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ABSTRACT

A series of varnishes was prepared in the Laboratory from various natural and commercial drying oils. The effects of varnish viscosity and oil length upon the durability and water vapor impedance of the films were studied. Though a maximum resistance to moisture transfer is highly desirable, it is often attained by sacrifice of other properties essential to durability. Durability is usually enhanced at longer oil lengths. Varnishes cooked to high viscosity generally have greater durability and higher moisture impedance. The alkyd varnishes are rather low in durability and moisture resistance. The commercial oils examined appear to be adequate.

INTRODUCTION

A. Authorization

1. This study was authorized by Bureau of Aeronautics letters Aer-E-2571-L2-51F38 0919E3 dated 10 July 1942 and Aer-E-2571-MVS F38-2-090781 dated 8 July 1942.

B. References

2. NRL Report No. P-2188 dated 10 November 1943 and NRL Report No. P-2030 dated 9 February 1943.

C. Background

3. The study of plywood finishing is a continuing problem of the Laboratory. Progress reports, referenced above, have been submitted and the results contained therein indicate the following:

a. The application of filler directly to the bare wood rather than over a sealer coat enhances the durability of the finishing system.

b. The primer surface coat, which is essentially a coat of very heavily pigmented sealer, offers no special advantage over a clear sealer coat.

c. A properly formulated phenolic resin type wood sealer is superior to the alkyd.

d. Pigmentation of the sealer generally results in increased durability of the finishing system, though there are hazards in over-pigmentation.

4. The product described by AN-S-17 is a low solids varnish, which by reason of its low viscosity is expected to penetrate the wood surface thereby investing fibers with a moisture resistant coating. Simultaneously it should afford improved adhesion for the coats to follow. Unreported observations of this Laboratory indicate that the sealer, even when thinned to dip viscosity, penetrates the wood very little. Since the penetration is negligible, any possible merit of a low viscosity, low solids varnish, seems to disappear. Since the sealer is shown to be primarily a surface film, it seems desirable to make the coating material one that offers a maximum of durability and moisture resistance. Specifically, the argument favors use of a high solids varnish, as typified by AN-TT-V-116 or -118 in place of their

low solid, low viscosity counterpart, AN-S-17.

5. Formulation of the vehicle is an open question though there are a number of points which are reasonably well established. Long oil phenolics are generally deemed superior, though studies at this Laboratory show that varnishes of high resin concentration are more resistant to moisture transfer. Tung is acknowledged as the superior oil. When it is not available, the selection of the best alternative is not easy nor is the issue of cooking the varnish to a high or to a low viscosity clarified.

6. The work reported here attempts to provide preliminary experimental data on the following points.

a. Selection of drying oils to use in formulating the most durable phenolic and alkyd sealer-varnishes. This includes a study of the relative merits of various commercial synthetic drying oils.

b. The effect of length of cook on the durabilities of phenolic varnishes.

c. The relative merits of phenolic and alkyd vehicles.

EXPERIMENTAL METHOD

7. A series of phenolic varnishes of 55% solids were prepared as listed in Table I below. The same resin, Bakelite BR-254, a paraphenyl phenol, was used throughout. The variables of the experiment were as follows:

a. Nature of the drying oil.

b. Oil length. The varnishes were prepared in three lengths, i.e., 15, 25, and 40 gallon, except where noted in the table.

c. Viscosity. By control of duration of cook, each varnish was prepared at two viscosities (at 55% solids), namely, B and H on the Gardner-Holdt scale. The exceptions are noted below.

8. The resin was added to the cold oil and heated during 30 minutes to a temperature of 300°C. Because the commercial synthetic oils are already viscous, it was not feasible to cook them to more than one viscosity, namely, H. Because of the high reactivity of tung oil, it is difficult to cook to a high viscosity varnish without risk of losing the batch

through gelation. As a consequence, the tung oil varnishes were cooked to viscosity B only.

9. A series of alkyd resin varnishes was also prepared using dehydrated castor oil and linseed oil only. These are listed in Table II. The concentration of phthalic anhydride was varied within the practical limits shown in the table. All alkyds were cooked to viscosity H. As with the phenolics, the solids content was 55%. Drier concentration in all varnishes was 0.03% cobalt and 0.3% lead, respectively, added as naphthenates.

TABLE I

FORMULATIONS OF EXPERIMENTAL PHENOLIC VARNISHES

Varnish No.	Viscosity	Drying oil	Oil length (gals/100# resin)
1	B	Tung	15
2	"	"	25
3	"	"	40
4	B	Dehydrated castor	15
5	"	" "	25
6	"	" "	40
7	B	Linseed	15
8	"	"	25
9	"	"	40
10	H	Commercial Oil #1	25
11	"	" " #2	25
12	"	" " #3	25
13	"	" " #4	25
14	"	" " #5	25
15	"	" " #6	25
16	H	Dehydrated Castor	15
17	"	" "	25
18	"	" "	40
19	H	Linseed	15
20	"	"	25
21	"	"	40

TABLE II

FORMULATIONS OF EXPERIMENTAL ALKYD VARNISHES

Varnish No.	Viscosity	Drying Oil	Phthalic anhydride percent
22	H	Dehydrated Castor	40
23	"	" "	50
24	H	Linseed	30
25	"	"	40
26	"	"	50
27		(Commercial Varnish A)	-

10. For evaluation of durability, panels of 3-ply mahogany plywood (AN-TT-P-511a) measuring 12" x 12" x 3/16" were pre-pared by sanding and filling, followed by a light sanding. All varnishes were adjusted to spray viscosity B by the addi-tion of xylene where necessary. Two coats were applied by spraying, allowing overnight drying between coats. Each panel was sawed so as to yield a 6" x 12" panel for roof exposure and a 3" x 9" piece for accelerated weathering. All cut edges were sealed with enamel and after the varnish films had aged one week, they were exposed to test.

11. For normal weathering the panels were placed in racks on the Laboratory roof in Washington, D. C., facing south and inclined at an angle of 45°. The surfaces were inspected once each month.

12. Accelerated weathering was performed in a National Carbon Company accelerated weathering unit. The test con-ditions are continuous exposure to light from a twin carbon arc, with an intermittent wetting by water spray (approximately 15 minutes every two hours). Almost invariably the varnish fails by cracking when exposed to accelerated weathering, and the time required for cracking to be initiated is taken as the index of film durability.

13. Moisture permeabilities of the varnishes were compared as follows: Single sheets of 1/32" mahogany veneer were given two spray coats of the respective varnishes. Discs were cut

from the coated veneer, the edges sealed with paraffin wax, and these were sealed to petri dishes, 60 mm. in diameter, containing anhydrous calcium chloride. The wood was held firmly in place by aluminum rings and bolts. The assembly is shown in Plate 6. The units were then maintained in an atmosphere that was approximately saturated at a temperature of 25° to 28°C. and they were weighed periodically.

14. This direct method of evaluating moisture permeability by maintaining a uniformly high vapor pressure gradient across the barrier is very old. However, most of this sort of work with coating materials has been done in one of two ways, both of which are open to criticism. The first consists in applying the coating to a surface to which it shows poor adhesion; e.g., mercury,amalgamated tin or plate glass from which the coating may be detached. The film is then sealed across a suitable vessel. The second method consists in applying the coating to a very permeable film such as cellophane.

15. In the first instance, the lack of adhesion would seem to be direct evidence that the molecular orientation within the film is not that which obtains when the varnish is applied to its proper substrate. Under these circumstances, it seems presumptuous to assume that the permeabilities of the detached film and of the film on a wood surface are equivalent. The same criticism applies with somewhat lesser force to any experiment in which the film is backed by a surface which differs widely from that to which the varnish might normally be applied.

16. Since the films here studied are applied to wood, they are regarded as having the orientation and permeabilities that they would have in service. The veneer itself has some moisture impedance but it is so low that comparisons of the varnishes are not impaired.

EXPERIMENTAL RESULTS

17. The conditions of the panels after 167 days of normal weathering are described in Tables III and IV. Each was rated on the basis of over-all appearance and integrity of the film, by classifying it in one of five groups running from "excellent" to "very poor". Especially in the case of the "excellent" and "good" groups the distinctions are quite arbitrary and further weathering may rearrange the members of two groups somewhat. However, either designation marks a definitely superior coating.

TABLE III

OUTDOOR WEATHERING OF PHENOLIC VARNISHES, 167 DAYS

Varnish No.	Drying oil	Oil length	Film condition
	LOW VISCOSITY ("B")		
1	Tung	15	Fair
2	"	25	Good
3	"	40	Excellent
4	Dehydrated Castor	15	Fair
5	" "	25	Fair
6	" "	40	Excellent
7	Linseed	15	Very poor
8	"	25	Very poor
9	"	40	Good
	HIGH VISCOSITY ("H")		
10	Commercial Oil #1	25	Good
11	" " #2	25	Good
12	" " #3	25	Good
13	" " #4	25	Excellent
14	" " #5	25	Good
15	" " #6	25	Fair
16	Dehydrated Castor	15	Fair
17	" "	25	Good
18	" "	40	Fair
19	Linseed	15	Poor
20	"	25	Good
21	"	40	Excellent
28	Commercial Phenolic Varnish	-	Poor

TABLE IV

OUTDOOR WEATHERING OF ALKYD VARNISHES, 167 DAYS

Varnish No.	Drying oil	Phthalic anhydride percent	Film condition
22	Dehydrated Castor	40	Fair
23	" "	50	Poor
24	Linseed	30	Poor
25	"	40	Good
26	"	50	Poor
27	Commercial Alkyd Varnish		Very poor

18. Data from the accelerated weathering determinations are summarized in Table V. As already mentioned, the index of durability is given as the number of hours required for the initial cracking. To facilitate comparisons, the approximate sequence of breakdown is given in the last column of the table.

19. Data on the permeabilities of the varnish films are depicted graphically in Plates 1 to 5.

DISCUSSION

20. The correlation between normal and accelerated weathering is usually quite poor when overall durability of the finish is being evaluated. It seems highly probable that the respective mechanisms of failure by the two methods are fundamentally different. For that reason, it is probably safest to regard the accelerated test not as a simple intensification of weathering but as a procedure which assesses a set of properties which may not be the properties responsible for durability in "normal" weathering. Since the latter varies with season, climate, and location, the significance of a single outdoor exposure in a given spot should not be overestimated. Accordingly, it is preferred to regard each method as independent and to base a judgment of general durability upon data from both sources, giving some extra weight to observations from roof exposure.

21. It is interesting to note that most of the laboratory formulated varnishes surpassed two commercial products in resistance to normal weathering. (The two items were not subject to accelerated weathering.) The tung oil varnishes were included in the study to serve as criteria for the other varnishes. At the low viscosity it is superior to linseed oil in normal weathering, though the margin in favor of tung oil over dehydrated castor oil in normal weathering is very slight. On accelerated weathering there is no difference between tung and linseed and dehydrated castor oil is slightly superior to either. An overall rating of the lower viscosities would probably credit the tung and the dehydrated castor oil as approximately equivalent and the linseed oil as inferior.

22. Of the three natural oils, only linseed and dehydrated castor oil were studied at the higher viscosity. The durabilities of both on normal weathering were not greatly altered by the extra cooking though the resistance to accelerated weathering was greatly improved.

23. With regard to oil length at low viscosity, the evidence of both normal and accelerated weathering favors the long varnishes with all three oils. At the higher viscosity, medium lengths of dehydrated castor oil and linseed oil are indicated.

24. The question of high versus low viscosity resolves itself generally in favor of the longer cooks.

25. Of the six commercial oils, five equalled or excelled tung at the same oil length though the higher viscosity probably accounts for it. At the same viscosity ("H") and the same oil length, linseed and dehydrated castor oil are superior.

26. It is generally held that a prime agent in the failure of an organic coating on wood is the dimensional charges of the wood as it gains and loses moisture. The durability of the film, therefore, is a function of its resistance to moisture transfer, all other factors being equal. High impermeability of a vehicle, however, is usually attained at a sacrifice of other desirable properties such as flexibility. Inevitably there is a compromise.

27. From a comparison of the data on low viscosity varnishes from Plate 1 and Tables III and V, it will be noted that durability varies inversely with resistance to moisture transfer. At the higher viscosity it is difficult to correlate durabilities and moisture resistance. However, separate

comparisons of each varnish at each oil length with viscosity as the variable, shows durability usually to vary directly with moisture resistance. For example, Plates 1 and 2 show that moisture resistance of 40 gallon linseed oil varnish is not significantly affected by increase in viscosity, and Tables III and V indicate that there is no great change in durability. At the other lengths of linseed oil there is an improvement both in moisture resistance and durability. The conspicuous exception is the 15 gallon dehydrated castor oil varnish, where the more viscous product is much more permeable to moisture, and also much more durable.

28. Plate 4 depicts the moisture transfer of the alkyds. In durability and moisture impedance they are inferior to the phenolics of comparable viscosity. The variations in moisture resistance among the alkyds is not reflected in their respective durabilities.

29. Plate 5 represents selected data from the first four figures. The two varnishes having the highest moisture impedance in each group have been plotted together to facilitate comparison. The lower moisture impedance of the alkyds is notable.

CONCLUSIONS

a. In general, the varnishes of longer oil length are more durable.

b. The varnishes of longer cook have both greater durability and better moisture impedance.

c. There is no necessary relationship between resistance to moisture transfer and general durability.

d. The phenolic varnishes formulated with tung oil appear to be excellent under normal weathering but inferior to many of the commercial synthetic oils and to dehydrated castor under accelerated weathering. The most successful varnish under normal weathering was made with Commercial Oil No. 6.

e. The alkyd varnishes appear to be inferior to the high viscosity phenolics and to the low viscosity phenolics with the exception of the linseed varnishes.

TABLE V

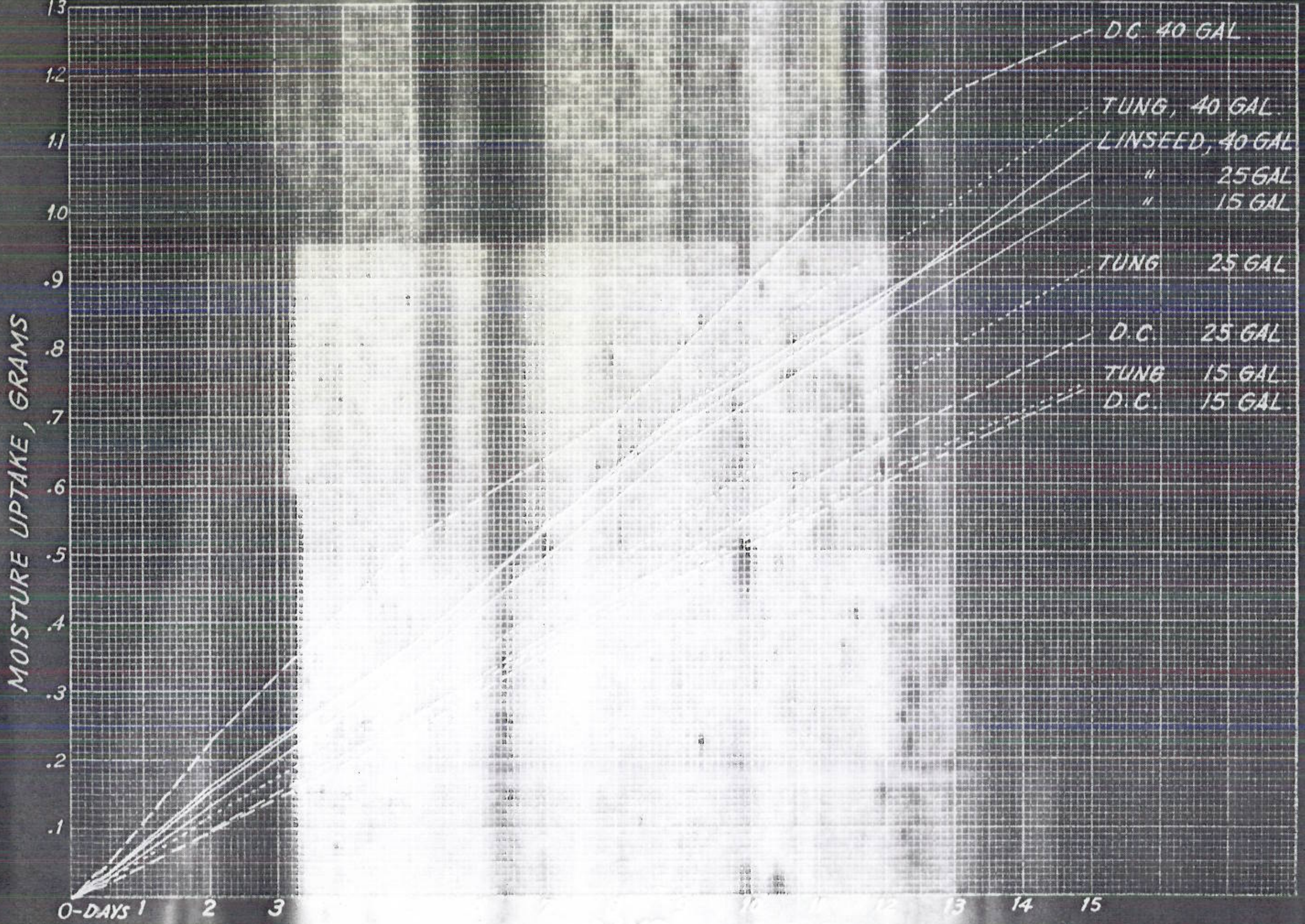
ACCELERATED WEATHERING

Varnish No.	Varnish formulation	Hours to initial cracking	Approximate Sequence of failure
PHENOLICS, LOW VISCOSITY ("B")			
1	15 gal. tung	160	2
2	25 " "	160	2
3	40 " "	365	5
4	15 gal. dehy. castor	189	3
5	25 " " "	189	3
6	40 " " "	365	5
7	15 gal. linseed	160	2
8	25 " "	160	2
9	40 " "	365	5
PHENOLICS, HIGH VISCOSITY ("H")			
10	25 gal. Commercial Oil #1	344	5
11	25 " " " #2	270	4
12	25 " " " #3	103	1
13	25 " " " #4	186	3
14	25 " " " #5	186	3
15	25 " " " #6	186	3
16	15 gal. dehy. castor (H.V.)	1310	8
17	25 " " " "	538	7
18	40 " " " "	396	6
19	15 gal. linseed (H.V.)	396	6
20	25 " " "	1230	8
21	40 " " "	354	5
ALKYDS, HIGH VISCOSITY ("H")			
22	Dehy. Castor Alkyd 40% ph.	262	4
23	" " " 50% "	262	4
24	Linseed 30% ph.	501	7
25	" 40% "	335	5
26	" 50% "	500	7

APPENDIX A

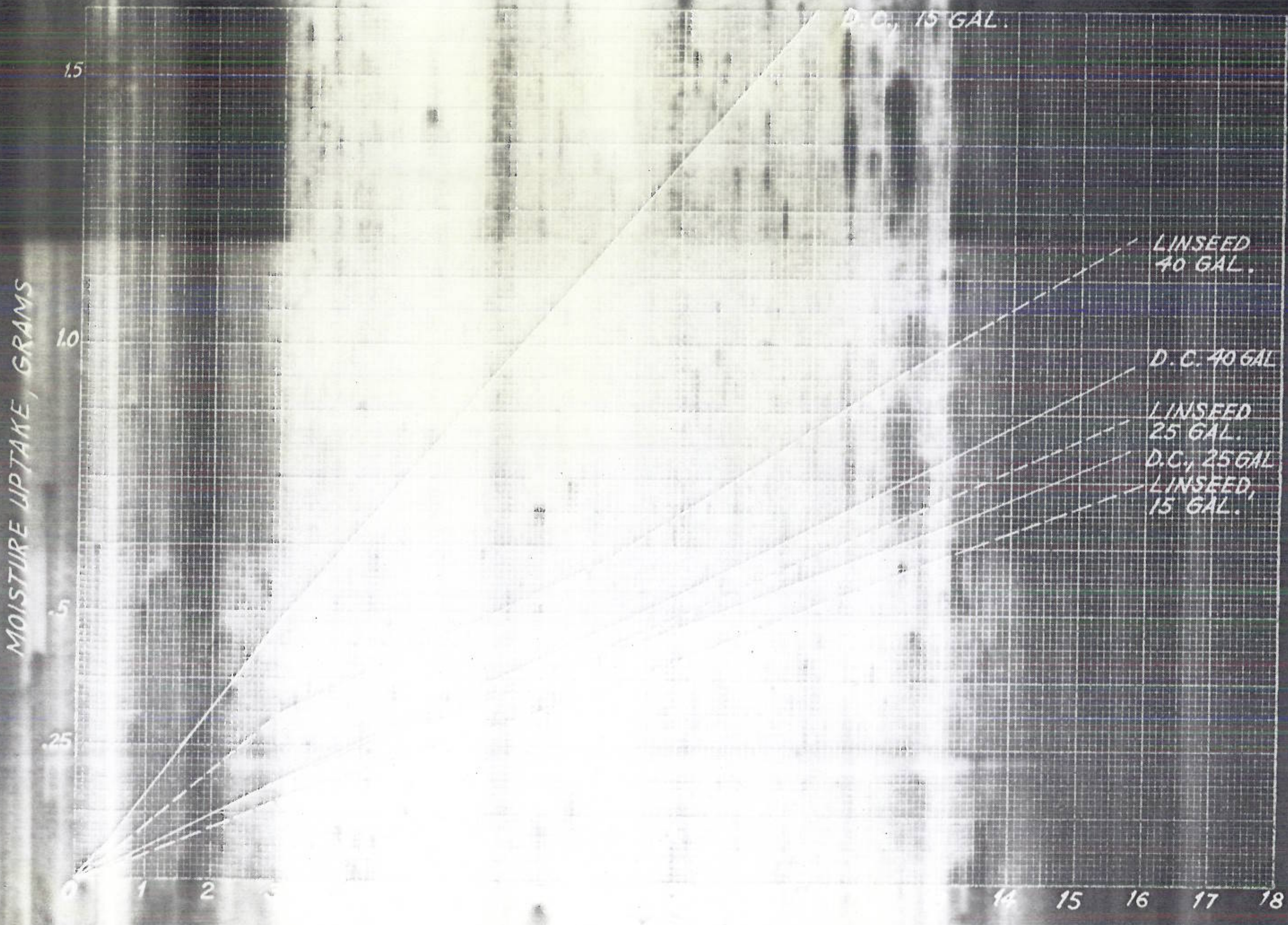
IDENTIFICATION OF COMMERCIAL DRYING OILS

Oil No.	Trade Name	Manufacturer
1	Roosenol #200	H. D. Roosen Co., Brooklyn, N.Y.
2	Selected #200	Pittsburgh Plate Glass, Pittsburgh, Pa.
3	Kellin	Spencer Kellogg, Baltimore, Md.
4	710 Oil (V-73)	National Lead, New York, N.Y.
5	G. F. Oil	E. I. duPont de Nemours & Co., Wilmington, Delaware
6	Kellsoy	Spencer Kellogg, Baltimore, Md.



WATER VAPOR PERMEABILITY OF LOW VISCOSITY NATURAL OIL PHENOLIC VARNISHES

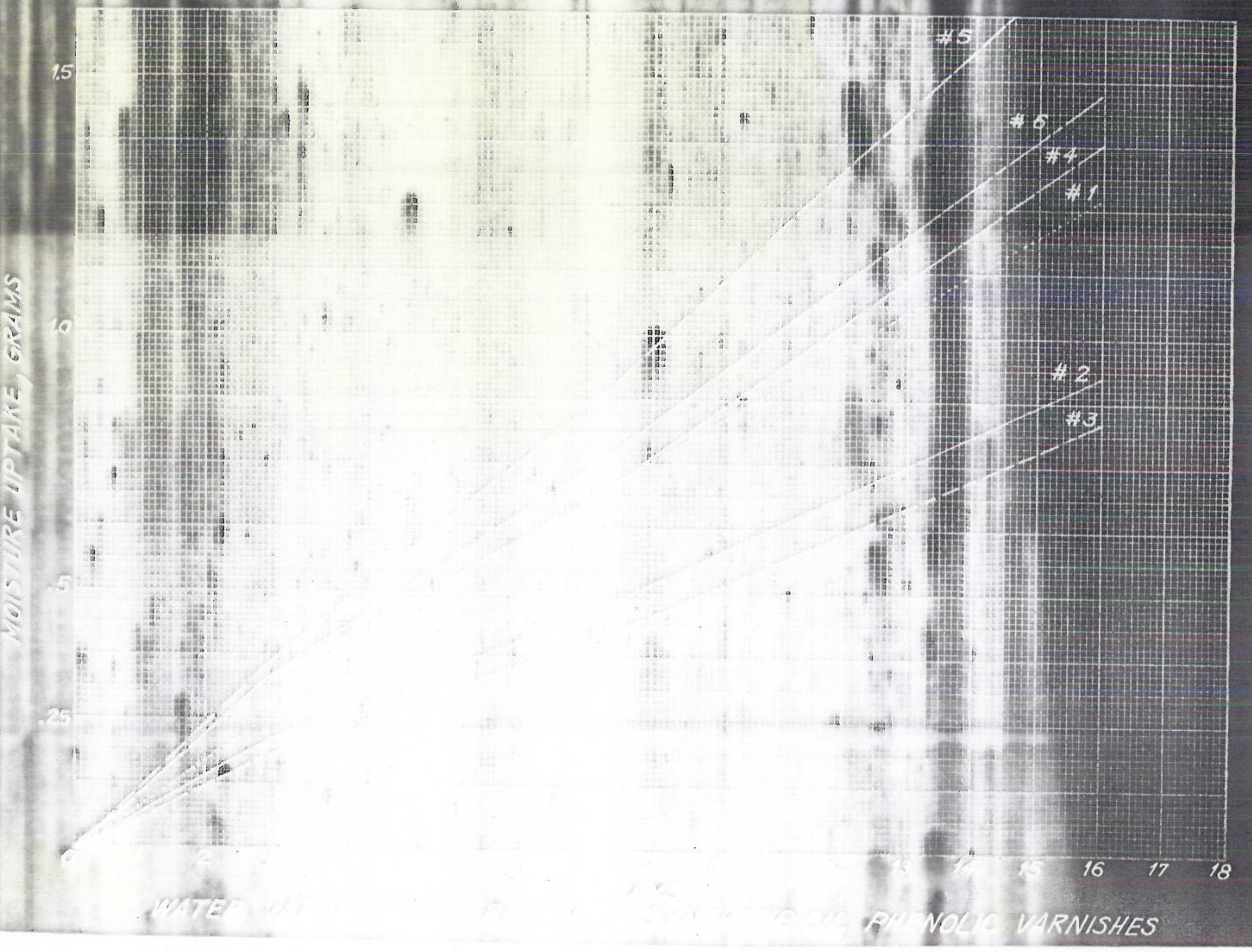
PLATE 1

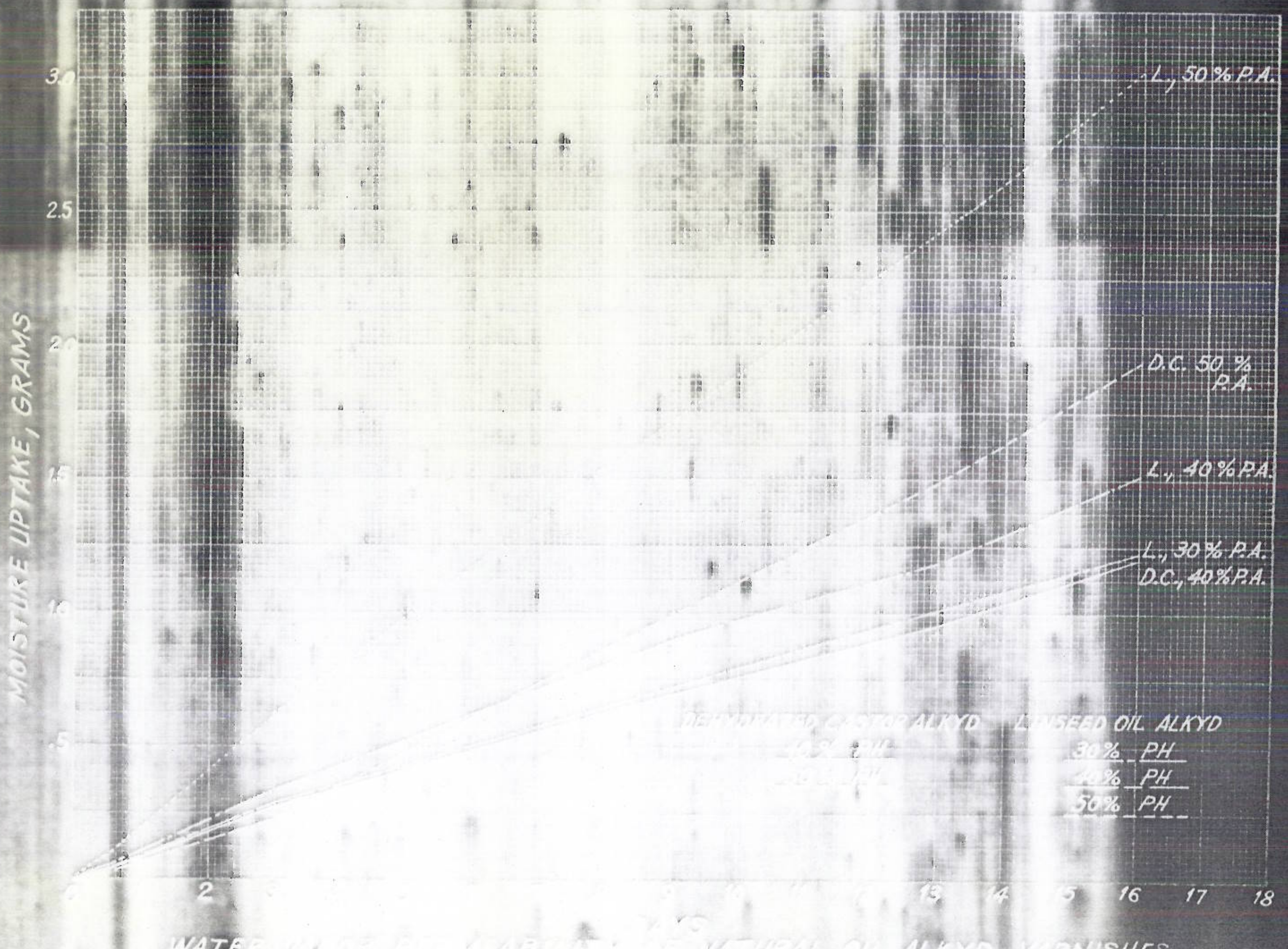


WATER VA[illegible] PHENOLIC VARNISHES

PLATE 2

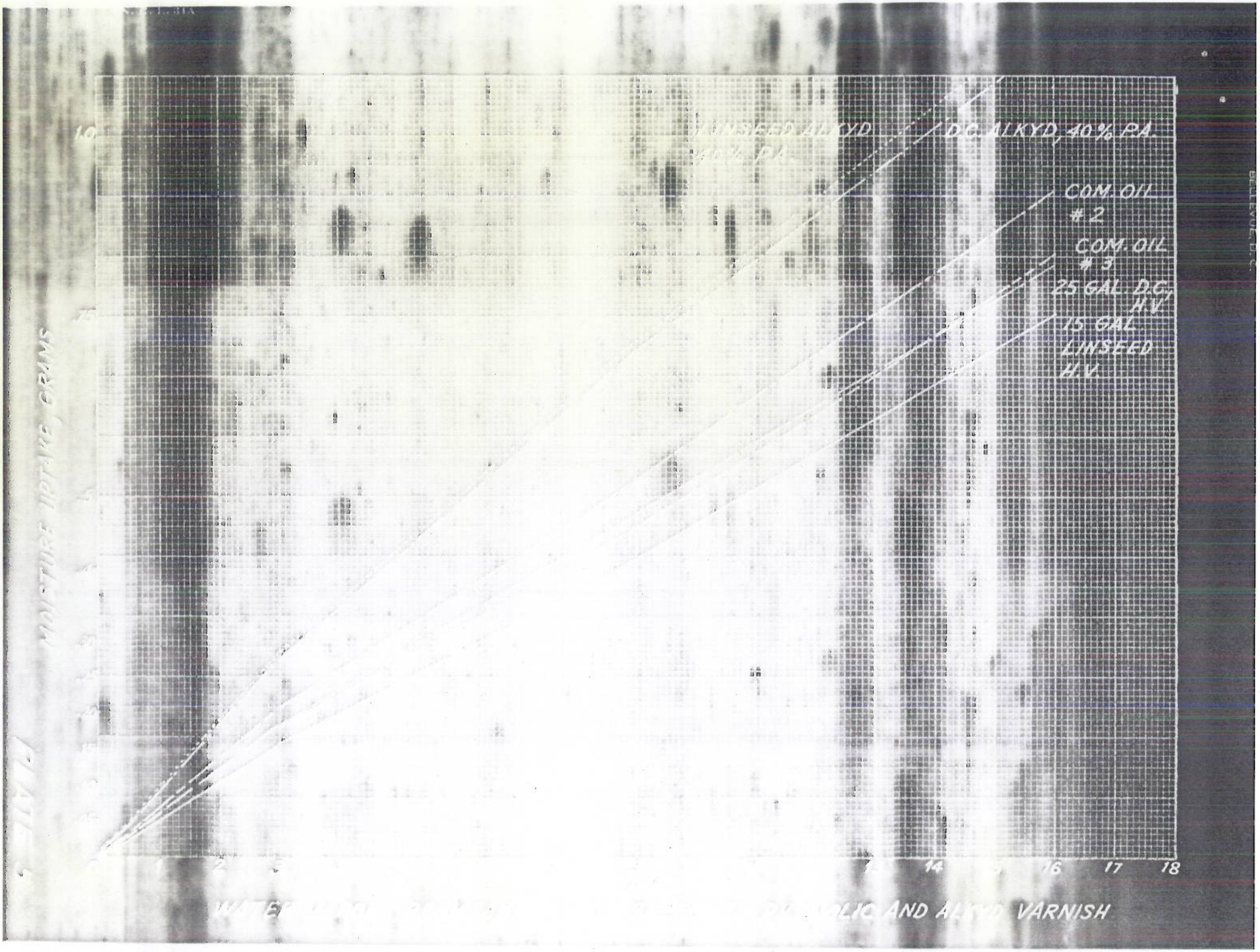
PLATE 3

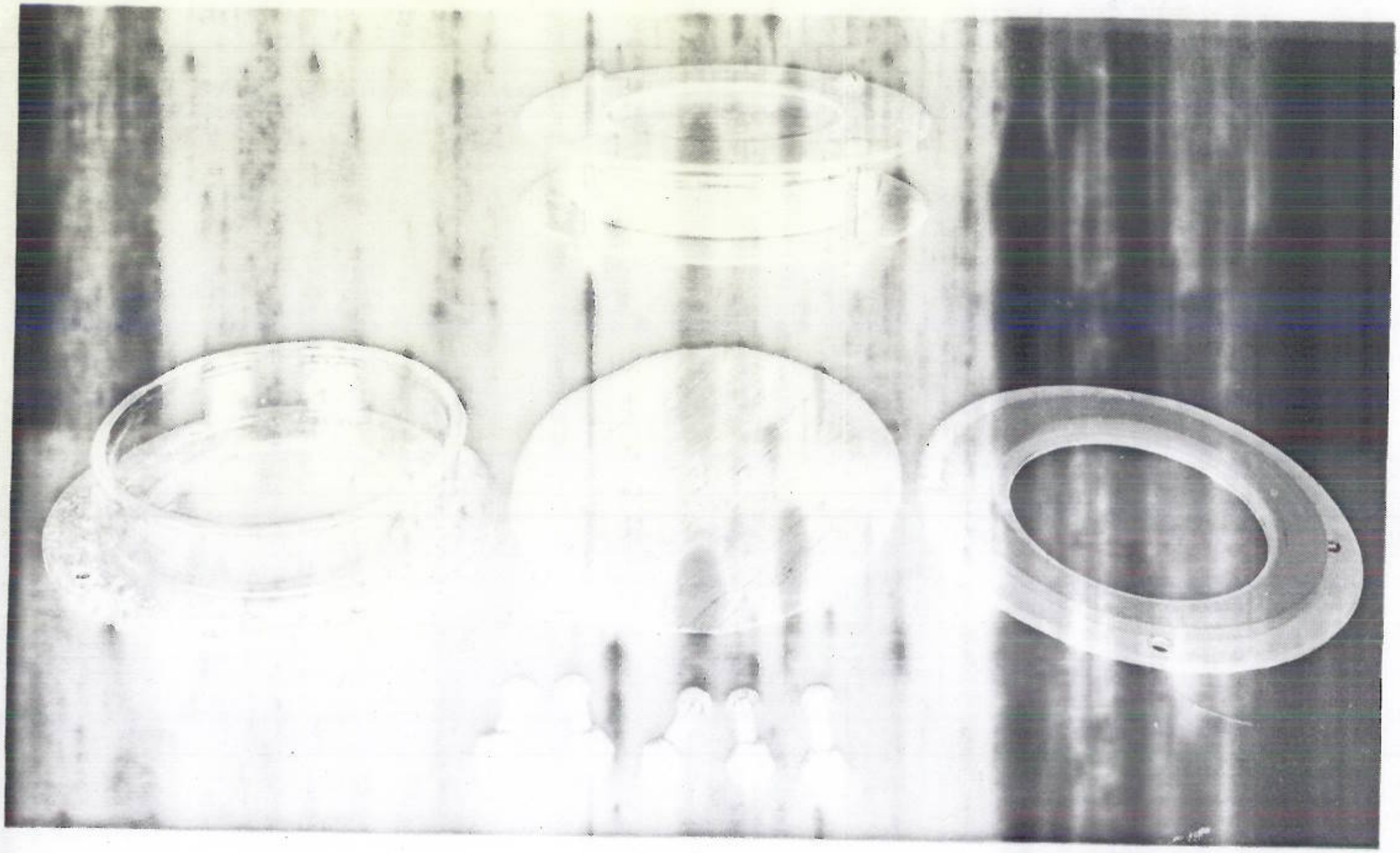

MOISTURE UPTAKE, GRAMS
1.5
1.0
.5
.25
0
2
13
14
15
16
17
18
#5
#6
#4
#1
#2
#3
WATER
PHENOLIC VARNISHES



WATER [illegible] NATURAL OIL ALKYD VARNISHES

PLATE 4


LINSEED ALKYD
40% P.A.
D.C. ALKYD, 40% P.A.
COM. OIL
#2
COM. OIL
#3
25 GAL. D.C.
H.V.
15 GAL.
LINSEED
H.V.
1.0
MOISTURE UPTAKE, GRAMS
14
16
17
18
WATER ... PHENOLIC AND AL... VARNISH
PLATE
BELLEVUE, D.C.



WATER VAPOR PERMEABILITY CELL

PLATE