St. Louis Research Report No. 1530

June 4, 1956

FINAL REPORT

ON

THE CONTINUOUS CHLORINATION OF BIPHENYL

Job No. 2-02-750.01-3040

Monsanto Chemical Company
Organic Chemicals Division
St. Louis Research Department

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INTRODUCTION

Aroclors are produced at the Anniston and WGK plants by the batch chlorination of biphenyl, terphenyl or a mixture of both.

The Anniston Plant expressed interest in converting their chlorination process to a continuous operation. The expected advantages are increased production, decreased labor costs, and product uniformity.

The continuous single stage chlorination of biphenyl to Aroclor 1142 and 1154 was previously attempted on a plant scale at Anniston. The products from these experimental runs were not comparable to batch production and were not considered acceptable to the customer. It was concluded that a multiple stage chlorination would be necessary to produce material that would be characteristic of batch product.

From the standpoint of isomer distribution, the continuous production of satisfactory Aroclor 1142 was considered to be a criteria of successful continuous chlorination and precluded the satisfactory manufacture of higher chlorinated products. The work reported herein concerns the multiple stage continuous chlorination of biphenyl to Aroclor 1142 and 1154 in the laboratory.

SUMMARY

Aroclors 1142 and 1154 were made in the laboratory by the continuous chlorination of biphenyl in three and four stages, respectively. The four stages represented 22, 32, 43 and 55% chlorination levels. The distilled products (Aroclors 1242 and 1254) compared favorably to laboratory produced batch material according to specification properties and infrared studies. The first two stages showed significant differences in isomer distribution in comparison to the batch product. However, these differences diminished in the 1142 and 1154 stages, the variations being of the same order of magnitude as the differences observed in previous infrared studies of samples of batchwise production lots. The infrared spectra of continuously processed Aroclor 1242 and 1254 are in good agreement with those of materials considered to be acceptable by General Electric, the prime customer of these products.

On the basis of laboratory work, a Tentative Process for the continuous production of crude Aroclors has been written.

CONCLUSIONS

Aroclor 1142 and 1154 can be made continuously in the laboratory which is characteristic of batch production. Aroclor 1121 as made in the laboratory by a single continuous stage chlorination was not comparable to batch material on the basis of isomer distribution. Because the demand for this product is small and is of minor interest in the continuous operation picture, however, a satisfactory product could be made in multiple stages.

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RECOMMENDATIONS

A Tentative Process for the continuous production of Aroclor 1142, 1148, 1154 and 1160 has been written on the basis of the work reported herein and a plant demonstration has been recommended. Future work should be directed toward the investigation of the continuous production of terphenyl Aroclors and is recommended in order to obtain maximum flexibility and efficiency in plant equipment.

REFERENCES

Progress Report No. 1, Job No. 2-02-750.01-3040, Aroclors - Process Investigation, October, November, December, 1955.

Report No. P-688, Job No. 2-02-750.01-3040, Tentative Process for the Continuous Chlorination of Biphenyl, R. A. Simone, March 23, 1956.

EXPERIMENTAL WORK

Apparatus (See Figure 1)

Chlorinator

The chlorinator was a glass cylindrical vessle equipped with an agitator, bottom inlet, overflow outlet, and chlorine feed tube. The overflow line contained a trap that forced the off-gas out of the top of the reactor. The reactor was wrapped with 1/8" nichrome ribbon for heating purposes.

Tower

The liquid feed was introduced through a 3/4 x 10" glass tower that was fitted to the top of the chlorinator. The feed was discharged through the tower into the side arm feed inlet line. The tower was packed with steel wool and was traced with nickrome ribbon. The reactor off-gas passed through the tower countercurrent to the liquid feed, in order to maintain full chlorine efficiency.

Pump

The liquid feed pump was an all glass syringe type, fitted with valves in the vacuum and pressure sides. The pump was driven by a variable speed Bodine motor through a 100:1 ratio Boston reduction gear. The delivery volume was regulated by adjustment of pump stroke and by motor speed. Motor speed was determined by a tachometer. The pump body and lines were immersed in a constant temperature bath to assure constant delivery and to avoid freezing.

Feed Reservoir

The feed reservoir was a glass pre-[illegible] the material in this vessel was maintained at the desired temperature by circulating [illegible] through the jacket from the constant [illegible]

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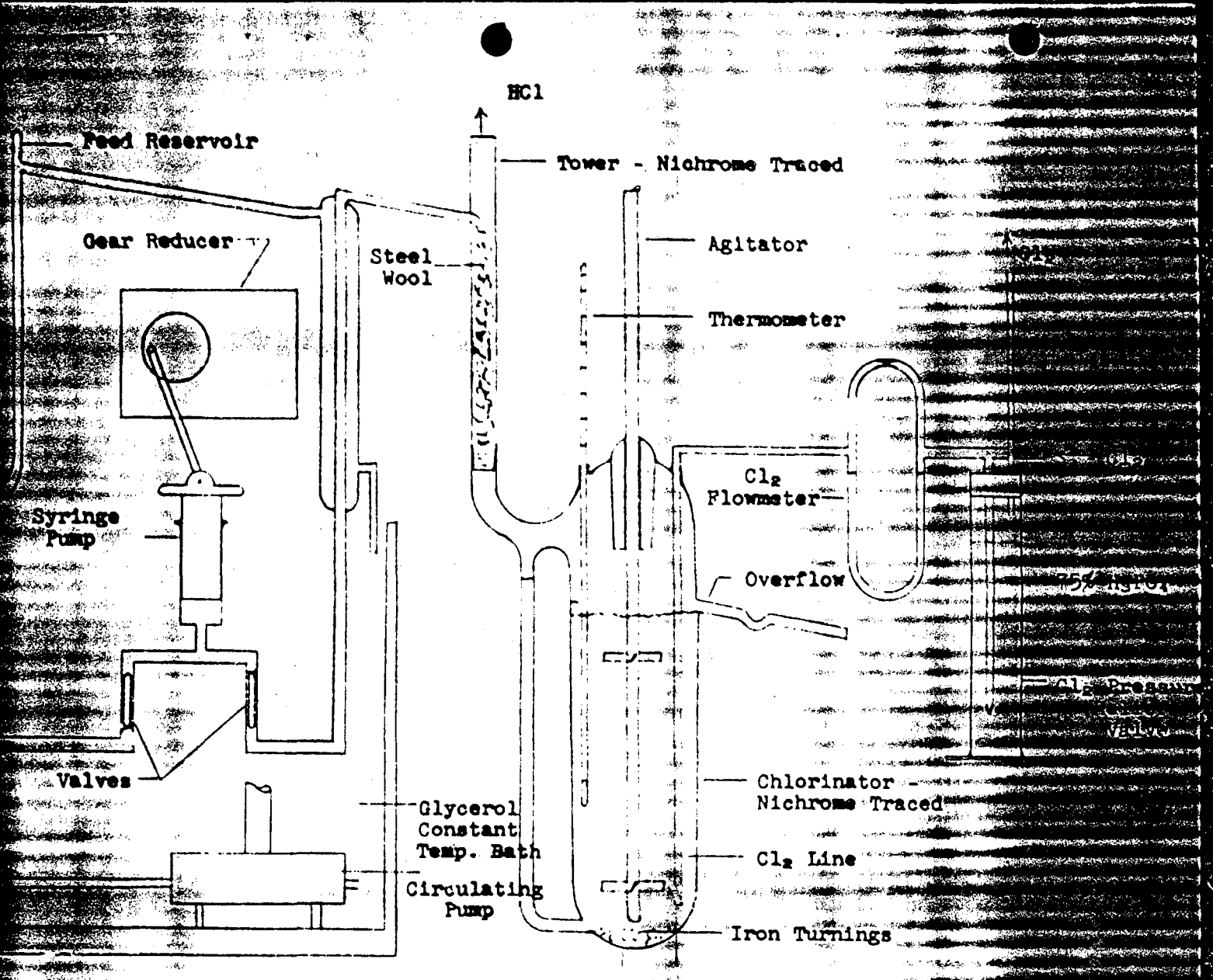

Figure I - Continuous Chlorination Apparatus

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temperature bath. The reservoir contained a pad of glass wool at the bottom to filter out solid material that would bind the valves or pump piston. The vessel was connected to the pump through a ball-socket glass joint.

Chlorine regulator

Chlorine was metered through a flowmeter containing 75% H_3PO_4. The orifice was calibrated against KI solution. The chlorine pressure was maintained constant by passing the gas through a pressure relief manometer containing 75% H_3PO_4 preceding the flowmeter. The chlorine was supplied from a cylinder.

Procedure

The pump delivery for each stage was calibrated by operating the pump at a constant speed and temperature while weighing the discharge over a definite period of time. The motor speed as determined by a tachometer was noted.

In the first stage, biphenyl was charged to the reservoir and chlorinator. Approximately 20 g. of iron turnings were added to the to the reactor and the biphenyl was chlorinated at 120-130°C to a level of 22% Cl_2, as determined by specific gravity at 25/15.5°C. The pump was then started and chlorine was introduced at the proper rate simultaneously. The bath temperature was 90°C and the chlorinator temperature was 120-130°C. The overflow gravity was determined every hour and any necessary adjustment in the Cl_2 flow was made in order to maintain a gravity of 1.185 to 1.191 at 25/15.5°C. Motor speed was also determined periodically. After 3000 ml. of the proper gravity material was discharged from the reactor, material to be used for the feed in the next stage was collected, which amounted to 16 liters. Approximately 5% of the biphenyl feed was lost by sublimation-entrainment. On completion of the first stage, the pump was adjusted to feed at the same rate as the first stage had discharged. The reactor contents were chlorinated to a level of 32% batchwise and continuous operation was resumed. The bath temperature was 60°C and the chlorinator temperature was 132-138°C. Three liters were allowed to discharge before collecting feed for the next stage. This stage was operated at a level of 32% Cl_2, corresponding to a gravity of 1.274 to 1.277 at 25/15.5°C. The third stage was started by batch chlorinating the previous stage to a level of 43% Cl_2 and continuously operating at a feed equal to second stage outlet at a chlorinator temperature of 144-147°C and an overflow gravity of 1.388 to 1.392 at 25/15.5°C.

Three liters were again discharged before collecting material. In the fourth stage, the feed rate was considerably reduced from the outage of the third stage, since two moles of chlorine were to be added per mole of liquid feed. The feed rate corresponding to the third stage outage would require a chlorine demand in excess of the chlorinator capacity. After batch chlorination to 55% Cl_2, the stage was operated at 14[illegible] to 15[illegible]°C with an overflow gravity of 1.500 to 1.505 at 25/15.5°C.

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[illegible] and operating periods for all stages are given in Table II of the Appendix.

Biphenyl was chlorinated batchwise to the level of each continuous stage in order to obtain samples for comparative analytical purposes.

Samples from each continuous stage and from each batch chlorination were purified by air blowing followed by vacuum distillation over 0.1% lime. The distillates were treated with 0.1% Attapulgus earth at 60-80°C for four hours and filtered. Each sample was analyzed for specification properties. In addition, infrared spectra of 5 and 10% carbon disulfide solutions were run for comparative purposes.

Data

The results of the conventional analyses of batch and continuous samples are given in Table I of the Appendix.

In the infrared studies, the only pure materials available for use as quantatative standards were biphenyl, 2-chlorobiphenyl, 4-chlorobiphenyl, 2,4-dichlorobiphenyl, 4,4'-dichlorobiphenyl, and 2,2'-dichlorobiphenyl.

The results of the studies using the above materials as a background are as follows:

Aroclor 1221	Batch	Continuous
Biphenyl	6.5%	15.4%
2-Chlorobiphenyl	39.1%	26.6%
4,4'-Dichlorobiphenyl	4.7%	5.4%

Aroclor 1232	Batch	Continuous
Biphenyl	0%	2.0%
2-Chlorobiphenyl	11.4%	13.1%
4,4'-Dichlorobiphenyl	11.5%	11.3%

Aroclor 1242	Batch	Continuous
Biphenyl	0%	0%
2-Chlorobiphenyl	0%	0%
2,4-Dichlorobiphenyl	45.2%	35.3%
4,4'-Dichlorobiphenyl	14.1%	14.9%

Aroclor 1254	Batch	Continuous
Biphenyl	0%	0%
2-Chlorobiphenyl	0%	0%
2,4-Dichlorobiphenyl	13.3%	12.3%
4,4'-Dichlorobiphenyl	14.1%	15.9%

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All of the background components could not be detected due to overlapping or interference of other constituents. 2,4-Dichlorobiphenyl could only be measured in the absence of biphenyl. No 2,2'-dichlorobiphenyl could be detected in any of the analyzed materials.

DISCUSSION

The conventional analysis indicates that only slight differences exist between batch and the corresponding continuous material from each stage. However, infrared studies show that marked differences exist at the 22 and 32% chlorination levels in comparison to batch product. These differences are to be expected since continuous operation will give a greater isomer distribution than batch processing, when a wide distribution is possible. The opportunity for a wide isomer distribution is greatest in the lower chlorination stages and tends to decrease as chlorination progresses. At the 43% chlorination stage, isomer distribution of the continuous material nearly approaches that of batch material, as interpreted from the infrared spectra. The quantatative values given for the background isomer in the infrared data are not conclusive, particularly in the case of 1242 and 1254, since all of the possible isomers were not available. Considerable overlapping of absorption bonds probably exists, making quantatative measurement of all possible isomers virtually impossible, without the aid of fractionation. In general, it is believed that the overall character of the infrared spectrum of each material is a more reliable basis of comparison than quantatative values based on incomplete background standard spectra.

The third and fourth stages were originally set up so that Aroclor 1242 and 1254 could be produced simultaneously. This would necessitate only partial utilization of the third stage overflow as feed for the fourth stage, with the remainder going to storage. It was later decided that the use of all four plant chlorinators for the continuous production of each Aroclor would be more practical. In the production of 1242 in the plant, this would involve the use of one more stage than used in the laboratory, and should assure the manufacture of material approaching batch characteristics.

In the Tentative Process for Continuous Chlorination of Biphenyl, four stages are to be used for the manufacture of Aroclor 1142, 1148, 1154, and 1160. At the maximum rate of chlorination, the production rate of 1142 will be approximately 3700 pounds per hour, with a total sojourn of 9.0 hours. This is slightly over the laboratory sojourn for 1142, which was 8.8 hours. Providing plant agitation is comparable to that in the laboratory, production at the maximum rate should approximate the laboratory continuous 1142.

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DESCRIPTION OF RECOMMENDED PROCESS

A description of the recommended process for the continuous production of Aroclors 1242, 1248, 1254, and 1260 is given in Report No. P-688, Job No. 12-02-750-01-3040, Tentative Process For Continuous Chlorination of Biphenyl, March, 1956.

In case further laboratory studies are to be made, the process should be demonstrated using feeds equivalent to those of the Tentative Process. The operation of all four stages simultaneously in the laboratory would be extremely difficult without elaborate instrumentation. Therefore, it is recommended that the chlorination be operated as four single stage continuous chlorinations, as described under the Procedure of this report.

MATERIAL SPECIFICATIONS, ANALYTICAL PROCEDURES

The raw, crude, and finished material specifications are the same as those given by present product specifications.

The analytical methods for finished Aroclors are those presently used on batch production. In addition, infrared spectra of 10% carbon disulfide solutions of finished Aroclors are to be run on all initial continuous plant production. A Perkin-Elmer Model 21 double-beam infrared spectrophotometer is available for these analyses at the St. Louis Research Department.

TOXICITY AND HAZARDS

The toxicity and hazards of the materials used in the process may be found under the same heading in the Tentative Process.

ACKNOWLEDGMENT

Acknowledgment is given to Dr. Bernard Katlafsky, of the Physical Group, for the infrared studies made during the project. The analytical work by the Queeny and WGK laboratories is also appreciated.

APPENDIX

(1) Table I - Laboratory Batch and Continuous Produced Aroclor Analytical Data

(2) Table II - Laboratory Continuous Chlorination Operating Data

(3) Table III - Laboratory Batch Chlorination Operating Data

(4) Infrared spectrograms
   a. Lab 1242 Batch
   b. Lab 1242 Continuous
   c. Plant 1242 Commercial Electro Standard
   d. Lab 1254 Batch
   e. Lab 1254 Continuous
   f. Plant 1254 Commercial Electro Standard

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(2) Notebook Pages

A-68790 to A-68800
A-73951 to A-73970

R. A. Simone

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Property										
Viscosity, SUS	39.9 at 100°F.	39.9 at 100°F.	38-41 at 100°F.	47.4 at 100°F.	47.2 at 100°F.	87.2 at 100°F.	88.0 at 100°F.	82-92 at 100°F.	45.5 at 210°F.	45.5 at 210°F.	44-48 at 210°F.
N_D 25°C.	1.6147	1.6145	None	1.6176	1.6178	1.6248	1.6249	1.6245-1.6265	1.6374	1.6378	1.6370-1.6390
Dielectric Constant at 1 Mc-100°C.			None				4.83	4.7-4.9		4.24	4.15-4.35
Resistivity ohm-cm at 100°C.			None				5000 x 10^9	500 x 10^9 Min.		20,800 x 10^9	500 x 10^9 Min.
Dielectric Strength - kv			None			40	38	35 Min.	41	44	35 Min.
Pour Point °C.			None			-18	-18	-14 or lower	10	10	7-12
% Chlorine	22.1*	22.2*	20.5-21.5	32.3	32.3	43.2*	43.4*	41.5-42.5	55.1	55.0	54.5-55.5
Specific Gravity	1.187 at 25/15.5°C.	1.189 at 25/15.5°C.	1.182 at 1.192 at 25/15.5°C.	1.275 at 25/15.5°C.	1.275 at 25/15.5°C.	1.388 at 25/45.5°C.	1.390 at 25/15.5°C.	1.381-1.392 at 25/15.5°C.	1.505 at 65/15.5°C.	1.501 at 65/15.5°C.	1.495-1.505 at 65/15.5°C.
Inorganic Chlorides			None			<0.1 PPM	<0.1 PPM	0.1 PPM Max.	0.1 PPM	0.1 PPM	0.1 PPM Max.
Corrosion Test Inorganic Chlorides			None			<0.1 PPM	<0.1 PPM	0.1 PPM Max.	0.1 PPM	0.1 PPM	0.1 PPM Max.
Distillation ASTM-D207, % by Wt. °C.											
1st. Drop	282.0	279.0	None	304.0	302.0	332.0	330.5		370.0	369.0	
5	284.0	282.0		305.5	304.0	333.0	332.0		372.5	371.0	
10	284.5	283.0		306.0	305.0	334.0	333.0	325 Min.	373.5	372.0	366-378
20	286.0	285.0		307.0	306.5	335.0	334.5		374.5	372.5	
30	287.0	286.5		308.5	308.0	335.5	335.5		375.5	374.0	
40	289.0	289.0		310.0	310.0	336.5	337.5		376.5	375.5	
50	290.5	291.5		311.0	313.0	338.0	339.5		378.0	377.0	372-383
60	292.5	295.0		313.5	316.0	340.0	341.5		379.5	379.5	
70	295.0	299.5		316.0	318.5	342.0	345.0		381.5	382.0	
80	299.5	305.5		320.0	323.0	345.0	348.5		384.0	385.5	
90	308.0	313.5		327.0	330.5	351.0	354.5	366 Max.	388.0	391.0	383-396

* Assuming that these analytical results are correct, there appears to be a discrepancy between specific gravity and percent chlorine in present product specifications for these Aroclors.

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TABLE II

Laboratory Continuous Operating Conditions

Stage	Approx. Lab Feeds Cl_2 g/Hr	Approx. Lab Feeds Liquid g/Hr	Approx. Lab Outage g/Hr	Chlorination Temp°C	Sp Gr Outage	Sojourn Time Hours Stage	Sojourn Time Hours Total
1121	104	192*	233	122-128	1.185-1.191 at 25/15.5°C	3.1	3.1
1132	70	233	267	134-138	1.274-1.277 at 25/15.5°C	3.0	6.1
1142	106	267	319	144-147	1.388-1.392 at 25/15.5°C	2.7	8.8
1154	83	162	204	147-153	1.500-1.505 at 65/15.5°C	4.6	13.4

*Approximately 5% biphenyl was lost by sublimation-entrainment.

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TABLE III

Laboratory Batch Chlorination Operating Conditions

Stage	Time (Hrs.)	Temp. °C.	Sp. Gr.	Specification Sp. Gr.
1121	6.0	120-126	1.187 at 25/15.5°C.	----
1132	7.0	120-138	1.278 at 25/15.5°C	1.384-1.397 at 25/15.5°C
1142	10	120-148	1.390 at 25/15.5°C.	1.384-1.397 at 25/15.5°C.
1154	16	120-153	1.505 at 65/15.5°C.	1.500-1.509 at 65/15.5°C.

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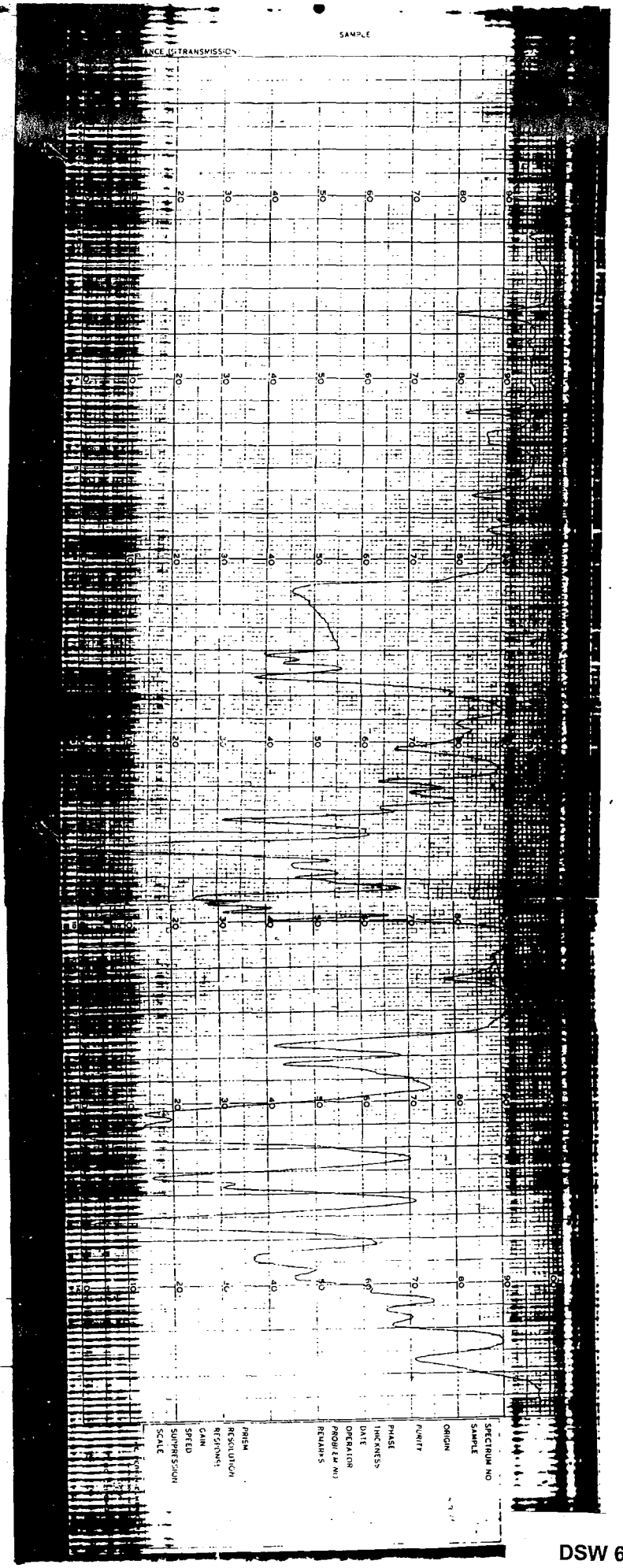

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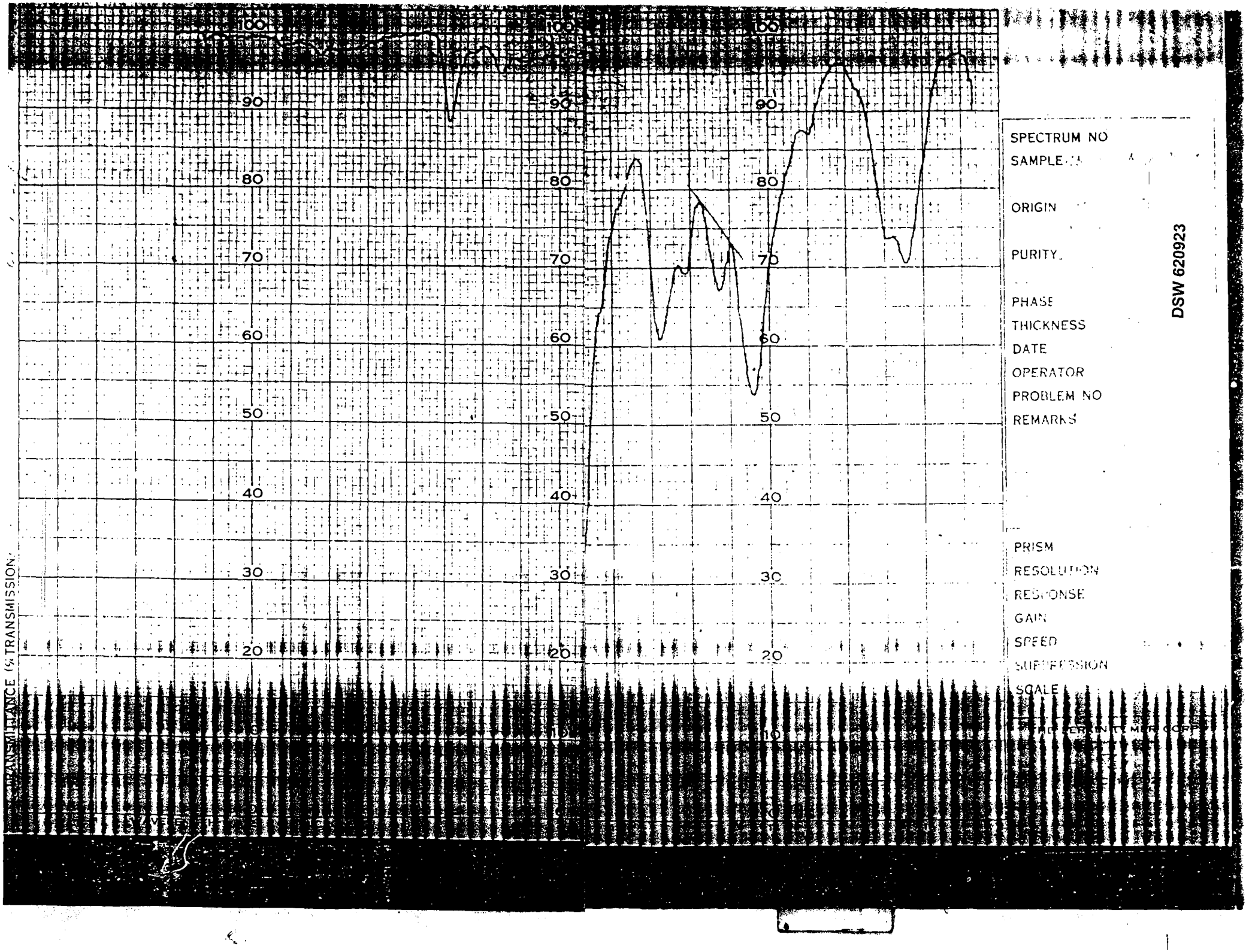

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