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STUDY OF INHIBITIVE PIGMENTS FOR IMPROVED
CORROSION RESISTANCE IN LUSTRELESS ONE
COAT AMMUNITION ENAMELS

Merrill Cohen, et al

Army Coating and Chemical Laboratory

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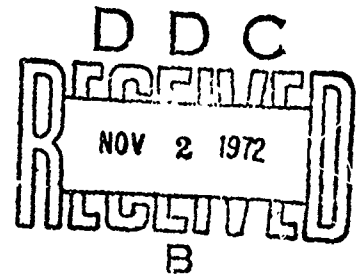
PROGRESS REPORT

STUDY OF INHIBITIVE PIGMENTS FOR IMPROVED
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ONE COAT AMMUNITION ENAMELS

BY

MERRILL COHEN
ANDREW A. O'BROCHTA
AND
MELVIN H. SANDLER

AUGUST 1972



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i-B

ABSTRACT

One coat ammunition enamels covered by Specification TT-E-516, "Enamel, Lustreless, Quick Drying, Styrenated Alkyd Type" were reformulated with white low tint strength inhibitive type pigmentations. The enamels were subjected to salt spray tests and exterior exposure at temperate and tropical zone sites. The data shows several of the experimental enamels will provide significantly improved corrosion resistance over the standard enamels.

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I. INTRODUCTION

During the past few years periodic reports from the field have indicated erratic performance of current specification one coat ammunition enamels conforming to Federal Specification TT-E-516 "Enamel, Lustreless, Quick Drying, Styrenated Alkyd Type". Most recently reported has been the occurrence of various degrees of corrosion on large caliber ammunition during shipment from the producer to the loading plant. This has further demonstrated the need to provide a higher degree of protection against atmospheric corrosion which may be encountered during the life cycle of such ammunition. A program was therefore undertaken to develop more corrosion resistant one coat ammunition enamels.

II. DETAILS OF TEST

In addition to providing corrosion resistance ammunition enamels are designed to meet production line requirements for ease of application and rapid drying characteristics. To avoid any change in these properties it was decided to initially concentrate on pigment modifications. Previous work at this laboratory had shown the use of zinc chromate as an inhibitive pigment in lustreless olive drab enamels appreciably improved salt spray resistance and exterior durability. However, since TT-E-516 includes seventeen colors and white, the use of colored inhibitive pigments would be precluded in the white and most of the other colors. Efforts were therefore directed toward the incorporation of white low tint strength or extender type pigments that have been reported to provide corrosion inhibitive properties. Those selected for the initial phase of this program were an experimental modified zinc molybdate (EZM), barium metaborate (BMB), tribasic lead phosphosilicate (TLP), and dibasic lead phosphite (DLP). Pigmentations for olive drab (OD) and white were formulated replacing a portion of the extender pigment with 15 and 30 percent concentrations of EZM, BMB, and TLP, by weight of total pigment. DLP was formulated at 10 percent of total pigment. Efforts to use higher amounts showed excessive viscosity increases with resultant tendencies toward gelation. Enamels (Tables A and B) were prepared substituting the revised pigmentations, at the same pigment volume concentration, in control olive drab and white enamels conforming to specification TT-E-516.

Salt spray testing was then conducted in accordance with the specification for up to 264 hours with daily examination for compliance. As can be seen in Tables C and D, EZM (Formulas A2 and A3) provided slight improvement in olive drab and none in white. All the others showed significantly improved corrosion resistance. Only the white enamel (B4) containing 15 percent BMB showing any failure at the end of 264 hours exposure compared to 48 hours for the control enamels (A1 and B1).

Test specimens were also placed on exterior exposure at Aberdeen Proving Ground (APG) and at breakwater and open field sites at Fort Sherman, Panama Canal Zone (1). All panels were scored, except for those at the Panama breakwater. Experience has shown this site to be extremely

severe on scored areas of one coat enamels and the spread of corrosion from the score could interfere with an effective evaluation of differences in the inhibitive properties of the enamels since only semi-annual inspections could be made. After 6 months exposure the panels at all sites were examined for corrosion. In addition those at APG and the open field sites were examined for chalking and color change in accordance with specification requirements. In efforts to additionally distinguish differences, score condition was rated as in Table E, surface condition as in Table F, substrate condition in accordance with Photos 0-10, (Appendix B); and lightness index difference determined as in method 6122 of Federal Test Method Std. No. 141. The data is tabulated in Tables G and H.

At APG, except for the EZM pigmented white enamels (B2 and B3), there was no significant difference between the control and modified enamels in either the white or olive drab colors, with all meeting specification requirements at this time. The EZM modified white enamels showed a significant color change to a blue shade which was immediately obvious to the eye and further confirmed by the significant change in lightness index difference. Appearance of the enamels after 6 months at the APG site is shown in Photo 11. At the tropical sites, which provide a more aggressive environment, differences in the corrosion resistance of the enamels was shown. The open field site, as expected, was less severe than the breakwater but nevertheless was beginning to show differences between the white enamels with the white control exhibiting noticeable surface corrosion. All the experimental white enamels provided significantly better corrosion resistance (Photo 12). There was no surface corrosion evident with the olive drab enamels. The breakwater site further confirmed the improved corrosion resistance. The white enamels are shown in Photos 13 and 14. The same trends were also evident for the olive drab enamels.

III. SUMMARY

Overall the most effective enamels were those modified with tribasic lead phosphosilicate with 30% concentration showing only a trace of corrosion at the breakwater site after 6 months exposure. Although not quite as effective as TLP the enamels using dibasic lead phosphite and barium metaborate were comparable and significantly better than the experimental zinc molybdate. Exposure studies are continuing and additional work has been initiated to study the effectiveness of these inhibitive type pigments in other colors covered by the specification.

IV. REFERENCE

1. Teitell, Leonard, Report R-1888, "Studies of the Effects of Tropical Environments in Materials", 1. Description of Exposure Sites Pittman-Dunn Research Laboratories, Frankford Arsenal, Philadelphia, Pa., May 1968.

APPENDIX A

TABLE A

Olive Drab Formulats Jns

Ingredient	A1	A2	A3	A4	A5	A6	A7	A8
Yellow iron oxide	133.1	134.7	135.6	136.4	138.6	141.5	134.7	138.8
Carbon black	4.0	4.0	4.0	4.1	4.1	4.2	4.0	4.1
Titanium dioxide	17.6	17.7	17.8	17.9	18.2	18.6	17.7	18.3
Acicular talc	79.9	60.2	39.3	61.0	40.2	64.2	39.1	69.3
Fibrous magnesium silicate	132.8	98.2	64.2	99.5	65.6	103.2	63.8	113.1
Zinc molybdate	--	55.6	111.8	--	--	--	--	--
Barium metaborate	--	--	--	56.3	114.4	--	--	--
Tribasic lead phosphosilicate	--	--	--	--	--	58.4	111.2	--
Dibasic lead phosphite	--	--	--	--	--	--	--	38.2
Styrenated alkyd resin (50%)	423.9	426.3	424.4	423.3	416.8	410.8	425.0	416.4
Xylene	238.0	237.6	239.7	241.1	248.5	255.4	239.2	249.0
Diethylamine	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Cobalt naphthenate	1.1	1.1	1.1	1.0	1.0	1.0	1.0	1.0
Antioxidant	1.1	1.1	1.1	1.0	1.0	1.0	1.0	1.0
Total Pounds	1032.7	1037.0	1039.5	1042.1	1048.9	1058.8	1037.2	1049.7
Total solids	56.3	56.3	56.3	56.3	56.2	56.2	56.2	56.2
Pigment on total paint, %	35.7	35.7	35.9	36.0	36.3	36.8	35.7	36.4
Vehicle solids on total paint, %	20.6	20.6	20.4	20.3	19.9	19.4	20.5	19.8
Pigment volume conc., %	37.7	37.7	37.7	37.7	37.7	37.7	37.7	37.7
Pigment to binder, ratio	1.74/1	1.74/1	1.76/1	1.77/1	1.83/1	1.89/1	1.74/1	1.83/1
Inhibitor, %	0	15	30	15	30	15	30	10

TABLE B

White Formulations

Ingredient	Pounds/100 gallons							
	B1	B2	B3	B4	B5	B6	B7	B8
Titanium dioxide, rutile	197.5	198.7	199.7	201.3	204.8	209.5	223.7	205.3
Acicular talc	38.3	25.8	14.4	26.2	14.7	27.2	15.1	30.7
Fibrous magnesium silicate	147.4	103.4	57.4	104.7	58.9	109.0	64.3	122.8
Zinc molybdate	--	57.9	116.3	--	--	--	--	--
Barium metaborate	--	--	--	58.6	119.2	--	--	--
Tribasic lead phosphosilicate	--	--	--	--	--	61.0	130.3	--
Dibasic lead phosphite	--	--	--	--	--	--	--	--
Styrenated alkyd resin (50%)	423.1	420.9	418.0	417.5	410.5	405.4	381.7	39.9
Xylene	239.9	242.5	246.4	246.4	254.4	260.2	286.2	411.5
Diethylamine	0.7	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Cobalt naphthenate, 6%	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Antioxidant	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Total pounds	1048.9	1051.7	1054.7	1057.2	1065.0	1074.8	1104.8	1066.0
Total solids	56.7	56.7	56.6	56.7	56.6	56.7	56.6	56.7
Pigment on total paint, %	36.5	36.7	36.8	37.0	37.3	37.8	39.3	37.4
Vehicle solids on total paint, %	20.2	20.0	19.8	19.7	19.3	18.9	17.3	19.3
Pigment volume conc., %	33.0	38.0	38.0	38.0	38.0	38.0	38.0	38.0
Pigment to binder, ratio	1.51/1	1.83/1	1.86/1	1.87/1	1.94/1	2.0/1	2.28/1	1.94/1
Inhibitor, %	0	15	30	15	30	15	30	10

TABLE C
5% Salt Spray Exposure
Olive Drab Formulations

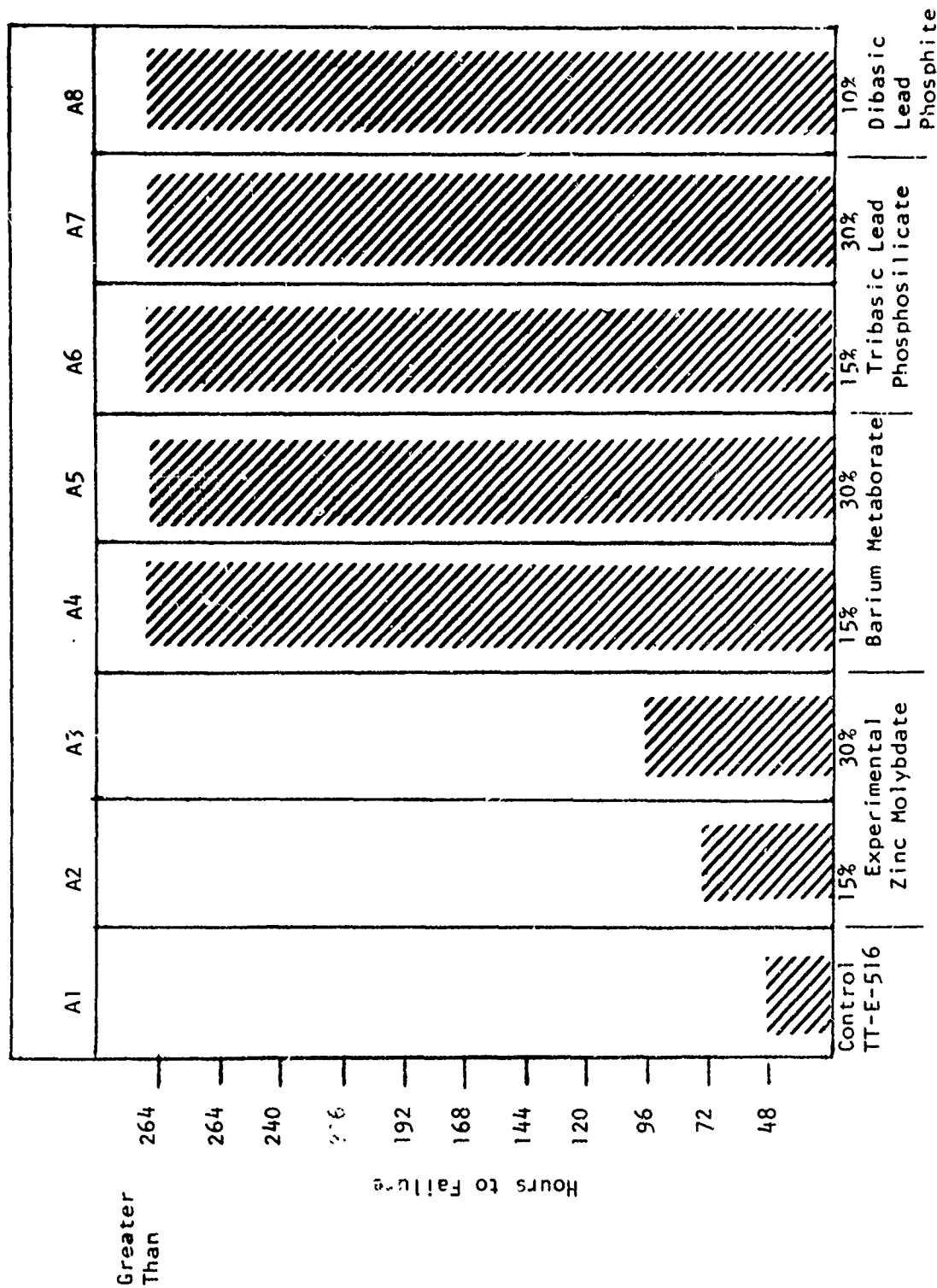


TABLE D
5% Salt Spray Exposure
White Formulations

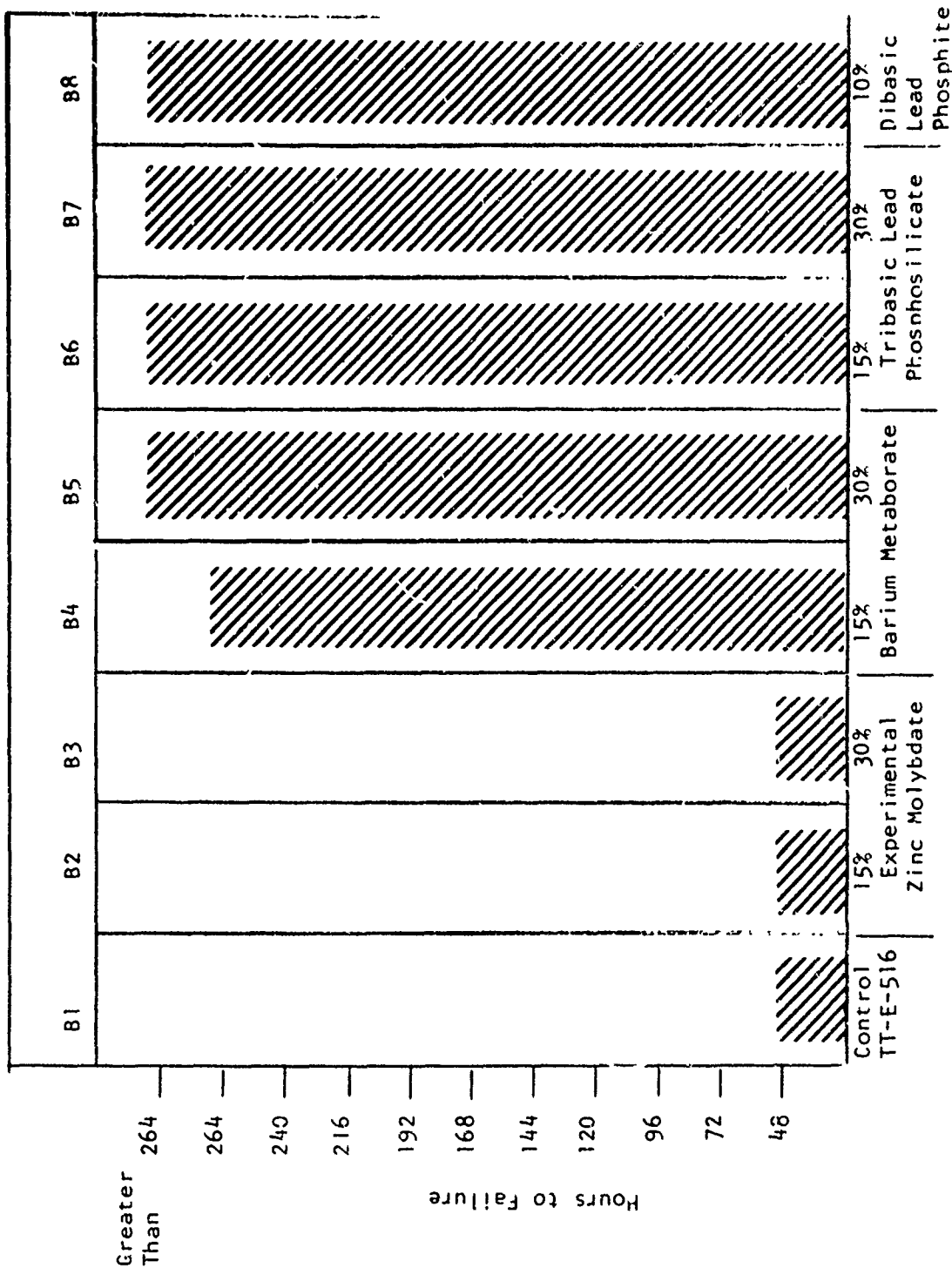


TABLE E
SCORE

I. Score Condition

<u>Rating</u>	<u>Corrosion and/or Blistering</u>
5	None - 1/32 inch
4	1/32 - 1/16 inch
3	1/16 - 1/8 inch
2	1/8 - 3/16 inch
1	3/16 - 1/4 inch
0	1/4 inch

II. Undercutting at Score

<u>Rating</u>	
5	None-intermittent
4	Continuous to 1/16 inch
3	Continuous to 1/16 - 1/8 inch
2	Continuous to 1/8 - 3/16 inch
1	Continuous to 3/16 - 1/4 inch
0	Continuous 1/4 inch

TABLE F

Surface Condition*

Rating

A. Corrosion Alone

5	None
4	ASTM D610-43 Photo No. 10, Type 1
3	ASTM D610-43 Photo No. 9, Type 1
2	ASTM D610-43 Photo No. 8, Type 1
1	ASTM D610-43 Photo No. 7, Type 1
0	ASTM D610-43 Photo No. 6, Type 1 or worse

Rating

B. Corrosion Accompanied by Blistering

5	None
4	Trace, less than 5 defects on 4x12 inch panel
3	ASTM D610-43 Photo No. 8, Type 2
2	ASTM D610-43 Photo No. 7, Type 2
1	ASTM D610-43 Photo No. 6, Type 2
0	ASTM D610-43 Photo No. 4, Type 2 or worse

Rating

C. Blistering Alone

5	None
4	Trace ASTM D714-56 Size 2 on 4x12 inch panel - 2 max. ASTM D714-56 Size 4 on 4x12 inch panel - 4 max. ASTM D714-56 Size 6 on 4x12 inch panel - 6 max. ASTM D714-56 Size 8 on 4x12 inch panel - 8 max.
3	ASTM D714-56 Few - Record blister size
2	ASTM D714-56 Medium - Record blister size
1	ASTM D714-56 Med-Dense - Record blister size
0	ASTM D714-56 Dense - Record blister size

*Select applicable condition.

TABLE G

6 Months Exterior Exposure - Olive Drab

Formula No.	APG			Panama Open Field			Panama Breakwater									
	Score C/B	U	Sur.	Sub.	Chalk	ΔL	Score C/B	U	Sur.	Sub.	Chalk	ΔL	Score C/B	U	Sur.	Sub.
A1	5	5	5	10	7	+0.43	5	5	5	9	8	+0.66	5	5	5	8
A2	5	5	5	10	8	+0.20	4	4	5	8	8	+1.71	4	4	5	3
A3	5	5	5	10	8	-0.15	5	5	5	10	8	+1.33	5	5	5	3
A4	5	5	A4	10	8	+0.55	5	5	5	10	8	+0.49	5	5	5	R
A5	5	5	A4	10	8	+1.16	5	5	5	10	8	+1.64	5	5	5	R
A6	5	5	5	10	8	-0.38	5	5	5	10	8	-0.46	5	5	5	8
A7	5	5	5	10	8	-0.08	5	5	5	10	8	+0.45	5	5	5	8
A8	5	5	5	10	8	-0.96	5	5	5	10	8	-0.52	5	5	5	8

TABLE H

6 Months Exterior Exposure - White

Formula No.	APG			Panama Open Field			Panama Breakwater									
	Score C/B	U	Sur.	Sub.	Chalk	ΔL	Score C/B	U	Sur.	Sub.	Chalk	ΔL	Score C/B	U	Sur.	Sub.
B1	5	5	5	10	7	-1.56	4	4	4	8	6	-0.23	4	4	4	7
B2	5	5	5	10	7	-4.14	4	4	4	10	6	-2.06	4	4	4	7
B3	5	5	5	10	7	-6.52	4	4	4	9	6	-2.91	4	4	4	6
B4	5	5	5	10	7	-0.12	3	3	3	10	6	-0.38	3	3	3	8
B5	5	5	5	10	7	+0.48	3	3	5	10	6	+0.23	3	3	5	8
B6	5	5	5	10	7	-0.93	5	5	5	10	6	-0.125	5	5	5	8
B7	5	5	5	10	7	-0.19	5	5	5	10	6	+0.11	5	5	5	9
B8	5	5	5	10	7	-0.59	4	4	4	10	6	-0.80	4	4	4	7

APPENDIX B



PHOTO NO. 0

SUBSTRATE CONDITION

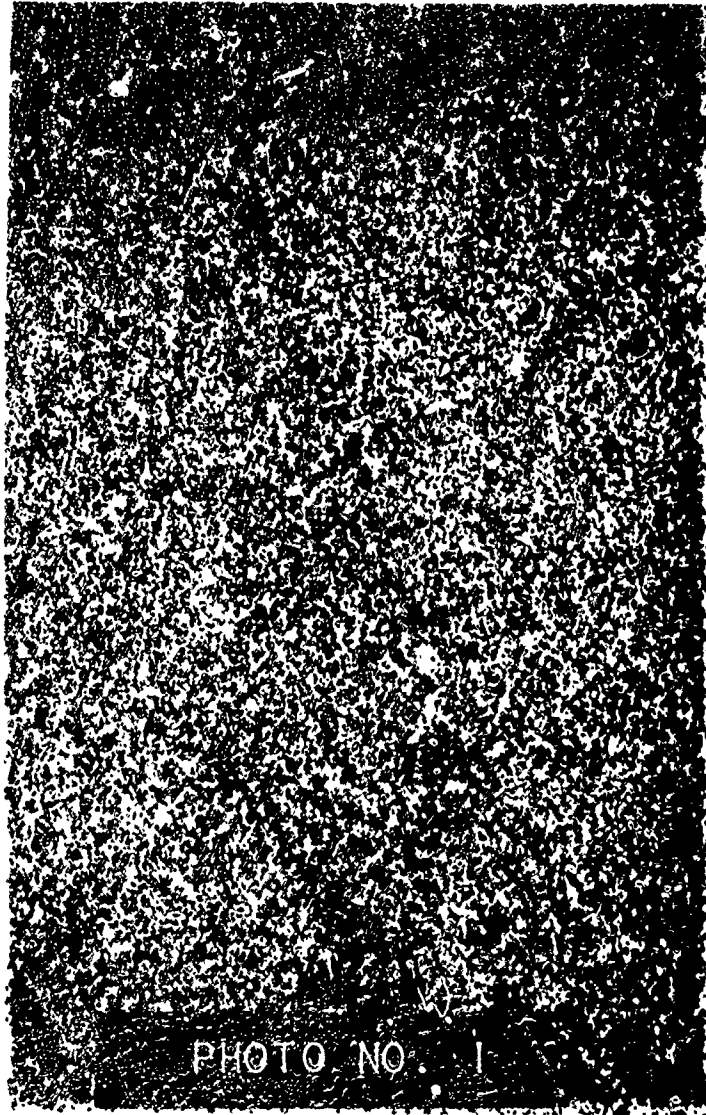


PHOTO NO. 1

SUBSTRATE CONDITION



PHOTO NO. 2

SUBSTRATE CONDITION

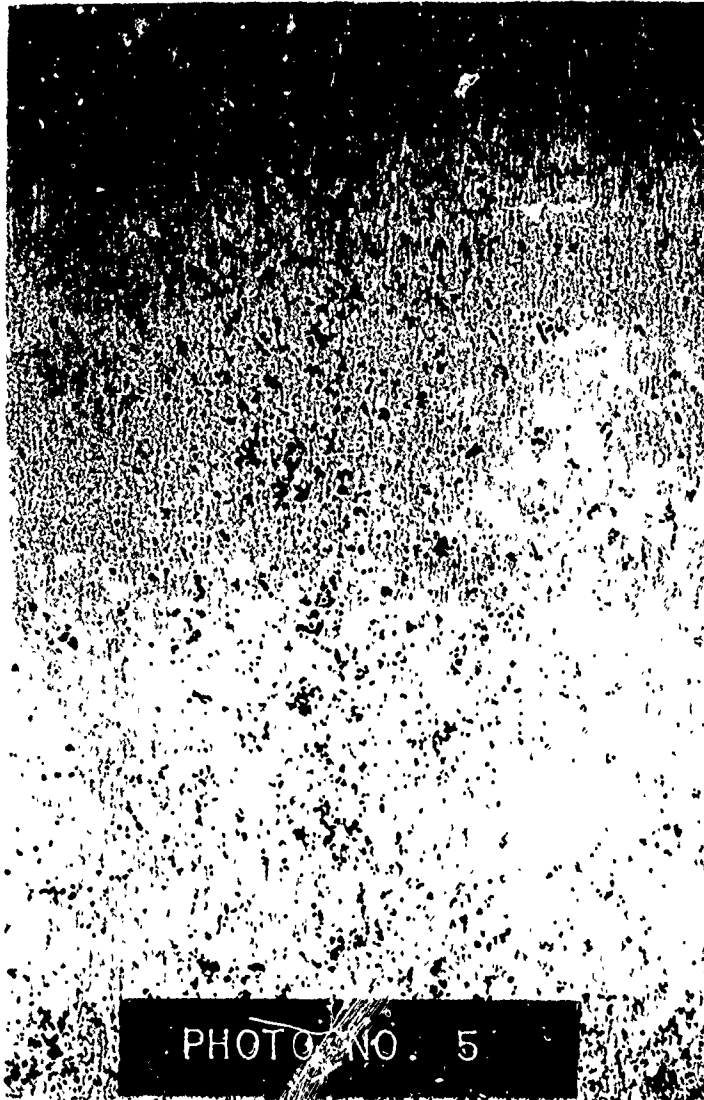


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SUBSTRATE CONDITION

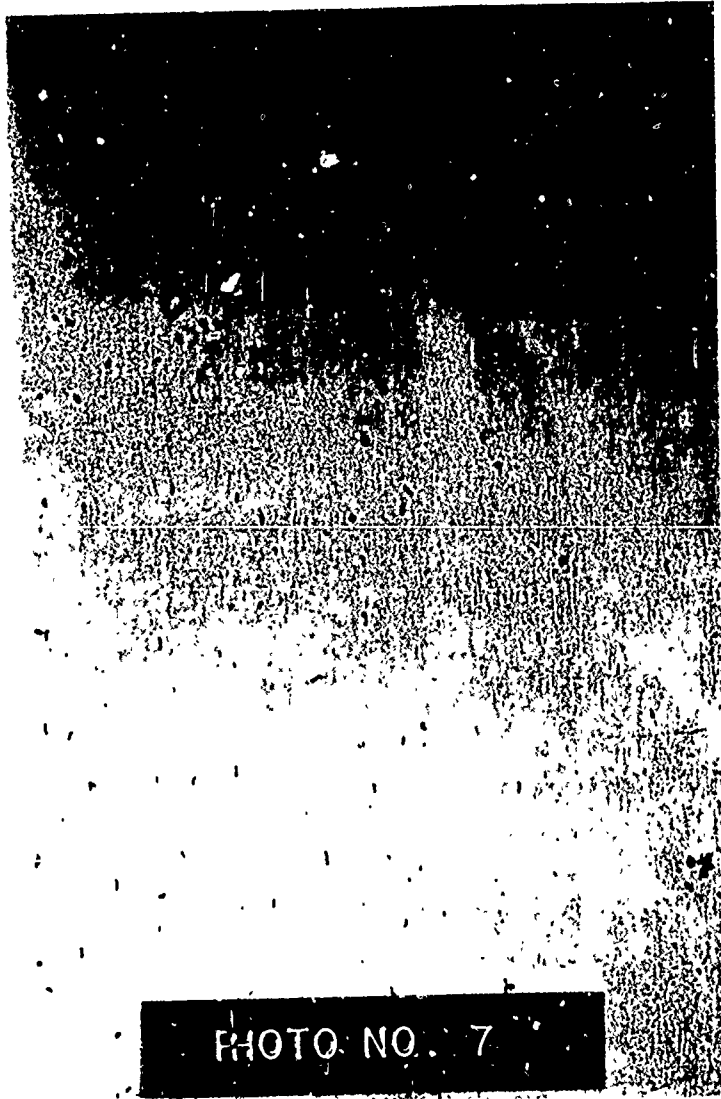


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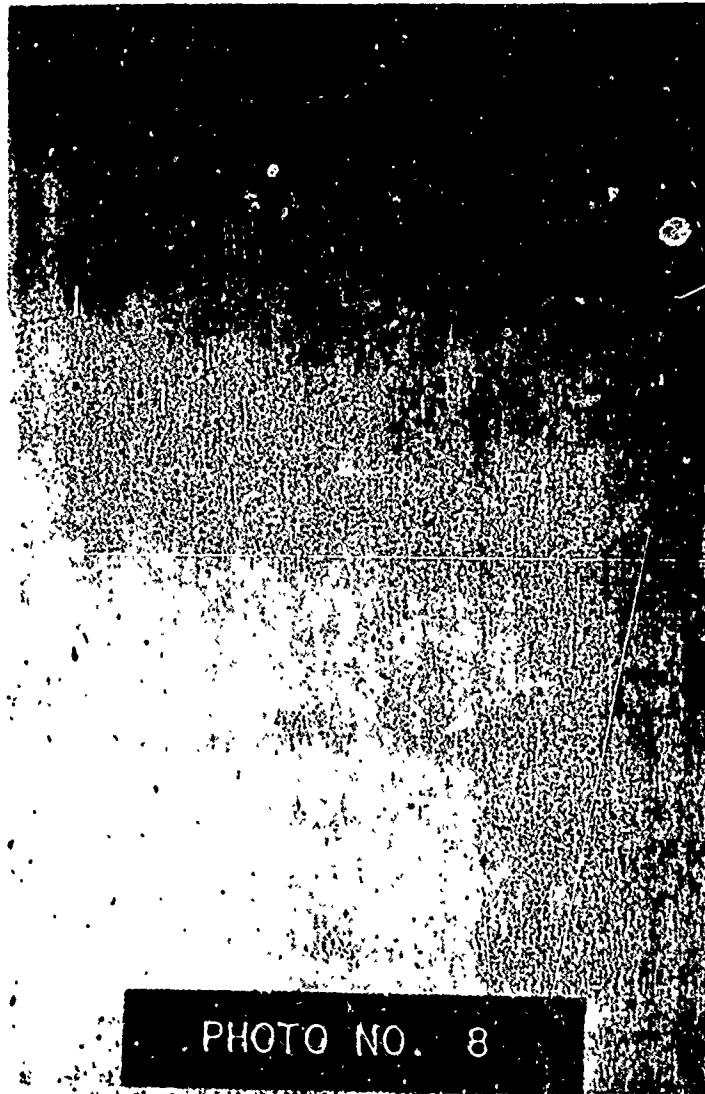
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SUBSTRATE CONDITION



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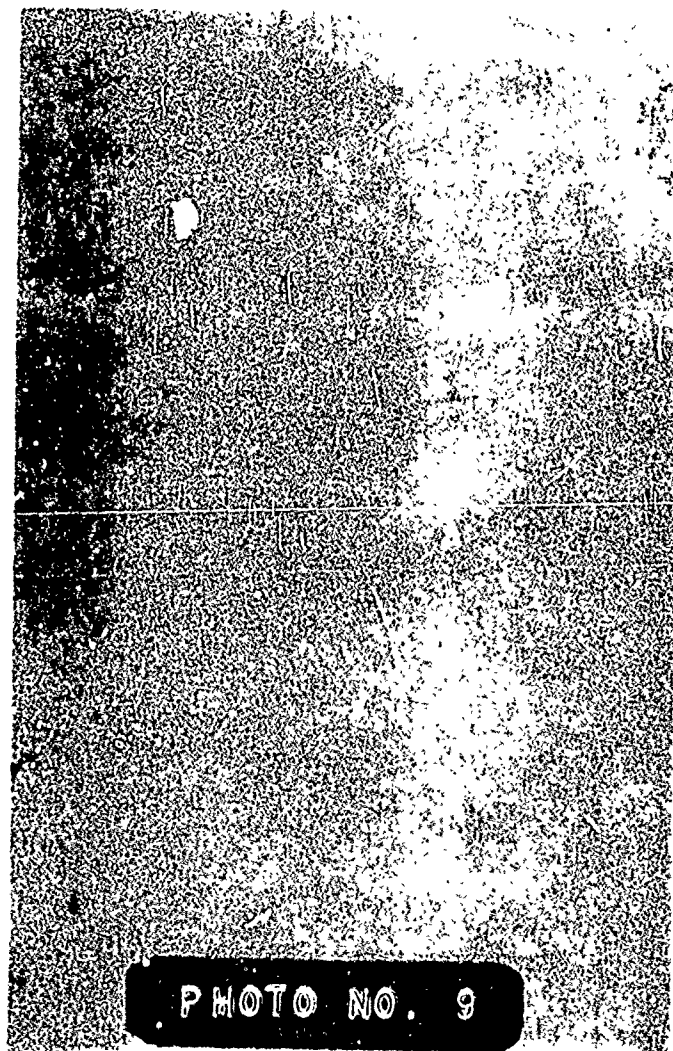
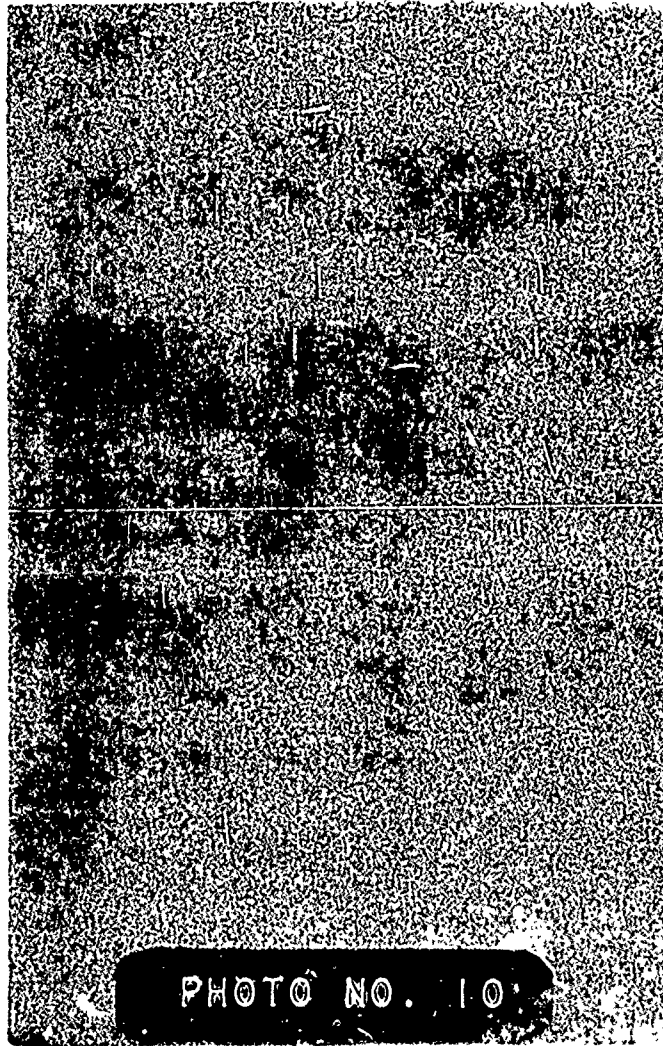


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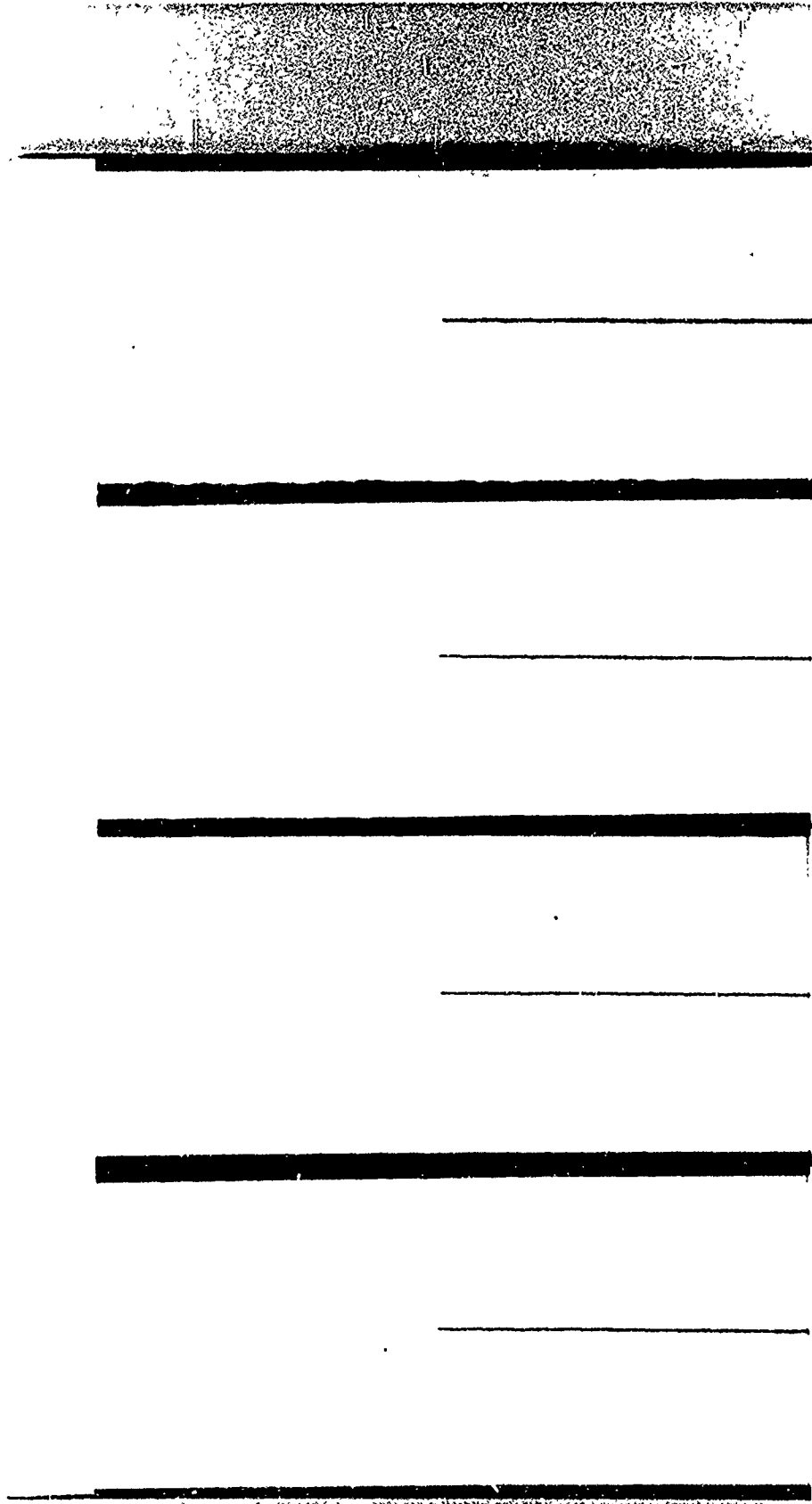
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PHOTO 11

6 MONTHS APG EXPOSURE



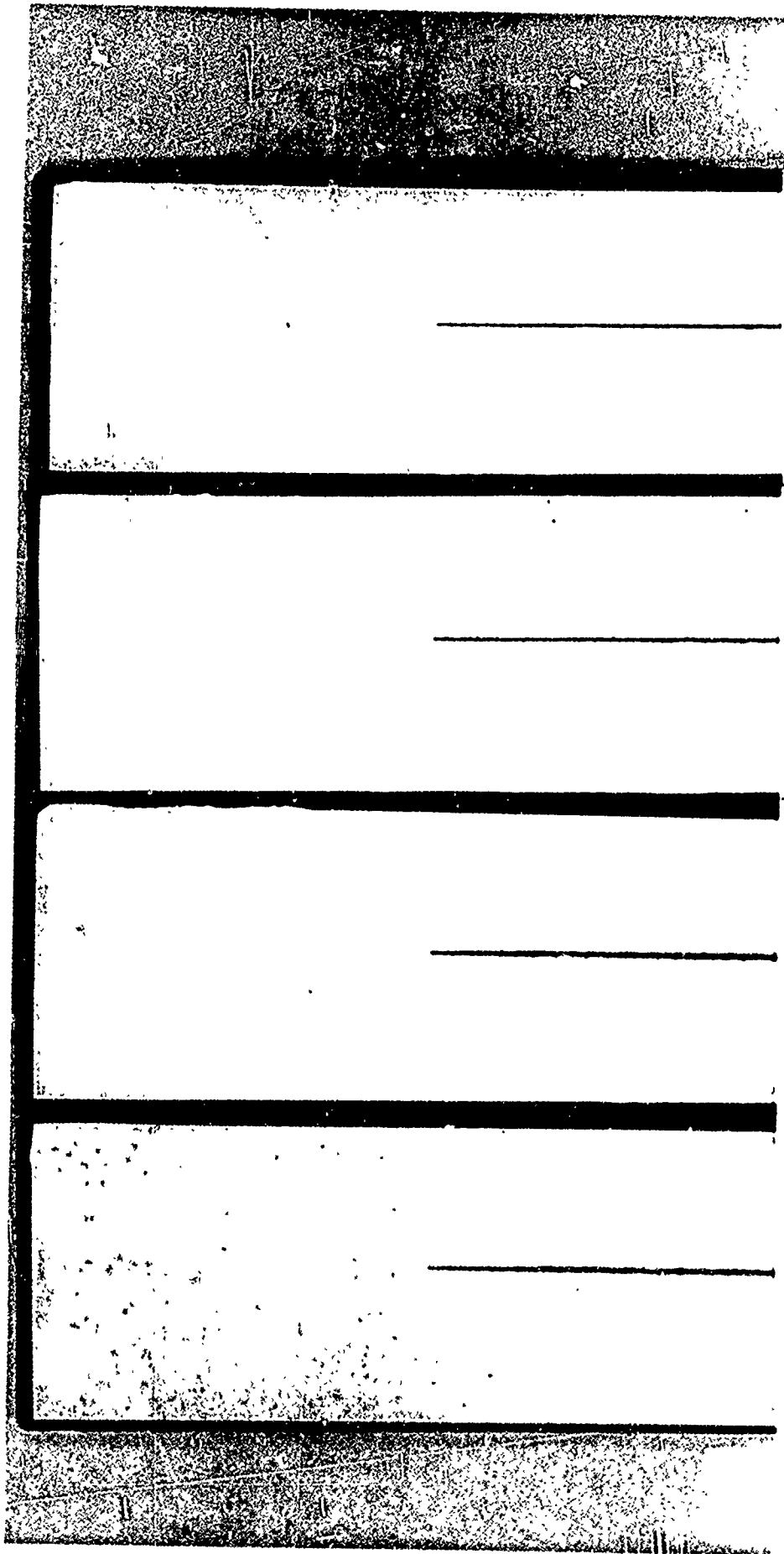
FORMULA B1
WHITE CONTROL

FORMULA B2
15% EXPERIMENTAL
ZINC MOLYBDATE

FORMULA B4
15% BARIUM
METABORATE

FORMULA B6
15% TRIBASIC LEAD
PHOSPHOSILICATE

PHOTO 12
6 MONTHS PANAMA EXPOSURE
OPEN FIELD



FORMULA B1
WHITE CONTROL

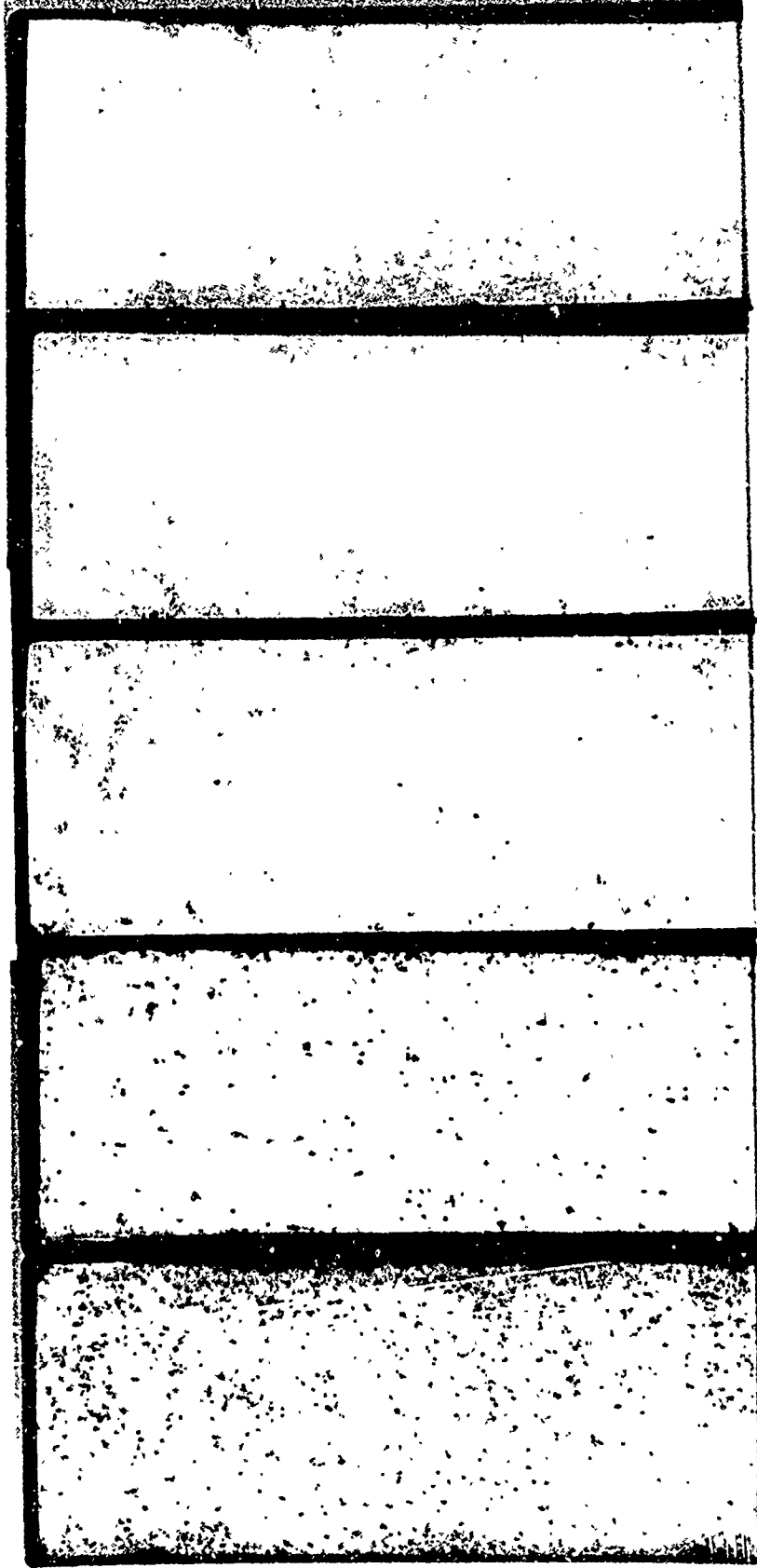
FORMULA B2
15% EXPERIMENTAL
ZINC MOLYBDATE

FORMULA B4
15% BARIUM
METABORATE

FORMULA B6
15% TRIBASIC LEAD
PHOSPHOSILICATE

PHOTO 13

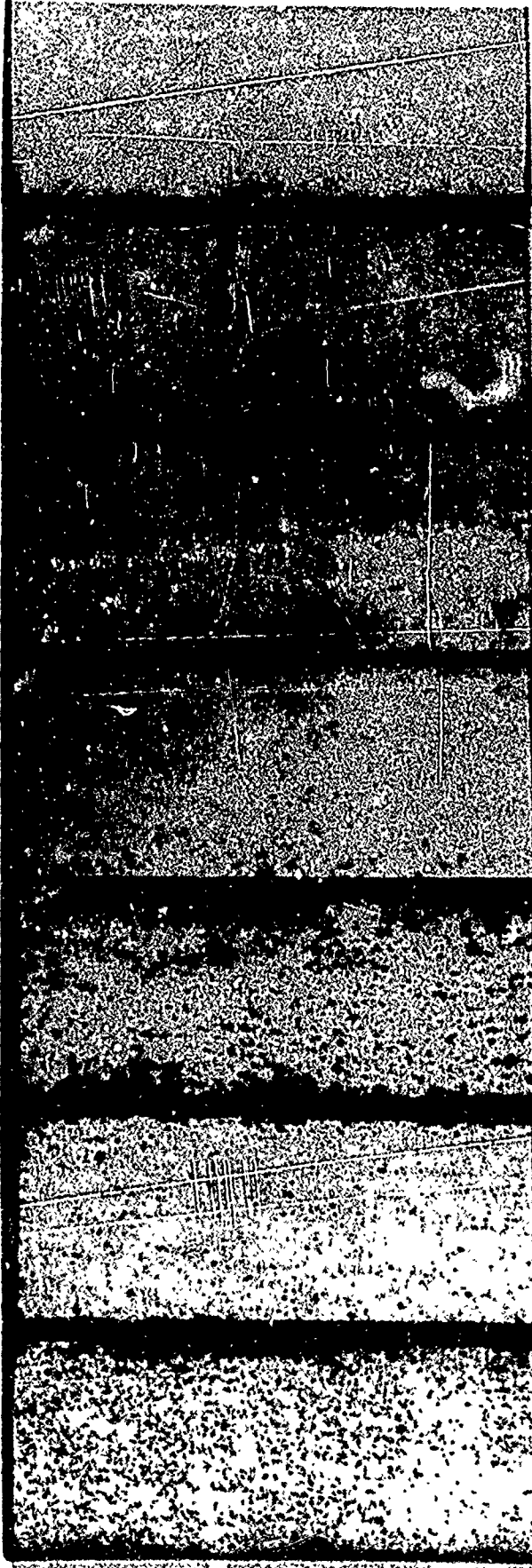
6 MONTHS PANAMA EXPOSURE
BREAKWATER



FORMULA B1	FORMULA B2	FORMULA B4	FORMULA B6	FORMULA B8
WHITE CONTROL	15% EXPERIMENTAL ZINC MOLYBDATE	15% BARIUM METABORATE	15% TRIPHASIC LEAD PHOSPHOSILICATE	10% DIBASIC LEAD PHOSPHITE

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PHOTO 14
6 MONTHS PANAMA EXPOSURE
BREAKWATER



FORMULA B1	FORMULA B2	FORMULA B3	FORMULA B4	FORMULA B5	FORMULA B6	FORMULA B:
WHITE CONTROL	EXPERIMENTAL ZINC MOLYBDATE	EXPERIMENTAL ZINC MOLYBDATE	BARIUM METABORATE	BARIUM METABORATE	TRIBASIC LEAD PHOSPHOSILICATE	TRIBASIC LEAD PHOSPHOSILICATE
	15%	30%	15%	30%	15%	30%