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REPORT NO. P-1021

DATE 31 January 1934

SUBJECT [redacted]

REPORT OF PROGRESS
ON
ANTIFOULING COATINGS

DECLASSIFIED by NRL Contract Declassification Team
Date: 15 APR 2016
Reviewer's name(s): A. THOMPSON, P. HANNA
Declassification authority: ______

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BY

NAVAL RESEARCH LABORATORY

BELLEVUE, D. C.

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ress on Antifouling Coatings.

31 January 1934

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NAVY DEPARTMENT

[redacted] BUREAU OF ENGINEERING

[redacted]

Report of Progress on Antifouling Coatings

NAVAL RESEARCH LABORATORY
ANACOSTIA STATION
WASHINGTON, D.C.

Number of Pages: Text - 5 Plates - 12 Table - 1.

Authorization: Bu.C&R let.S19-1-(3)(S) of 1 July 1933.

Date of Test: 25 August 1933 to 23 November 1933.

Reported by:

Walter Rosett, Asst. Chemist.

Approved by:

H.R. Greenlee, Captain, U.S.N.,
Director.

[redacted]

Distribution:
BuEng. (5)
Norfolk Navy Yard

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AUTHORIZATION:

1. This problem was authorized by Bureau of Construction & Repair confidential letter S19-1-(3)(S) of 1 July 1933 and forwarded by Bureau of Engineering first endorsement C-S19/L5(4-1-Ds) of 6 July 1933.

STATEMENT OF PROBLEM:

2. During the early part of 1930, the question of protective coatings was discussed at this Laboratory. In the literature and in practice, the production of antifouling surfaces for ships had all been based on attempts at poisoning the fouling organisms. In general, the effectiveness of poisons depends on their toxicity, their concentration, this on their solubility. Thus, the more soluble the poison in the paint film, the more effective it will be to prevent fouling, and the shorter the time it will be effective, since the supply of unsaturated solvent, sea water, is to all intents and purposes infinite. It seemed to the Laboratory that a fresh method of approach to the problem was to try to produce surfaces such that there would be a force in a direction away from the surface, either a surface tension or small electrical force, so that the minute organisms could not approach closely enough to adhere.

WORK DONE AT LABORATORY:

3. Accordingly, a number of metallic soap paints were made up and applied to steel test panels. Among these was one on the surface of which powdered metallic selenium had been roughly melted. These panels were suspended beneath the water at Norfolk for about four months. Some of them proved about as good as the standard Navy antifouling paint. The panel having a metallic selenium surface was, however, markedly better in that it had no fouling of any kind. The coating had become loosened in some places because of corrosion of the steel plate. Other panels containing metallic selenium and tellurium in suspension in paint vehicles showed no unique result.

It was decided, therefore, to work in the direction of producing durable surfaces of selenium, etc., and permission was requested on 5 June 1933 to continue this work officially. Authorization was given shortly afterwards.

METHODS:

4. By August, 1933, a number of test panels had been prepared by methods developed at the Laboratory consisting essentially of immersing steel in a bath of molten selenium at about 450° C for five minutes, the excess selenium being removed by squeezing between steel rollers.

For these experiments, sand blasted mild steel panels 12" x 12" were used. The treatments were as follows:

Panel #1 was dipped in a dilute acidic copper sulphate solution, washed in water, dried, and dipped in a selenium bath at a temperature of about 450° C for about five minutes.

Panel #2 was washed in hot carbon tetrachloride, dried, and copper dipped as above, and then treated with selenium as above.

Panel #3, the untreated sand blasted plate, was given a double dip in the selenium bath.

Panel #4 was treated the same as panel #3.

Panel #6 and #7 were sand blasted plates with one coating each of standard Navy anticorrosive and antifouling paints.

These photographs show the panels before shipment to Norfolk for test. No photographs were taken of the standard Navy panels.

Results of the test showed much corrosion and consequent loosening of the protective coating.

DATA OBTAINED:

5. These plates were exposed at Norfolk Navy Yard from 25 August 1933 to 23 November 1933. Plates #9 and #10 are photographs of the panels after exposure. The panels were in the following condition as reported by Norfolk Navy Yard at time of inspection after exposure:

Fronts of Panels

#1. Fouling: Light bryozoan slime and scattered very small barnacles on portions of film remaining on panel. Grade (not considering 3/4 of area covered by heavy rust and therefore no fouling) - 85.

Corrosion: Heavy on 3/4 of area; light where film remains - Grade 20.

Film: Remaining film mushy and thin. Grades (considering all) 20; (considering only remaining film - 60).

#2. Fouling: Light bryozoan slime and few scattered hydroids (small) on remaining portion of film. Grade (not considering about 1/2 area covered by rust) - 85.

Corrosion: Heavy on 1/2 area; light on remaining film. Grades (considering all) - 40; (considering only remaining film - 70).

Film: Fair, washed thin and 1/2 ruined by rust. Grade 40.

#3. Fouling: Light bryozoan slime and few small ascidians and short hydroids on remaining film. Grade (not considering 1/2 area covered by rust) - 80.

Corrosion: About 1/2 area covered by heavy rust; remainder has light rust - Grade (considering all) - 10.

Film: Ruined by rust.

#4. Fouling: Light bryozoan slime and a few hydroids on remaining film - Grade (not considering 3/4 of area covered by rust) - 70.

Corrosion: Heavy on 3/4 of area and remaining film full of light rust - Grade 0.

Film: Ruined by rust.

#6. Fouling: Light slime - Grade 90.

Corrosion: Moderate. Grade 80 (no rust except on few spots where film is not intact).

Film: Bare under few rust spots; remainder excellent - 80. (Note: Film dried out similarly to a shellac film; that is, cracked and spalled).

#7. Same as #6.

Backs of Panels

#1. Fouling: Light slime and short hydroids - Grade (not considering 1/2 of area covered by rust) - 85.

Corrosion: Heavy on 1/2 area; sufficient on remainder of area to ruin film. Grade 0.

Film: Thin; ruined by rust.

#2. Fouling: Light slime and hydroids - Grade (not considering area covered by heavy rust) - 75.

Corrosion: Heavy on 3/4 area; remainder has considerable light rust - Grade 0.

Film: Ruined by rust.

#3. Fouling: Slime and short hydroids. Grade (not considering area covered by heavy rust) - 80.

Corrosion: Heavy on 3/4 area; remaining film contains much rust - Grade 10.

Film: Ruined by rust; mushy, thin. Grade 0.

#4. Fouling: Light slime and short hydroids; three barnacles 1/2" diameter and a few small ascidians - Grade (not considering area covered by heavy rust) - Grade 70.

Corrosion: Heavy on 1/3 area. Remaining film full of rust. Grade 0.

Film: Ruined.

#6. Same as #7.

[redacted]

#7. Fouling: Very light bryozoan slime and two small ascidians. Grade 88.

Corrosion: Very light - Grade 95.

Film: Excellent.

Wood frame (painted with Navy antifouling paint No. 16): Fouling: Considerable slime; few hydroids; no shell growth. Grade 75.

Galvanized iron weights attached to frame. Fouling: Practically covered with barnacles about 1/2" diameter.

Plate #11 is a photomicrograph of a steel specimen treated in a selenium bath at a temperature of about 450° C for about five minutes. The light portion is the polished steel shading off into a reaction zone which probably consists of a mixture of iron selenide and selenium, this in turn shading off into the thin coating of pure selenium.

Plate #12 is the same specimen under high magnification. The reaction or bonding zone can be more clearly distinguished.

It was determined the continue the research by developing alloys of selenium, sulphur and tellurium in the hope of developing a more plastic, adherent surface which would still retain the antifouling properties of selenium.

A large number of these alloys was prepared and from these a number chosen for salt spray corrosion tests. While making these alloys a number were found to possess unusual physical and electrical properties. These are dealt with in the appendix to this report.

Ten of the most promising of these alloys were chosen for corrosion tests. These alloys were as follows:

Alloy	Selenium %	Tellurium %	Sulphur %
1	70	0	30
2	63	12	25
3	65	5	30
4	60	5	35
5	60	10	30
6	55	5	40
7	65	2	33
8	70	2	28
9	60	2	38
10	100	0	0

RESULTS OF TEST:

6. A 21 day salt spray test of 2" x 4" mild steel samples coated with ten of these alloys by dipping gave the following results:

In all cases corrosion started at the edges, and wherever blisters occurred in the coating; thereafter working underneath the protective coating. The pure selenium coated plate was between 30 and [redacted]

[redacted]

roded in spots appearing on both sides of the plate. The corrosion had not, as on some of the other plates, eaten into the plate. Of the remaining samples, several showed bad flaking and corrosion on one side with hardly any on the other. Wherever the coating remained, it was tough and in good condition.

CONCLUSIONS:

7. (a) The selenium groups of metals appear to have value as antifouling agents.

(b) The anticorrosive properties of the selenium groups must be greatly improved before the antifouling properties can be properly evaluated.

RECOMMENDATIONS:

8. It is recommended that work with the selenium group be continued along the following lines:

(a) Improve anticorrosive properties by developing an anticorrosive coating to be applied to the steel before the antifouling coating is applied. Test anticorrosive properties by salt spray test.

(b) When anticorrosive properties have been sufficiently developed, prepare standard antifouling test panels for further test at Norfolk.

APPENDIX

9. While making the selenium, tellurium and sulphur alloys, a number were found to possess unusual physical and electrical properties. Measurements of the dielectric constants and power loss factor of these alloys were made both freshly cast and after ageing about two weeks. Results are shown in Table 1.

[redacted]

Those samples marked "A" and "B" were found to retain their plasticity to a marked degree.

There is a possibility of some of the alloys finding a use in radio or electrical work.

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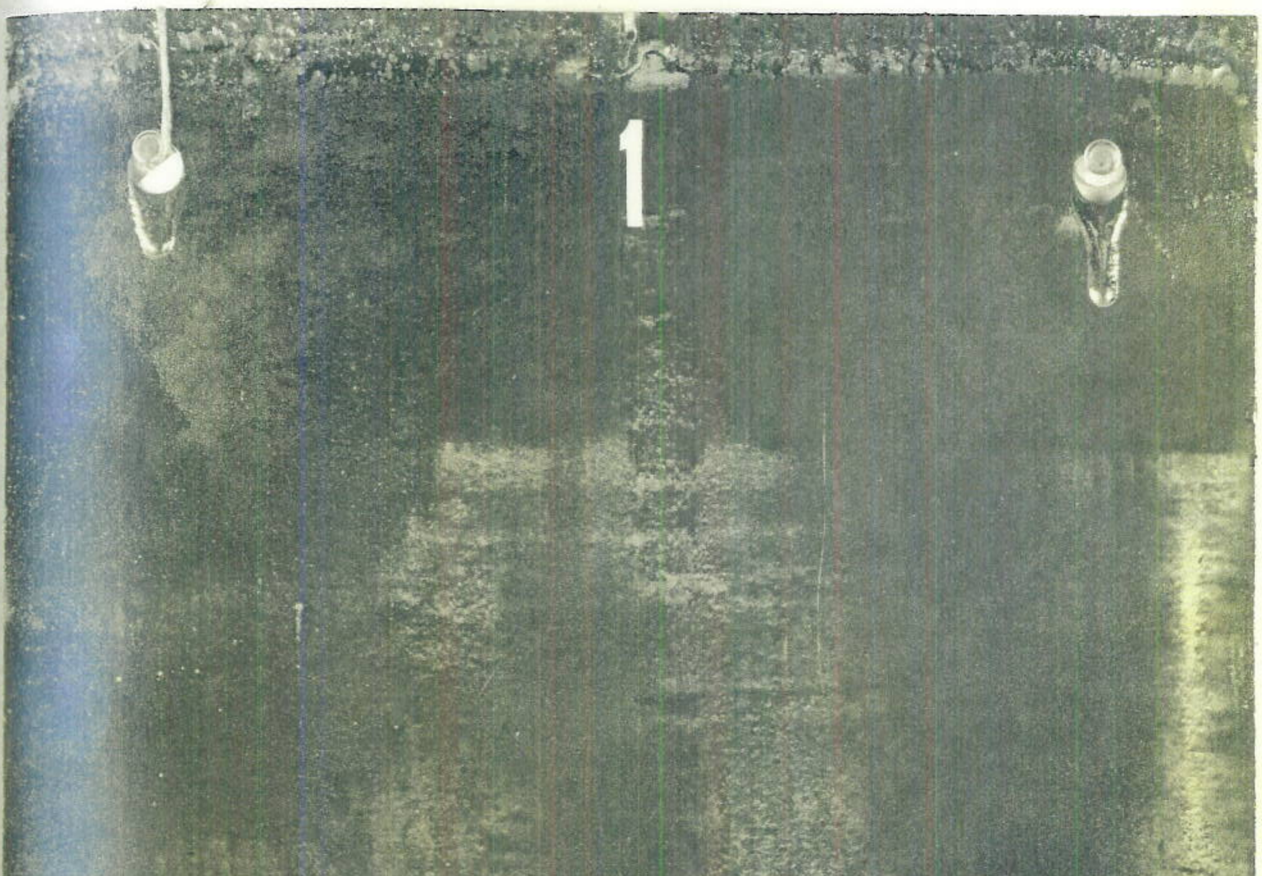

Plate #1. Front view of Panel #1 before test.

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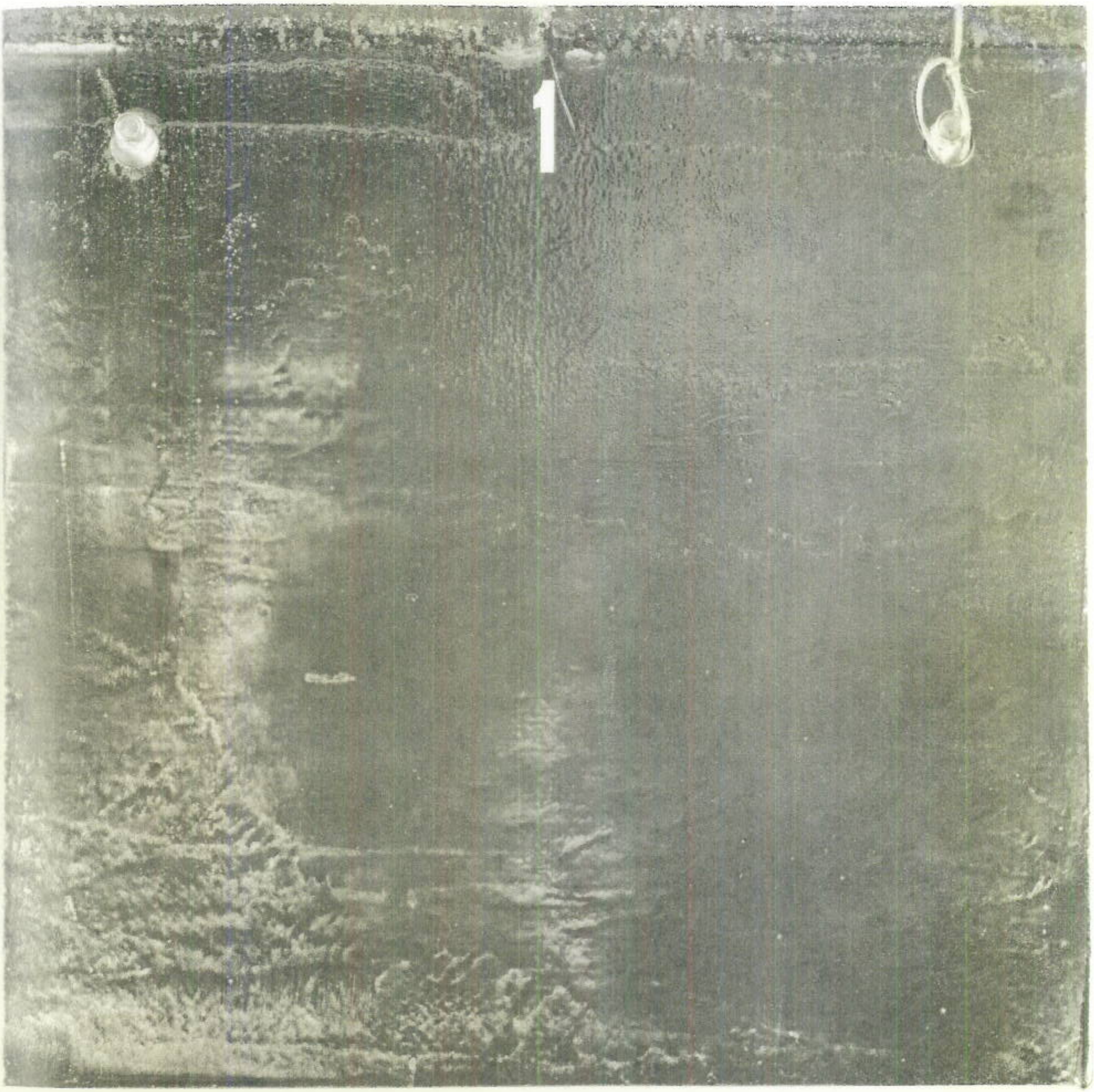

Plate #2. Back view of Panel #1 before test.

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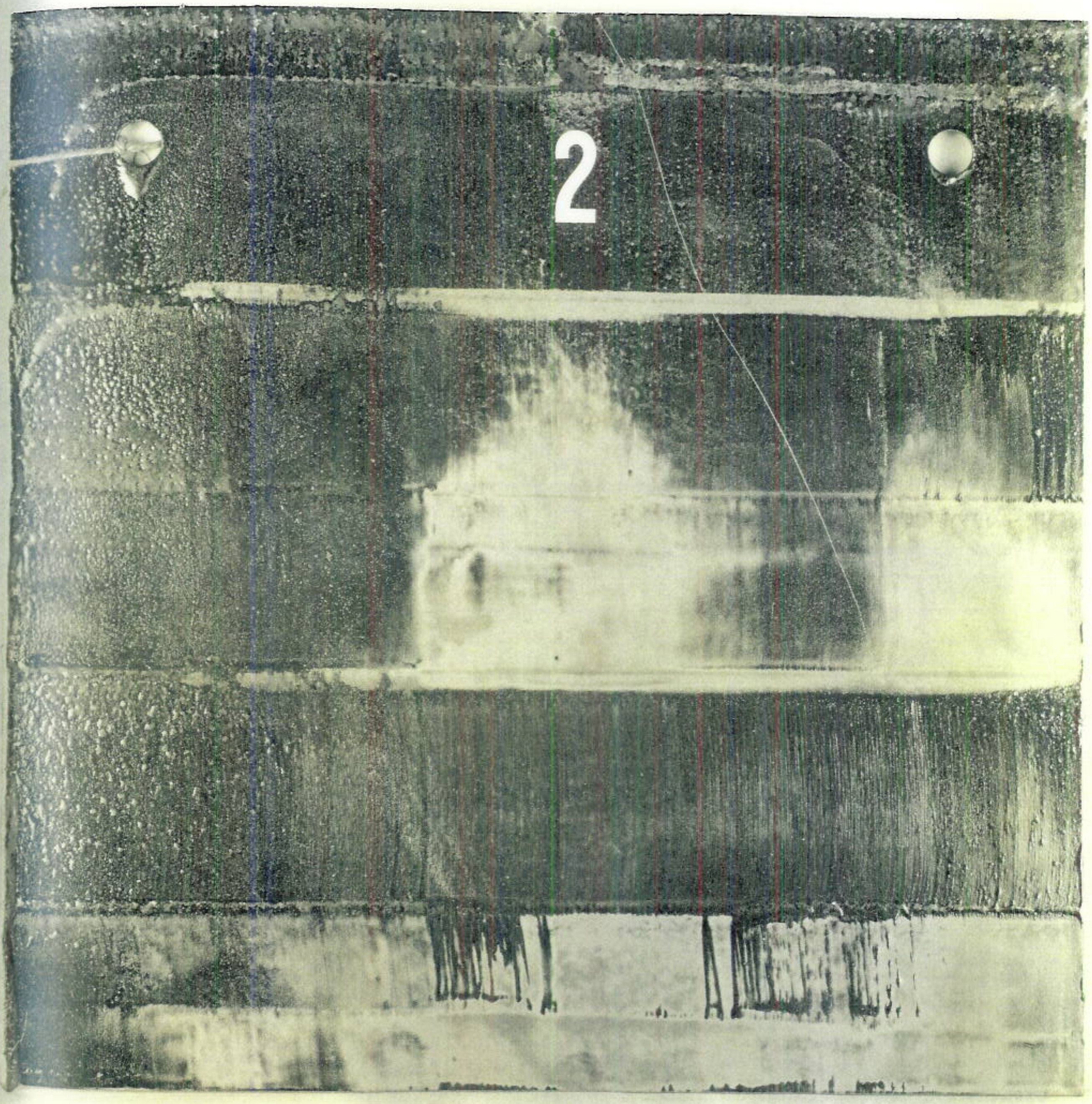

Plate #3. Front view of Panel #2 before test.

Plate #4. Back view of Panel #2 before test.

[redacted]

[redacted]

Plate #5. Front view of Panel #3 before test.

 [redacted] [redacted]

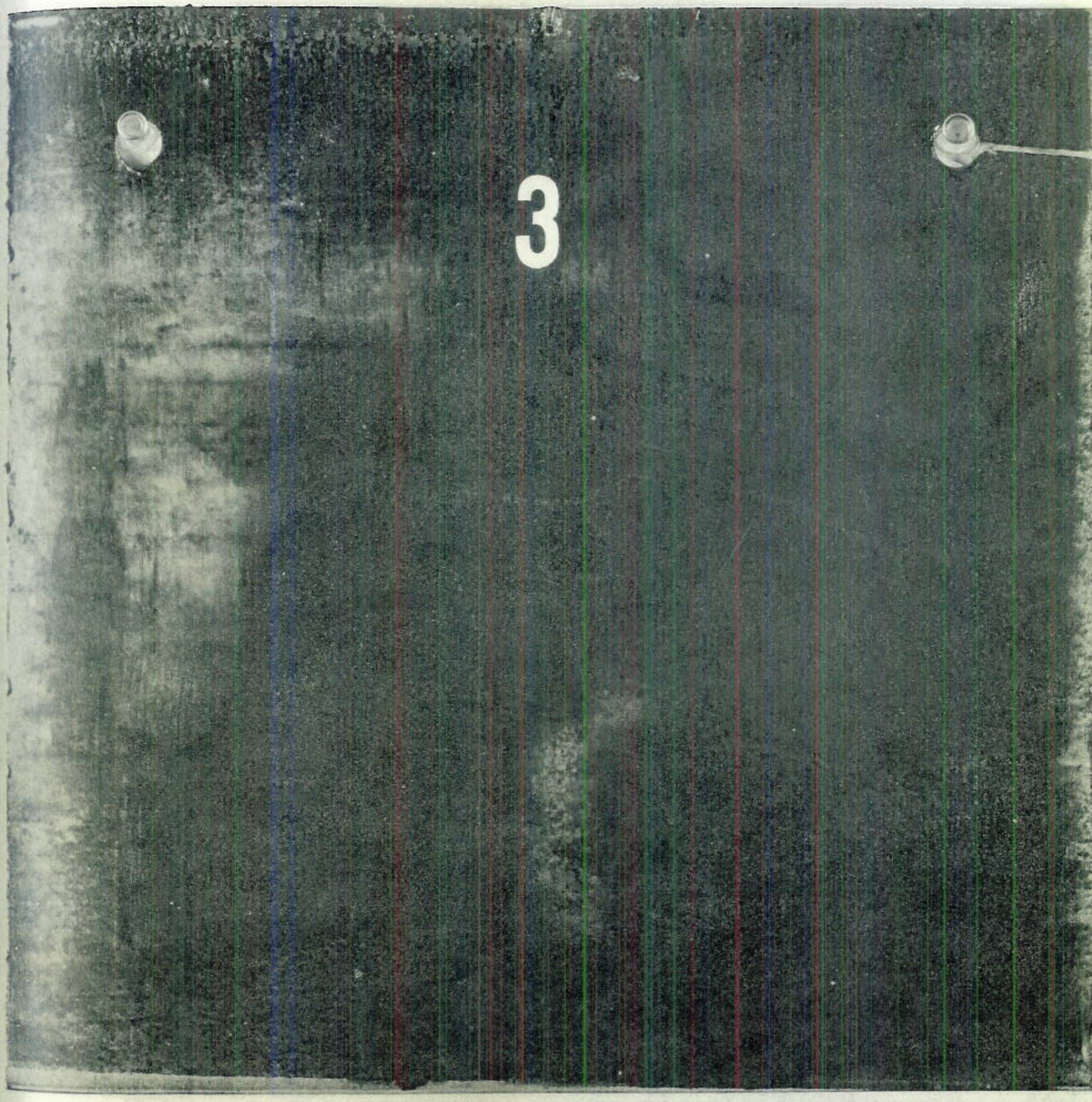

Plate #6. Back view of Panel #3 before test.

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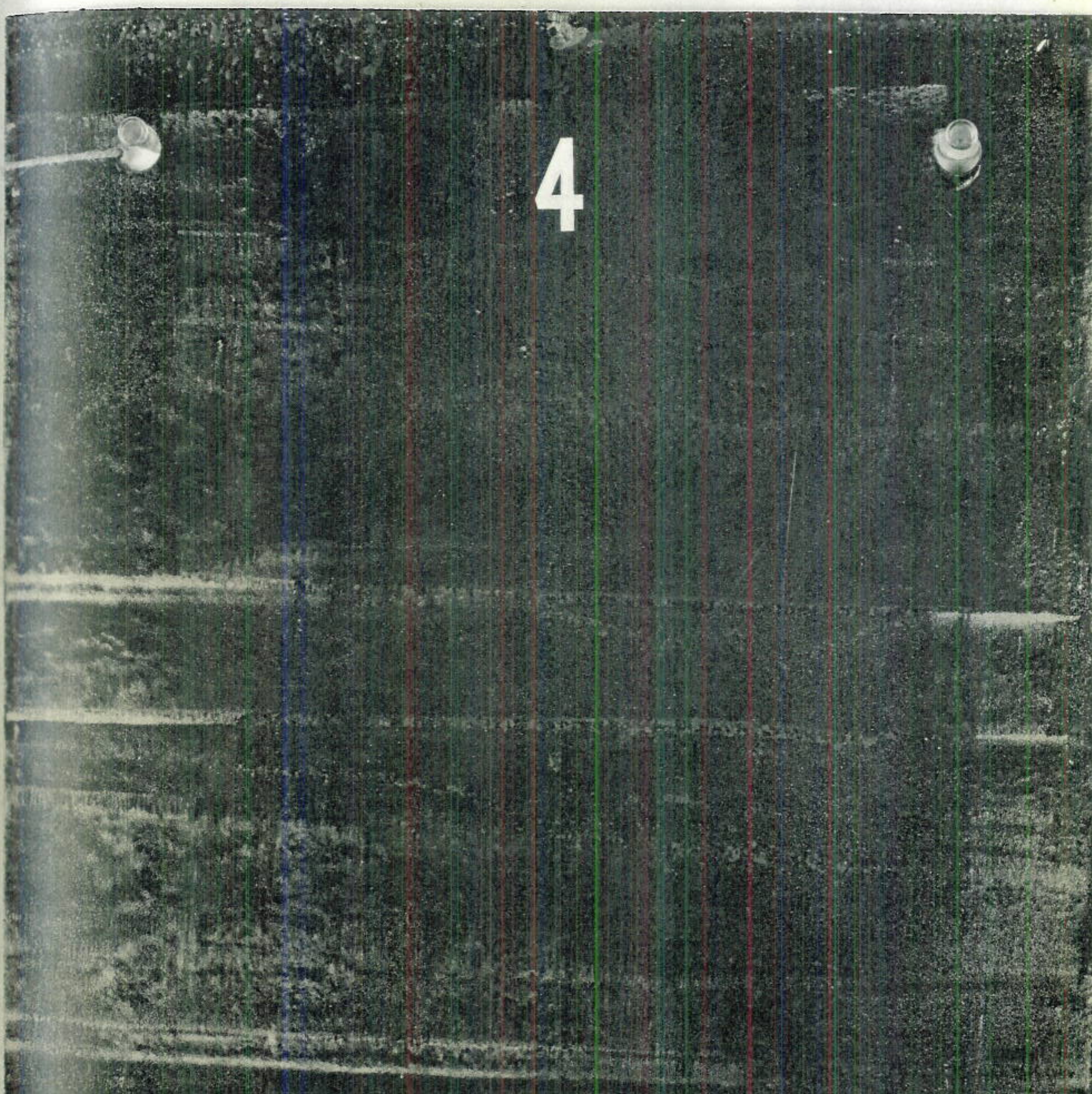

Plate #7. Front view of Panel #4 before test.

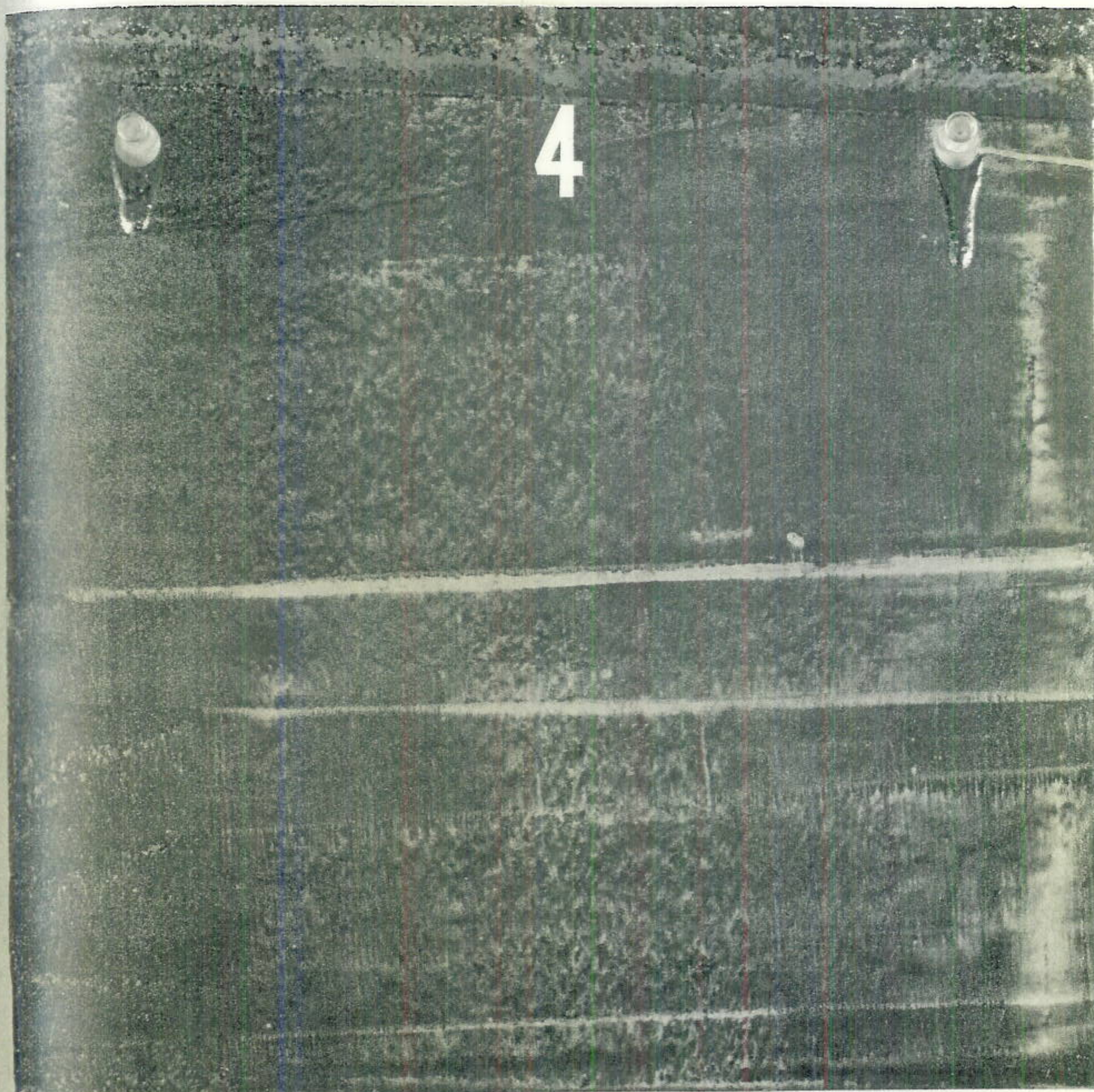

Plate #8. Back view of Panel #4 before test.

[redacted] [redacted]

Plate #9. Photograph of Panels Nos. 1, 2, 3, 4, 6, 7 after exposure. Front view.

Plate #10. Photograph of Panels Nos. 1,2,3,4,6,7 after exposure. Back view.

[redacted]

[redacted]

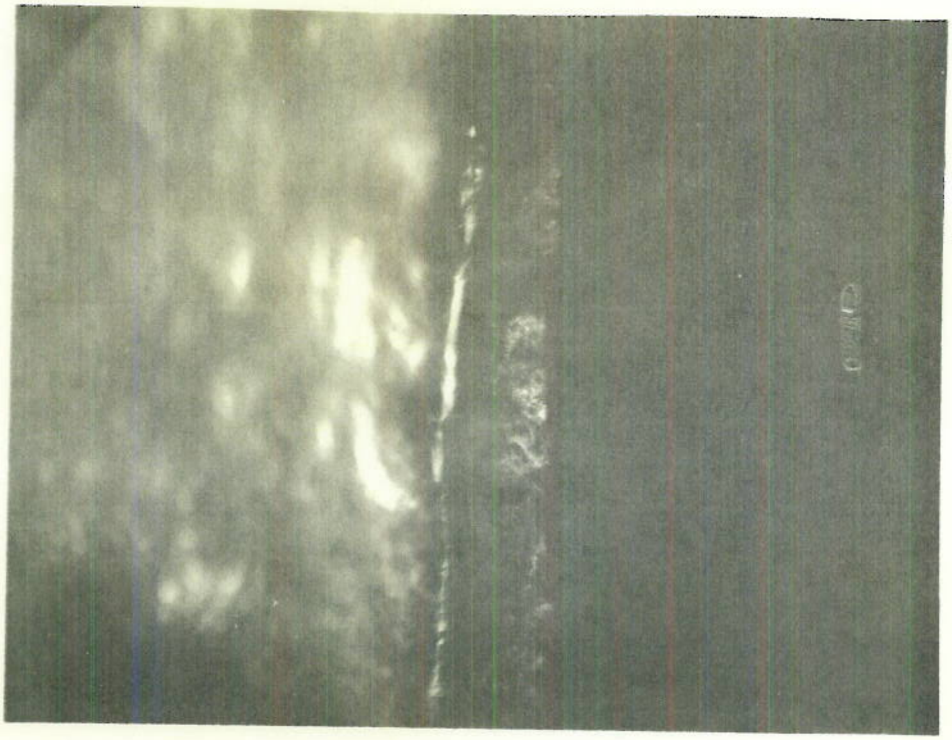

Plate 12

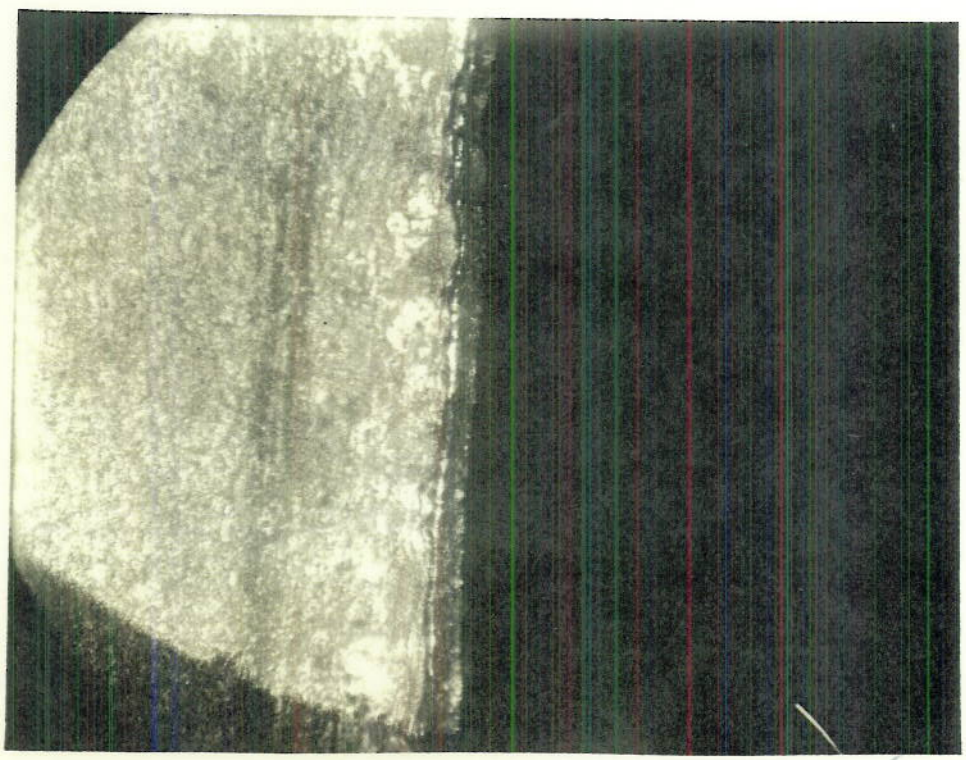

Plate 11

TABLE 1.

Sample No.	Date Cast	Date Tested	% SE	% Te	% S	Flexibility at 22°C 11-20-33	Dielectric constant K	Dielec. Const. K Measured on 11-15-33	Phase Difference %	Phase Diff. Measured 11-15-33	Loss Factor K x Phase Diff. in %	Loss Factor K x Phase Diff. in % Measured on 11-15-33
58	10-25-33	10-23-33	35	–	65		4.22	2.67	0.55	.22	2.31	0.60
27			40	–	60		4.01	2.95	0.65	.29	2.60	.86
57			45	–	55		4.00		0.69		2.76	
56			55	–	45		3.62		0.56		2.03	
19			60	–	40		3.78	4.02	0.57	.64	2.11	2.55
55	10-24-33		65	–	35		5.13	5.05	0.71	.71	3.62	3.58
18			70	–	30	B	4.95		0.69		3.44	
54			75	–	25		4.82	5.19	0.63	.69	3.05	3.60
62	10-27-33	10-27-33	25	10	65		3.27	2.69	0.47	.33	1.53	.87
32	10-26-33	10-27-33	30	10	60		4.25		0.80		3.42	
31	10-26-33	10-27-33	40	10	50		4.81		0.85		4.09	
61	10-27-33	10-28-33	45	10	45		4.78	3.67	0.96	.47	4.58	1.73
59	10-26-33	10-27-33	50	10	40		4.46	4.40	0.71	.78	3.17	3.43
60	10-26-33	10-27-33	60	10	30	B	4.81	4.20	0.77	.69	3.70	2.95
68		11-1-33	30	5	65		3.50		0.43		1.50	
67		11-1-33	35	5	60		3.54	2.88	0.51	.37	1.80	1.17
66	10-30-33	11-1-33	40	5	55		4.29		0.88		3.77	
65	10-28-33	10-30-33	45	5	50		4.26		0.78		3.33	
64		10-30-33	50	5	45		4.64		0.77		3.56	
63		10-30-33	55	5	40	A	4.72	4.28	0.74	.74	3.49	3.15
47	10-28-33	10-30-33	60	5	35	A	4.61	4.62	0.66	.75	3.05	3.48
42	10-27-33	10-28-33	65	5	30	B	4.71	4.95	0.69	.80	3.25	3.98
70	10-31-33	11-1-33	65	2	33	A	4.37	4.33	0.63	.61	2.77	2.64
71	10-31-33	11-1-33	70	2	28	A	5.08	4.52	0.75	.65	3.81	2.94
72	10-23-33	10-26-33	60	2	38	A	4.70	3.31	0.68	.49	3.18	1.62
35	10-31-33	11-1-33	63	12	25	B	4.84	5.39	0.67	.76	3.25	4.09 Pro.Atomic
25	10-26-33	10-27-33	25	25	50		10.13		2.61		26.45	Wts.tested
25	10-26-33	10-27-33	25	25	50		8.44		1.97		16.61	on diff.date
25	10-26-33	10-28-33	25	25	50		8.28		2.17		18.00	
25	10-26-33	10-28-33	25	25	50		8.84	6.75	2.28	2.81	20.20	18.95
	10-30-33	10-30-33	–	–	100		3.78		0.06		0.24	Fresh cast sulphur
	10-30-33	10-30-33					3.26		0.51		1.66	Victron E
							3.16		1.74		5.54	Victron E
							3.40		0.67		2.28	Amer.Hard Rubber
							4.33		0.44		1.93	"Parock"

Aver.Freq. 440 KC (Approx.) A = Excellent
Sample 6 x 6-1/4 inches. B = Very good