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PROGRESS REPORT
TECHNICAL SERVICES DEPARTMENT
ANNISTON, ALABAMA PLANT

JOB NO. 370-481 **REPORT NO.** 5 **DATE** June 2, 1967

TITLE: QUALITY OF LIQUID AROCLORS

OBJECTIVE: (This report) Present details of a systematic study made to identify sources of variability in electrical grade Aroclor.

PERSONNEL: W. B. Dunlap, Charles McIlwain (L. C. Fuhrmeister)

REPORTED BY: W. B. Dunlap

SUMMARY: Due to the high quality requirements of export grade electrical Aroclors, a systematic survey was made to isolate existing sources of variability, as planned in Report #4, Job 370-481, May 2, 1967. This survey revealed the following facts:

1. High resistivity (15,000 x 10^9 ohm-cm) exists at the blend tank but is degraded by passing through the system to the storage tank.

2. Possible sources of contamination have been found to be atmospheric, exposure to iron through ruptured tank linings and old, threaded galvanized pipe, unacceptable gaskets and packing, and exposure of drum loading to weather.

3. Unreliability in reported quality arises in contaminated samples and imprecise analysis, with sampling error controlling by a factor of 4:1. Difference between duplicates of single tests on different samples, statistically calculated, could be as high as ± 100%.

4. The test method devised by the Anniston PR&D group has better precision than the routine lab test and twice the accuracy (PR&D values average higher by factor of 1.8).

RECOMMENDATIONS (including improvements planned and underway by TSD engineers)

1. Replace tanks and lines with aluminum.

2. Close the entire system under a nitrogen pad.

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(continued)

3. Initiate a PR&D study of water washing of crude Aroclor to eliminate air blowing and need for lime in the still.

4. Develop a bomb sampling system.

5. As a referee method upgrade the routine lab test to match the PR&D method.

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SURVEY OF LOW RESISTIVITY

ELECTRICAL GRADE LIQUID AROCLORS

CONTENTS

SURVEY OF LOW RESISTIVITY ELECTRICAL GRADE LIQUID AROCLORS

I. OBJECTIVES AND SCOPE

The high quality requirement of export grade Aroclor (10,000 x 10^9 Min. resistivity - see Appendix L) has made this product extremely sensitive to process contamination. Multiple treatment with earth is frequently required, with some material failing to upgrade to minimum requirements, and consequently being sold as regular. A systematic study has been made to isolate sources of contamination within the process and to spell out the limits of reliability in sampling and electrical testing.

This survey has been designed to quantify answers to the following questions:

1. Does material at the refining step (earth treatment) exceed resistivity specification minimum?

2. If quality is high at the refining step, what are the subsequent sources of contamination which cause minimal quality in final product?

3. What are the analytical and sampling components of the overall observed quality variability?

If question No. 1 is answered in the negative, we then have the problem of defining the factors which make it impossible to upgrade Aroclor. Solution of this problem will require systematic laboratory and plant study of chlorine, biphenyl, blowing air, chlorination control, still operation, etc. Defining these variables is out of the scope of the present survey.

II. PROCEDURE

A. Process piping and material flow sheet appear in Appendix A. Over a five-day period a survey was made of resistivity values from blend tank to finished container, analyzing blend tank (after lab filtration), filtrate receiver, storage tank, and finished containers (drums or car). Multiple samples were taken at the storage tank to permit determination of sampling and analytical variability. Selected samples were further checked by the PR&D group in order to compare the two testing situations. During this period supplementary data was recorded to monitor the environment, raw materials, and operating controls. Complete details of procedure will be found in Report No. 4, Job 370-481, which set up the study.

B. A study was made of previous surveys in this field. A laboratory investigation was made in 1956 and subsequent limited investigations have been carried out by the Aroclor Department supervisors. Lately, J. G. Bryant of Anniston Plant PR&D group made one series of observations. These findings are included in this report.

C. A search for causes followed the diagnostic study. These findings are included, along with recommendations for correction and further study.

III. OBSERVATIONS AND DATA

General Note: Weighing the significance of Aroclor electrical data, particularly Resistivity, involves an understanding of certain critical facts related to the test itself: (1) The test procedure is an arbitrary selection of conditions which has been accepted to permit reproducibility, (2) Given this specific test sequence, there are remaining variables in the area of cell cleaning and material handling which profoundly affect test results, and (3) Given this specific test sequence, these outside variables will predominantly cause low values rather than high. This leads to the generality that "the highest value is the most accurate value" in a series of replicate tests on the same material.

A. Degradation During Forward Flow

1. The five-day survey is summarized in Appendix B -- "Batch-Sample Summary" and Appendix C -- "Progress of Resistivity Through the System." All resistivities were measured by a special analytical laboratory analyst using a clean test cell for every determination and, therefore, are not necessarily indicative of accuracy or precision of routine lab testing.

   Appendix C shows resistivities of all material flowing to the storage tank and into final containers. Blend tank values are inconsistent, since some are much higher than corresponding filtrated material while others are much lower. Interpretation of this phenomenon is treated later in this report from the viewpoint of one or all of three factors which have strong statistical correlation: operator variability, atmospheric contamination, and run sequence in the still. Each filtrate sample can be paired with the corresponding blend tank, but the corresponding storage tank sample is a composite of all previous material. Hence, the final sample of the storage tank is to be compared with the average of contributing filtrates and blend tanks, as well as the following drums or tank car. These weighted averages are tabulated below:

Batches	Blend Tank	Filtrate Tank	Storage Tank #2	Storage Tank #5	Drums	Final Lot
535	14,900	4,480	2,900		2,600	AI-123
536-538	20,000	9,810	2,100		1,320	AI-124
539-543	6,100	10,740	7,200		6,900	AI-1006
544-545	3,200	5,260		3,200	3,300	AI-125
546	12,800	5,900		4,000		

Discussion: (1) A perfectly consistent drop exists between filtrate tank and storage tank.

(2) With plant filtration practice unchanged throughout this study, it is difficult to interpret an increase

from blend tank to filtrate, except as a consequence of contamination, either during the lab filtration which was required to remove earth prior to analysis, or by the operator in sampling the tank. Both alternatives are possible and are treated below in detail. With the axiom that errors are on the low side, these low blend tank values would be expected to be at least equal to the corresponding filtrate tanks.

(3) The equality of storage tank with shipping containers is surprising in light of the historical evidence of lower drum and higher car values. This probably reflects the extreme care that was used throughout the experiment.

2. Previous Studies -- V. R. Haupt, J. W. Molloy, and J. R. Savage conducted informal experiments during their tenure as Department Supervisors. These were primarily designed to define the optimum sojourn time in the blend tank for earth treatment. All studies indicated a rise in resistivity followed by a decline, with a maximum at 1 1/2 - 2 1/2 hours earth treatment.

In 1956 W. B. Dunlap carried out a laboratory-plant study designed to measure the effect of operating variables. The results were published as "Analytical Laboratory Investigation #3," July 26, 1956 and appeared in Appendix D "1956 Study-Effect of Duration of Earth Treatment and Storage on Plant Batches," and in the following summary. This data confirms and quantifies the observation of the Department Supervisors.

Table I

Summary of 1956 Investigation

(1) Effect of hot aging in original glass sample bottle

Average of 10 lots -	sample as received	1790×10^9
	after 30 hours @ 90°	4370

(2) Value of earth treatment in plant - Resistivity went up with earth treatment to a maximum in 2 hours, then fell off. The decline continued through the filter tank and storage tank until the resistivity in the storage was 7 - 12% of maximum value in the blend tank.

(3) Effect of variables in laboratory earth treatment - Resistivity increased rapidly with treating time for first hour, then continued at slower rate, but showed no decline as found in plant treatment; 80°C was more effective than 150° for treating temperature; higher resistivities were obtained with more earth, but the greatest proportional rise was obtained in the first 0.05%.

(4) Decline of resistivity from filtrate tank to storage tank is further demonstrated by an extended study of Aroclor after leaving the filtrate tank. Averages of all Aroclor 1242 production over a 15 day period show:

Filtrate tank	5210×10^9
Storage tank	1160
Tank car	2900

3. Conclusions on Degradation in Forward Flow

   a. Contamination from blend tank to storage tank.

   b. Progressive contamination within the blend tank which is compensated by earth absorption until earth saturation is reached, after which degradation occurs.

   c. Stable quality going to drums, improved quality going to tank cars (in the <5,000 resistivity range).

B. Sampling - Analytical Variability

1. Appendix E summarizes data comprising the experiment statistically designed to separate sampling, testing, and loading variability. Appendix F summarizes duplicate tests on the same sample by PR&D, using different cells for each element of the pair.

2. Variability related to resistivity level - The PR&D data is extensive enough to get an idea of the correlation between analytical variability and the resistivity level. Statistically the correlation is very significant. Some curvature in the relationship is indicated. More extensive data might prove that the regression is not linear, but the burden of present evidence, up to 50,000, shows no great deviation from a straight line. Obviously, then, the standard deviation of resistivity test data is not constant, but must be considered relative to the resistivity level. For simplicity, the constant variability parameter has been taken as $\frac{\sigma}{R}$. Therefore, in the following study of components of variability, the standard deviation is given in terms of σR.

3. Analytical Laboratory test variability - The analytical test precision measured here will inevitably be better than routine testing. In this study one analyst of proven reliability was used; the test cell was cleaned each time before using. Precision figured across all analysts and procedures would be higher.

   Test variability is calculated from 4 pairs of duplicates, expressing the parameter as a function of the resistivity.

Table II

Lot	Sample	Averages: Lot Average	Averages: Sample Average	Difference Between Tests $d_{(Test)}$	$\frac{d_{(Test)}}{R}$
536	1	4400	5200	1800	.34
	2		3500	1100	.31
	Difference between samples		1700		
537	1	3900	2600	1200	.46
	2		5250	100	.02
	Difference between samples		2650		

Average $\frac{d_{(T)}}{R} = .28$

Analytical Std. Deviation = $S_{(t)} = (.28)(.886)R = .25R$

4. Storage tank sampling error - The storage tank is sampled from a 1/4" valve and nipple attached to the circulation line. Routine procedure is to rinse a warm sample bottle and cap twice, catch a full bottle, cap tightly, label, and carry to the laboratory. In the laboratory the lip of the bottle is wiped with tissue paper and Aroclor is poured into the test cell. Routine sampling methods were followed in the study.

Combined sampling and analytical error is calculated from the two "differences between the samples" in Table II, recognizing that each sample average comprises two test values. From this combined error the sampling error is separated by analyses of variance technique.

Table III

Difference between samples $d_{(sample + test)}$	$\frac{d_{(sample + test)}}{R}$
1700	.39
2650	.67
Average	.53

Std. Dev (sampling + testing) = $S_{(st)} = (.53)(.886)\ R = .47R$

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$$S_{st}^2 = S_s^2 + \frac{S_t^2}{N} \qquad N = \text{number tests per sample}$$

$$(.47R)^2 = S_s^2 + \frac{(.25R)^2}{2}$$

$$S_s = \begin{matrix}\text{storage tank} \\ \text{sampling error}\end{matrix} = .43R$$

5. Variability of drums and drum sampling - Drum sampling is done with a glass thief, by pressurizing the drum and forcing Aroclor into a sample bottle which has been previously rinsed twice from the storage tank sample port. Drum-to-drum variability cannot be extricated from its combination with drum sampling error in the present study. The combined variability is determined from three ranges of three.

Table IV

Lot	Range of 3 Samples d_{ds}	Average of 3 Samples	$\frac{d_{ds}}{R}$
123	1,600	2,600	.61
124	750	1,300	.58
1006	7,600	6,700	.88
		Average =	.69

Std. Dev (Drums, drum sampling, testing) = (.69)(.591) R = .40R

$$S_{dst}^2 = S_{ds}^2 + S_t^2$$

$$(.40R)^2 = S_{ds}^2 + (.25R)^2$$

$$S_{ds} = \begin{matrix}\text{drum} \\ \text{sampling error}\end{matrix} = .32R$$

6. PR&D test precision - Appendix F presents a series of duplicate tests made by the PR&D method. Analytical precision of this method is calculated from the differences and expressed as a function of resistivity.

$$\text{Ave.}\frac{d}{R} = \frac{5.64}{24} = .24$$

Std. Dev (PR&D test) = S_{pt} = (.24)(.886)R = .21R

C. Accuracy of Resistivity Data

Precision of test data has been examined above, dealing with inability of resistivity tests to obtain the same values on repetitive tests. Accuracy

of the test refers to its ability to determine the true resistivity level by the average of a large number of repetitive tests. (Refer to "General Note" under III above.) Under the specified conditions of cell charging, temperature and test time, higher test data are considered to be closer to the true resistivity.

1. Table V presents the five test pairs which compare the PR&D test with the special lab procedure employed in the plant study.

Table V

Batch	Lab Test	PR&D Test
541 St. Tk.	11,100	10,800
542 St. Tk.	900	9,200
543 St. Tk.	7,200	10,000
544 St. Tk.	1,900	2,900
546 Filt. Tk.	8,300	20,700
Average	5,880	10,720

2. Using the standard deviations for analytical precision previously established for these two test methods, we can easily set up a statistical test to determine the significance of this difference in average. This test takes the form of the following "t" ratio:

$$t = \frac{10,720 - 5,880}{\sqrt{\frac{(.25R)^2 + (.21R)^2}{5}}} = \frac{4,840}{\sqrt{\frac{[(.25)(5880)]^2 + [(.21)(10,720)]^2}{5}}}$$

$$t = 4.0$$

This ratio is highly significant. We are led to the conclusion, therefore, that the PR&D method gives higher resistivities, in the order of 1.8 magnitude.

PR&D test = 1.8 X special lab test

The superiority of the PR&D test would be greater, of course, over the routine test used by the lab, in which a cell is not pre-cleaned before each test and several analysts of varying abilities are employed.

D. Summary of Conclusions on Sampling-Analytical Variability

1. Specific sources of variability in resistivity test data

Analytical (special lab test) Std. Dev. = .25R

Sampling storage tank Std. Dev. = .43R

Drum + drum sampling — Std. Dev. = .32R

PR&D analytical — Std. Dev. = .21R

2. Amount of variability in resistivity data is a direct, roughly linear function of the resistivity level itself.

3. The greatest source of error is in storage tank sampling. To statistically bring this error down to magnitude of the test error, it would be necessary to test four samples and average the results.

4. The PR&D test is more <u>accurate</u> than the lab test by a ratio of roughly 2:1.

5. Confidence in various sampling-testing combinations

   a. One storage tank sample, one lab test

      Overall std. dev. = .50R

      Expected range of 80% of replicate measurements = ± .94R

      <u>Range of the reported value = approximately ± the test value</u>

   b. Two storage tank samples, one lab test each

      Overall std. dev. = .35R

      Expected range of 80% of replicate measurements = ± .65R

      <u>Range of the reported value = ± 2/3 test value</u>

   c. One drum sample, one lab test

      Overall std. dev. = .40R

      Expected range of 80% replicate measurements = ± .58R

      (This value is less than the corresponding value of (b) due to greater confidence in a std. dev. figured from 6 pairs as compared to 2 for storage tank.)

      <u>Range of reported value = ± 1/2 test value</u>

   d. One drum sample, one PR&D test

      Overall std. dev. = .38R

      Expected range of 80% replicate measurements = ± .50R

      <u>Range of reported value = ± 1/2 test value</u>

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IV. SEARCH FOR CAUSES OF QUALITY DEGRADATION

A. Factors in Forward Flow of Material

1. Changes in properties of upstream components - Raw materials, control of chlorinators, personnel on chlorinators and blowing variables are all upstream variables which could be expected to influence liquid Aroclor quality in the blend tank. However, an inspection of flow rates and stream size quickly reveals that batch-to-batch variations from these causes are impossible. Ahead of the still are the continuous blow tank (500 gal., kept 2/3 full), the catch tank (1000 gal., kept 2/3 full), the #4 blow tank (containing 0 - 2400 gal., pumped out when full). Forward flow from chlorinators is 7.5 gal./min. With the damping effect only very long term effects in the chlorinators will be revealed in the distilled Aroclor.

2. Changes of incidental factors - Appendix G shows graphically the sequence of batches through the system, related to time, and to other variables which are time-oriented. The factors revealed are the only ones of many studied which showed any possible shift during the 7 days covered by the survey.

   The conspicuous aberration in the experimental data shown in Appendix C is the profound change in relationship of blend tank to filtrate tank samples between batches 535 - 538, 539 - 547, and 546 - 547. As discussed above (III A-1) this can be found to coincide approximately with the three factors on the chart. Statistically speaking, these are <u>all</u> strongly correlated with blend tank observations and cannot be separated into specific individual effects. Strong statistical correlation does not <u>prove</u> a cause and effect relationship. However, in considering corrective action these factors certainly should be carefully investigated.

   a. Wind direction. The parathion department releases small amounts of mercaptan-type odors and considerable SO_2; the PNP department releases PNCB vapors and assorted fumes; the chlorine department releases chlorine and hypochlorite fumes. These departments are all west of the Aroclor department and laboratory. During the first period (535 - 539) the wind was steadily toward the west; during the second (540 - 547) it was 180° reversed, blowing these air-borne contaminants toward the Aroclor plant and laboratory.

      The effect of air-borne contaminants would be pronounced during exposure of samples and sampling equipment. This occurred during dip-cup sampling of blend tank and filtrate tank. However, the filtrate tank did not show the abrupt drop of the blend tank, and the tanks were sampled identically, using same equipment and method. Air-borne contaminants could also effect the testing, particularly with exposure of blend tank material during the lab filtration required to remove earth. Inevitably, considerable air would be pulled through the filter paper. It seems more likely that the harmful effect of outside fumes was suffered in the lab. This is consistent with the experience of two other occasions when very small concentrations of vapors (paint fumes, scorched phenolic plastic smoke) made

reliable resistivity testing impossible. This test is apparently very sensitive to extremely small amounts of fouling material.

b. Operator participation. Statistically speaking, the participation of operators K-H is strongly involved in the shift of blend tank data. However, K-H also sampled the filtrate tank, without evidence of a shift of any kind. This factor should be discounted.

c. Still run sequence. No. 3 still is chain-fed until 6 receivers have been filled, then bottoms are pumped out. This sequence during the experiment is shown on the chart. The initial high period shows perfect correlation with the first sequence (runs 3 - 6); the low period fits the full middle sequence (runs 1 - 6); the last high period approximately coincides with the last sequence (runs 1 - 3). Only batch 545 is outside the perfect correlation. We cannot ignore the possibility that the middle sequence in the still was heavily fouled (air-borne contaminants, contaminated lime?) and purged only by pumping out, after which a relatively good sequence would start (but still not equal to the high level of the first sequence).

d. Corrective measures.

(1) Close up the entire system from the stills downstream. Air-borne contamination should be excluded. This can be done by sealing the system under N_2. Exposure in the blend tank will be prevented by use of a continuous treatment column; process changes have been proposed to eliminate the need for lime, making possible an unbroken N_2 pad in the still. If lime is needed, an airlock for introducing lime can be installed. Closing the system will also prevent the fouling which occurs at present whenever heavy rain blows through the still area over the blend tank.

(2) Carefully protect lime and earth. These additives carry with them all fouling material to which they are exposed. At present no protection is provided other than the shipping bags. While drying in the oven, earth is exposed to circulating air from outside.

(3) Elimination of Aroclor blowing. All air-borne vapors are included in the air blown through crude Aroclor to remove HCl. If high quality is as sensitive to plant fumes as this survey indicates, serious quality damage may be continually inflicted by present blowing methods. Two proposals have been advanced to eliminate air blowing.

3. Equipment, materials contamination

a. Tank linings. Adequate inspection of linings is not possible without tank entry and cleaning of all interior surfaces. This has not been possible. Prevailing opinion is that the blend tanks have considerable amounts of exposed steel. In the past, exposed tank steel has

proved to be heavily oxidized. This oxide is dissolved in the Aroclor, requiring removal by earth. This has been assumed to account for the blend tank degradation observed in past studies. (See above III A-2.) Steel tanks, with fragile zinc-tin linings should be replaced by aluminum or stainless steel.

b. Pipe lines. Pipe lines from stills to storage tanks are galvanized iron with threaded joints and a few flanged joints. Much of it is very old. The prevailing opinion is that much of the interior galvanizing has worn away. Threaded joints inevitably expose Aroclor to bare steel. These lines are adequate to produce 500 x 10^9 Min. Aroclor but are probably involved in the high level degradation from tank to tank proved by this survey. <u>They should be replaced with aluminum</u>.

c. Pumps and valves. Bronze and stainless steel are specified and are apparently used. Peerless pumps on process tanks and Durco pumps on storage tanks #5 and #6 have mechanical seals with Teflon inner rings. The Blackmer pumps on the still receivers and the Taber submerged pumps on other storage tanks have packed seals. Valves are Nordstrom plug valves and packed stem gate valves. The plug valves are not lubricated. (Some silicone lubricant has been used very infrequently to open a frozen valve.) Metals in these fixtures are acceptable by present standards. <u>Packing material is not approved</u>, and is discussed below.

d. Packings and gaskets. Packing is Raybestos-Manhattan #365; gaskets are Garlock 7021 or its equivalent, SEPCO #200. Appendix H gives specifications of these materials. The packing is lubricant-impregnated, permitting hydrocarbon contaminant to enter the Aroclor. Hydrocarbons are extremely detrimental to electrical Aroclor quality. Gasket material is a high-sulfur, SBR-bonded material which is not approved for chlorinated aromatics by the manufacturer. <u>If present technology is inadequate to specify inert materials here, research should be initiated to provide such information</u>.

e. Drumming facilities. The plant study did not show a drop in resistivity in loading. However, significant sources of contamination were observed here which could cause serious harm. Appendix I presents photographs of drum loading equipment. Material from the loading line passes through a sac filter, into a funnel resting in the bung hole. Filling continues until gross weight is reached, the loading line is swung over, a drip can suspended under the sac filter, the bung cap screwed in and the drum moved out. During loading the bung cap rests on a heavily-fouled plywood cover used to protect drum stencils from splashed Aroclor. At this time the drip can rests in a pool of dirty Aroclor on an old drum lid. While drums are being shifted the loading funnel rests on the old drum lid and, in turn, supports the plywood cover. Occasional contamination inevitably enters from contact of drip can with inside of funnel, from contact of bung cap with the fouled plywood cover, and from contact of loading funnel with contaminants on the old drum lid.

During the interim between loadings the funnel and plywood cover rest on the drum lid as shown, in the open, with no cover. It must be considered that HCl fumes from the blowing tanks is frequently strong in this area; all exposed surfaces are fouled with chlorides.

The loading area is open to the west where drums are laid out, stencilled, and the bungs loosened for loading. During rains with even slight wind from the west this area is soaked, with serious risk of admitting water into the drums. Also, the exposed funnel and plywood drum cover are open to rain. The second sheet of Appendix J presents pictures taken by J. G. Bryant during such a rain while loading was being carried out, with rain water drops plainly visible on funnel and plywood and a pool of water on the old drum lid.

The entire drumming operation needs to be automated with adequate protection. Consideration should be given to a preliminary drum rinse with hot Aroclor, followed by nitrogen pad during drum loading. Anniston PR&D work has indicated a drop in high-level resistivity by merely pouring through the air. Subsurface transfer of Aroclor to the drum would prevent this. Some of these improvement are already being considered by Anniston PR&D.

f. Drum materials. J. G. Bryant has done extensive research on drum linings, finding that present double phenolic linings crack in service, exposing Aroclor to steel. This work is reported on Job 322, Reports #11 and #7, J. G. Bryant. It is significant that foreign competitive material with very high resistivity is protected by galvanized drums.

B. Sampling Factor in Degradation of Reported Quality

1. Sample containers - Samples are sent to the laboratory in brown glass jugs with polyethylene-lined phenolic caps. Before taking the sample, the jug is rinsed twice with the sample material, cap in place. This study has shown that sampling errors far exceed analytical. A sample container is needed which can be purged with hot Aroclor, remain sealed and padded with N_2 until filled with sample. A sampling bomb of aluminum or stainless, connected to the circulating line with hand disconnects and valves, purged by continuous circulation, then removed and sent to the laboratory would fulfill this need. The laboratory would force out the sample under reduced N_2 pressure, returning the N_2-filled bomb to the plant for re-use.

2. Storage tank sampling - This is the greatest single error in sampling-testing procedures. It undoubtedly reflects the exposed conditions of storage tank sampling and the heavily-fouled condition of the sample port valves and all other surfaces in the area. There is no roof to protect the sampling location from rain. Use of the sampling bomb described above would completely eliminate this problem.

3. Drum samples - There is no provision at present to obtain a representative sample of a drum lot. A sample and reserve sample are generally taken -- each comes from a different single drum. Obviously this fails to provide a valid measure of lot quality. It also fails to monitor drum cleanliness. It exaggerates the sampling error. The sampling bomb described above should be connected through a sample line to whatever drum loading system is eventually installed, using a small peristaltic pump and silicone tubing. This would continually sample a small portion from all drums during loading, making the bomb sample a valid lot composite.

4. Tank car samples - The sample system above, consisting of bomb sampler and sampling pump should be installed to obtain a sample during tank car loading. Homogeneity is not a problem, but this system will best protect quality.

C. Analytical Factor in Degradation of Reported Quality

Test method. Three test methods are pertinent to this study. All use identical test cells, resistance meters and measurement procedures. Essential differences exist in other features treated below.

1. PR&D method - Cells are given routine cleaning, then repeatedly rinsed and tested with high quality Aroclor until a maximum is reached. Verification of cell purity is shown by increase of resistivity when cell is stored in Aroclor overnight. The cell is not cleaned again until low quality material is tested, after which it must be re-cleaned and conditioned to permit high values. This method, its history and supporting data is given by Report #15, Job No. 370-322, J. G. Bryant, 5/3/67. This method has given average values higher than the special lab method by a factor of 1.8 and is the most accurate and precise test available at the Anniston Plant.

2. Special laboratory test - This procedure, used throughout the present study, is identical to the PR&D test except in personnel, environment, and cell preparation. One highly talented analyst performed all tests; all were conducted in the routine laboratory environment; cells were given the routine cleaning before each test, with no conditioning.

3. Routine analytical lab method - This method is identical to the special test above except in personnel and cell preparation. All analysts make the test; the cell is cleaned only when the test falls below 1000 x 10^9 on regular material (for export grade Aroclor a clean cell is always used). Accuracy and precision of this method is inevitably at a lower level than the above, thus easily explaining well-known examples of widely divergent checks on the same material.

The present study has clearly demonstrated the superiority of the PR&D method. This superiority may be the result of cell cleaning, test environment, or personnel. A simple statistically designed study can separate these variables and should be carried out to place plant testing at its maximum practical capability. The design of this test is given in Appendix K.

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V. SUMMARY CONCLUSIONS RELATED TO CAUSES OF LOW RESISTIVITY

A. The answer to the first fundamental question advanced under "I - Objectives and Scope" is affirmative. We do make Aroclor at the refining step which is good enough to meet minimum resistivity specification of $10,000 \times 10^9$ ohm-cm.

B. Serious degradation does exist from blend tank to storage tank. This may be as great at 10:1, with greatest drop at the highest values. Possible sources of contamination have been identified as:

1. Atmospheric contamination -- particularly fumes from other plant departments.

2. Broken tank linings which permit contact of Aroclor with iron oxide.

3. Very old galvanized iron pipe lines with threaded joints. Iron is exposed to Aroclor and oxidation in threaded joints. Protective galvanizing on inner surfaces has probably been lost.

4. Unacceptable packing in pumps and valves.

5. Unacceptable gaskets in equipment and flanged joints.

6. Drum loading facilities seriously exposed to weather, plant fumes, and general contamination.

C. Variability (error in reproducibility) was found to be an approximate direct function of the resistivity level and hence must be expressed as a function of R. Checks between duplicate tests will tend to be twice as far apart at 20,000 as compared to 10,000. A test which will be reproduced at $\pm$ 2,000 at the 10,000 level may show $\pm$ 4,000 at the 20,000 level.

D. Sampling error was found to be the single greatest source of imprecision in reported resistivity data. This numerically amounts to:

Storage tank sampling : std. dev. = .43R

Drum and drum sampling : std. dev. = .32R

It would be necessary to sample four times, take one test on each sample and average all four to bring the sampling error equal to the error of one analytical test.

E. Analytical variability is high. Even under the carefully controlled conditions of the study, the standard deviation of analyses was .25R. This will make duplicate tests on one sample fall within 43,000 to 57,000 at 50,000 level and 4,300 to 5,700 at the 5,000 level.

Precision of the routine control test would be expected to fall below that of the controlled study. The above values would probably be ceiling for the routine control test.

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F. The PR&D test method gives resistivity values almost twice as high as the special laboratory method used in the study, and hence is much more accurate, especially at the high levels demanded for future production. This advantage would be expected to be higher in comparison with the routine control procedure.

VI. SUMMARY OF RECOMMENDATIONS TO OBTAIN FUTURE REQUIRED HIGH RESISTIVITY LEVELS

A. Related to Plant Equipment Changes (some recommendations have been in progress).

1. Replace present zinc-tin lined tanks with aluminum.

2. Replace existing galvanized threaded pipe with aluminum.

3. Replace present batch earth treatment with the continuous treatment column.

4. Close up the entire system and provide a nitrogen blanket.

5. Initiate a PR&D study to determine feasibility of water washing crude Aroclor to eliminate air blowing and lime in the still.

B. Related to Materials in Contact With Aroclor

1. Initiate a research study to select suitable packing and gasket materials.

2. Complete the well-advanced PR&D search for acceptable drum linings.

C. Related to Analytical and Sampling Capabilities

1. Design and install a bomb sampler for use in storage tank, drum, and tank car sampling under nitrogen.

2. Execute a carefully designed study to determine what factors in the PR&D test method are responsible for its superiority (cell preparation, personnel, environment). These findings can then be used to upgrade the routine lab test.

W. B. Dunlap

/dp

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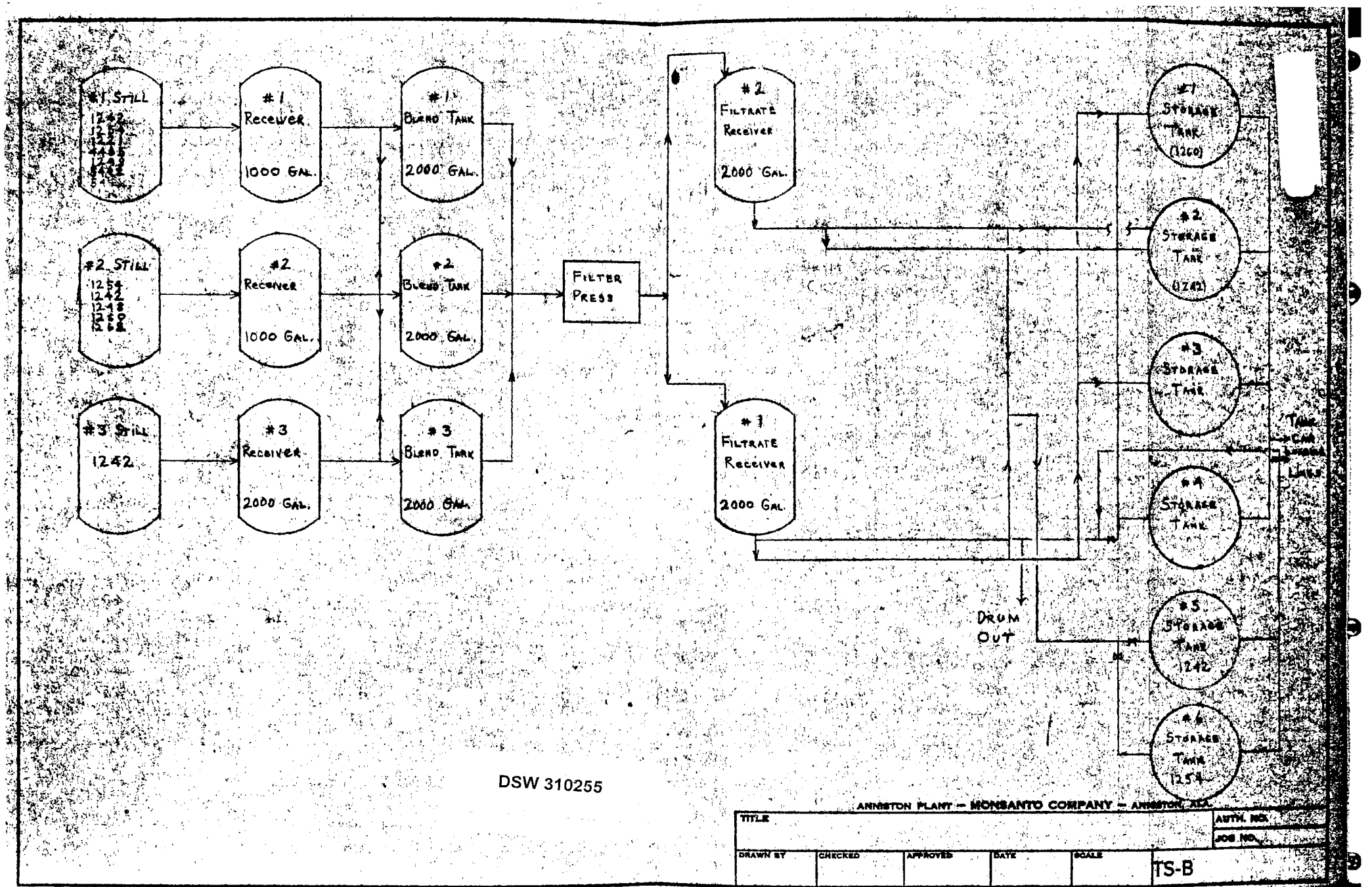

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STLCOPCB4070242

Appendix B

Batch-Sample Data Summary

Batch	Source	Electrical Tests				Previous Material in Lines or tank		Notes
		Resist. ($\times 10^9$)	60 Cycle P.F.	1000 Cycle P.F.	D.K.	Aroclor	Batch No.	
535	B.T. #3	14,900	.37	.11	4.82	1242	534	Treated 2 hrs.
	F.T. #2	5,600	1.24	.17	4.84	1242	534	
	S.T. #2 before transfer	4,000	2.40	.24	4.78	1242	534	
	After transfer #535	4,000	2.35	.24	4.84			
	Before drumming	1,700	2.67	.25	4.72			
	Drums - early drmg.	2,600	2.32	.24	4.86	1254	1021	Lot 123
	middle drmg.	3,400	1.92	.20	4.82			
	late drmg.	1,800	2.63	.24	4.85			
536	B.T. #3	23,100	.34	.11	4.74	1242	535	Treated 2 hrs.
	F.T. #2	15,900	.88	.15	4.78	1242	#5 S.T.	
	S.T. #2 Sple. 1							
	Test 1	(4,400	1.59	.18	4.83	1242	536	
	Test 2	(6,200	1.36	.17	4.83			
	Sple. 2							
	Test 1	(2,900	2.55	.25	4.84			
	Test 2	(4,000	1.08	.20	4.80			
537	B.T. #3	12,000	.34	.10	4.85	1242	536	Treated 2 hrs.
	F.T. #2	5,600	.99	.15	4.90	1242	536	
	S.T. #2 Sple. 1							
	Test 1	(3,200	1.89	.21	4.83	1242	536	
	Test 2	(2,000	2.27	.22	4.90			
	Sple. 2							
	Test 1	(5,200	1.54	.18	4.80			
	Test 2	(5,300	1.45	.18	4.77			
538	B.T. #3	23,400	.35	.10	4.87	1242	537	Treated 2 hrs.
	F.T. #2	9,300	.70	.13	4.82	1248	59-60	
	S.T. #2 before drmg.	2,100				1242	537	
	Drums - early drmg.	1.700	3.30	.30	4.85	1254	18	Lot 124
	middle drmg.	950	4.26	.36	4.80			
	late drmg.	1,300	2.58	.25	4.82			
539	B.T. #3	2,400	1.04	.16	4.84	1242	538	Treated 2 1/4 hrs.
	F.T. #2	4,800	1.72	.18	4.85	1254	231-32	
	S.T. #2	4,100	1.20	.17	4.90	1242	538	
540	B.T. #3	5,200	.96	.15	4.88	1242	539	Treated 4 3/4 hrs.
	F.T. #2	19,900	.57	.11	4.84	1242	539	
	S.T. #2	5,200	.87	.14	4.82	1242	539	

Appendix B (continued)

Batch	Source	Electrical Tests				Previous Material in Lines or tank		Notes
		Resist. ($\times 10^9$)	60 Cycle P.F.	1000 Cycle P.F.	D.K.	Aroclor	Batch No.	
541	B.T. #3	9,100	.32	.10	4.86	1242	540	Treated 2 hrs.
	F.T. #2	7,400	.77	.13	4.89	1248	61-62	
	S.T. #2	(11,100	.70	.13	4.81	1242	540	
	PR&D check	(10,800	.36					
542	B.T. #3	4,500	.97	.13	4.82	1242	541	Treated 3 hrs.
	F.T. #2	28,700	.37	.11	4.85	1254	235-36	
	S.T. #2	(900	3.00	.27	4.76	1242	541	
	PR&D check	(9,200	.36					
543	B.T. #3	8,400	.47	.11	4.89	1242	542	Treated 2 1/2 hrs.
	F.T. #2	14,000	.76	.13	4.86	1254	237-38	
	S.T. #2 before drmg.	(7,200	.70	.13	4.85	1242	542	
	PR&D check	(10,000	.42					
	Drums - early drmg.	4,900	1.00	.15	4.85	1254	19	Lot 1006
	middle drmg.	4,600	1.20	.17	4.86			
	late drmg.	11,300	.63	.12	4.82			
544	B.T. #3	5,300	.85	.14	4.90	1242	543	Treated 3 1/4 hrs.
	F.T. #2	4,100	.90	.14	4.82	1242	543	
	S.T. #5 before transfer	(1,900	1.77	.19	4.88	1242	#5 S.T.	S.T. heel
	PR&D check	(2,900	1.02					
	after transfer #544	2,900	1.04	.15	4.86	1242	#5 S.T.	
545	B.T. #3	8,900	.54	.12	4.87	1242	544	Treated 2 1/2 hrs.
	F.T. #2	15,800	.47	.11	4.83	1242	544	
	S.T. #5	3,200	1.41	.18	4.77	1242	544	
	Tank Car MONX 8606	3,300	1.47	.19	4.82			Lot 125
546	B.T. #3	12,800	.31	.11	4.77	1242	545	Treated 2 hrs.
	F.T. #2	(8,300	.64	.12	4.85	1248	65	
	PR&D check	(20,700						
	S.T. #5	4,000	.71	.14	4.82	1242	545	
547	B.T. #3	4,800	.58	.12	4.85	1242	546	
	F.T. #2	3,600	1.27	.17	4.77	1254	241-242	

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Appendix C

Progress of Resistivity Through the System
(Analytical Lab Data Only - PR&D Not Involved)

Batch	Blend	Filtrate Tank (Gal.)	Filtrate Tank Resist. (x 10^9)	Storage Tank #2 (Gal.)	Storage Tank #2 Resist.	Storage Tank #5 (Gal.)	Storage Tank #5 Resist.	Tank Car or Drums
Storage tank heel				(4,900)	4,000			Lot 123
535	14,900	(2,130)	5,600	(7,000)	4,000)			(Drums
					1,700)			(2600
								(3400
								(1800
								(Ave. = 2600
Storage tank heel				(450)	above			
536	23,100	(2,040)	15,900	(2,480)	(4,400			
					(6,200			
					(2,900			
					(4,000			
				Ave. =	4,400			
537	12,000	(1,900)	5,600	(4,380)	(3,200			
					(2,000			
					(5,200			Lot 124
					(5,300			(Drums
				Ave. =	3,900			(1700
538	23,400	(2,620)	9,300	(7,010)	2,100			(950
								(1300
								(Ave. = 1320
Storage tank heel				0				
539	2,400	(2,050)	4,800	(2,050)	4,100			
540	5,200	(2,080)	19,900	(4,130)	5,200			
541	9,100	(2,350)	7,400	(6,730)	11,100			Lot 1006
542	4,500	(1,920)	28,700	(8,380)	900			(Drums
543	8,400	(2,410)	14,000	(10,793)	7,200			(4900
								(4600
								(11,100
								(Ave. = 6900
Storage tank heel						(5,960)	1,900	
544	5,300	(2,480)	4,100			(8,130)	2,900	
545	8,900	(2,170)	15,800			(10,300)	3,200	(Tank Car
							3,200	(3300
Storage tank heel						(1,780)	above	
546	12,800	(2,010)	8,300			(3,790)	4,000	
547	4,800	(2,170)	3,600			(5,963)	-----	

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Appendix C (continued)

Batch	Blend	Filtrate Tank		Storage Tank				Tank Car or Drums
				#2		#5		
		(Gal.)	Resist. ($\times 10^9$)	(Gal.)	Resist.	(Gal.)	Resist.	
	Weighted average resistivities going to storage tank compared to final composite resistivities in storage tank and shipment							
535	14,900		4,480	2,900				2,600
536-538	20,000		9,810	2,100				1,320
539-543	6,100		10,740	7,200				6,900
544-545	3,200		5,260			3,200		3,300
546	12,800		5,900			4,000		

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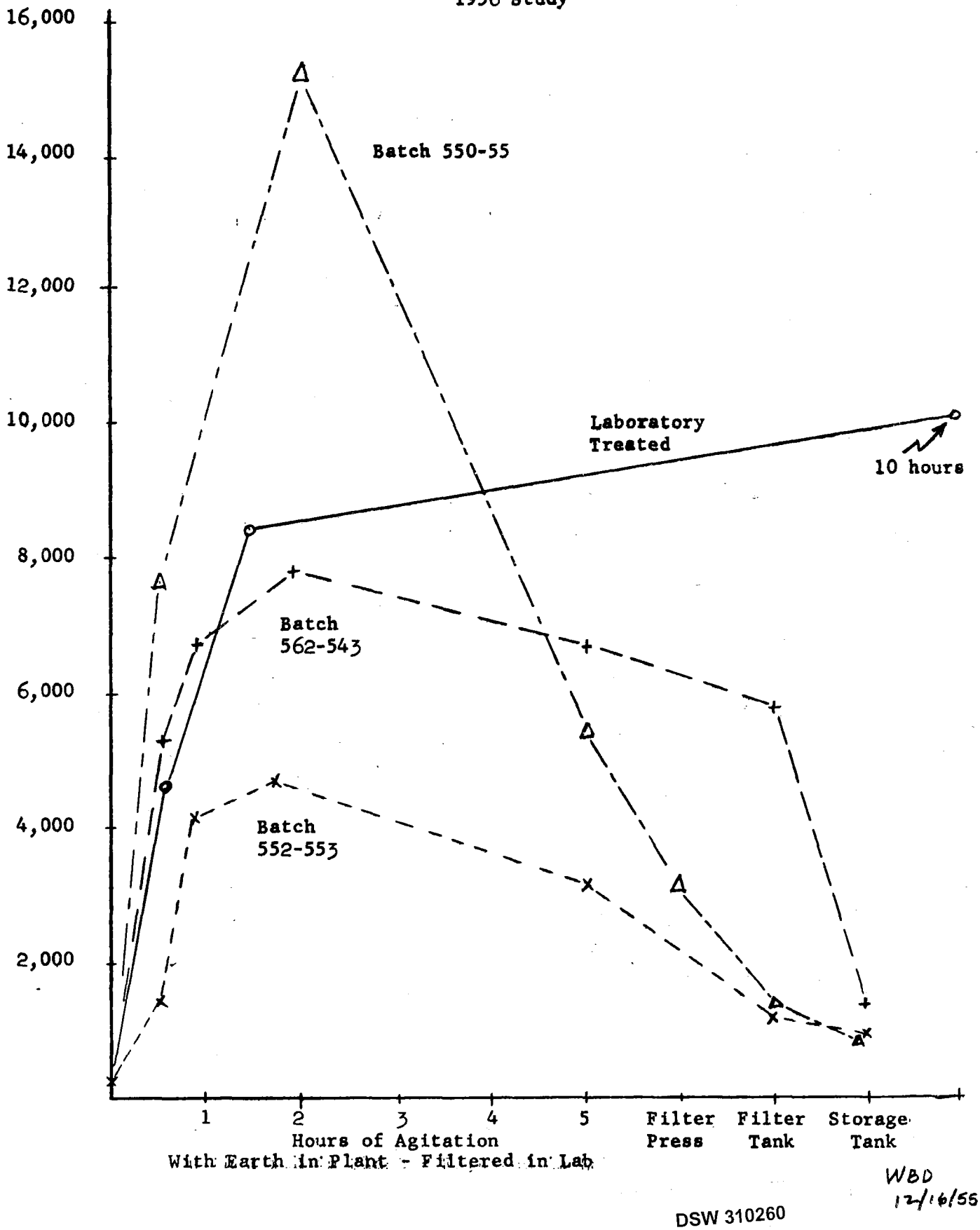
APPENDIX D

Effect of Duration of Earth Treatment and
Storage on Plant Batches
1956 Study



WBD
12/16/55

DSW 310260

Appendix E

Recapitulation of Data Arranged for Statistical Analyses of Variability Sampling, Testing, Drums

Lot	Sample	Test	Resistivity	P.F. 60	P.F. 1000	D.K.
536	1	1	4,400	1.59	.18	4.83
		2	6,200	1.36	.17	4.83
	2	1	2,900	2.55	.25	4.84
		2	4,000	1.08	.20	4.80
537	1	1	3,200	1.89	.21	4.83
		2	2,000	2.27	.22	4.90
	2	1	5,200	1.54	.18	4.80
		2	5,300	1.45	.18	4.77
			Drums			
123	Early		2,600	2.32	.24	4.86
	Middle		3,400	1.92	.20	4.82
	Late		1,800	2.36	.24	4.85
124	Early		1,700	3.30	.30	4.85
	Middle		950	4.26	.36	4.80
	Late		1,300	2.58	.25	4.82
1006	Early		4,900	1.00	.15	4.85
	Middle		4,600	1.20	.17	4.86
	Late		11,300	.63	.12	4.82

Appendix F

Duplicate Tests by PR&D Method
(Resistivity values obtained by multiplying table value by 0.795×10^9)

		Test 1	Test 2
2/15/67	#3	22,000	22,000
2/16	#4	24,000	19,000
2/30	#1	16,500	14,500
	#2	14,000	11,000
2/22	#1	43,000	37,000
	#4	30,000	35,000
2/27	#1	31,000	34,000
	#2	29,000	32,000
	#3	27,000	40,000
	#4	25,000	40,000
3/1	#1	22,000	33,000
	#2	21,000	27,000
	#3	24,000	43,000
3/8	#3	25,000	30,000
3/9	#1	60,000	50,000
	#2	32,000	27,000
	#3	25,000	28,000
3/15	#1	26,000	21,000
	#2	22,000	17,000
	#3	23,500	15,500
3/17	#1	12,500	12,500
	#2	14,500	14,000
	#3	12,500	18,000
3/20	#2	14,500	14,000

Note: Test 1 and Test 2 made on different cells

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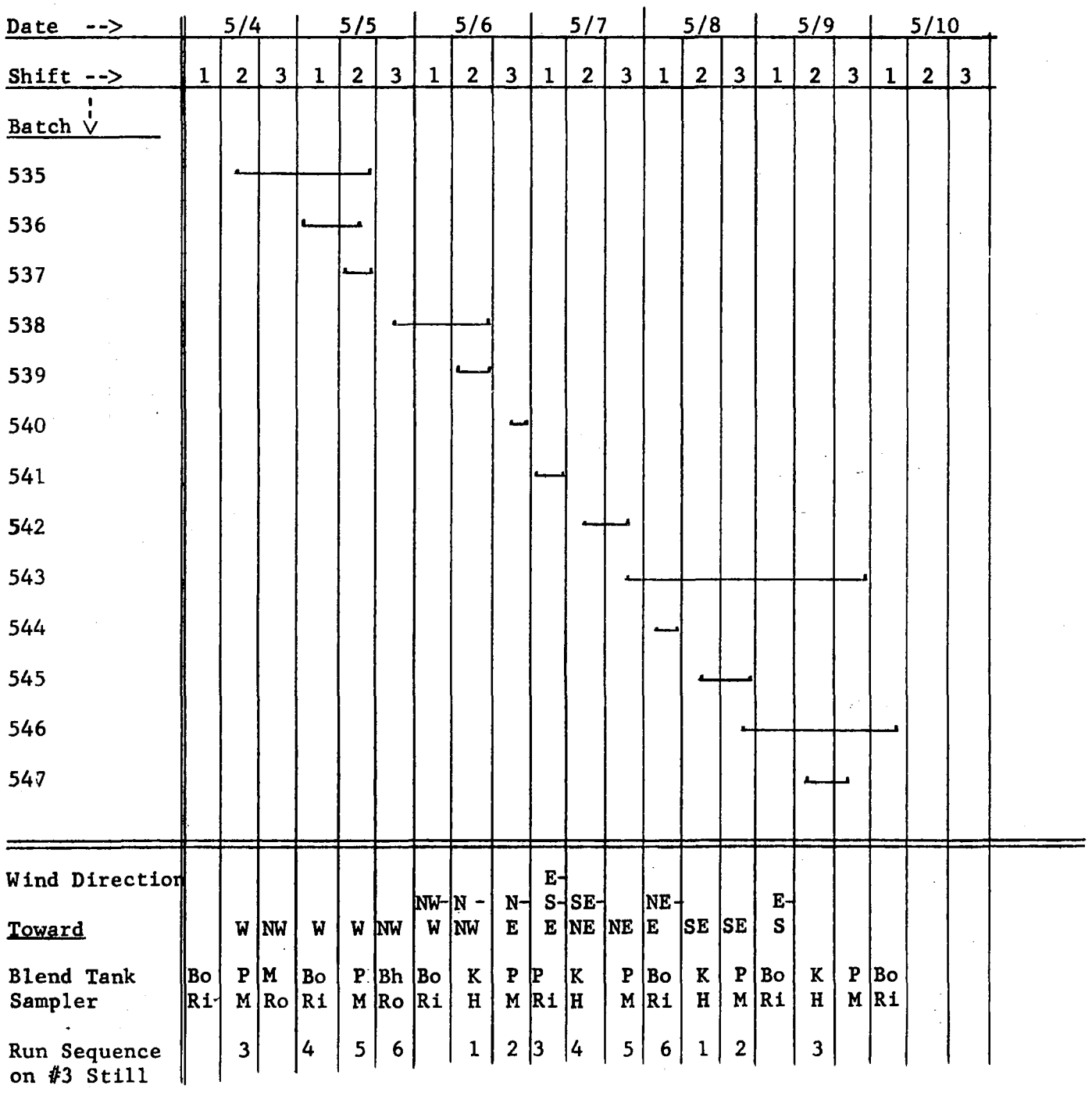
Appendix G

Forward Flow of Material
Related to Relevant External Factors



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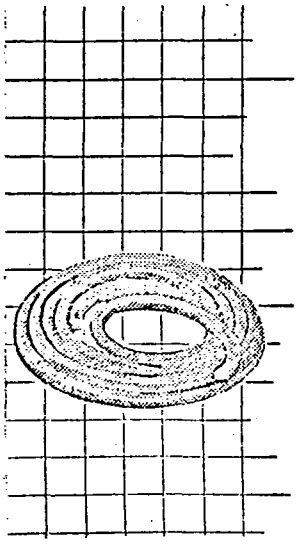
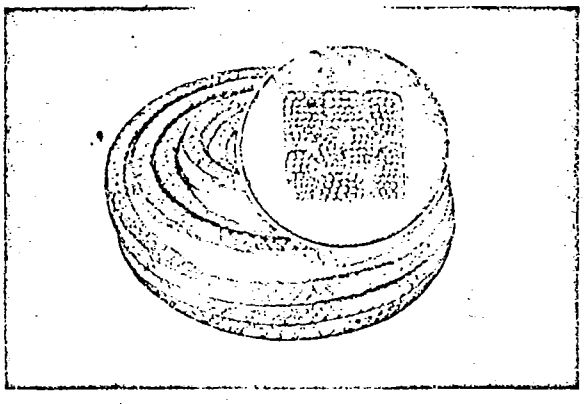
APPENDIX H

SPECIFICATIONS ON PACKING MATERIALS



R/M SQUARE PLAITED BRAID PACKING

R/M No. 365 (Non-metallic) **R/M No. 366 (Wire-inserted)**
R/M No. 365-R (Rings) **R/M No. 366-R (Rings)**



PACKAGING SPECIFICATIONS

Size	Approx. lbs. per box	Continuous Coils per box	Approx. lbs. per 100 ft.	Feet per box
1/8"	Spools	—	1 1/2	—
3/16"	Spools	—	2 1/2	—
1/4"	Spools	—	4 1/2	—
5/16"	10 1/4	7	5 1/4	200
3/8"	11 3/8	5	10 1/4	110
7/16"	12 3/4	5	12 1/4	100
1/2"	12	5	16 1/2	72
9/16"	12	4	20 1/4	59
5/8"	12	4	31	40
3/4"	12 1/4	3	34	36
7/8"	14 1/4	3	50	28 1/2
1"	10 1/4	2	58 1/2	17 1/2

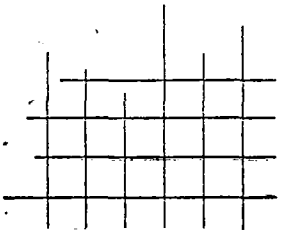
We Stock 365C.

DESCRIPTION: Constructed of asbestos yarns, plaited braid, thoroughly impregnated with special, heavy bodied lubricant and graphite, resulting in soft, pliable low friction packing. Available as R/M No. 366 with wire insertion.

SERVICE RECOMMENDATIONS: A general purpose packing for use against steam, water, air, oil and caustics. Particularly efficient as centrifugal and rotary pump packing. Use R/M No. 365-1571-C lubricant for use against gasoline and light oils.

STANDARD SIZES: 1/8" to 1 1/4" in increments of 1/16".

STANDARD PACKAGES: Coil form, boxed; and 25 lb. reels. 1/8", 3/16", 1/4" available on 1/4 lb., 1 lb., 5 lb. spools. 5/16", 3/8" available on 1 lb. and 5 lb. spools. 5/16" and up, coil form, boxed.



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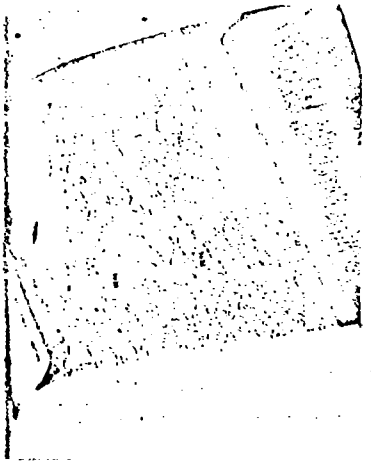
APPENDIX H

Continued



GARLOCK COMPRESSED ASBESTOS SHEET GASKETING

Garlock Compressed Asbestos Sheet combines white or blue asbestos with a variety of binders . . . bonded under pressure and vulcanized into a homogeneous sheet. All styles are tough and durable with sufficient compressibility to seal properly, yet resist plastic flow under heavy bolt loads. Ideal for high pressure/high temperature applications employing rigid flanges with adequate bolting capacity. For basic information covering four popular styles, see chart below. Contact your Garlock representative on other styles.

7021

MATERIAL	Compressed Chrysotile asbestos with SBR binder
TENSILE STRENGTH	With grain 6800 psi. Across grain 2500 psi. Average 5000 psi
APPLICATION	Hot oil service at high temperature—steam or hot gases up to 700°F
EQUIPMENT	On flanges of cracking stills and other refinery equipment, pipe lines, compressors, internal combustion engines; other high temperature applications
THICKNESSES (inches)	1/64, 1/32, 1/16, 3/32, 1/8, 3/16, 1/4

SHEET SIZES (inches)	40 x 40	50 x 50	60 x 60	75 x 75	120 x 120	150 x 150
NOMINAL WEIGHTS* (pounds per sheet)	6.0	9.4	13.5	21.1	54.0	84.4

GARLOCK MATERIALS

medium	METALS	NATURAL RUBBER	SBR
Gases Air	Satisfactory except lead melts above 600°F.	Satisfactory but becomes tacky above 200°F.	Satisfactory but hardens above 250°F.
Oxygen	Satisfactory except lead melts above 600°F	Limited depending on conditions.	Limited depending on conditions.
Halogens (Chlorine, Bromine, etc.)	Satisfactory all free from water. Otherwise attacked.	Hardens on exposed surfaces.	Hardens on exposed surfaces.
Other Hot Gases or Dry Steam	Satisfactory below melting point. Hot compressed H_2 embrittles steel.	Satisfactory but becomes tacky above 200°F.	Satisfactory but hardens above 250°F.
LIQUIDS Water (including all neutral water-soluble salts, sugar solutions, etc.)	Satisfactory except for iron rusting.	Satisfactory but becomes tacky above 200°F.	Satisfactory but hardens above 250°F.
Alkaline Solutions	Satisfactory except lead, tin, zinc, aluminum and alloys.	Limited, depending on conditions, exposed surfaces become tacky.	Satisfactory but exposed surfaces swell.
Weak Acid Solutions (including Acetic and other organic acids, sulphurous acid and low concentration of sulphuric acid and hydrochloric)	Copper, its alloys and stainless irons satisfactory; aluminum satisfactory in organic acids only and lead in all but acetic acid.	Satisfactory all free from acid-soluble fillers.	Satisfactory all free from acid-soluble fillers.
Strong Acids Hydrochloric Acid	Not recommended except Hastelloy, gold and platinum.	Limited depending on conditions.	Limited depending on conditions.
Sulfuric Acid Dilute up to 50%	Not recommended except Duriron, lead, gold and platinum.	Limited depending on conditions.	Limited depending on conditions.
Concentrated Sulfuric Acid	Limited depending on conditions.	Not recommended.	Not recommended.
Concentrated Acetic Acid (Glacial)	Limited depending on conditions.	Limited depending on conditions.	Limited depending on conditions.
Nitric Acid	Not recommended except Duriron, gold and platinum. (Stainless Steel in concentrate but not dilute.)	Not recommended.	Not recommended.
Aqua Ammonia	Satisfactory except copper and its alloys.	Satisfactory but becomes tacky above 200°F.	Satisfactory but hardens above 250°F.
Liquid Ammonia (Anhydrous)	Satisfactory except copper and its alloys.	Limited depending on conditions.	Limited depending on conditions.
Liquid Chlorine, Bromine, etc.	Satisfactory if completely free from water. Otherwise attacks all metals.	Not recommended.	Not recommended.
SOLVENTS Aliphatic (Gasoline, etc.)	Satisfactory.	Not recommended.	Not recommended.
Aromatic Types (Benzol, etc.) or chlorinated Types (Carbontetra-chloride, etc.)	Satisfactory.	Not recommended.	Not recommended.
Acetone	Satisfactory.	Limited depending on conditions. Butyl preferred.	Limited depending on conditions.
Alcohol	Satisfactory.	Satisfactory.	Satisfactory.
OILS	Satisfactory except high-sulphur fuel oils attack copper, iron and alloys.	Not recommended.	Not recommended.

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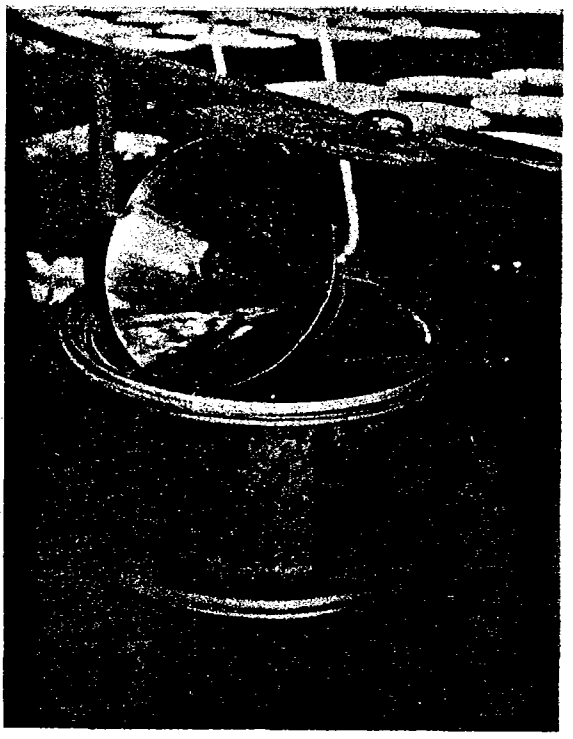
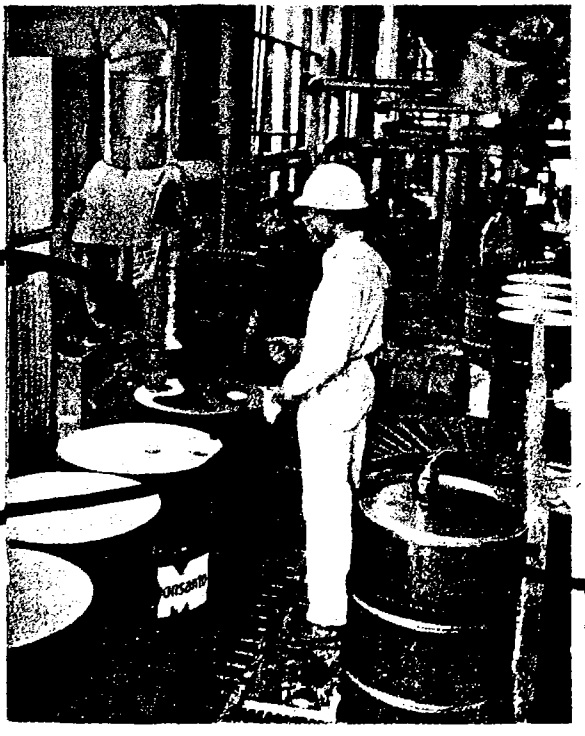
APPENDIX I

Sources of Contamination in Drum Loading

Actual loading - drip can on spout, cap on plywood drum cover, funnel in next drum to be filled.



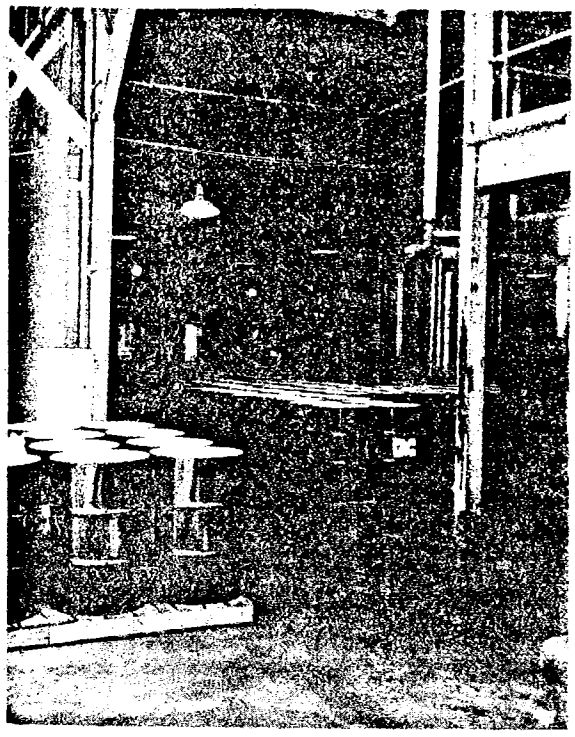
Between-loading exposure of equipment - Funnel resting in pool on old drum lid, plywood drum cover on top.



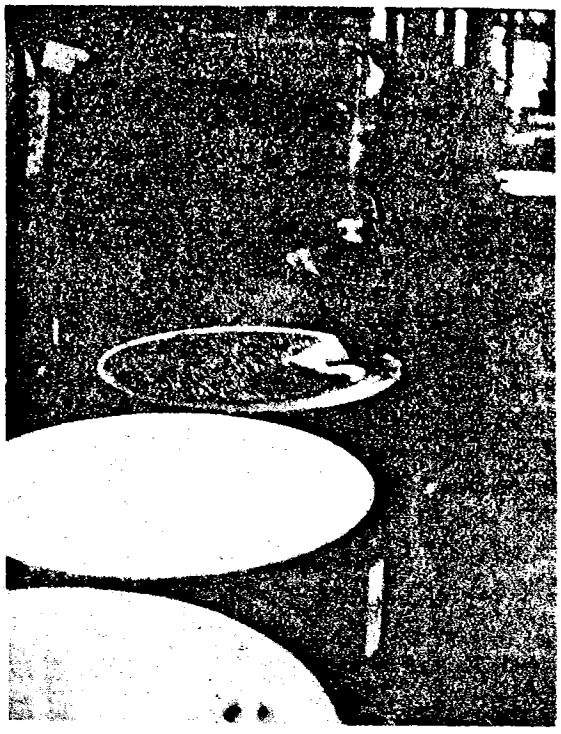
Actual loading - drip can resting on old drum lid, cap on plywood drum cover.

APPENDIX J

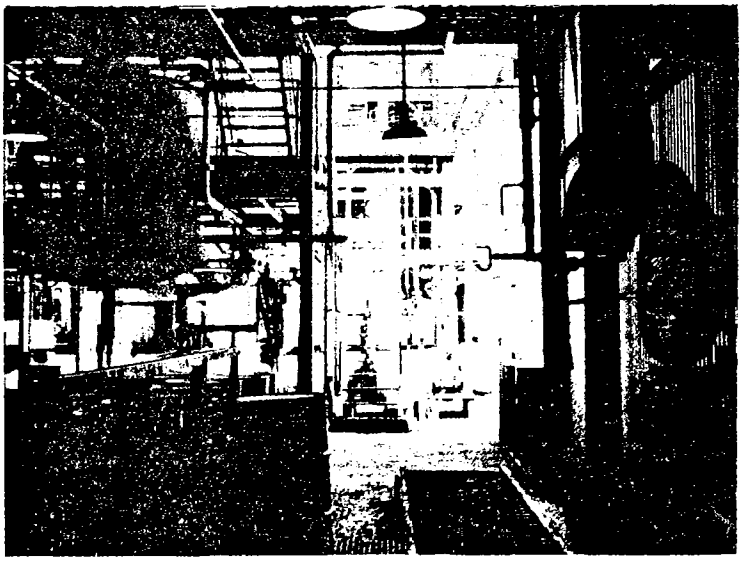
Exposure of Drum Loading to Weather



Weather exposure in Drum loading. Showing open end of building toward west.



Actual loading of drums after rainstorm - water droplets plainly visible on funnel and plywood drum cover.



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APPENDIX K

Laboratory - PR&D Study Designed to Separate Factors Involved in PR&D Superiority

Location →		PR&D		Lab	
Personnel →		BW	DY	BW	DY
Method	PR&D	1	1 2	1 3	2
	Lab	1 3	2	3	3 2

Numbers Refer to Samples 1, 2, 3 From Same Drum

12 tests required, using 3 samples from the same drum, four tests per sample. No repetition is necessary.
Each factor evaluated between averages of four tests. Possible interaction can be evaluated.
Comparisons between conditions will be evaluated against analytical precision information generated by this study.

Note - sample bottles and sampling technique must be very carefully planned to minimize the sample-to-sample differences unavoidably introduced by using 3 samples.

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Appendix L

Organic Division Quality Goals for Electrical Grade Aroclor

Color	10 APHA Max.
Water	20 ppm Max.
Resistivity	10,000 x 10^9 ohm-cm Min.
Power Factor @ 60 cycles	0.2% Max.
Thermal Chemical Chloride Stability	0.1 ppm Max.

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