0.26	
4	11/12/-14	KI-480 & 482	0.50	0.37	
5	11/25-27	KI-488 & 489	0.64	0.35	
6	12/22-29	KI-492 & 493	1.81	0.40	

The only explanation for the 1.81 analysis is that most of the biphenyl for lot KI-492 came from a tank car that was analyzed later and found to contain 160 ppm H_2O. The biphenyl used for lot KI-493 analyzed at 75 ppm H_2O, a more "normal" level.

Discounting Test 6, the average improvement in TCC when going from 150°C to 195°C was 0.49 ppm to 0.31 ppm.

High temperature Lot KI-448 was life tested at Electric Utilities and found to be "equal to" or "slightly better than" the Aroclor normally sent them by WGK.

Little work has been done with Aroclor 1254, but the response to chlorinator condition changes should be very similar to 1242. This was verified by two 1254 profiles, one at 150°C and the other at 195°C.

As soon as instrumentation changes can be completed all chlorination of biphenyl in the batch plant will be done at 195°C.

2. Starting chlorination temperature was of concern because under normal conditions chlorination is begun at about 110-120°C, the temperature of the biphenyl in storage. Heat of reaction takes the temperature to 150°C in about one-half hour and to 195°C in about one hour. Laboratory work could not establish that a harmful effect was produced by beginning chlorination at the lower temperature. The chlorinators are steam jacketed but the heat transfer is very poor and so this quality aspect was not checked in the plant.

I. CHLORINATION (Continued)

3. Catalyst particle size as well as concentration was considered. It was originally observed that the particle size of an Anniston $FeCl_3$ sample was much smaller than normal WGK $FeCl_3$, although both get catalyst from the same supplier, McKesson & Robbins. A WGK sample was pulverized and resulting particle size determined. Later it was noticed that WGK $FeCl_3$ was not always coarse, but that it varied. Since McKesson & Robbins is the only domestic supplier of anhydrous ferric chloride, and since particle size has not been definitely linked to Aroclor quality, no further work was done. For a comparison of $FeCl_3$ particle size see Appendix A.

4. Circulation of the catalyst prior to chlorination gets as much ferric chloride into solution as possible (about 0.03%). During several test runs the biphenyl/catalyst mix was circulated for one-half hour before chlorination. No significant quality improvement resulted.

5. Basket removal from the chlorinators was completed during December 1966. Electrical grade 1242 quality (all at 150°C) before and after catalyst basket removal was as follows:

Date	No. of Lots	Catalyst Baskets	TCC ppm	Resistivity x 10^9	Power Factor
1966	35	Yes	0.59	2,650	2.25
1967	37	No	0.45	3,625	1.50
1968 YTD	6	No	0.34	3,025	2.01

Removal of the catalyst baskets was the only known process or equipment change made between 1966 and 1967. While it cannot be said that basket removal has improved quality, neither has it degraded quality.

6. The level of catalyst addition to crude 1142 after the new plant start-up is yet to be determined. If carry-through is sufficient, no addition may be necessary to chlorinate to 1148, 1154, and 1160 in the batch plant.

B. Sparger Design

The following sparger designs have been used in the chlorinators:

1. Pancake design, holes up
2. Pancake design, holes down
3. Ring with crossbar, holes up
4. Cross-arm, holes down

DSW 296891

I. CHLORINATION (Continued)

B. Sparger Design (Cont'd)

Aroclor quality cannot be correlated to sparger design in the plant. It has been observed that when the sparger holes are up, they become plugged with ferric chloride. The drain hole(s) also plug. If the chlorine line enters the side of the sparger, the area immediately above the entry erodes away. This is a maintenance problem and indicates uneven distribution of the chlorine gas. For these reasons the cross-arm design (See Appendix B) is the replacement being used in the batch plant, and is approximately the design to be used in the new plant.

C. Circulating Pumps

Unless excellent seals are available, it is better to steam trace the circulating pumps than to use back plates. At least in one instance water was leaking into the process stream at the circulating pump. Hydrated ferric chloride is not a catalyst to the chlorination reaction.

D. Filtration of Crude

Undissolved ferric chloride does not harm crude aroclor (there is some evidence that it is desirable) but it can become a maintenance problem and operational nuisance. At a 0.05% concentration it can be "lived with". During plant tests using 0.20% ferric chloride the crude was filtered with a Fulflow filter which was available (54-10" cartridges). Glass filament cartridges with a 5 micron rating removed about two-thirds of the undissolved catalyst. Each set of cartridges would remove only 40-50 lbs. of undissolved catalyst before the pressure drop across the filter reached 50 psi and the rate was very slow.

Obviously, the above filtration method would be appropriate only for tests of relatively short duration. If routine filtration is needed a centrifugal filter capable of producing relatively high G's is needed. Estimated cost of purchase and installation is $30,000 (± 25%) for a 40 gpm rate.

E. Off-Gas Condensate

At 150°C chlorination, off-gas losses represent a 0.6% biphenyl yield loss worth $7,000 in 1968. At 195°C, the losses amount to 3.5% or $37,000. This increased loss (worth $30,000 in 1968) closely follows the relative increase in vapor pressure. (See Appendix C). By 5/1/68 the old Brink demister elements will be replaced and losses will be remeasured.

I. CHLORINATION (Continued)

E. (Cont'd)

In the batch plant off-gas condensate is sewered. With the start-up of the new plant, condensate from all the chlorinators will be used periodically for non-electrical grade Aroclor production.

F. Biphenyl Quality

Methyl diphenyl is a known impurity in biphenyl which can cause instability. This impurity seems to be under control in the biphenyl process at Anniston. Water content is being questioned, however, for water can hydrate $FeCl_3$ and make it useless as a catalyst. On two specific occasions water was suspect of causing problems:

1. Biphenyl would chlorinate only very slowly in the lab and when analyzed contained 120-180 ppm H_2O in the flaked material.
2. Aroclor 1242 produced in the plant analyzed at 1.81 ppm TCC whereas normal is 0.3-0.6 ppm. A tank car sample of the biphenyl contained 150 ppm H_2O.

From several samplings, 30 ppm H_2O in tank cars and 50 ppm H_2O in flaked biphenyl appears "normal". A firm baseline will be established by daily sampling and analysis of the biphenyl storage tank to begin by 4/1/68. Further work will depend upon results of routine analysis.

G. Chlorine Quality

Under normal operating conditions, 500 ppm Br_2 in the Cl_2 supply can cause Aroclor instability as demonstrated in the laboratory. A test was run in the plant where chlorine with 700-800 ppm bromine was used to chlorinate biphenyl at 195°C and 0.20% $FeCl_3$. A "normal" analysis resulted:

Thermal Chemical Cl_2 Chlorides	0.47 ppm
Resistivity x 10^9 ohm-cm	5000
Power Factor, %	1.56

This work resulted from an anticipated contract to purchase Esterhazy KCl for chlorine production in the DeNora plant at a raw material savings of $1 M/year. This KCl may have as much as 500-600 ppm bromine. At present the Esterhazy KCl received averages 400 ppm Br_2. The former level (prior to mid 1967) was about 200-250 ppm Br_2.

By 4/1/68 the bromine content of the chlorine actually received in the Aroclor department will be monitored on a routine basis. This was done on a spot basis during July-August 1967 and the bromine level was 100-160 ppm.

II. DISTILLATION

A. Tangential Separator

To date there have been no quality problems identified with Still #2. Periodically, color is a problem with Still #1, especially when trying to run at higher rates. It is thought that the color is due to entrainment. Still #2 is equipped with a separator different in design from #1 separator. Since full capacity is needed to meet the 1968 sales forecast, a new separator for Still #1 will be evaluated by 6/1/68.

B. Re-Lime and Boil-Down Frequency

There have been no known quality problems due to re-liming or boil-down frequency. This frequency, however, has not been established and has been left to the judgment of the department foreman. This is an unnecessary responsibility and could lead to quality problems. PR & D will establish a re-lime and boil-down frequency by 5/1/68.

III. EARTH TREATMENT AND STORAGE

A. Attapulgus Clay versus Bauxite

In a brief test attapulgus clay and bauxite were compared for the purpose of improving Aroclor electrical properties. The following conditions were used to treat 2,000 gallon batches of distilled Aroclor 1242:

Kind of Earth	Lbs.	Time	No. of Runs	Average Final Power Factor
Atta. clay	20	1/2 hr.	5	0.71%
Atta. clay	60	2 hrs.	2	0.63
Bauxite	20	1/2 hr.	3	0.49
Bauxite	60	2 hrs.	2	0.80

After the indicated agitation time the batches were circulated through a Sparkler filter. As soon as circulation began, power factor readings were taken on a temporary in-line instrument until equilihrium was reached. See Appendix D for results.

Because of the briefness of the test and the inaccuracies involved in taking readings, it can only be said that there is no obvious difference in clean-up properties between attapulgus clay and bouxite. No further work is planned.

III. EARTH TREATMENT AND STORAGE (Continued)

B. Porocel Column

Part of the current Aroclor expansion is the installation of four porocel columns, one for each major liquid Aroclor produced. These will be used for up-grading the electrical properties instead of the current blending and filtration procedure. Excellent results have been obtained with the column at Anniston. On one occasion two samples of distilled un-earth-treated Aroclor 1242 produced at WGK was column treated at Anniston to a TCC of 0.12 ppm on each. By batch treatment TCC was 0.38 and 0.30 ppm. For other results and plant scale-up details see J. G. Bryant's report 370-322-19.

C. Nitrogen Blanket

The present nitrogen blanketing system on the finished goods storage tanks has never worked properly and has not been in use. It will be made operable by 5/1/68. All new storage tanks, porocel columns and auxiliary tanks will be nitrogen blanketed.

IV. FUTURE WORK

A. Determine off-gas losses after new Brink demister elements are installed and chlorination is at 195°C.

B. Assist in setting up monitoring of water in biphenyl.

C. Assist in setting up monitoring of bromine in chlorine.

D. Evaluate tangential separator for Still #1.

E. Assist in determining proper re-lime and boil-down frequency.

F. Assist in determining up-grading capabilities of porocel column on WGK Aroclor.

G. Make nitrogen blanketing system operable.

H. Determine catalyst addition to batch chlorinators when starting with 1142 (PR & D).

DSW 296895

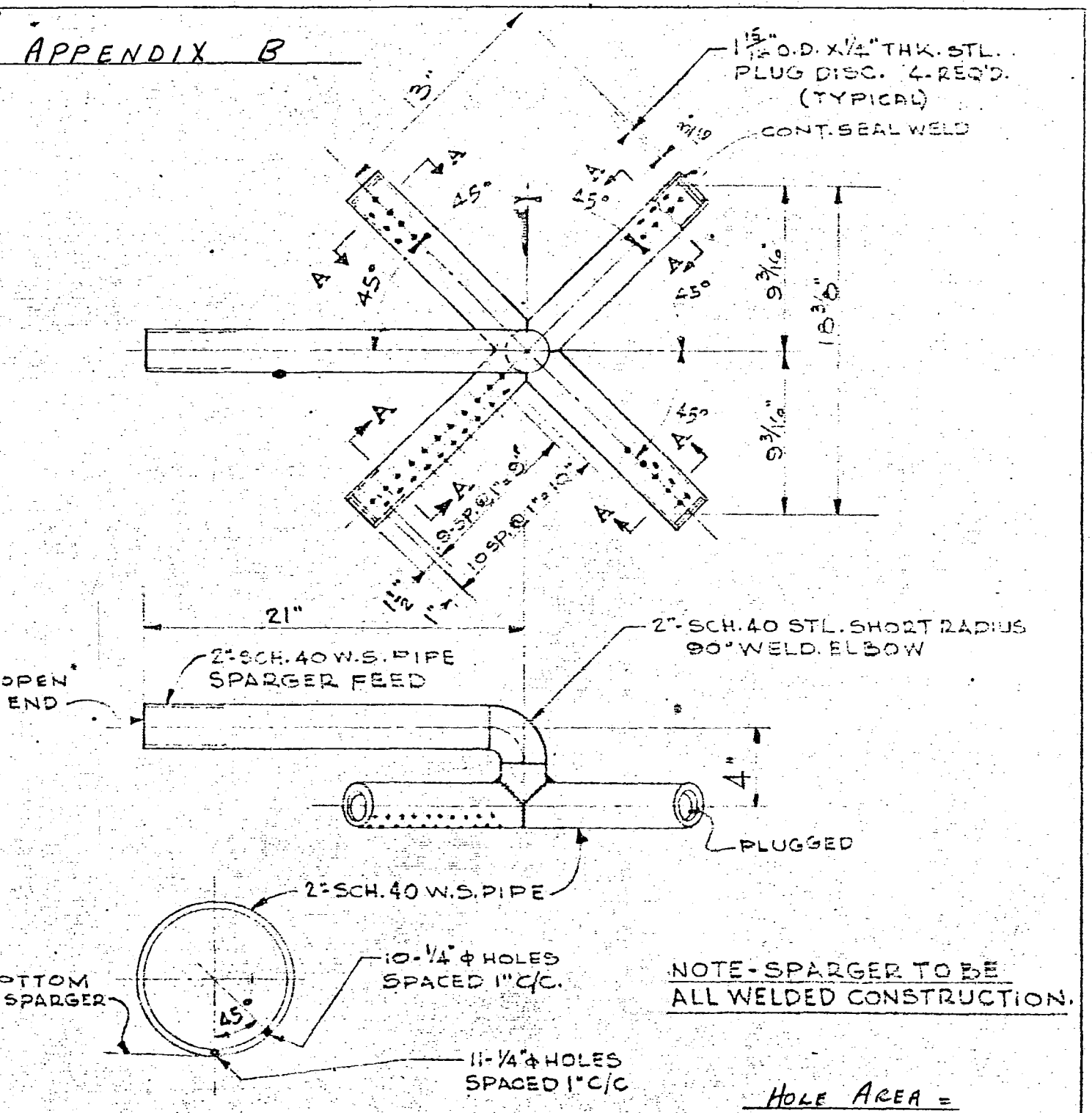
APPENDIX A

FERRIC CHLORIDE PARTICLE SIZE

% By Wt. Less Than	WGK #1 Fresh	WGK #1 Used	Ann. #1	WGK #2 Pulv.	Ann. #2	WGK #3	WGK #4
1 Micron		21.63	6.60	0.86			5.37
2		40.93	13.20	1.72			17.20
3		57.89	16.98	3.44			39.78
5		72.51	24.52	6.89			69.89
10	17.39	90.64	42.45	24.13	8.48	13.13	91.39
15		95.61	76.41	54.31			95.70
20	40.57		93.39	79.31	21.81	35.00	
30	61.35			98.30	44.84	57.50	
60	88.40				75.15	85.00	
80	92.75				84.24	92.50	
100	96.13				89.70	95.00	
150	97.79				96.36	99.30	
Date	5/8/67	5/8/67	5/25/67	5/25/67	7/6/67	7/6/67	7/6/67

DSW 296896

APPENDIX B



SECTION "A-A"
TYPICAL FOR ALL SPARGERS
3" = 1'-0"

NOTE - SPARGER TO BE ALL WELDED CONSTRUCTION.

HOLE AREA = 4.1 in.²

DSW 296897

MONSANTO COMPANY

ORGANIC CHEMICALS DIVISION
MONSANTO, ILLINOIS

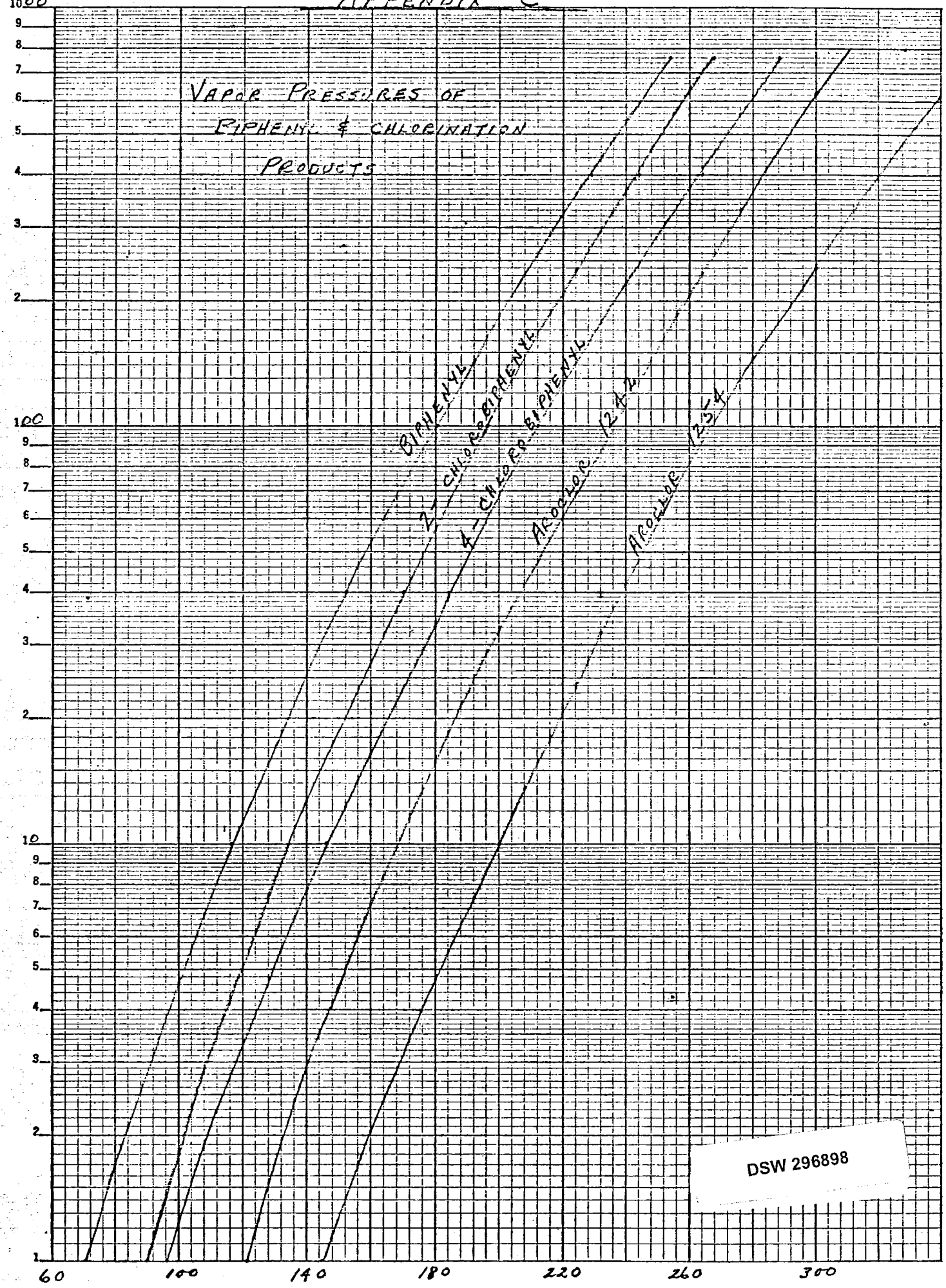
	BY	DATE		BY	DATE
DRAWN	GREGOWICZ	7-21-67	APPD.		
CKD.			APPD.		
DSGN. APPD.			APPD.		

TITLE
DETAIL - CHLORINATOR SPARGER

SCALE	JOB NO.	EST. NO.
AS NOTED	MINOR	

DEPT. No.	IDENTITY	DRAWING NUMBER	REV.
246	260	TS-A-8282	0

APPENDIX C



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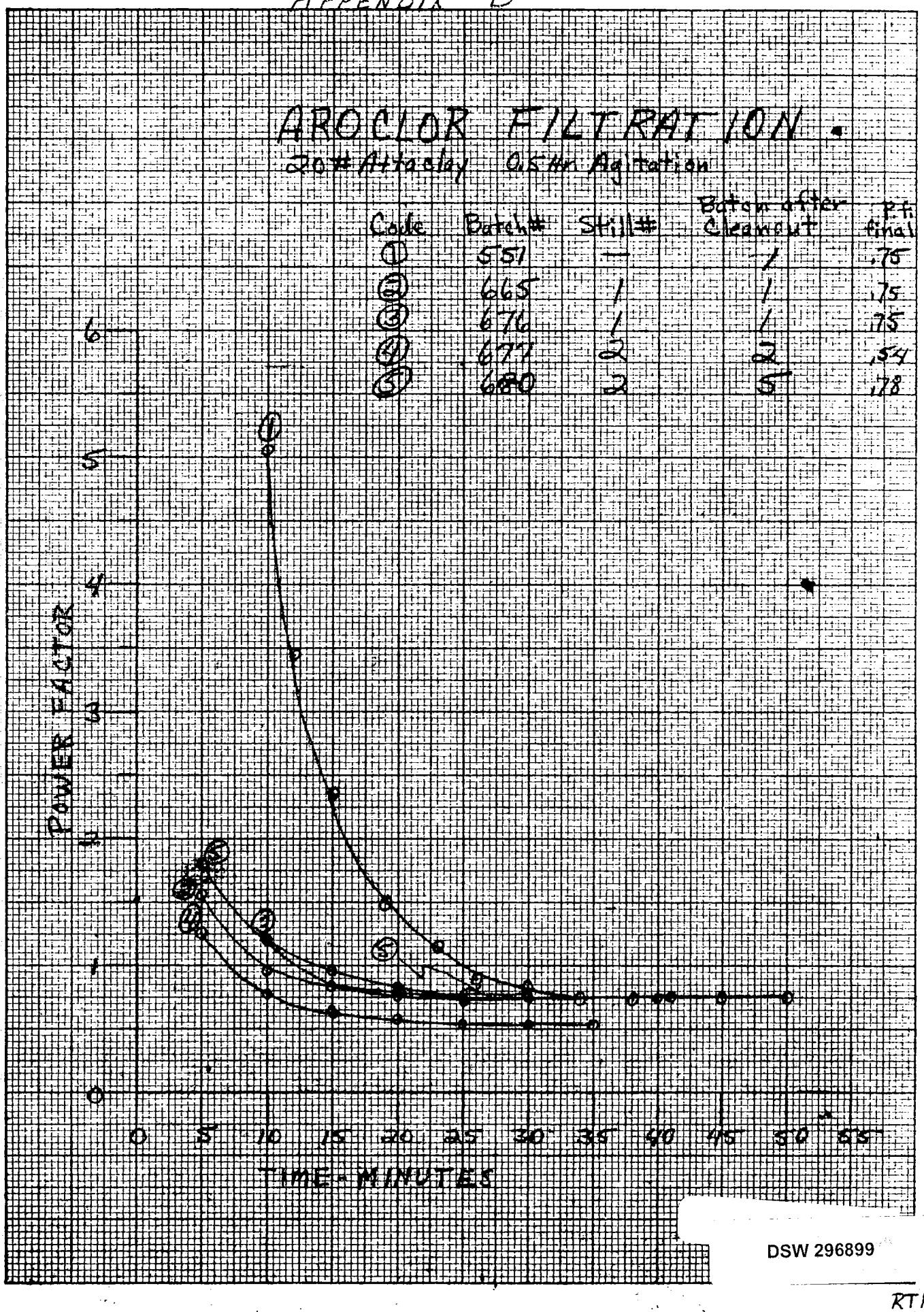
STLCOPCB4066811

APPENDIX D

AROCLOR FILTRATION

20# Attaclay 0.5 hr Agitation

Code	Batch #	Still #	Batch after Cleanout	P.F. final
①	551	—	1	.75
②	665	1	1	.75
③	676	1	1	.75
④	677	2	2	.54
⑤	680	2	5	.78

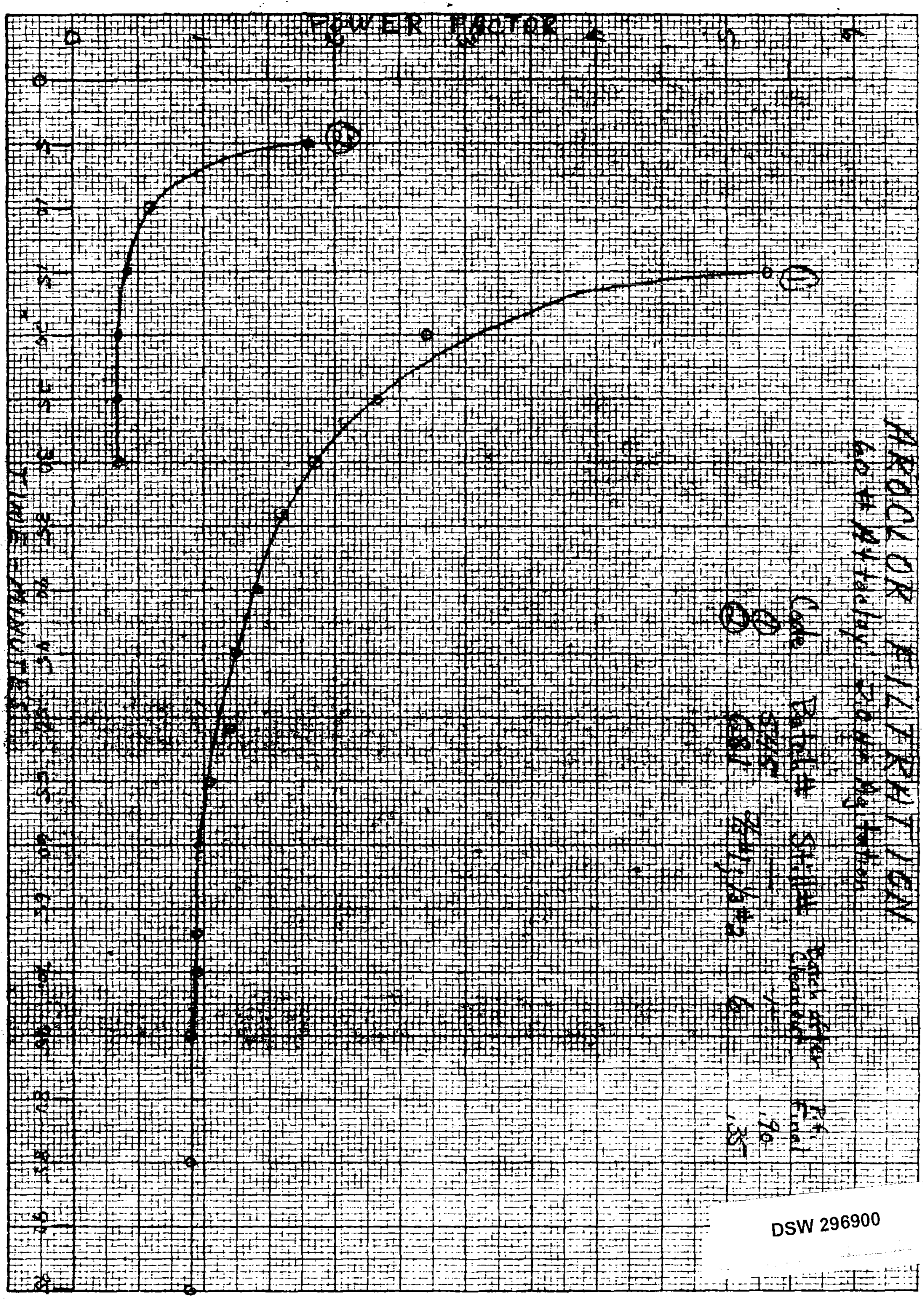


K&E 10 X 10 TO ½ INCH 46 1323
7 X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.

DSW 296899

RTK
6/8/67

APPENDIX D

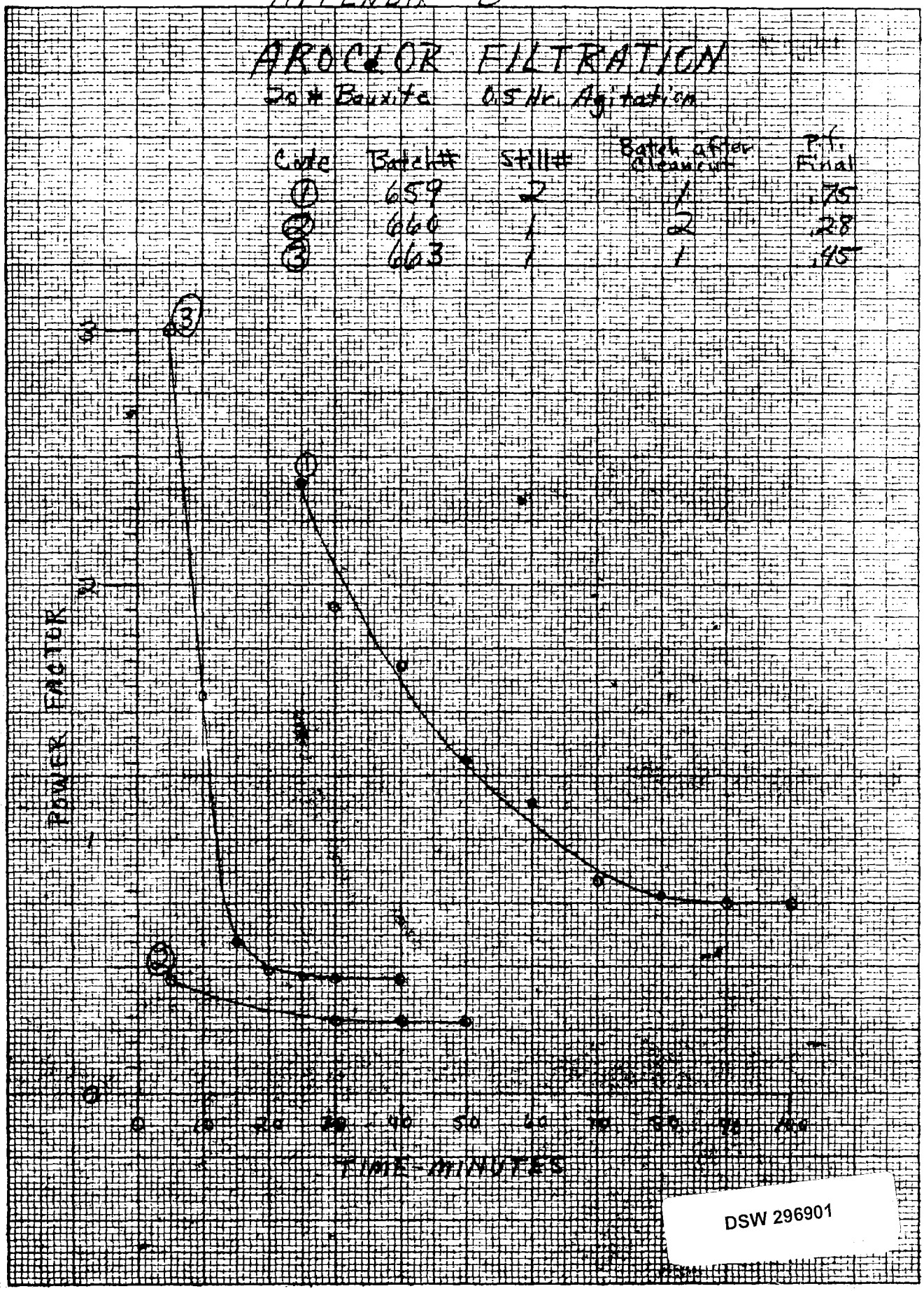


APPENDIX C

AROCLOR FILTRATION

3% Bauxite 0.5 Hr. Agitation

Code	Batch #	Still #	Batch after cleanout	P.F. Final
1	659	2	1	.75
2	660	1	2	.28
3	663	1	1	.45



KOE 10 X 10 TO ½ INCH 46 1323
KEUFFEL & ESSER CO.

DSW 296901

RTK
6/8/67

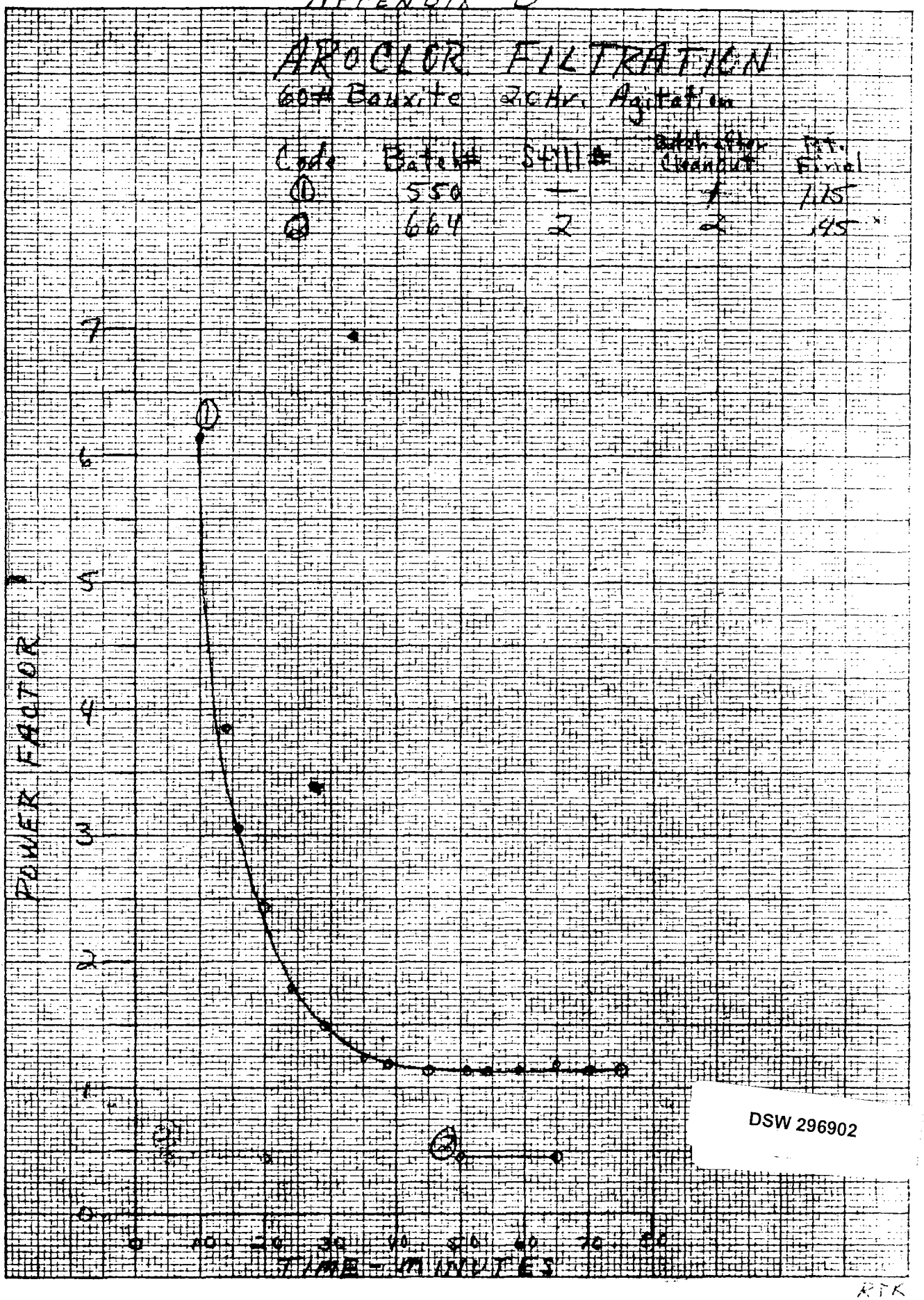
STLCOPCB4066814

APPENDIX D

AROCLOR FILTRATION

60# Bauxite 24 Hr. Agitation

Code	Batch #	Still #	Batch Filter Cleanout	Rel. Final
①	550	—	1	115
②	664	2	2	145



DSW 296902

RTK