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Acetone Extraction of "Phenolic Materials"

NAVAL RESEARCH LABORATORY
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INTRODUCTION

(a) Authorization

1. This problem was authorized by Bureau of Engineering Project Order No. 42/38 of 9 July 1937.

(b) Statement of Problem

2. The problem is to study the acetone extraction of phenolic materials. This acetone extraction test was proposed by the Bureau of Engineering as a specification for obtaining information on the relative cure of molded phenolic materials. This test has been accepted as an ASTM tentative method and is designated as D-494-38T.

(c) Theoretical Considerations

3. The phenolic material studied is a thermo-setting solid produced by the condensation of phenol and formaldehyde. In the final product there remains some unreacted phenol and formaldehyde, some partially condensed, the dye that is often added to give color, and asbestos and a fibre to give the finished product strength. Of these products the unreacted base materials are readily soluble in acetone and the partially condensed product and the dye to a lesser extent. The ingredients soluble in acetone are extracted and the acetone is evaporated and the residue is weighed, giving a measure of the soluble constituents. This residue is believed to be a measure of the cure of the finished product. An incompletely cured product should have a larger per cent of acetone soluble components and one completely cured or over-cured should have a low per cent of soluble material.

4. Of the extractable materials, free phenol is found to be one of the constituents. It is detectable during the evaporation of the acetone for during the evaporation the free phenol is lost. Therefore the final residue consists of the material that is soluble in acetone minus the phenol that is volatilized during the evaporation of acetone. If the amount of uncombined phenol could be determined, it possibly would give a measure of the cure equally as well as the extraction test.

METHODS

(a) Materials

5. The materials studied in this investigation were commonly used commercial products furnished by leading manufacturers in this field. The source and designation of each sample is given in paragraph 10 of the appendix. The acetone used for these extractions complied with Federal Specification O-A-51a.

(b) Equipment

6. The extraction apparatus and oven for carrying out the evaporation were designed to conform with specifications received from the

Brooklyn Navy Yard. It consists of a Wiley-Richardson extraction apparatus with a suitable heating unit. The drying chamber is constructed so that the base is heated and controlled thermostatically and is ventilated with preheated air. It was found that the best ventilation could be had by using a vacuum sweeper type of blower. The distillation output used for the phenol determination was of the same design as that for ammonium distillations.

(c) Procedure

7. Samples of Bakelite for the extraction were prepared by milling the molded material. By this method the bakelite was heated less than if the sample were drilled. The method used is as follows: The sample is fed at the rate of 1 inch per minute at 35 r.p.m. using a 4-inch diameter mill tool of 22 teeth. These millings after a little working in a mortar will pass through the required 40 mesh sieve.

8. Three grams of the bakelite millings prepared in the standard manner were accurately weighed out and folded into a filter paper. Fifty cubic centimeters of acetone were placed in the flask and the rate of heating was adjusted so that the siphons emptied 15 to 20 times per hour. Then the samples were put in the siphons and the extractions continued for 4 hours. The contents were then poured into individually weighed tinfoil dishes and the flasks washed sparingly three times. The washings were added to the extraction solution. The tinfoil dishes were then placed in the oven maintaining a temperature of $50^\circ \pm 2^\circ C$ and were dried to a constant weight. It was observed that during the evaporation of the extract free phenol was present in the escaping vapors and the residue remaining was found to be the partially condensed phenol formaldehyde resins and dyes.

DATA OBTAINED

9. Averages of determinations made on the samples examined appear below in Table 1. The individual analysis from which these results were averaged appear in the appendix, paragraph 11.

TABLE 1

Residue from Acetone Extraction, Per Cent

Sample	Operator #1	Operator #2
A	1.74	1.83
B	0.95	1.01
C	5.09	4.99
D	1.66	-
BA	5.59	-
BB	6.38	-
BC	4.71	-
BD	10.97	-
X	1.75	-

10. The values listed in Table 1 were obtained after the samples were extracted for four hours with acetone. In order to determine the completeness of the extraction at the end of four hours, several samples were run for four additional hours with the following results.

TABLE 2

Sample	Extraction at 4 hrs. Per Cent	Extraction at 8 hrs. Per Cent	$\frac{4 \text{ hrs.}}{8 \text{ hrs.}} \times 100$
A	1.69	1.97	85.7
A	1.68	1.92	87.8
B	0.97	1.09	89.0
B	0.93	1.07	86.8
C	5.18	5.34	97.0
C	5.18	5.27	98.3

The foregoing figures indicate that four hours are sufficient for the extraction of 85 per cent or more of that found in eight hours. Although some additional material may be extracted by further treatment, it does not appear advisable to extend the extraction time to eight hours. However, it is necessary to maintain uniform conditions throughout all determinations as uncontrolled conditions would introduce considerable error.

11. As already pointed out, it has been suggested that the amount of uncombined phenol and bakelite possibly would give some measure of the extent of cure. Methods were developed for the determination of this phenol in the millings directly and also in the acetone extract. The details of each method are described in the appendix. The results of each method applied to a number of samples are given together in Table 3.

TABLE 3

Sample	Phenol - Per Cent found in Acetone Extract	Phenol - Per Cent found directly in Millings
C	0.23	0.42
BC	0.45	0.60
BD	0.97	1.03
X	0.38	0.50

It is apparent that the values obtained directly from the millings are uniformly higher than those from the acetone extract.

12. It is significant to note that the ratio of phenol to the total residue is approximately the same (8 to 12 per cent) in various samples examined. This is shown in Table 4.

TABLE 4

Sample	Residue from Extraction Per Cent	Phenol Found Per Cent	Ratio of Phenol to Total Residue Per Cent
C	5.04	0.42	12.0
BA	5.58	0.67	9.5
BB	6.38	0.73	8.5
BC	4.71	0.60	7.9
BD	10.96	1.03	10.6

13. Of the samples studied, (B), (C), and (D) had been tested for electrical properties as described in Naval Research Laboratory Report No. R-1117 wherein they are designated as products numbers 4, 3, and 1, respectively. Table 5 compares some of their electrical properties with the amount of material extractable from them with acetone.

TABLE 5

Sample	Acetone Extract Per Cent	Phenol Found Per Cent	Breakdown Voltage Volts	Loss Factor Decimal Fraction
B	1.79	-	5000	1.58
C	5.05	0.60	8000	0.129
D	1.66	-	1300	-

From the data it is apparent that no definite relationship exists between the percentage of the insulator extractable with acetone and its electrical properties.

14. The relationship existing between the time and temperature of the curing process and the extractable materials is shown in Table 6. For samples (BC) and (BD) no definite information was submitted from the manufacturers as to the curing time and temperature. It was merely indicated that (BC) was cured for a longer period and (BD) a shorter period than either samples (BA) and (BB).

TABLE 6

Sample	Curing Time Minutes	Curing Temperature °F.	Acetone Extract Per Cent	Phenol Per Cent
BA	10	320	5.59	0.67
BB	5	280	6.38	0.73
BC	More than 10	320 or above	4.71	0.60
BD	Less than 5	280 or less	10.97	1.03

CONCLUSIONS AND RECOMMENDATIONS

15. The acetone extraction of phenolic molded and laminated products was found to give reproducible results for individual products. Apparently results can be duplicated on a given sample to within ± 1 per cent.

16. From the information and data obtained, it is apparent that the material extractable as well as the free phenol present varies inversely as the degree of curing. If additional quantitative data should bear this out, the determination of the extract in free phenol present should serve as an index to the extent of curing.

17. It was shown that the suggested time for the extraction (4 hours) is not sufficient to quantitatively remove all extractable material. The time involved for complete removal makes the operation impractical, but if strict adherence to the outlined procedure is followed, results are obtained which are easily reproducible and reliable.

18. From the data thus far obtained the electrical properties may not be reliably correlated with the free phenol content or the acetone extractable substances. This phase of the problem deserves further study. However, the fact appears established that the free phenol present occurs in a definite proportion to the total extract as from 8 to 12 per cent.

SUMMARY

19. The method of analysis of bakelite by determining the amount of acetone-soluble material has been studied. It has been shown that by strict adherence of the outlined procedure results are reproducible which give a good index to the cure of the material being studied.

20. An additional method was developed whereby phenol may be determined directly in the millings. Should further tests bear out the results obtained herein by this procedure, it offers a quicker and more direct determination of the extent of curing bakelite type insulators.

APPENDIX

DETAILS OF METHODS EMPLOYED IN THESE STUDIES

1. The method for determining the relative cure of phenolic materials as tentatively accepted by ASTM, D-494-38T, assumes that during the evaporation of the acetone from the extract the same relative amount of extractables are lost by evaporation in each determination. To amply verify this assumption experiments to confirm this fact were conducted.

Determination of Phenol in Acetone Solution

2. In order to get some idea as to the amount of free phenol in the extract before evaporation, a method was sought whereby the phenol could be determined in this extract. The method evolved consists of brominating the phenol in acetone so that acetone can be evaporated without the loss of phenol. Bromine is added to the acetone and water solution of phenol, and the excess bromine removed with a slight excess of sodium bisulfite. Sodium hydroxide is added and the precipitated tribromphenol dissolved. The solution is heated on a hot plate for complete removal of the acetone. The alkaline solution is allowed to cool and is acidified, precipitating the tribromphenols. A large excess of freshly prepared saturated bromine water is added and the precipitate allowed to stand for 4 hours. Tribromphenol bromide forms. Next sodium bisulphite is added in large excess and after stirring, the precipitate is allowed to stand for 5 minutes. The tribromphenol is filtered off and weighed. The results are within 2 per cent of the theoretical. The determinations as made are given below in tabular form.

Results of Determinations of Known
Solutions of Phenol in Acetone

TABLE I

Weight Phenol Taken	Weight Phenol Found
.0200 gm.	.0204 gm.
.0200	.0213
.0100	.0082
.0100	.0096
.0100	.0110
.01035	.0105
.01035	.0102
.01035	.0103
.0100	.0095
.0100	.0091
.0200	.0196
.0200	.0190
.0400	.0384
.0400	.0370
.0026	.0021

Effect of Time of Standing of Precipitate in Presence of Excess $NaHSO_3$ before Filtration

Weight Phenol Taken	Time	Weight Phenol Found
.0400 gm.	1 min.	.0421 gm.
.0400	5 min.	.0396
.0400	10 min.	.0394

Effect of Adding Too Much $NaHSO_3$ in First Reduction of Bromine before Evaporation

Weight Phenol Taken		Weight Phenol Found
.0100 gm.	Excess $NaHSO_3$	.0077 gm.
.0100	Excess $NaHSO_3$	.0059
.0100	Slight excess	.0102
.0100		.00998
.0100		.0102

Determination of Total Free Phenol

3. Using the foregoing method for the determination of phenol in acetone, the acetone extract is treated as follows: Water is added to the extract and the acetone distilled off. The phenol going over with the acetone is determined by the method as outlined in paragraph 2 above. The aqueous residue left from the removal of the acetone is completely distilled and the remainder of the phenol distilling with the water is determined volumetrically.

Determination of Phenol in Millings Directly

4. An attempt was made to determine the free phenol in bakelite millings directly. The millings were placed in water acidified with phosphoric acid and the water distilled over so as to carry all of the free phenol present in the aqueous solution. Phosphoric acid was employed in the distillation of phenol from water solutions as recommended by the chemical laboratory of the Chicago Health Department. The phenol in the distillate was determined volumetrically by an adaptation of the Francis[1] method for determination of unsaturates. A slightly higher per cent of phenol was determined by this method than is found in the acetone extract, as shown by the following:

Ref. 1 - Francis, Ind. Eng. Chem. 18, 821 (1926).

Sample	Phenol in Acetone Extract Per Cent	Phenol in Water Extract Per Cent
C	0.23	0.42
BC	0.45	0.60
BD	0.97	1.03
X	0.38	0.50

5. Acetone has found some application as a substitute for formaldehyde in the manufacture of certain plastics. For this reason it was deemed worthwhile to investigate the possibility of a reaction between acetone and the phenols, such as might occur during the evaporation of the acetone. In order to show the effect of various amounts of phenol on the acetone and the extractable constituents during this evaporation, a series of four runs was made, varying the conditions each time. The results of these determinations made on the same sample of bakelite are shown graphically in Plate 1. Curve 1 represents a regular run in which 3 grams of milled bakelite was extracted for four hours with 50 cc of acetone. The extract was evaporated in the usual manner and the first weighing made at the end of three hours. Subsequent weighings were made periodically to approximate constant weight. At this point 40 milligrams of phenol and 40 cc of acetone were added and evaporation repeated to constant weight. This final weight was found to agree closely with that from the first evaporation, indicating that both the added phenol and the acetone were removed. Three additional runs were made, the curves of which also appear on Plate 1. As shown in Curve 2, Plate I, extraction was carried out as usual, but 80 milligrams of phenol was added to the extract before evaporation started. At constant weight 40 milligrams of phenol and 40 cc of acetone were added and evaporation repeated. This final weight agreed with that from the first evaporation, again showing the complete removal of the added phenol. In runs 3 and 4, 80 milligrams of phenol were added to the extraction liquid (the acetone) and to the milled sample, respectively. At constant weight, 40 cc of acetone were added to each and evaporation repeated.

6. From observation of curves 2, 3 and 4, it is apparent that all of the added phenol has not evaporated, otherwise there would be the same amount of residue in the dishes of the evaporation as shown by curve 1. It is seen then, that there is retention of the phenol by the extracted material and more was retained when the added phenol was originally in contact with the chips. When additional acetone is added to the residues, as shown by curves 3' and 4', more of this phenol evaporates. Thus it follows that the phenol does not combine with the other condensed phenol material but, because of similar physical character to these materials, is held in the mass of non-volatile material that was extracted by the acetone.

7. To further investigate the possible error due to reaction between acetone and the phenol, the phenol was determined without evaporating the acetone. Water was added to the extract which was then treated

with bromine, after which the acetone could be evaporated without loss of phenol. The residue in this water was filtered and weighed. The amount of free phenol that was present being known from a previous determination, an allowance was made for its bromination. The weight of residue less the added weight due to the bromination of phenol divided by the number of grams of sample gives per cent of extracted material. The determination does not allow for bromination of other higher condensed phenols. The only observation that can be made from the results is that as they are of the same order of magnitude as the regular extractions, there is no reaction between the acetone and the extracted material during the evaporation of the acetone.

Per cent residue by above method	12.1	12.6
Per cent residue by regular method	10.8	11.1

Loss of Phenol during Evaporation of Acetone

8. Knowing that phenol is lost during the evaporation of the acetone, an investigation was carried out to observe the behavior of solutions of phenol in acetone when evaporated by the prescribed procedure. This investigation was carried out under various conditions. The significant facts are:

(a) The amount of phenol lost varies critically with the position of the evaporating dish in the oven.

(b) It is impossible to stop any one evaporation at exactly the point where the acetone is gone and only phenol remains.

The data are shown in Table II.

TABLE II

EVAPORATION OF PHENOL-ACETONE SOLUTIONS AT 50°C.

Run No.	Grams Phenol in 40 cc Acetone	Time (Minutes) Evaporated	Weight of Residue Gms.	Amount Phenol Lost Gms.	Per Cent Phenol Lost
1	0.808	60	0.144	0.664	82
2	0.808	60	0.251	0.557	69
3	0.808	60	0.492	0.316	39
4	0.808	60	0.508	0.300	37
5	0.808	60	0.608	0.200	25
6	0.808	60	0.631	0.177	22
7	0.808	60	0.563	0.245	30+
8	0.952	60	0.271	0.681	71
9	1.059	60	0.431	0.628	56
10	1.300	60	0.872	0.428	33-
11	1.316	60	0.896	0.420	32
12	1.416	60	1.194	0.222	15.6
13	1.439	60	1.278	0.161	11.2
14	1.371	60	1.172	0.199	14.5

TABLE II (CONTINUED)

Run No.	Grams Phenol in 40 cc Acetone	Time (Minutes) Evaporated	Weight of Residue Gms.	Amount Phenol Lost Gms.	Per Cent Phenol Lost
15	0.338	60	0.044	0.293	87
16	0.132	60	0.014	0.118	90-
17	0.144	60	0.056	0.088	61
18	0.300	120	0.001	0.300-	100-
19	0.300	120	0.001	0.300-	100-
20	0.300	120	0.022	0.280-	93
21	0.300	30	0.047	0.250+	84
22	0.500	30	0.070	0.430	86
23	0.666	37	0.338	0.328	49
24	0.300	37	0.132	0.168	56
25	0.300	37	0.144	0.156	52
26	0.808	10	0.807	0.001	0
27	0.808	10	0.986	-	-
28	0.808	10	0.749	0.059	7.3
29	0.808	10	0.643	0.165	20.0+
30	0.808	10	0.506	0.302	37
31	0.808	10	0.687	0.121	15
32	0.808	10	0.623	0.185	23
33	0.300	103	0.118	0.180	60
34	0.300	103	0.170	0.130	43+
35	0.300	103	0.298	0.000+	0
36	0.300	103	0.256	0.040+	7.5

9. The method of determining phenol in bakelite chips by extraction of water and subsequent distillation of the entire mixture is described in paragraph 4. It appears more specific than extraction with acetone. The acetone extraction may be influenced by fillers present in the bakelite and plasticizers and reagents used to form the resin. Phenol is appreciably soluble in water and volatile with steam. When the bakelite chips are digested in boiling water the phenols are extracted and at the same time distill over with water, while the other organic materials remain behind.

Evaporation of Acetone at Room Temperature

10. An experiment was carried out to determine the loss of phenol when a phenol-acetone solution was allowed to evaporate at room temperature with the forced air draft. Forty cc of acetone containing 0.300 grams of phenol were placed in each of two tinfoil dishes and allowed to evaporate at room temperature. These were weighed from time to time as follows:

TABLE III

	1		2	
Time Hours	Weight Lost in Grams	Per Cent Lost	Weight Lost in Grams	Per Cent Lost
18	.0843	28	.1005	33
26	.1987	66	.2187	73
42	.2837	94	.2870	96
70	.2944	98	.2935	98
94	.2965	99	.2945	98
163	.2980	99+	.2957	99+
193	.2980	99+	.2962	99+

The above data are plotted on Plate 2. From the curve (Plate 2) it is evident that if pure phenol is present in quantity greater than 0.02 gram, the loss during evaporation at room temperature is quite appreciable. On the other hand, if the quantity of phenol is less than 0.015 gram, the rate of evaporation is very slow.

11. Numerous extractions were made on some of the samples submitted to check the method as accepted by ASTM. The figures given in the main body of the report for the percentage extractable with acetone are averages derived from the following individual determinations.

TABLE IV

Percentage by Weight Extractions with Acetone

Sample	A	B	C	D	BA	BB	BC	BD	X
1	1.73	0.96	5.18	1.66	6.65	6.3	4.78	11.08	1.7
2	1.75	0.94	5.17	1.69	5.52	6.5	4.65	10.85	1.8
3	1.72	0.96	5.18	1.68					
4	1.72	0.98	5.18	1.69					
5	1.71	0.97	5.20	1.70					
6	1.71	0.92	5.17	1.70					
7	1.73	0.97	5.19	1.67					
8	1.72	0.93	5.17	1.67					
9	1.68	0.94	4.95	1.64					
10	1.71	0.91	4.98	1.66					
11	1.69	0.92	4.96	1.69					
12	1.69		5.03						
13	1.68		5.00						
14	1.68		5.27						
15	1.68		5.27						
16	1.77		5.26						
17	1.74		5.24						
18	1.74		5.00						
19	1.75		4.97						
20	1.75								
21	1.75								
22	1.74								
23	1.78								

12. The samples of bakelite used in this investigation were obtained from the following sources:

Sample	History
A	Continental Fiber.
B	Textolite 1841A - General Electric Co. - Referred to in NRL Report No. R-1117 as product #4.
C	G.E. #2008 - General Electric Co. - Referred to in NRL Report No. R-1117 as product #3.
D	Spauldite - Spaulding Fibre Co. - Referred to in NRL Report No. R-1117 as product #1.
BA) BB) BC) BD)	Different grades of Bakelite furnished by the Bakelite Corporation.
X	Manufacturer unknown.

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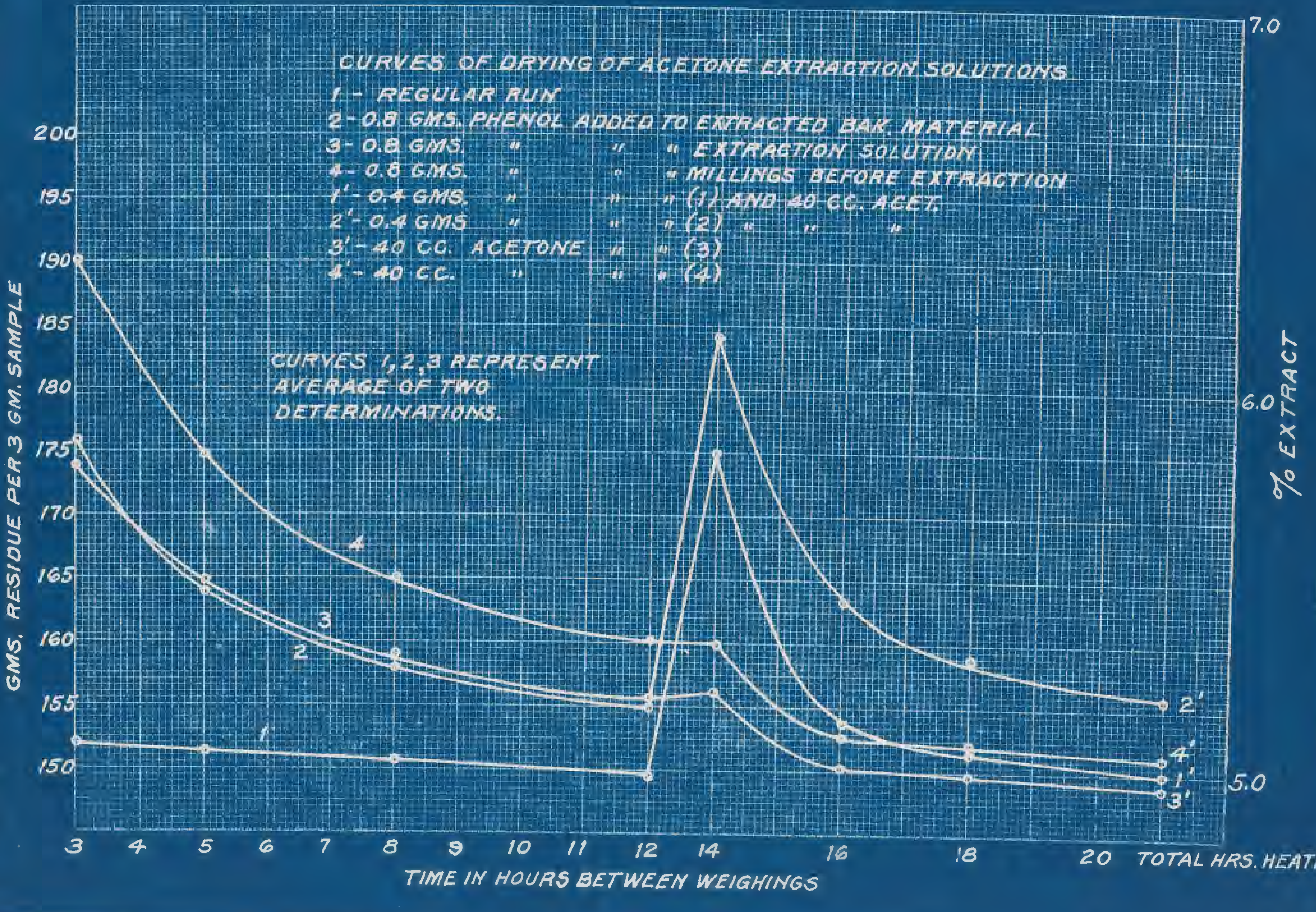

PLATE 1

IF SHEET IS READ THIS WAY (HORIZONTALLY) THIS MUST BE TOP. IF SHEET IS READ THE OTHER WAY (VERTICALLY) THIS MUST BE LEFT-HAND SIDE.

N. R. L. 31A

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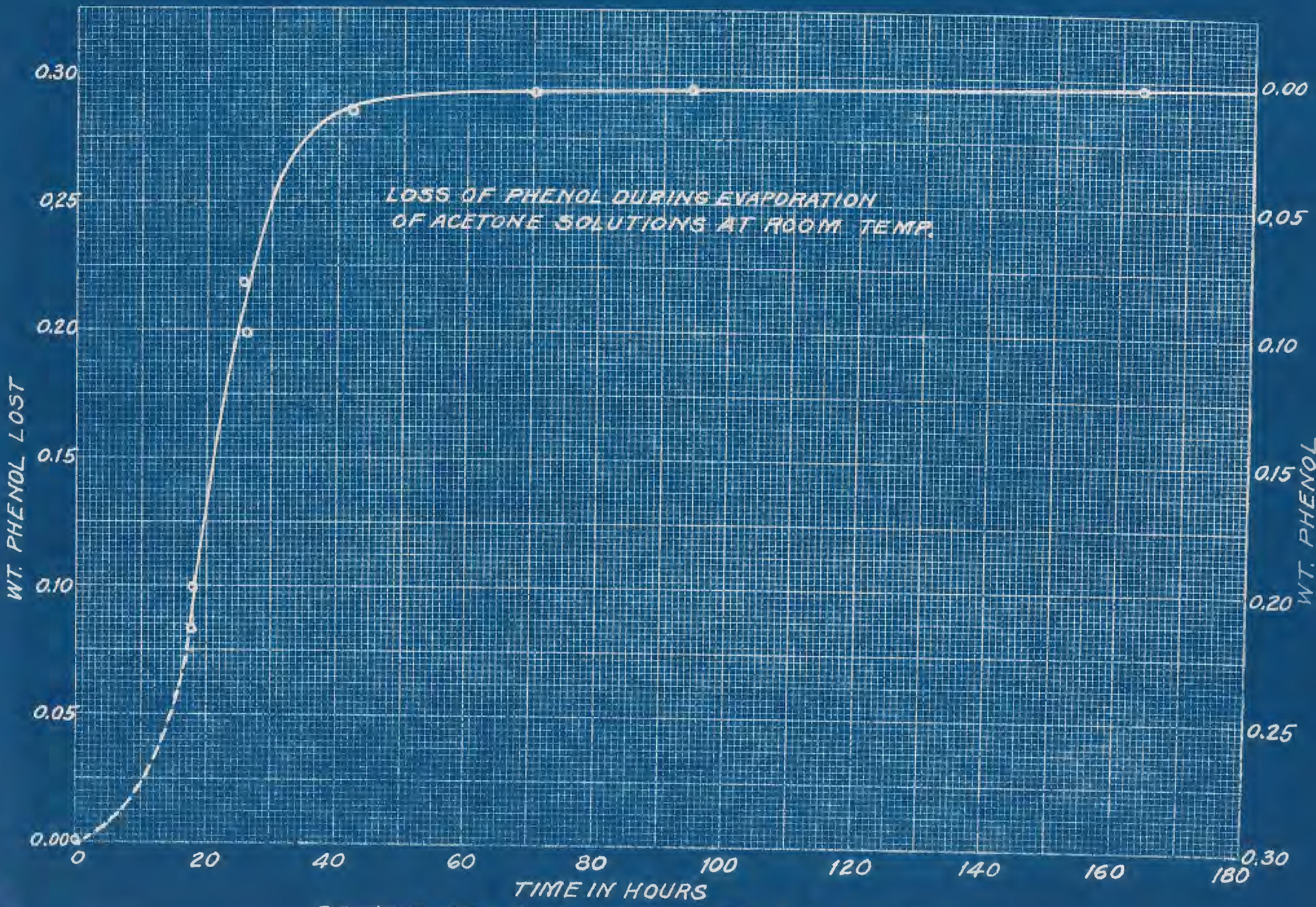

LOSS OF PHENOL DURING EVAPORATION
OF ACETONE SOLUTIONS AT ROOM TEMP.

STARTING WITH 40 CC. ACETONE AND 0.30 G. PHENOL.

PLATE 2