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NAVAL RESEARCH LABORATORY

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PROTECTIVE COATINGS SECTION - CHEMISTRY DIVISION

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INVESTIGATION OF CUPROUS OXIDE ANTI-FOULING PAINT - II INACTIVATION OF HIGHLY PIGMENTED FILMS CONTAINING METALLIC COPPER

By
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Report No. P-2922

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ABSTRACT

An earlier investigation has established the fact that highly pigmented films containing metallic copper perform as cathodes when applied to steel surfaces and immersed in the sea. It is a well recognized fact that copper cathodes are readily fouled when exposed to environments of high fouling intensity. The present investigation describes experiments designed to establish the degree to which highly pigmented films containing metallic copper may become inactivated when in contact with steel. The findings are in close agreement with predictions made from electrical conductivity measurements on similar films. Films pigmented with cuprous oxide are not inactivated irrespective of pigment-volume ratio. Films containing metallic copper become inactivated at pigment volumes above 30% when applied to steel surfaces, but continue to afford ample protection when used over wood surfaces. The conclusion is reached that for paints intended for application to steel, metallic copper pigments should be avoided at concentrations above 25% pigment volume.

INTRODUCTION

A. Authorization

1. These studies were authorized by Bureau of Ships letter S19-1-(3) (60177)(336) dated 9 November 1944.

B. Statement of Problem

2. Accrued shortages of toxic pigment used in anti-fouling paint in the early stages of the war necessitated a divergence from cuprous oxide. The most likely substitutes consisted of copper metal in the form of powder and flake and several so-called copper pigments which were produced primarily to eleviate the shortage. Prejudices of long standing have militated against the use of pigments other than cuprous oxide due to the accepted theory that metallic pigments accelerate the corrosion of steel. The fact has been established that accelerated corrosion, attributable to anti-fouling paints, is accompanied by a corresponding inactivation of the paint itself. The object of this report is to determine the relative efficiencies of a number of anti-fouling pigments as compared with cuprous oxide when dispersed in representative anti-fouling matrices.

C. Known Facts Bearing on the Problem

3. The role of copper pigments in anti-fouling paints has been described in detail in NRL Report No. P-2676 dated 1 November 1945. Data are presented in this report to indicate that at high pigment volumes copper-bearing anti-fouling paints may be expected to perform as active cathodes when applied to steel panels and immersed in the sea. Highly pigmented films coupled with steel were shown to possess resistances of sufficiently low magnitude so that appreciable galvanic currents were produced when such films were coupled with steel.

4. In a monthly report of the Woods Hole Oceanographic Institution to the Bureau of Ships dated 1 September 1944, experiments were described in which an anti-fouling paint containing copper flake applied to a wood panel was completely inactivated by the simple mechanism of attaching an iron strip in contact with the surface of the paint. In addition to rendering the paint susceptible to attack by fouling organisms, the rate of corrosion of the iron strip was many times greater than that of a similar specimen attached to a paint of extremely low pigment volume. From the Woods Hole data it was apparent that perhaps somewhere a critical value for pigment volume relationship exists between 20 and 30%. For the type of matrices studied it was apparent that below 25% no inactivation of the paint need be expected although the film is in direct contact with steel, while above this pigmentation inactivation may occur.

5. The data reported in NRL Report No. P-2676 substantiate this view inasmuch as the most highly pigmented films were shown to produce galvanic currents when coupled with steel. It is the purpose of the present discussion to further establish this view by actual exposure data

and to determine performance characteristics of several pigments containing varying amounts of metallic copper.

D. <u>Narrative of Original Work on the Problem at this Laboratory</u>

6. Previous evidence having indicated a critical pigment-volume value somewhere between 20 and 30%, two series of paints were prepared representing the extremes of high and low pigmentation that have been found practical for producing an effective anti-fouling paint. In order not to be misled by any peculiar characteristics of a single matrix, three vehicles of varying compositions were pigmented at pigmentations of 12% and 36%. In order to study the performance of these materials the paints were applied to three types of panels which were selected as being most likely to demonstrate the active performance of the paint. One panel consisted of plywood to which three coats of anti-fouling paint were applied. This panel eliminates all possibility of corrosion or inactivation of the paint due to contact with metal. A second panel of steel was given two coats of fast drying anti-corrosive primer, Navy Department Specification 52P81, with the exception of a 1" square window which was prepared in the center of one side of the panel. This window was intended to permit direct contact of the paint to the metal. A third panel was completely covered with two coats of the primer. Both steel panels received three coats of anti-fouling paint.

7. All panels were immersed in Biscayne Bay at Miami Beach, Florida, at the station of the Woods Hole Oceanographic Institution. The formulations of 12% pigment-volume exhibited severe physical failure in a matter of a few days after exposure in the form of checking and "alligatoring". However, they continued to repel any severe fouling attack until they were removed at the end of three months, at which time their physical condition had deteriorated to such a point that further exposure appeared meaningless. The formulations of 36% pigment volume exhibited superior physical behavior. Extreme differences were soon manifest, however, as to their ability to repel the attachment of fouling. These differences were obviously attributable to the chemical characteristics of the pigments themselves, and on this basis the hypothesis promulgated by NRL Report No. P-2676 appeared to be amply substantiated. In addition, definite recommendations appear in order as to critical pigment-volume relationships that are permissible for metallic pigmentation where use is intended over steel.

METHODS AND DATA OBTAINED

A. <u>Materials</u>

8. In addition to the normal supplies of cuprous oxide, copper flake and powder, two new pigments were introduced as a result of the acute shortage. A material known as Cement Copper was introduced by the C. K. Williams Company, which on the average consisted of 85-87%

metallic copper, the remainder being cuprous oxide. Another product manufactured by the H. H. Robertson Company, and known simply as Copper Pigment contained approximately the same percentages of copper and cuprous oxide as the Cement Copper. These two products were given equal consideration in the current study along with the materials which had been used over longer periods. The complete list of the pigments investigated are included in Table I.

TABLE I

A. Cuprous Oxide	-	Charles Lennig
B. Cuprous Oxide	-	Metals Refining Company
C. Cement Copper	-	C. K. Williams Company
D. Copper Pigment	-	H. H. Robertson Company
E. Copper Flake	-	Metals Disintegrating Company
F. Copper Powder	-	Phelphs-Dodge
G. Copper Powder	-	Charles Hardy, Inc.

9. The matrices in which the pigments were dispersed consisted of rosin methyl abietate and Pliolite S-1 in varying proportions. The composition of the vehicles is set forth in Table II.

TABLE II

Composition of Vehicles

	Percent by Wt.		
	A	B	C
W. W. Rosin	87	75	75
Methyl Abietate	12	20	5
Pliolite S-1	1	5	20

10. Panels 6 x 12" were prepared from "Weld Wood" and cold rolled steel. The steel primer meeting requirements of Navy Department Specification 52P81 was obtained from the Norfolk Navy Yard.

EXPERIMENTAL

11. The three matrices described in Table II were pigmented at pigment volumes of 12 and 35% with each of the pigments listed in Table I. Exposure panels were prepared which were immersed at the Beach Boat Slips testing site of the Woods Hole Oceanographic Institution at Miami Beach, Florida. Their condition was noted after the first several days and at monthly intervals. Detailed reports were prepared at each reading and forwarded to the laboratory for correlation. The panels of 12% pigment volume were removed after a period of three months due to severe physical failure, while formulations at 35% pigment volume were still performing 100% and undoubtedly would have continued for several additional months. It was believed, however, that the object of the experiment had been accomplished and all panels were removed and returned to the laboratory for final inspection.

DATA OBTAINED

12. Detailed data on the performance of each formulation as recorded in the monthly reports is not reproduced here; however, the fouling data from these reports have been abstracted and arranged in Tables III through VI. Table III containing the data for the three months' exposure of the 12% pigment volume formulations, does not disclose any significant differences in the performance of the pigmentation whether applied to wood or steel. However, this is not true of the formulations at 36% pigment volume. It is believed that references to Plates 1 through 21 present a clearer picture of the effect of each pigment during its exposure period than may be gained from the tabulated data.

DISCUSSION AND SUMMARY

13. In order to appreciate fully the preferred performance of the pigments containing little or no metallic copper when applied to steel, a careful study of the curves of Plates 1 through 21 must be made. The curves have been arranged for each pigment in the same order listed in Table I, therefore, by referring to successive plates, for example, 1, 2, and 3, it is possible to observe the properties of cuprous oxide from one source in three different matrices. Likewise, Plates 4 through 6 indicate similar behavior for cuprous oxide B in the same three vehicles. By reproducing the curve for each pigment in each material any discrepancies resulting from a single observation may be detected and readily discounted.

14. In the cases of cuprous oxide, regardless of its source, it may be seen from Plates 1 through 6 that it renders an almost perfect performance up to the time the experiment was terminated. It performs almost equally as well when applied to wood or steel, and the variables in the matrix appear to have little or no effect on its efficiency. There is possibly an infinitesimal difference in favor of the curpous oxide from source B; however, when it is considered that a panel is given a reading of 90 or 95% when only a half dozen forms of marine life have attached, such a differentiation is probably unjustified.

15. Plates 7 through 12 represent the performance of Cement Copper and Copper Pigment when applied to wood and steel. In order to appreciate the position of these materials lying between that of cuprous oxide and metallic copper pigments, it should be remembered that each contains a predominantly high percentage of copper metal. In the case of Pigment D, the copper metal is described by its manufacturer as being surrounded by an envelope of cuprous oxide which, if unremoved during the grinding process, should be expected to perform more nearly like the oxide rather than the metal. Plates 10 through 12 partially substantiate this view. Perhaps the most significant observation that may be made from examination of these curves is the superior performance when applied to wood. An exception to this is seen in the case of Pigment D which would have further bearing on the fact that the active surfaces are comprised of cuprous oxide rather than metallic copper. In such cases the inferior performance to pure cuprous oxide must be attributable to other causes.

The remainder of the curves, Plates 13 through 21, present the most positive evidence of inactivation of metallic copper paints applied to steel. For the most part performance over wood is practically as good as for cuprous oxide, only slight failure occurring during the last month. It is highly significant that in the majority of cases a performance rating of 0% was given each of the metallic pigments at the end of 3 or 4 months with initial failure often occurring at the first inspection. Since no similar failures were recorded for the metallic pigments at 12% pigment volume, the conclusion is almost inescapable that at higher pigmentation the pigments have been inactivated due to their contact with steel. This view is further enhanced by the fact that a similar reduction in the protective value of the pigments applied to wood was not observed.

CONCLUSIONS

16. The data presented herein strongly support the view that metallic copper in the form of flake or powder, when applied to steel at high pigment volumes, is to a large degree inactivated and will permit the attachment of fouling within a brief period after exposure.

17. The same pigments applied at the same concentration to wood do not exhibit such behavior and will offer continued protection over extended periods of time.

18. Metallic pigments applied at low pigment volumes do not appear affected by the contact with steel and may be expected to perform adequately for moderate periods. Their total life expectancy was not a primary concern of this investigation.

19. Cuprous oxide, when largely free of contaminating metallic copper may be expected to perform equally well whether applied to steel or wood irrespective of the degree of pigmentation.

ACKNOWLEDGMENT

20. The value of the cooperation of Mr. Charles M. Weiss of the Woods Hole Oceanographic Institution cannot be overestimated for his part in exposing the panels at Miami Beach and preparation of the monthly reports on their condition

TABLE III

Exposure Data for Matrices A, B, and C at 12% P/V

Pigment	Panel Materials	% Protection by Months Matrix A 1	 2	 3	 Matrix B 1	 2	 3	 Matrix C 1	 2	 3
Cu_2O CL	Steel	83	87	100*	90	22	45	100	31	51
" "	Window	100	80	100	100	40	57	100	87	92
" "	Wood	100	100	100	90	50	92	100	40 87	77 100
Cu_2O MR	Steel	100	91	100	100	41	80	77	50	88
" "	Window	100	91	100	100	40 91	87(100)	85	25	85
" "	Wood	100	100	100	100	74	92	100	50	91
Cement Cu	Steel	100	88	100	100	60	85	100	80	94
" "	Window	100	85	92	91	71	93	100	86	100
" "	Wood	100	100	100	100	81	86	100	89	90
CuP - Robert	Steel	100	89	100	100	50	63	100	90	90
" "	Window	100	93	100	92	77	90	89	85	84
" "	Wood	100	100	100	100	80	85	100	72	72
CuFlake MD	Steel	100	89	100	100	94	100	100	100	100
" "	Window	100	100	100	100	94	93	100	100	100
" "	Wood	100	100	100	100	100	100	100	100	100
CuPowder PD	Steel	100	100	100	100	91	100	100	90	100
" "	Window	100	93	100	100	92	90	100	92	100
" "	Wood	100	100	100	100	100	100	100	100	100
CuPowder CH	Steel	72	30	77	63	0	0	61	°89	0, 94
" "	Window	100	100	75(100)	77	5	72	83	11	53
" "	Wood	100	87	100	89	80	87	85	20	0

*In some instance loosely adhering fouling disappears - usually consisting of encrustating bryazoa.

TABLE IV

Exposure Data for Matrix A at 36% P/V

Panel No.	Pigment	Panel Material	Monthly Ratings for Fouling Resistances in % Protection 1	3	4	5	6	7	8
1	a. Cuprous oxide	Steel	100	100	100	100	100	100	94
22	" "	Window	100	100	100	100	100	92	92
43	" "	Wood	100	100	100	100	100	100	100
2	b. Cuprous oxide	Steel	100	100	100	100	100	100	100
23	" "	Window	100	100	100	100	100	100	100
44	" "	Wood	100	100	100	100	100	100	100
3	c. Cement Copper	Steel	100	72	65	55	45	35	0
24	" "	Window	100	85	80	77	58	34	0
45	" "	Wood	100	100	100	100	95	80	20
4	d. Cu Pigment	Steel	100	100	100	100	100	95	70
25	" "	Window	100	100	100	100	100	95	100
46	" "	Wood	100	100	100	100	95	87	34
5	e. CuFlake	Steel	100	0	0	0	0	0	0
26	" "	Window	85	15	0	0	0	0	0
47	" "	Wood	100	100	100	100	100	100	80
6	f. CuPowder	Steel	100	0	0	0	0	0	0
27	" "	Window	100	40	0	0	0	0	0
48	" "	Wood	100	100	100	100	100	100	100
7	g. CuPowder	Steel	45	0	0	0	0	0	0
28	" "	Window	70	0	0	0	0	0	0
49	" "	Wood	100	100	100	100	100	100	100

TABLE V

Exposure Data for Matrix B at 36% P/V

Panel No.	Pigment	Panel Material	Monthly Ratings of Fouling Resistances in % Protection 1	3	4	5	6	7	8
8	Cu_2O CL	Steel	100	100	100	100	100	100	100
29	" "	Window	100	100	100	100	100	100	100
50	" "	Wood	100	100	100	100	100	100	100
9	Cu_2O MR	Steel	100	100	100	100	100	100	95
30	" "	Window	100	100	100	100	100	100	100
51	" "	Wood	100	100	100	100	100	100	100
10	Cement Cu	Steel	100	89	81	65	50(100)	37(91)	0
31	" "	Window	100	85	84	70	63	44	0
52	" "	Wood	100	100	100	100	95	95	35
11	CuP Robert	Steel	100	100	100	100	100	95	85
32	" "	Window	100	100	100	100	100	92	94
53	" "	Wood	100	100	100	100	95	95	15
12	CuFlake MD	Steel	100	0	0	0	0	0	0
33	" "	Window	87	25	0	0	0	0	0
54	" "	Wood	100	100	100	100	100	100	85
13	CuPowder PD	Steel	42	0	0	0	0	0	0
34	" "	Window	60	47	0	0	0	0	0
55	" "	Wood	100	100	100	100	100	100	90
14	CuPowder CH	Steel	70	0	0	0	0	0	0
35	" "	Window	52	0	0	0	0	0	0
56	" "	Wood	100	100	100	100	100	100	88

TABLE VI

Exposure Data for Matrix C at 36% P/V

Panel No.	Pigment	Panel Material	Monthly Ratings of Fouling Resistances in % Protection 1	3	4	5	6	7	8
15	Cu_2O CL	Steel	100	100	100	100	100	100	85
36	" "	Window	100	100	100	100	100	100	90
57	" "	Wood	100	100	100	100	100	100	100
16	Cu_2O MR	Steel	100	100	100	100	100	100	100
37	" "	Window	100	100	100	100	100	100	95
58	" "	Wood	100	100	100	100	100	100	100
					70	100	100	91	0
17	Cement Cu	Steel	100	79	100	55	58	38	20
38	" "	Window	100	84	85	67	60	43	0
59	" "	Wood	100	100	100	100	95	93	75
18	CuPigment	Steel	100	100	100	100	100	95	34
39	" "	Window	100	100	100	100	100	100	100
60	" "	Wood	100	100	100	100	95	95	24
									90
19	CuFlake	Steel	0	0	0	0	0	0	0
40	" "	Window	20	0	0	0	0	0	0
61	" "	Wood	100	100	100	100	100	95	85
20	CuPowder	Steel	55	0	0	0	0	0	0
41	" "	Window	90	0	0	0	0	0	0
62	" "	Wood	100	100	100	100	100	100	85
21	CuPowder	Steel	90	0	0	0	0	0	0
42	" "	Window	20	0	0	0	0	0	0
63	" "	Wood	100	100	100	100	100	100	90

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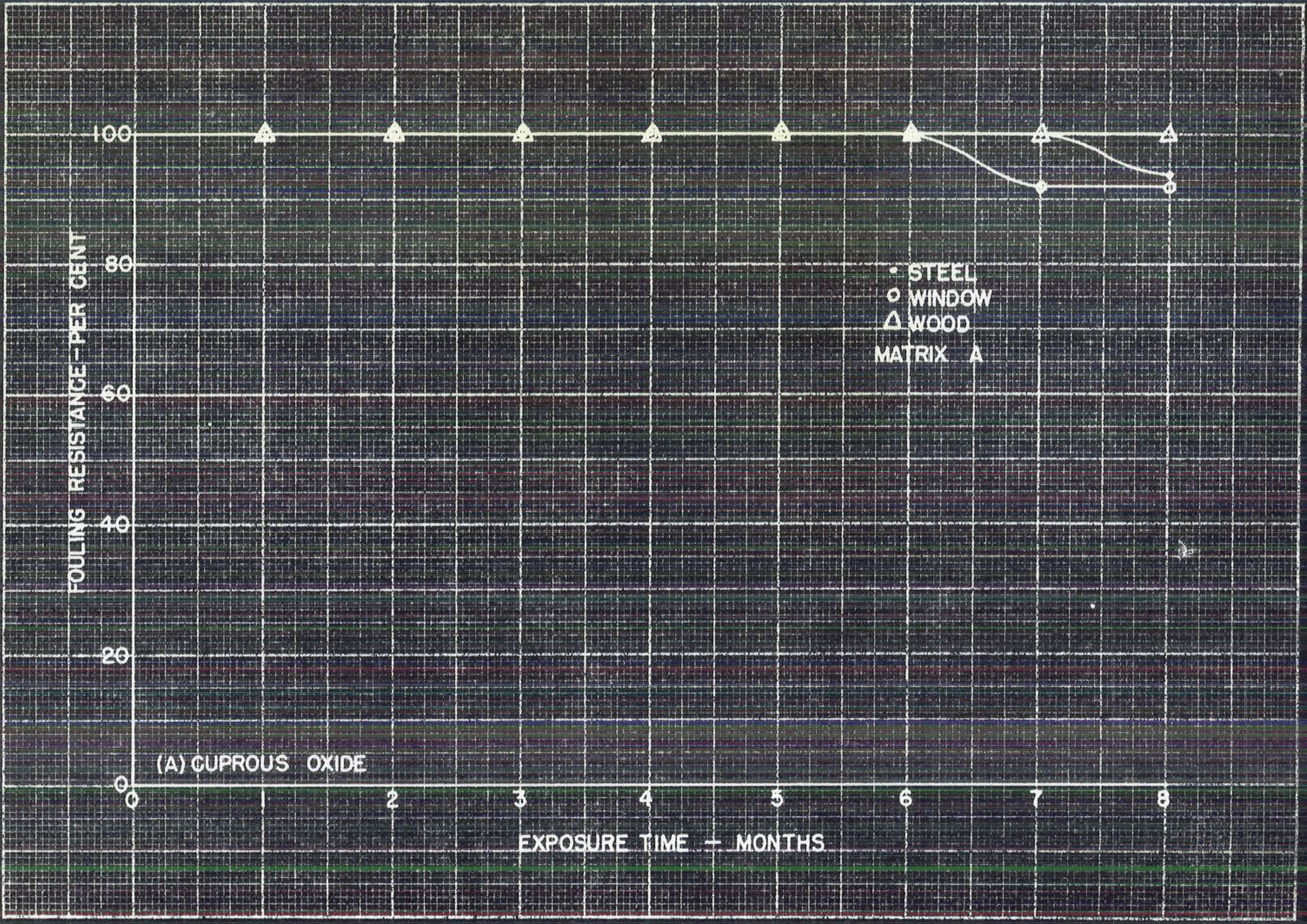
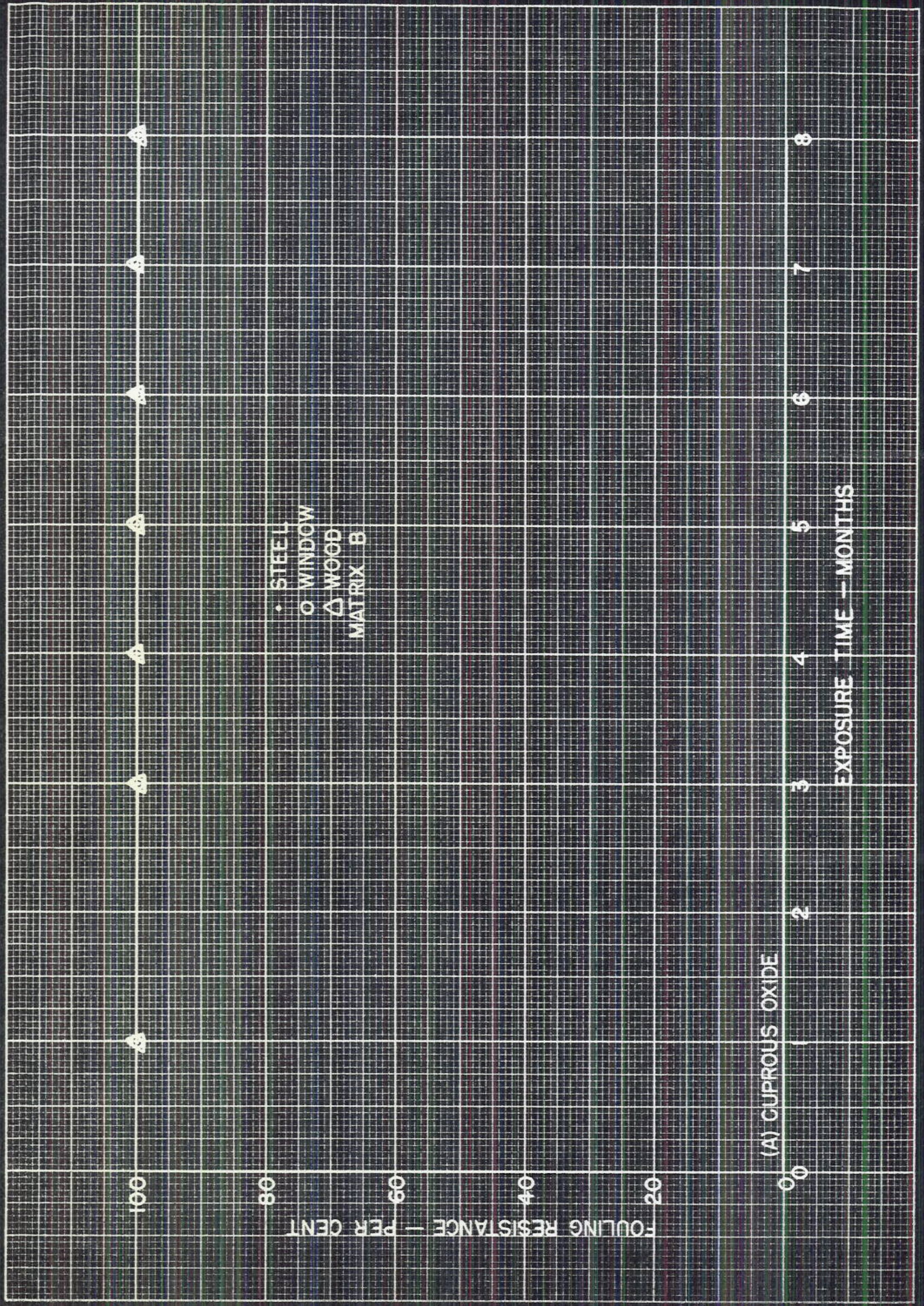


PLATE I



FOULING RESISTANCE – PER CENT
0
20
40
60
80
100
EXPOSURE TIME – MONTHS
0
1
2
3
4
5
6
7
8
· STEEL
○ WINDOW
△ WOOD
MATRIX B
(A) CUPROUS OXIDE

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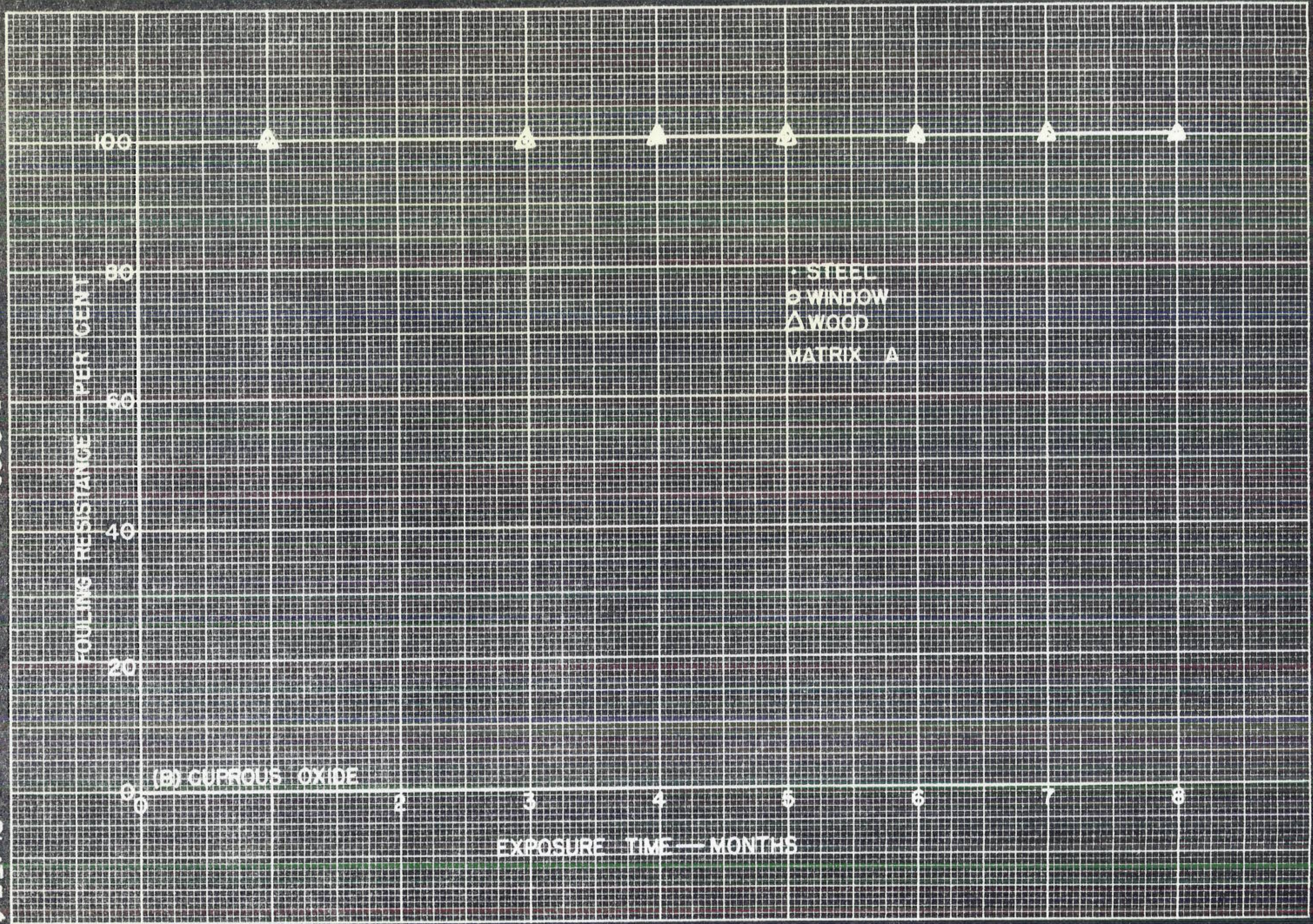
PLATE 3



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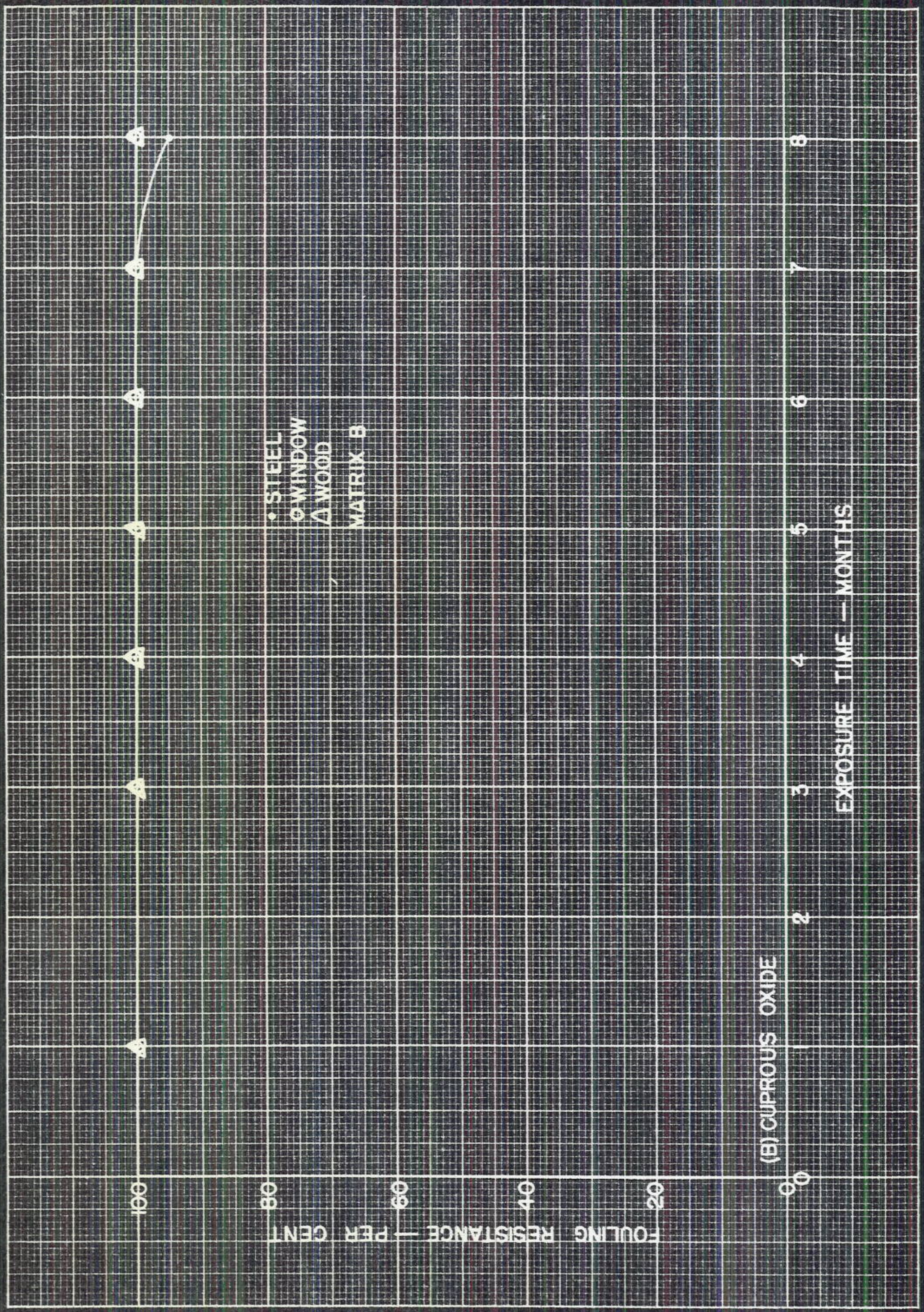

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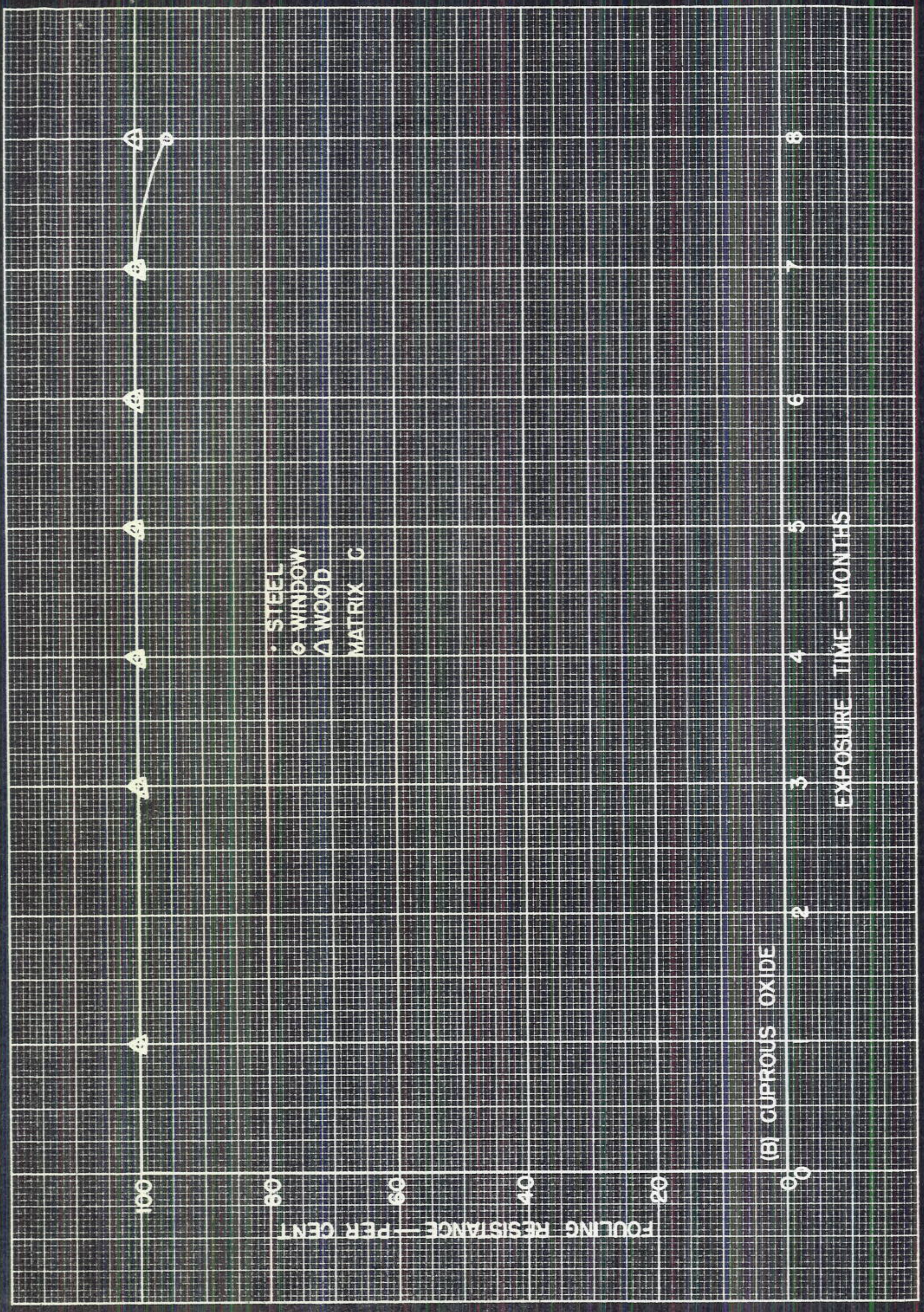

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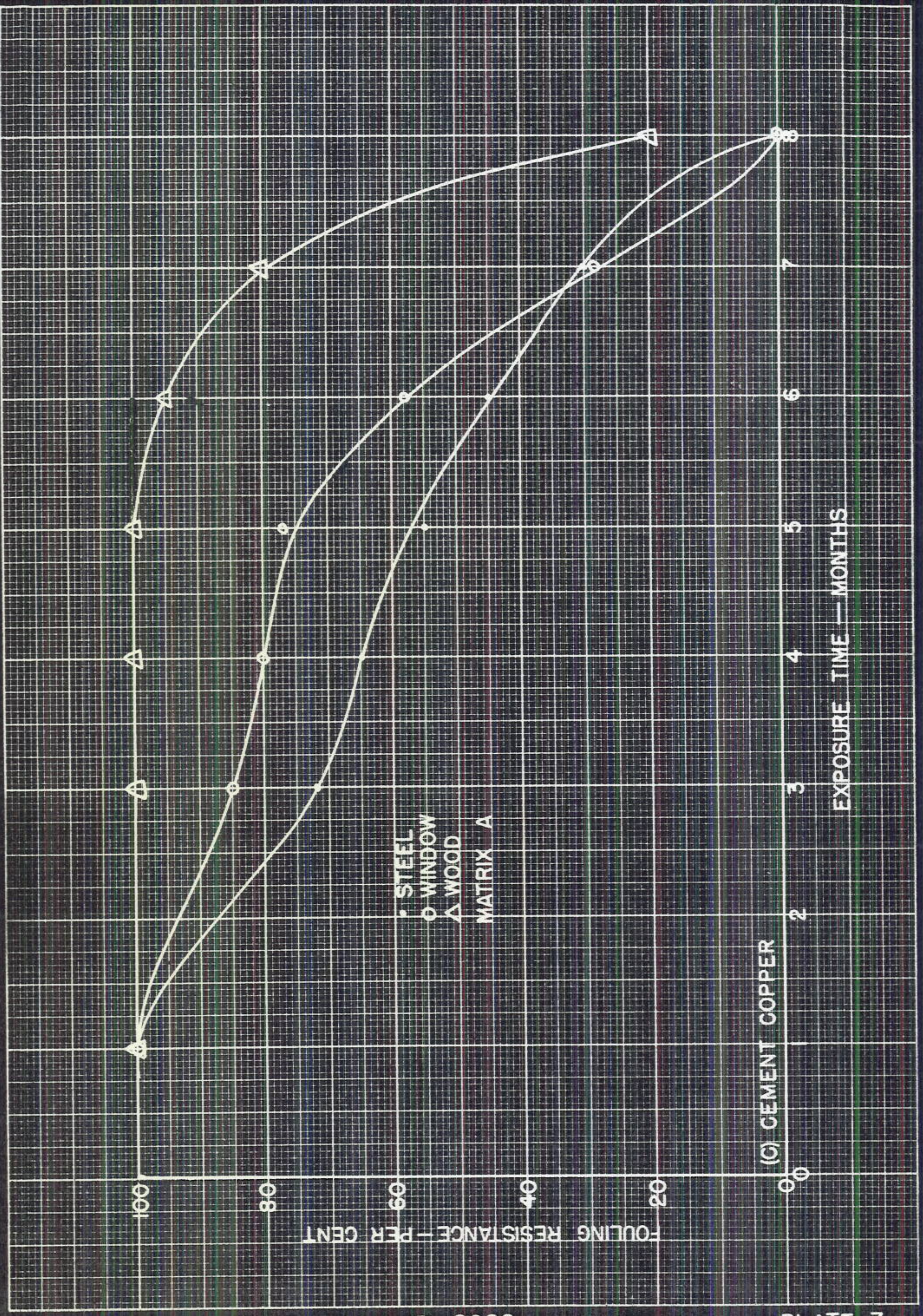
(C) CEMENT COPPER
• STEEL
o WINDOW
△ WOOD
MATRIX A
EXPOSURE TIME — MONTHS
FOULING RESISTANCE – PER CENT
0
1
2
3
4
5
6
7
8
0
20
40
60
80
100

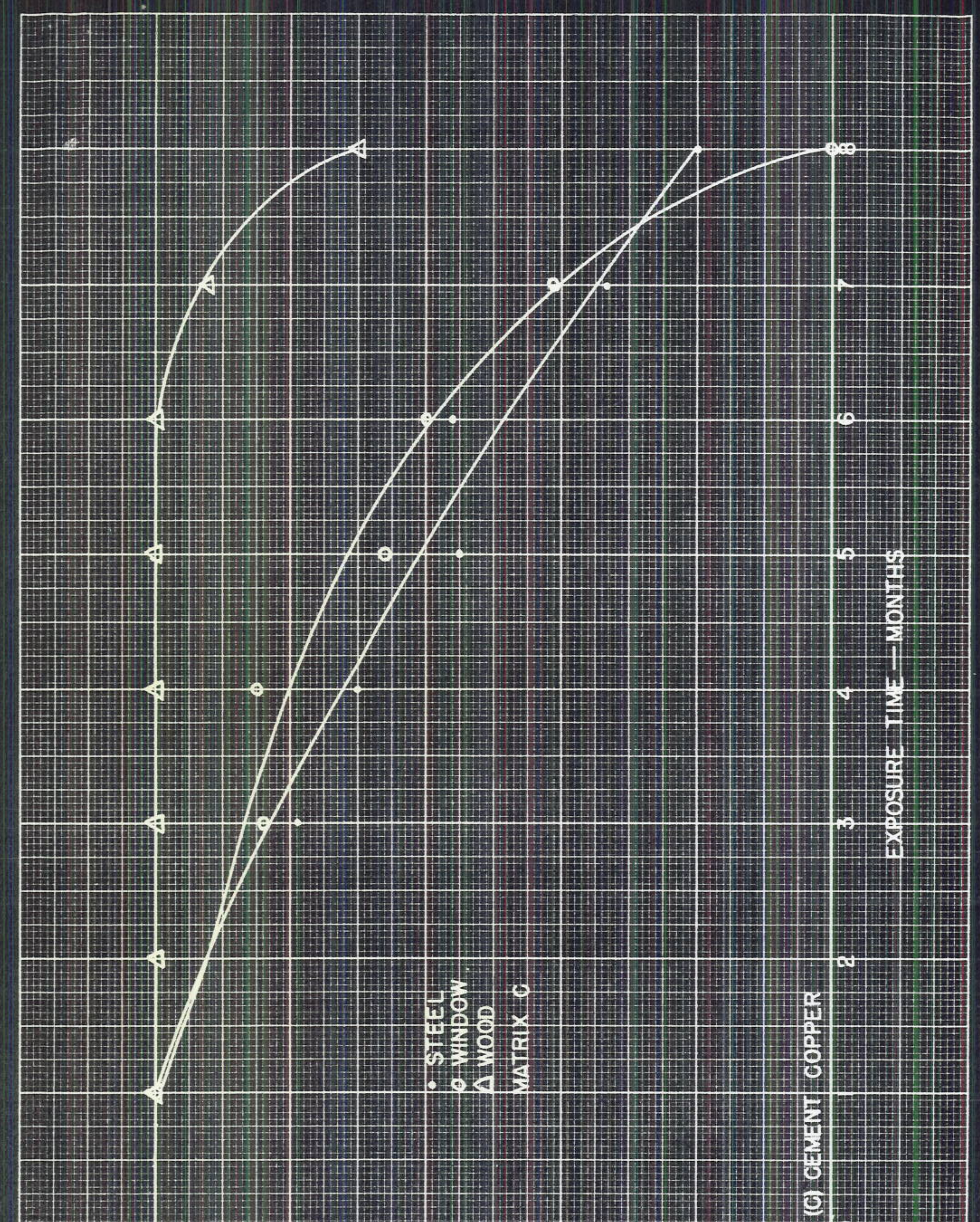

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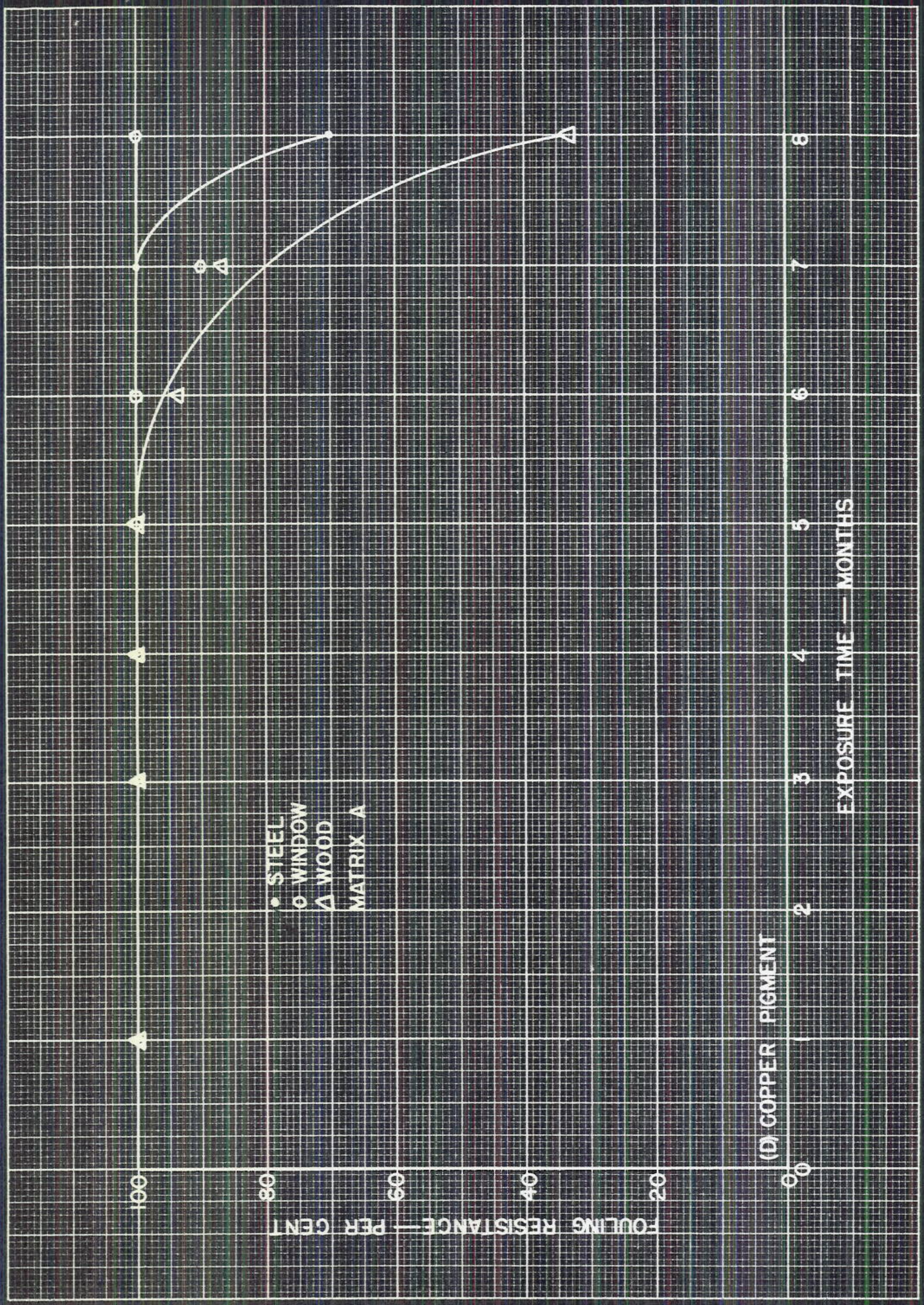
PLATE 9



(D) COPPER PIGMENT
• STEEL
o WINDOW
Δ WOOD
MATRIX A
FOULING RESISTANCE — PER CENT
100
80
60
40
20
0
EXPOSURE TIME — MONTHS
0
1
2
3
4
5
6
7
8

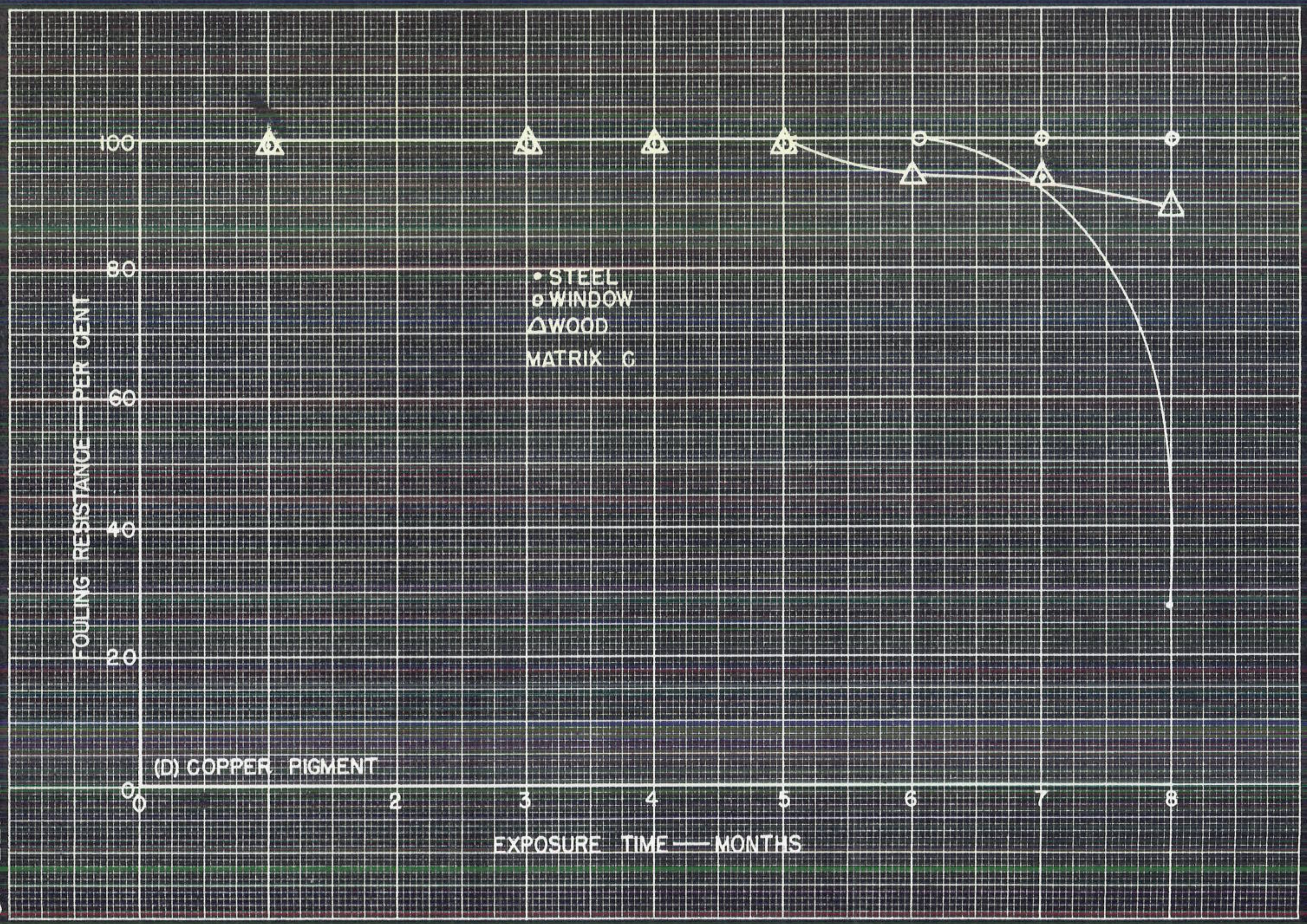


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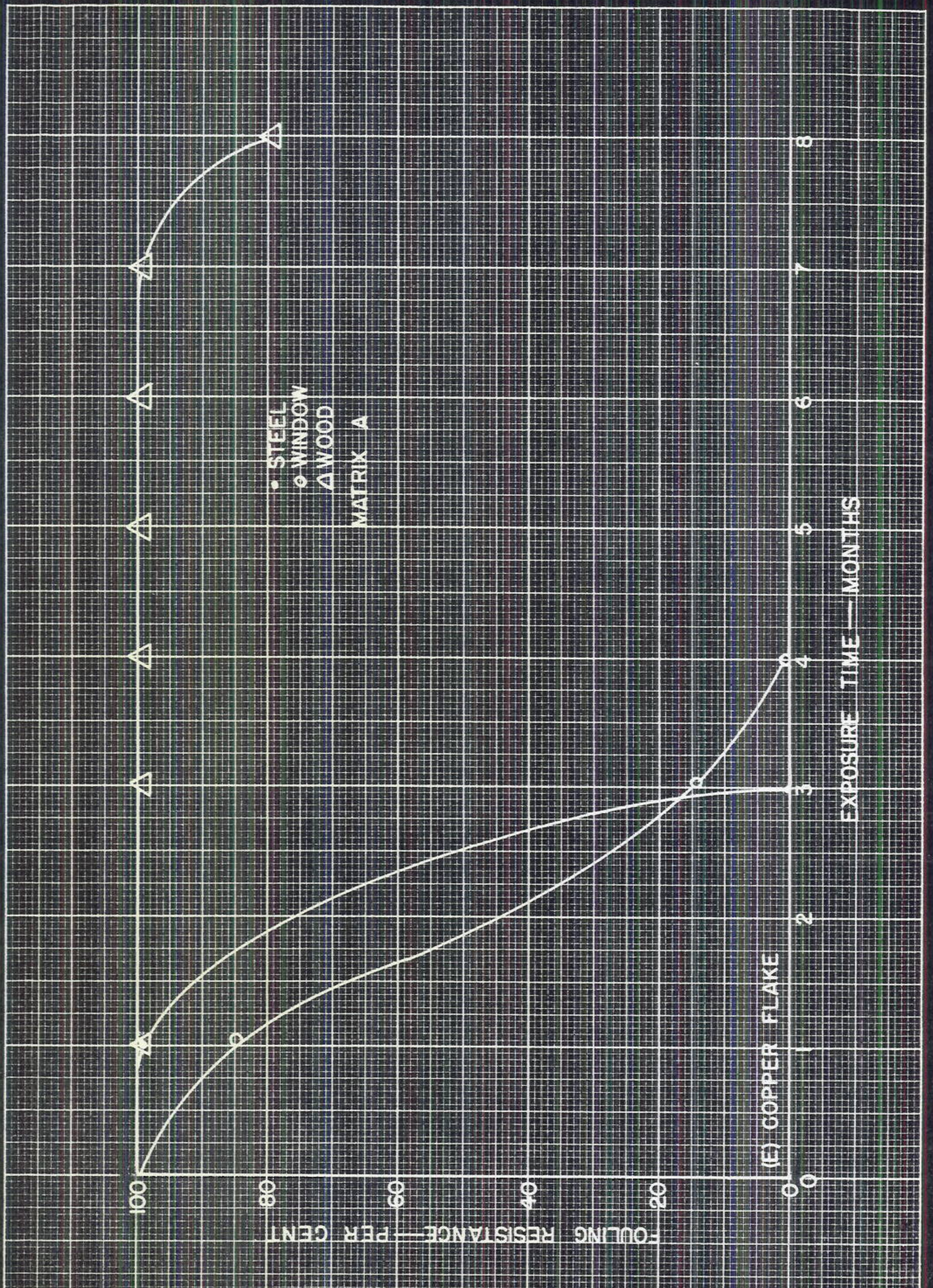
PLATE 12



• STEEL
o WINDOW
Δ WOOD
MATRIX A
(E) COPPER FLAKE
FOULING RESISTANCE — PER CENT
EXPOSURE TIME — MONTHS
100
80
60
40
20
0
0
1
2
3
4
5
6
7
8

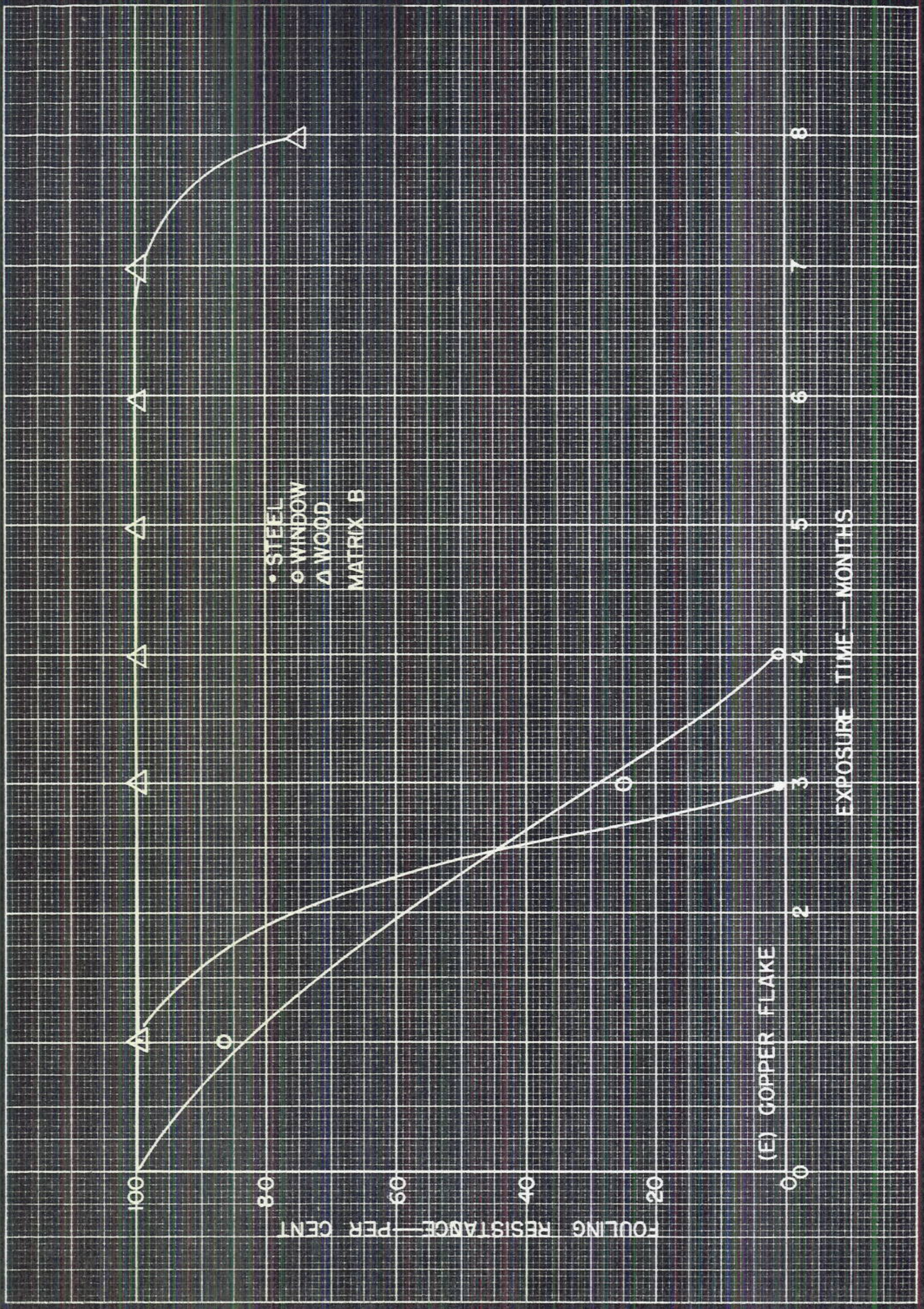


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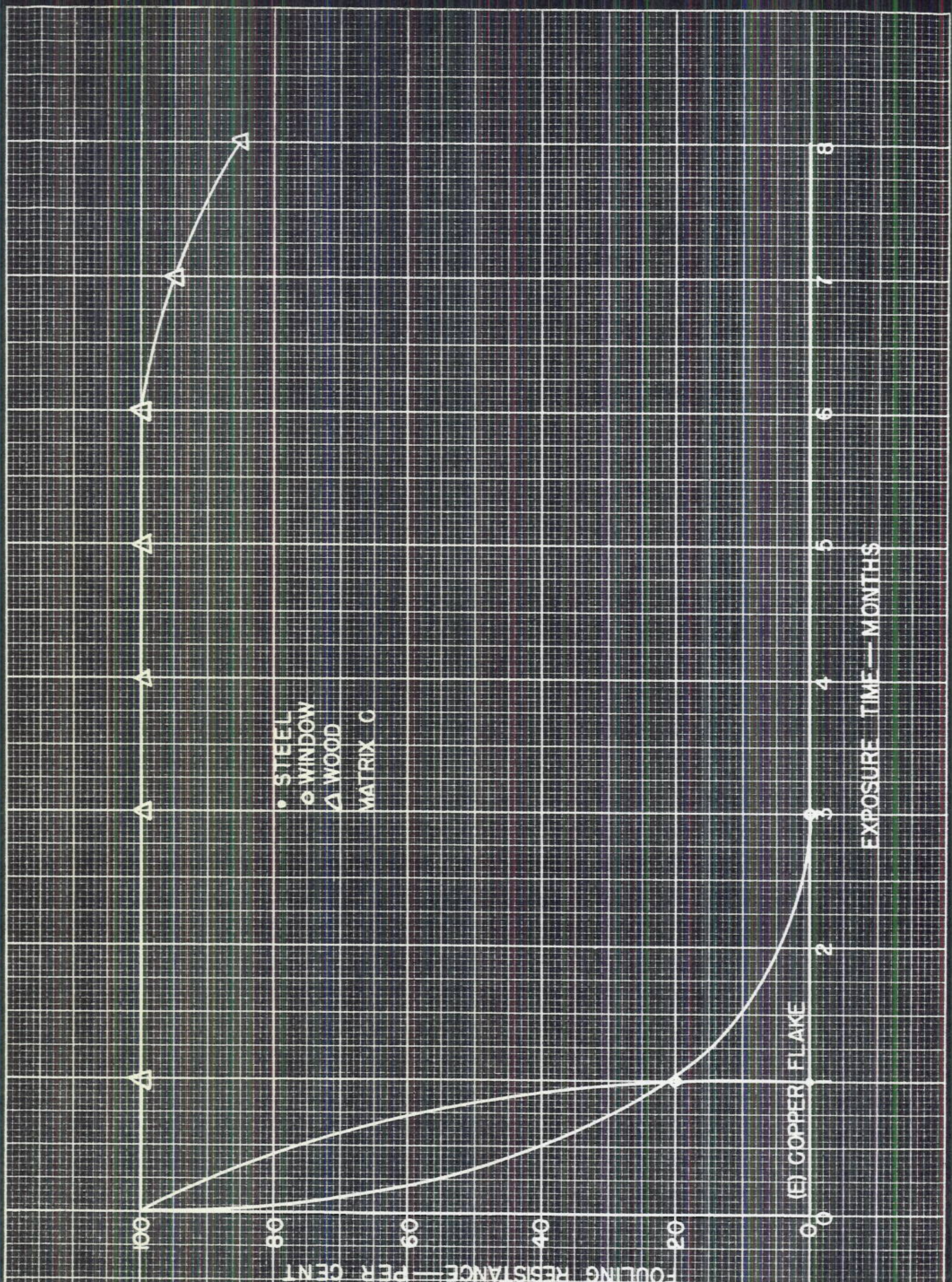
PLATE 14



• STEEL
⊖ WINDOW
Δ WOOD
MATRIX C
(E) COPPER FLAKE
FOULING RESISTANCE — PER CENT
EXPOSURE TIME — MONTHS
100
80
60
40
20
0
0
1
2
3
4
5
6
7
8

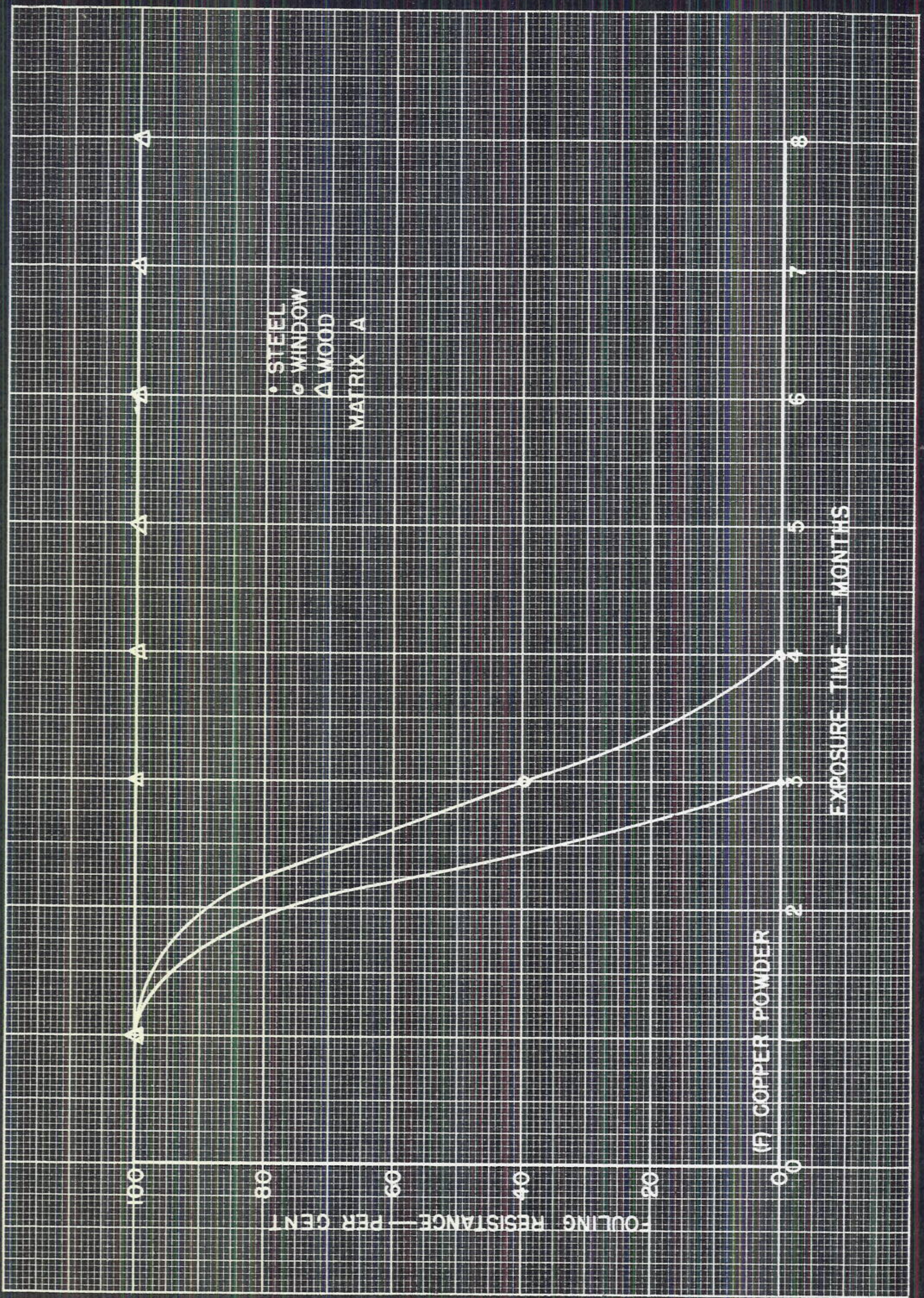


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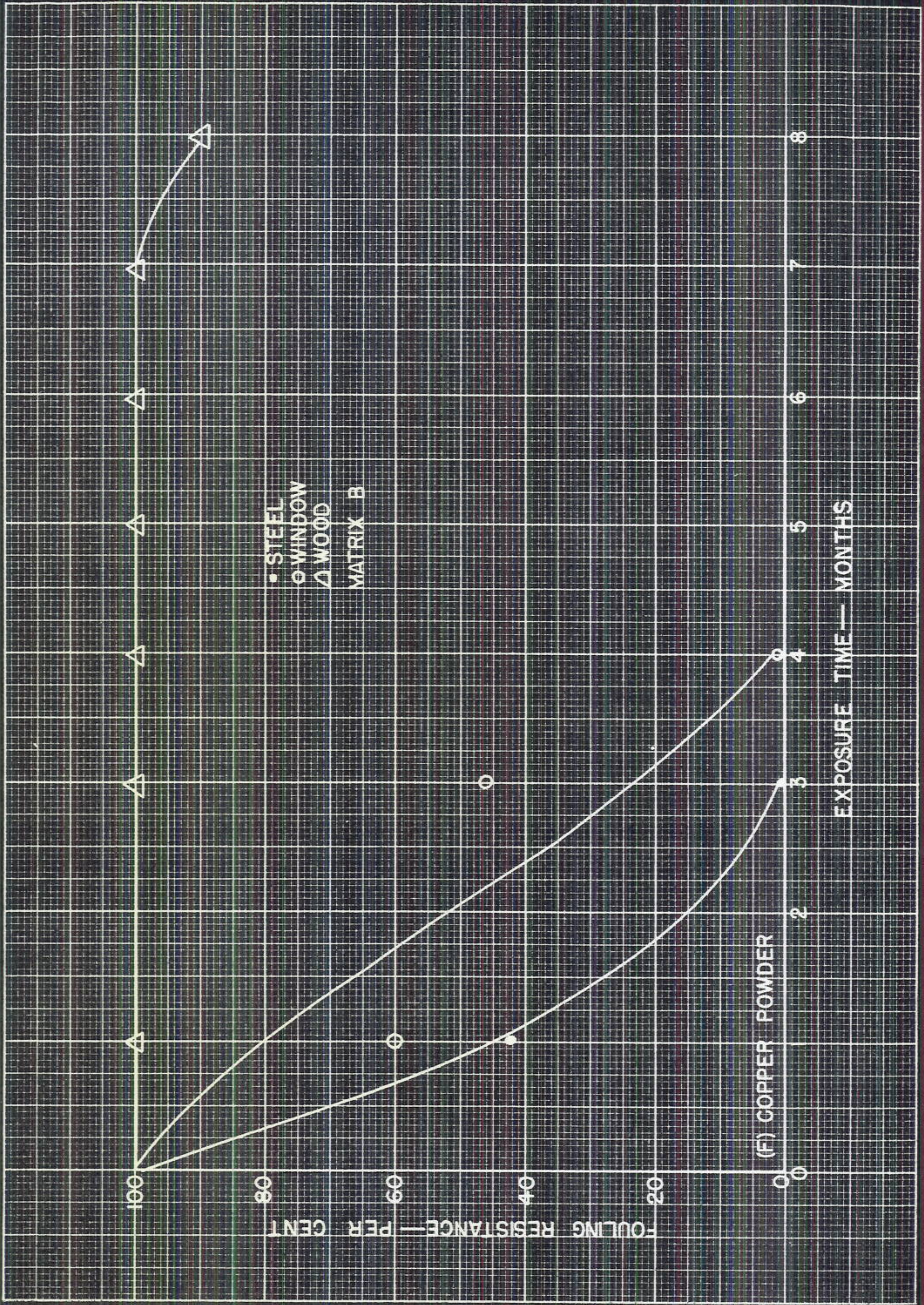
PLATE 16


• STEEL
⊖ WINDOW
Δ WOOD
MATRIX B
(F) COPPER POWDER
FOULING RESISTANCE — PER CENT
100
80
60
40
20
0
EXPOSURE TIME — MONTHS
0
1
2
3
4
5
6
7
8

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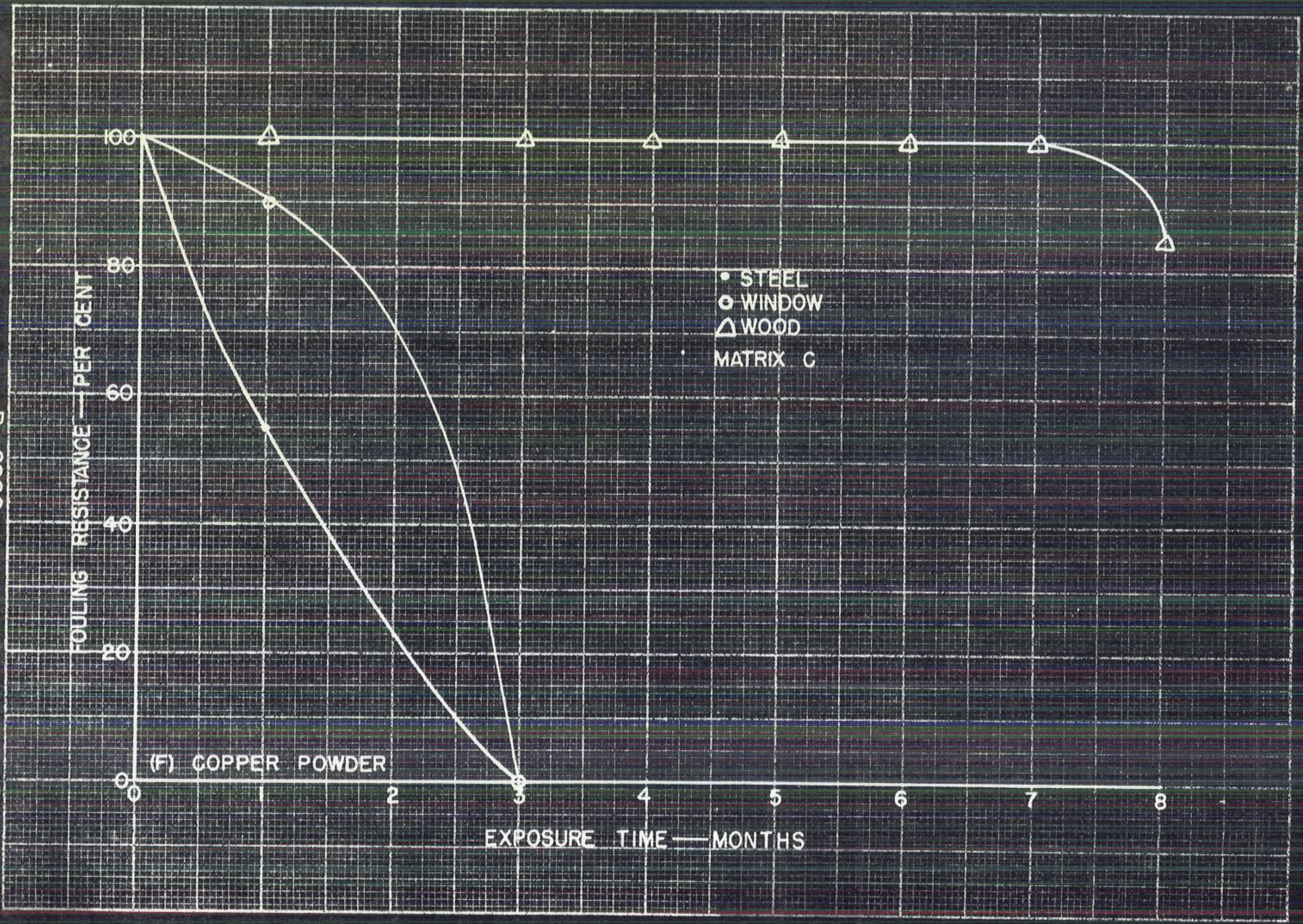

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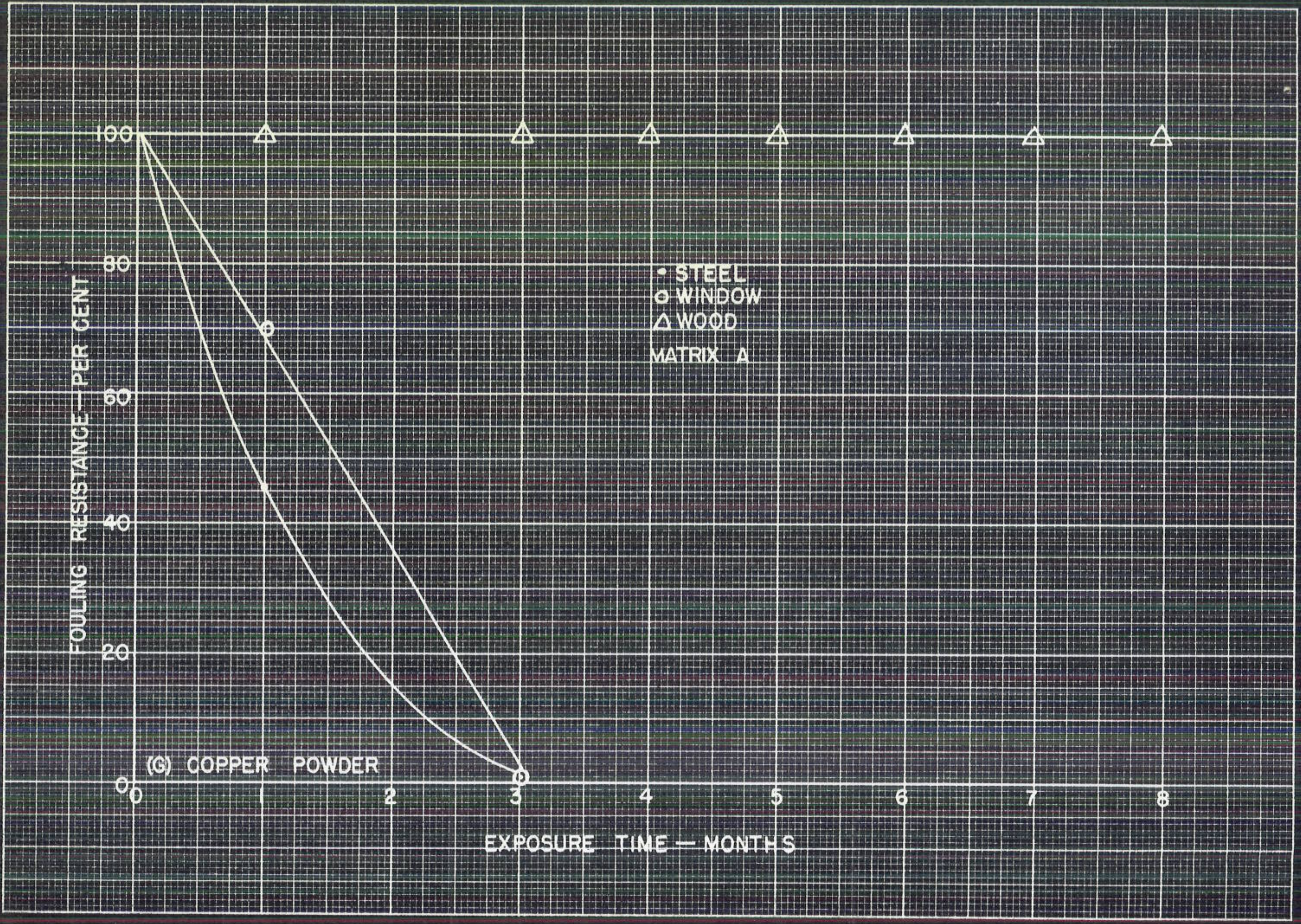

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PLATE 19

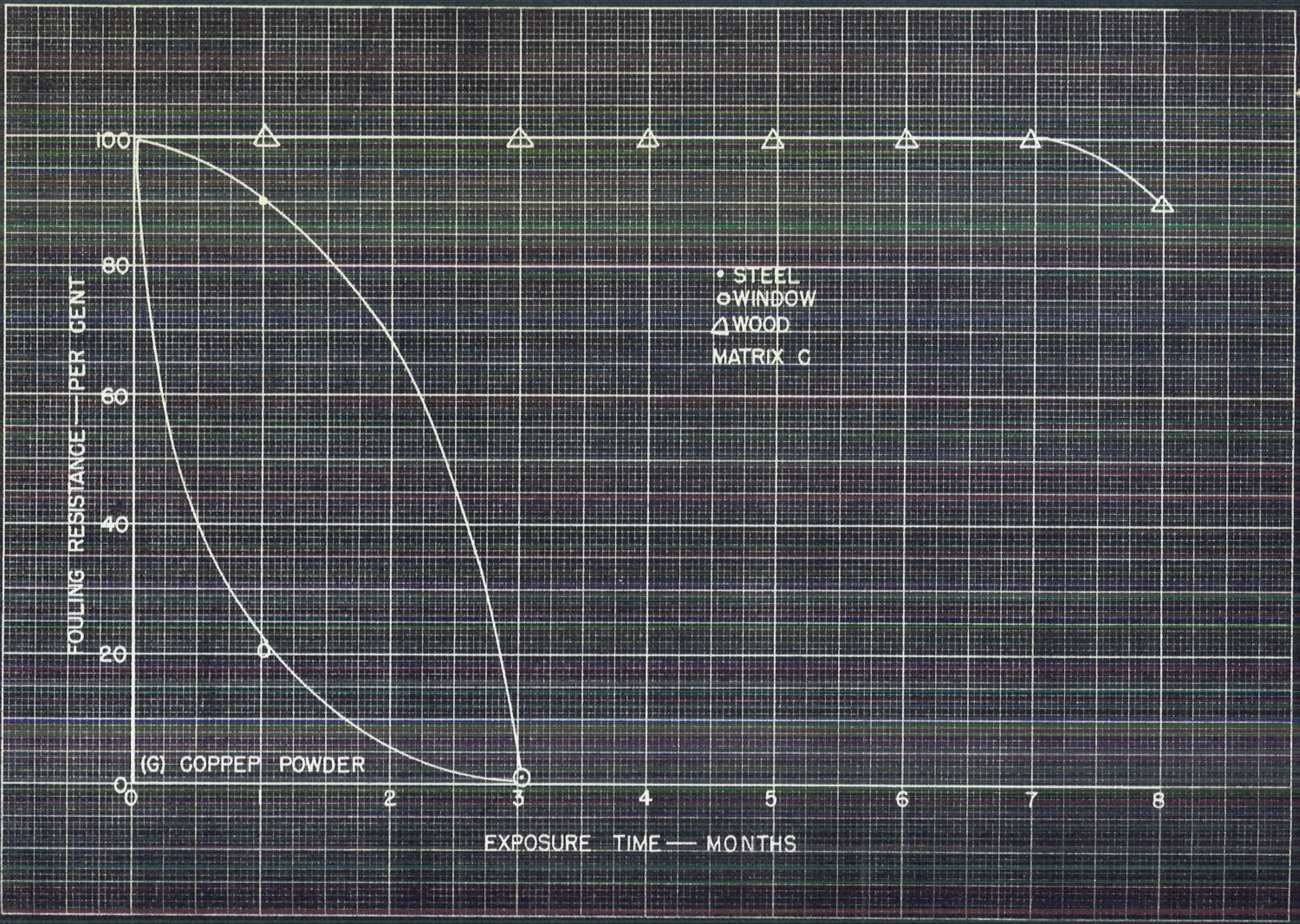

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PLATE 21