Navy Department - Office of Research and Inventions

NAVAL RESEARCH LABORATORY
Washington, D.C.

* * *

CHEMISTRY DIVISION - PROTECTIVE COATINGS SECTION

28 August 1945

FR-2628

AN EXAMINATION OF TOXIC AGENTS FOR FUNGICIDAL COATING-MATERIALS PART IV

By Wilson M. Whaley, W. L. Clark,
W. E. Weaver, and J. M. Leonard

- Report P-2628 -

* * *

DISTRIBUTION STATEMENT A APPLIES
Further distribution authorized by
UNLIMITED only.

Approved by:

Allen L. Alexander, Head, Protective Coatings Section

Dr. P. Borgstrom
Superintendent, Chemistry Division

Rear Adm. A. H. Van Keuren, USN(Ret.)
Director, Naval Research Laboratory

Preliminary Pages	a-d
Numbered Pages	5
Plates	23
Distribution	e

NRL Problem No. S14R-C

TABLE OF CONTENTS

Page No.

ABSTRACT

INTRODUCTION

A. Authorization 1
B. References 1
C. Background 1

EXPERIMENTAL

A. Method 1
B. Observations 2

DISCUSSION 2

SUMMARY & CONCLUSIONS 2

RECOMMENDATIONS 3

ACKNOWLEDGMENT 3

TABLE I . . . . . 4&5

APPENDIX A

Abstract

Fifteen chemical compounds have been examined as components of fungicidal lacquers and varnishes. Acetoxymercurimesitylene and acetoxymercuri-o-phenylphenol gave good results and are now being further investigated for corrosiveness and durability. The need for coordinated work in this field has been emphasized.

INTRODUCTION

A. Authorization

1. The study of tropical deterioration of electronic equipment is authorized under Bureau of Ships Project Order No. 212/45.

B. References

2. Previous reports of this Laboratory pertinent to this report are:

(a) NRL Report No. P-2518 dated 15 May 1945
(b) NRL Report No. P-2611 dated 1 August 1945
(c) NRL Report No. P-2626 dated 23 August 1945

C. Background

3. It is not intended that the reports of this series should enlarge upon existent literature which describes the many difficulties encountered in tropical regions of the world. The present purpose is to emphasize that current remedial measures are not adequate. Toxic agents usually used in lacquers and varnishes have been shown to be ineffective in acceptable concentrations (reference (a)) and to lack persistence of toxicity (reference (b)). A series of new fungicides was examined (reference (c)) with very little success.

4. Up to this time a few fungicides have been fairly effective as toxic agents for coating-materials, although there are existent drawbacks to the use of each one. Phenylmercuric salicylate is effective at 5-10% but is not very persistent and is considered dangerous to humans in such concentration, though the latter point will bear investigation. Pentachlorophenol, fairly good at 10%, is not durable and cannot be used at elevated concentrations because of corrosive tendencies. Pyridylmercuric chloride, not completely effective at 10%, is durable, but is corrosive, and salicylanilide has not met the claims made for it. o-Hydroxybiphenyl, which has been effective at 10% (reference (c)), has not been examined for corrosiveness or durability.

5. This Laboratory consequently holds the opinion that a safe and entirely reliable coating-material for electronic equipment is yet to be found, and the work contained in this report is part of a continuing project on the synthesis and evaluation of fungicides suitable for the task.

EXPERIMENTAL

A. Method

6. The procedure used in reference (a) will be described only briefly. Fifteen fungicides were milled into varnish and lacquer in three concentrations, and then the coatings were applied to 3-centimeter squares of paper by a single dip. After drying in the laboratory for one week, the specimens were placed on a modified Czapek's agar containing only 0.1% glucose. In contact with each sample was a specimen of paper coated only

with the non-toxic vehicle. The Petri dishes were then inoculated with a mixed spore-suspension of four species of mold in relative concentrations calculated to allow optimum growth of all four. The dishes were then incubated, and inspected weekly for the presence or absence of growth upon each "toxic" specimen.

B. Observations

7. The data thus obtained are presented in Table I, supplemented by photographic plates 1 to 23. The photographs were taken after the last observations recorded in the table except that all the observations allowed in the eighth week column were photographed at eight weeks. Although weekly readings were taken, only the first, second, fourth, and eighth readings are tabulated in the interest of simplification and without distortion of the overall picture.

DISCUSSION

8. The findings reported are somewhat more encouraging than those of previous reports. The fungicidal action of these compounds still depends upon a high concentration in the vehicle, and since the best are mercurials, this constitutes a drawback.

9. Of the six mercurials examined, two were effective at 5% concentration for no less than three weeks, and at 10% for at least twice as long. These were acetoxymercurimesitylene and acetoxymercuri-o-phenylphenol. The mercurated naphthylamines exhibited slight fungicidity, but not sufficient to deserve further consideration.

10. None of the other nine compounds showed a high level of toxicity, although p-aminophenyl thiocyanate was slightly active. Since ammonium thiocyanate was not effective, it is apparent that the thiocyanate ion is not the reason for the activity of p-aminophenyl thiocyanate. Perhaps the effect is due more to the amino group. The amides examined were ineffective, which is not amazing. The sulfur compounds were useless. Age-old use of sulfur and its derivatives as agricultural fungicides has given sulfur a reputation which does not seem to be commensurate with its relative level of toxicity.

11. The apparent effectiveness of acetoxymercurimesitylene and acetoxymercuri-o-phenylphenol is heartening, and further evaluation of their usefulness is under way. A word of caution is recommended, however, for data on corrosiveness and durability are not yet available. Even if this data were available and favorable, the question of health-hazard must be explored before acceptance is suggested.

SUMMARY AND CONCLUSIONS

12. Fifteen different organic and inorganic compounds were milled into lacquer and varnish vehicles at three concentrations. The resultant coating-materials were examined for fungus-resistance by a method previously reported. Two mercurials, acetoxymercurimesitylene and acetoxy-

mercuri-o-phenylphenol, were found to be relatively good and worthy of further investigation.

13. On the basis of data so far obtained the following conclusions are drawn:

(a) The continuing evaluation of toxic agents for coating-materials has performed an important service by pointing out the inefficacy of current practices for fungus-proofing electronic equipment.

(b) The work done has also pointed out some interesting new possibilities as toxic agents for coating-materials, though it must be emphasized that they are not yet fully investigated.

RECOMMENDATIONS

14. The following recommendations are made:

(a) That efforts to uncover compounds which are potent, durable, specific, and non-deleterious continue.

(b) That adequate, modern facilities for the close and controlled simulation of tropical conditions be established at this Laboratory.

ACKNOWLEDGMENT

15. The cooperation of Lt.(jg) Dorothy Molnar, USNR, of the Protective Coatings Section is gratefully acknowledged, for the preparation of the photographic plates 1 to 23, and for analytical work on compounds prepared here.

TABLE I

FUNGUS RESISTANCE OF VARNISHES AND LACQUERS

Fungicide	% Conc.	Fungus Growth(1) Varnish 1 wk.	Varnish 2 wks.	Varnish 4 wks.	Varnish 8 wks.	Lacquer 1 wk.	Lacquer 2 wks.	Lacquer 4 wks.	Lacquer 8 wks.
Acetoxymercuri-mesitylene (517)	1	2	3	3		0	1	2	2
	5	0	0	0	3(a)	0	0	0	2(b)
	10	0	0	0	3	0	0	0	3(b)
Bis(acetoxymercuri)-mesitylene (518)	1	not compatible				3	3		
	5					0	0	3	
	10					not compatible			
Acetoxymercuri-1-naphthylamine (519)	1	2	2	2		3	3		
	5	0	0	2		3	3		
	10	0	0	0		1	3		
Acetoxymercuri-2-naphthylamine (520)	1	3	3			3	3		
	5	1	3	3		1	1	2	2
	10	0	0	3		2	3		
Hydroxymercuri-salicylic acid anhydride (521)	1	3	3			3	3		
	5	3	3			3	3		
	10	2	2			3	3		
Acetoxymercuri-o-phenylphenol (522)	1	3	3			3	3		
	5	0	0	1	3(c)	0	0	1	3(b)
	10	0	0	0	1(a)	0	0	0	1(c)
Furfuramide (1600)	1	3	3			3	3		
	5	3	3			3	3		
	10	3	3			3	3		
p-Toluene-sulfonylamide (1601)	1	3	3			3	3		
	5	3	3			3	3		
	10	3	3			3	3		
o-Toluene-sulfonylamide (1602)	1	3	3			3	3		
	5	3	3			3	3		
	10	3	3			3	3		
Ammonium thiocyanate (1751)	1	3	3			3	3		
	5	3	3			3	3		
	10	3	3			3	3		
Benzyl thiocyanate (1752)	1	3	3			3	3		
	5	3	3			3	3		
	10	3	3			3	3		

Table I (continued)

Fungicide	% Conc.	Fungus Growth(1) Varnish 1 wk.	Varnish 2 wks.	Varnish 4 wks.	Varnish 8 wks.	Lacquer 1 wk.	Lacquer 2 wks.	Lacquer 4 wks.	Lacquer 8 wks.
p-Aminophenyl thiocyanate (1753)	1	2	3			3	3		
	5	2	3			3	3		
	10	0	0	0	3	1	1	2	3(b)
2-Mercapto-thiazoline (1852)	1	3	3			3	3		
	5	3	3			3	3		
	10	3	3			3	3		
2,2'-Dibenzothiazolyl-disulfide (1853)	1	3	3			3	3		
	5	3	3			3	3		
	10	3	3			3	3		
2-Phenylbenzo-thiazole (1854)	1	3	3			3	3		
	5	3	3			3	3		
	10	3	3			3	3		

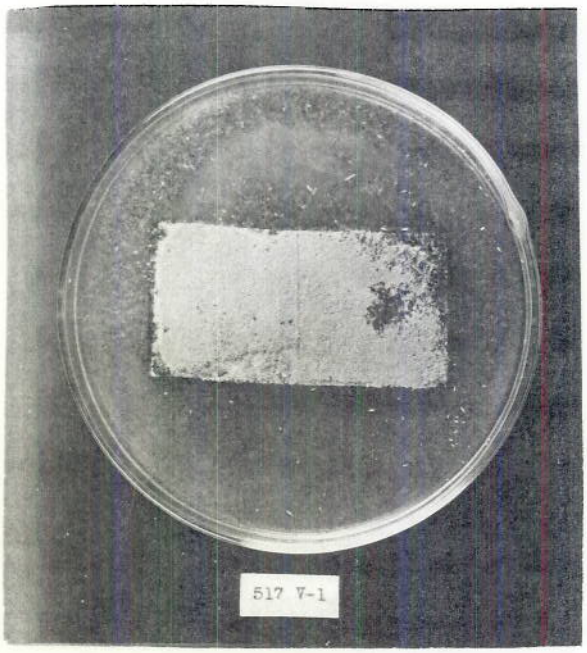
(1) The samples were run in triplicate, the numbers in the table indicating the number of samples showing growth.

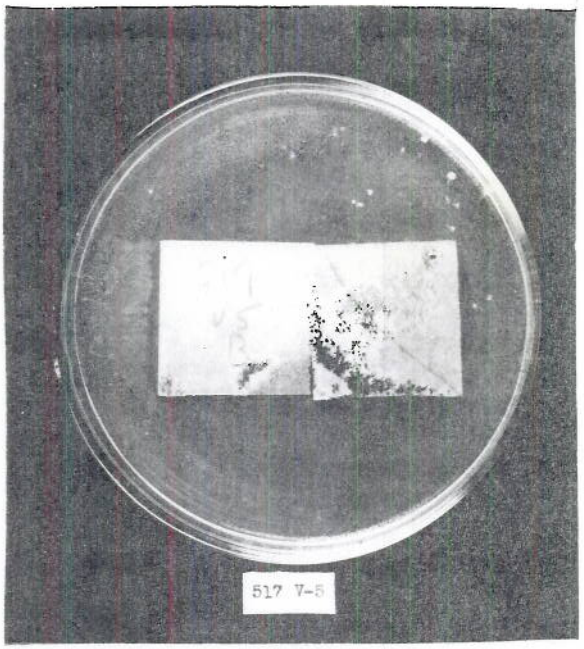
(a) At six weeks.
(b) At seven weeks.
(c) At five weeks.

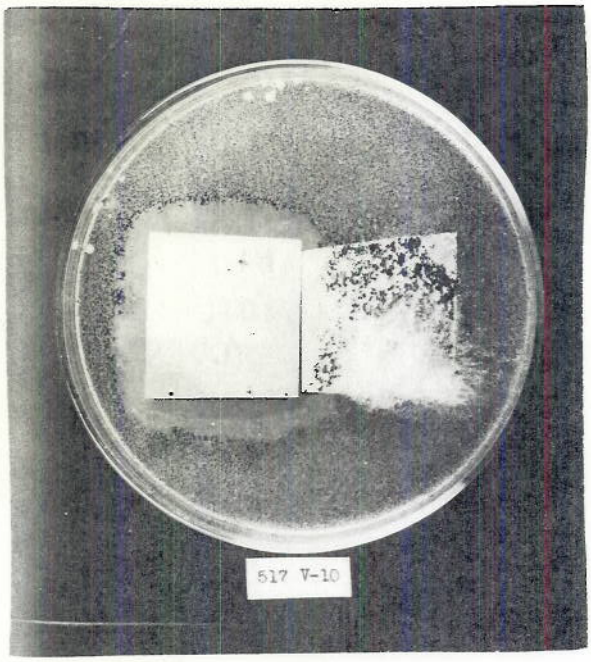
APPENDIX A

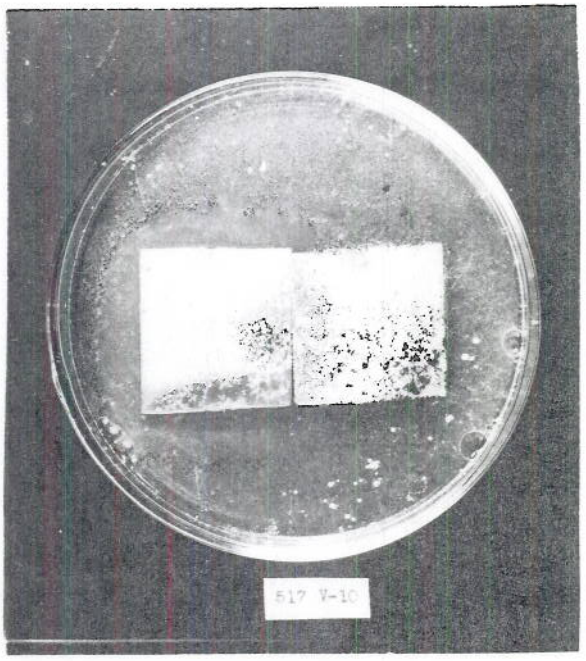
IDENTIFICATION OF TOXIC AGENTS

Laboratory Number	Chemical Name	Commercial Designation	Source
517	Acetoxymercurimesitylene		NRL synthesis
518	Bis(acetoxymercuri)-mesitylene		NRL synthesis
519	Acetoxymercuri-1-naphthylamine		NRL synthesis
520	Acetoxymercuri-2-naphthylamine		NRL synthesis
521	Hydroxymercurisalicylic acid anhydride		NRL synthesis
522	Acetoxymercuri-o-phenylphenol		NRL synthesis
1600	Furfuramide	#P1942	Eastman Kodak Co. Rochester, N.Y.
1601	p-Toluenesulfonylamide	#423	Eastman Kodak Co.
1602	o-Toluenesulfonylamide	#594	Eastman Kodak Co.
1751	Ammonium thiocyanate	#1128	City Chem. Corp. New York City
1752	Benzyl thiocyanate		NRL synthesis
1753	p-Aminophenyl thiocyanate		NRL synthesis
1852	2-Mercaptothiazoline	#P5444	Eastman Kodak Co.
1853	2,2'-Dibenzothiazolyldisulfide	#P5432	Eastman Kodak Co.
1854	2-Phenylbenzothiazole	#2265	Eastman Kodak Co.



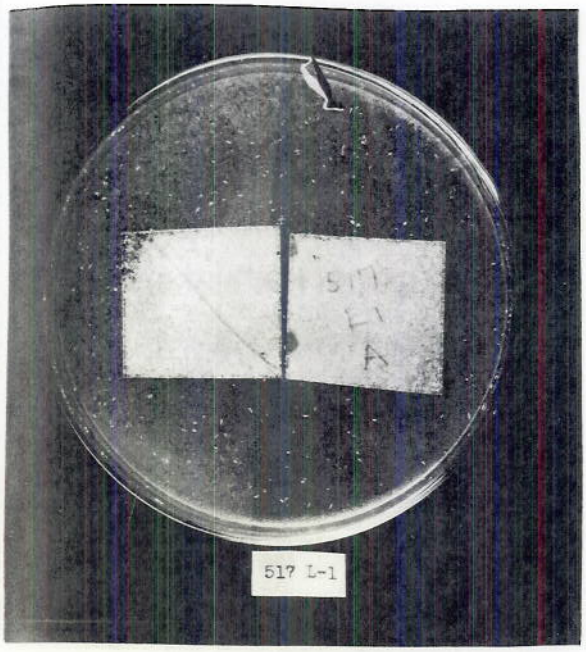


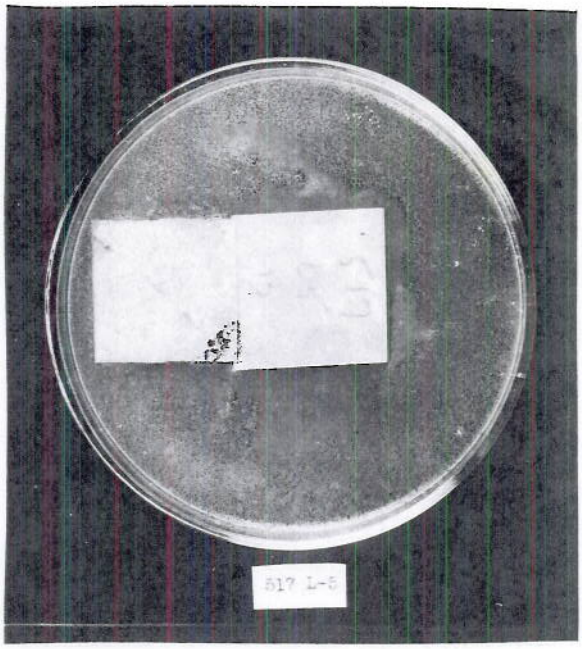


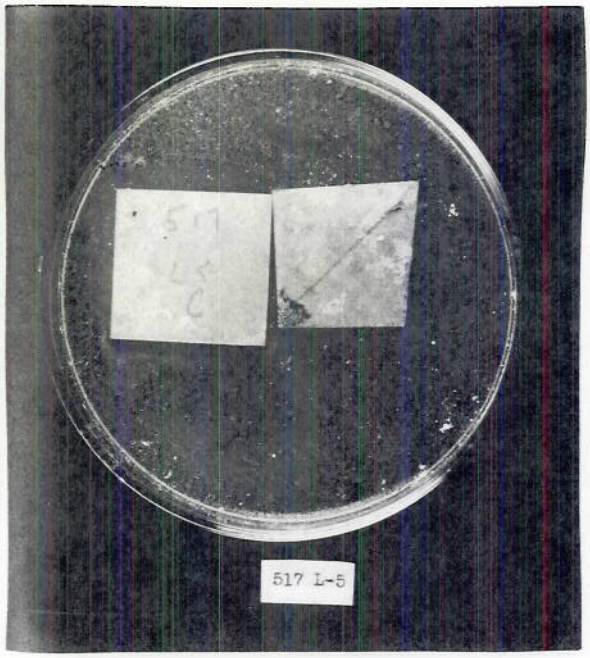


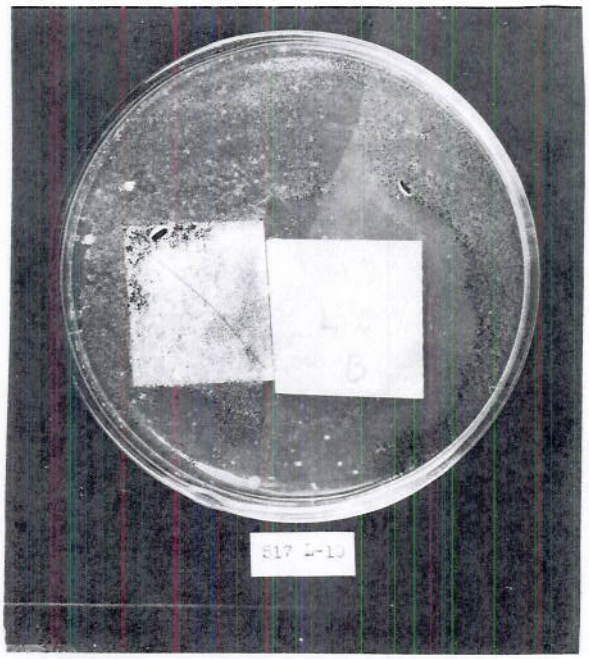
FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE I



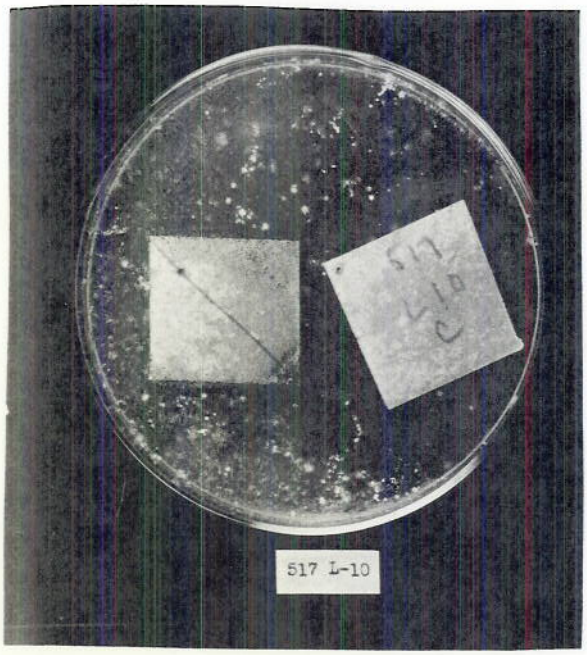


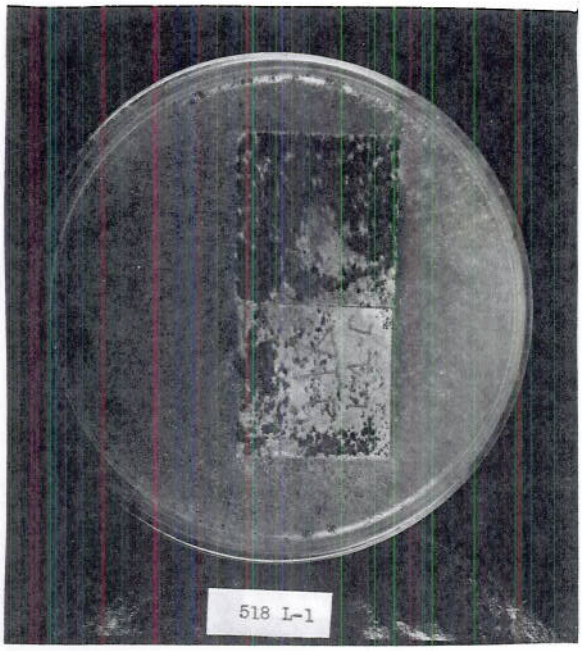


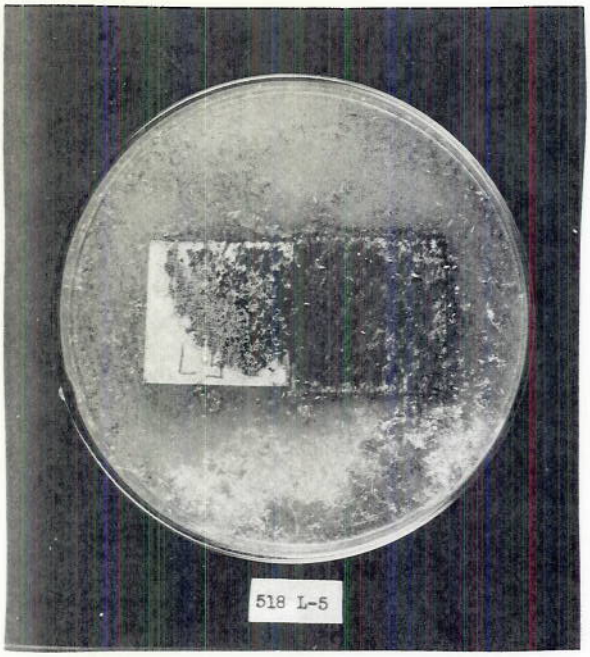


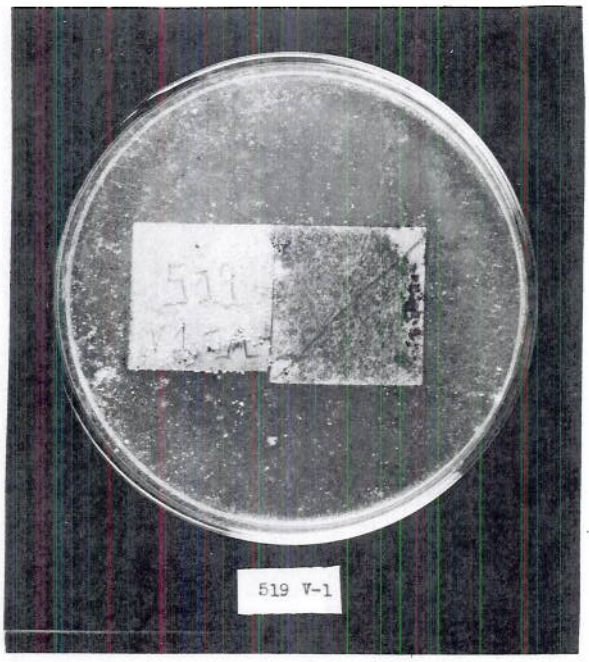
FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 2



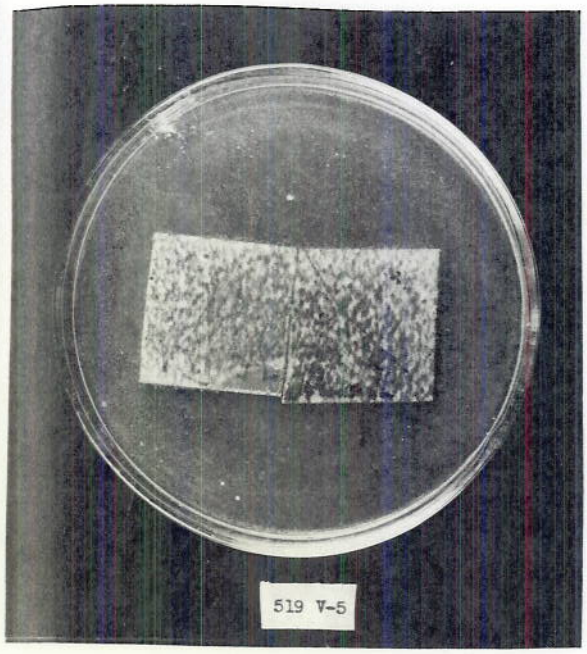


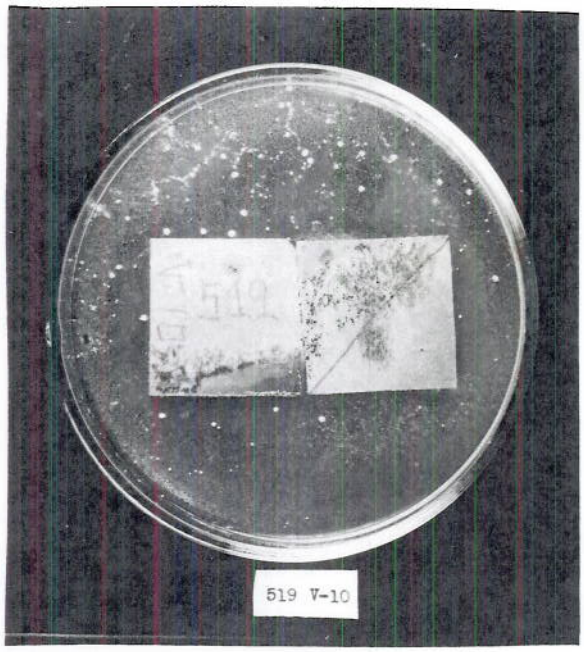


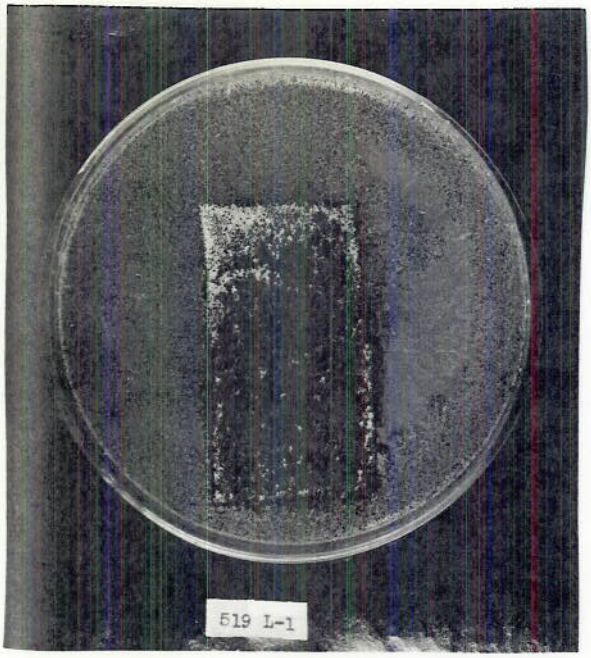


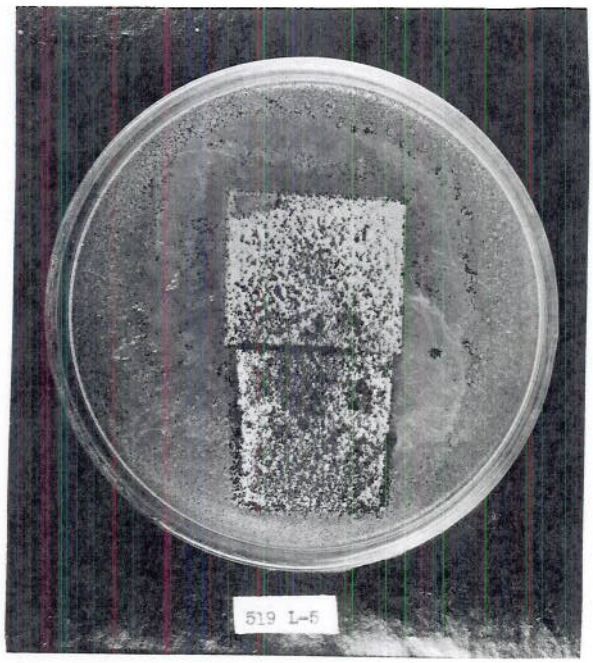
FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 3



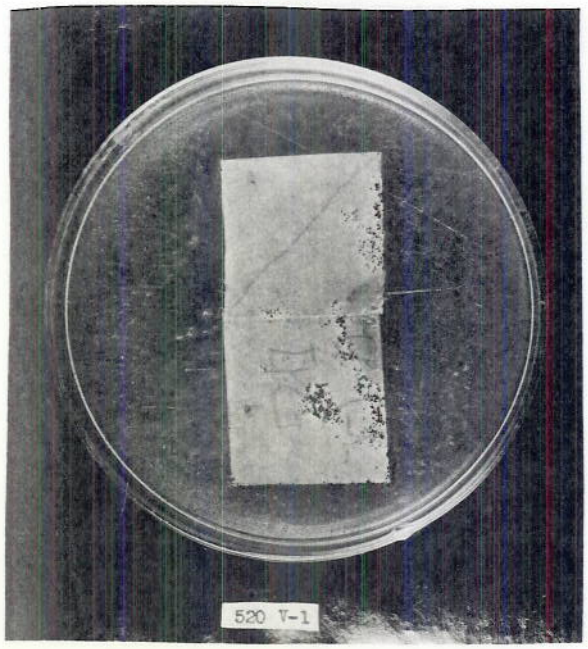


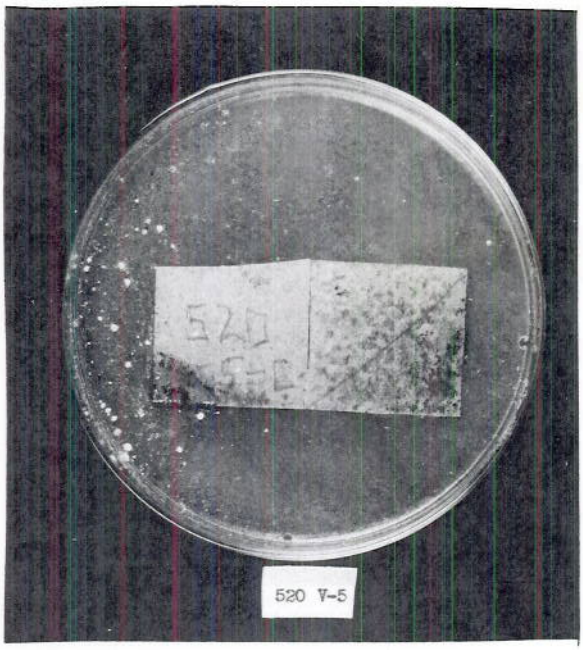


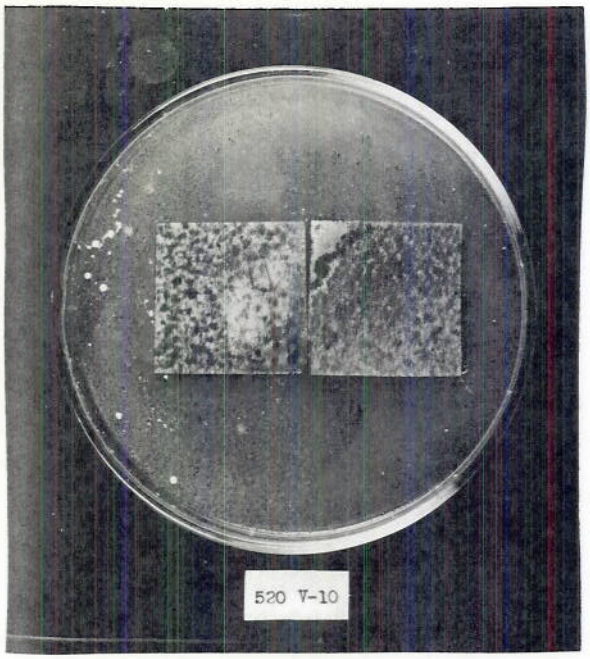


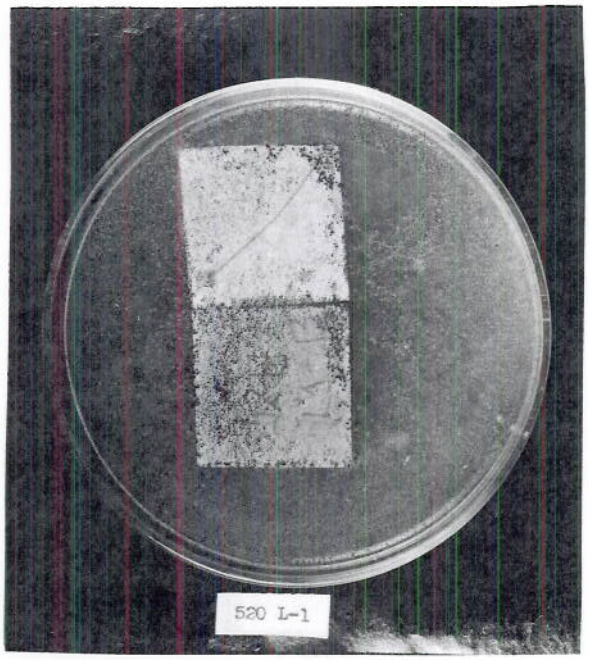
FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 4



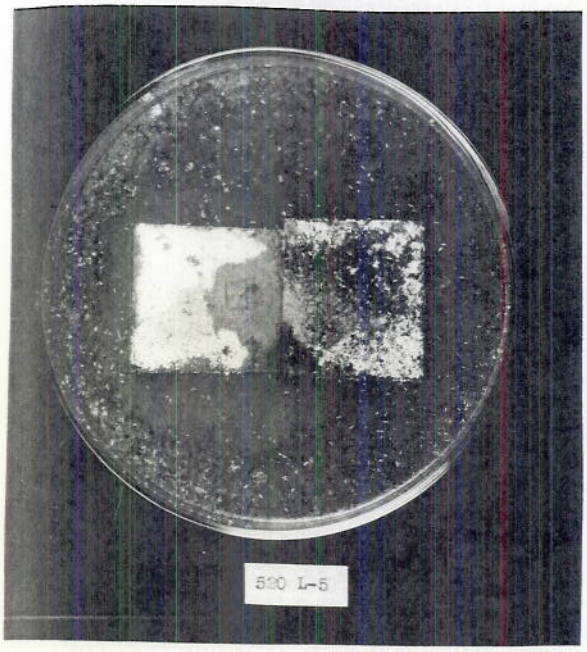


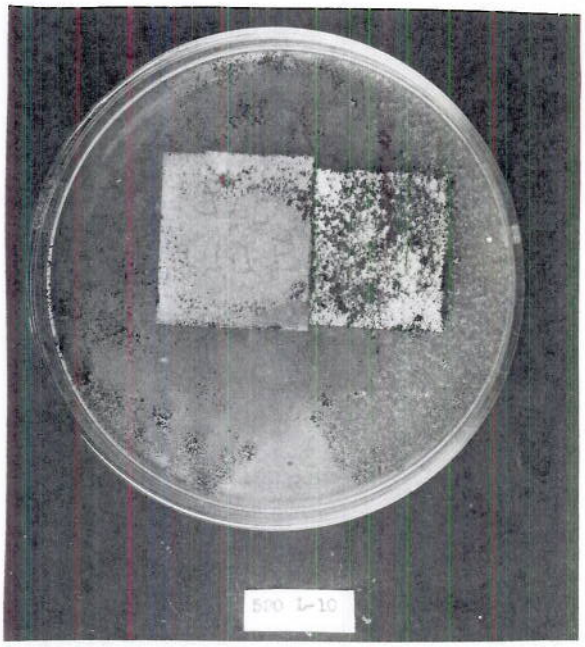


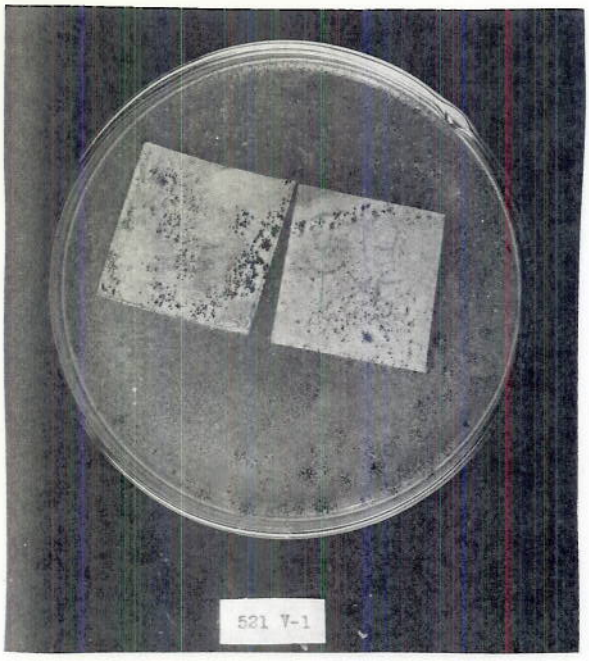


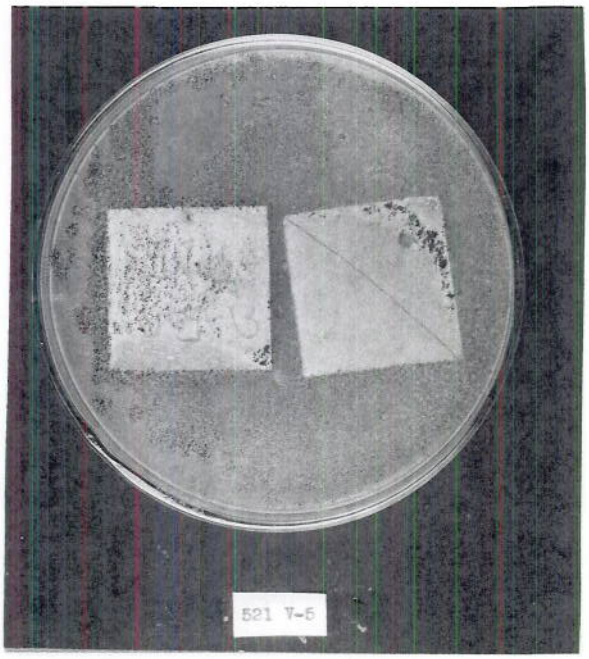
FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 5



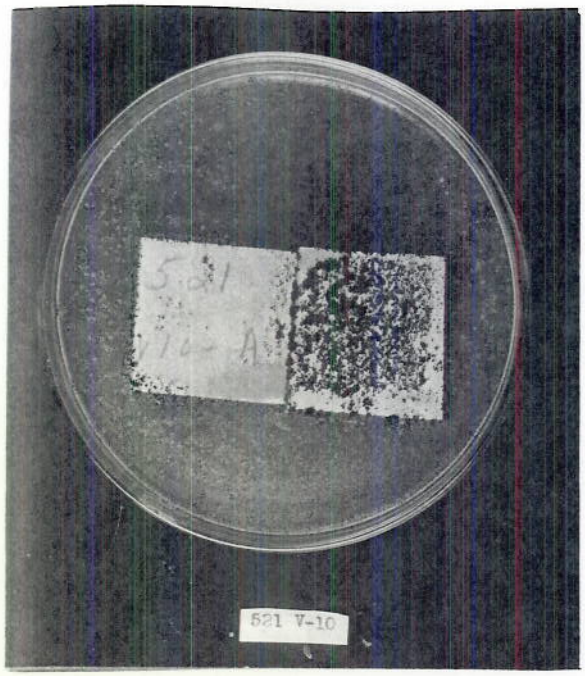


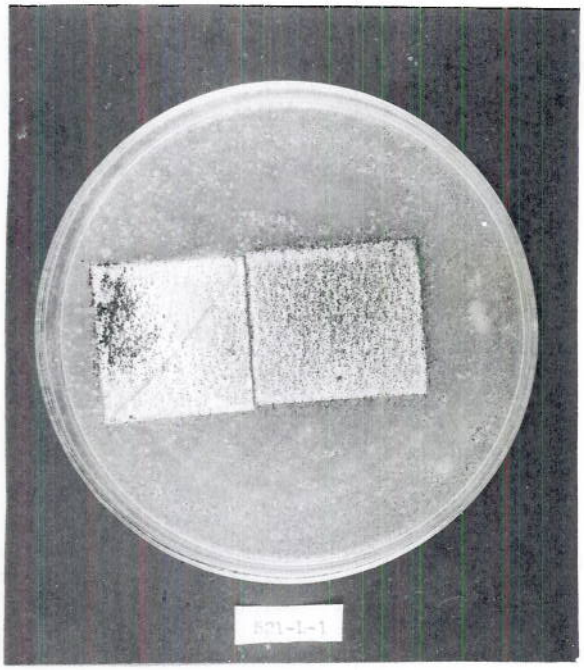


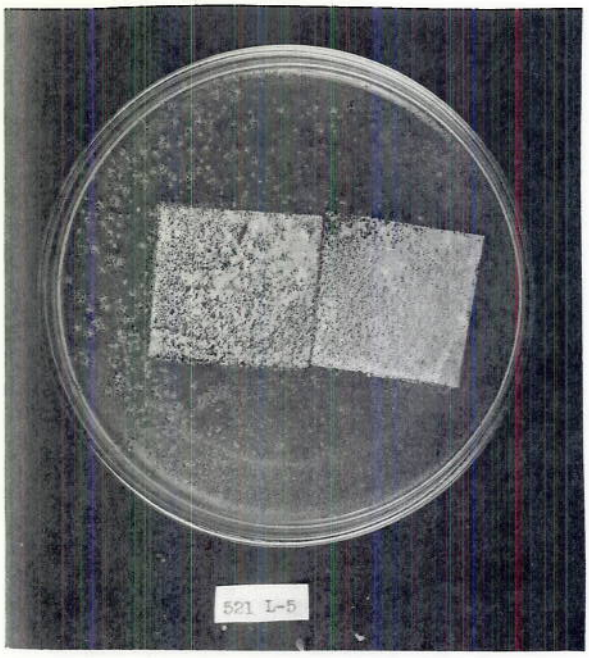


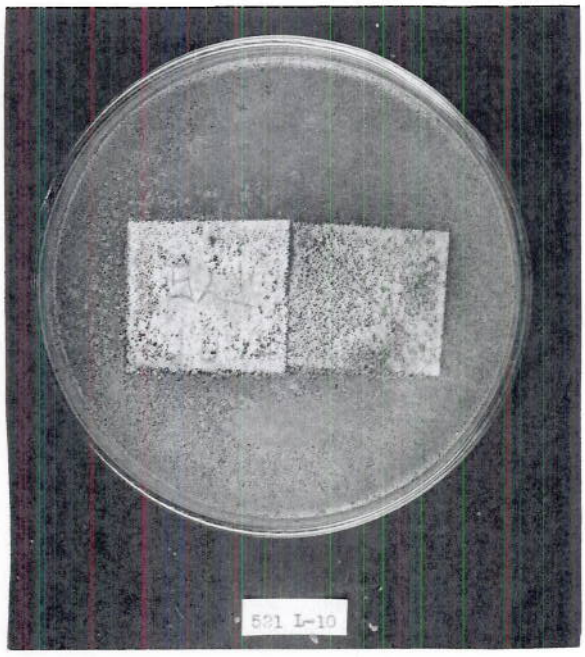
FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 6



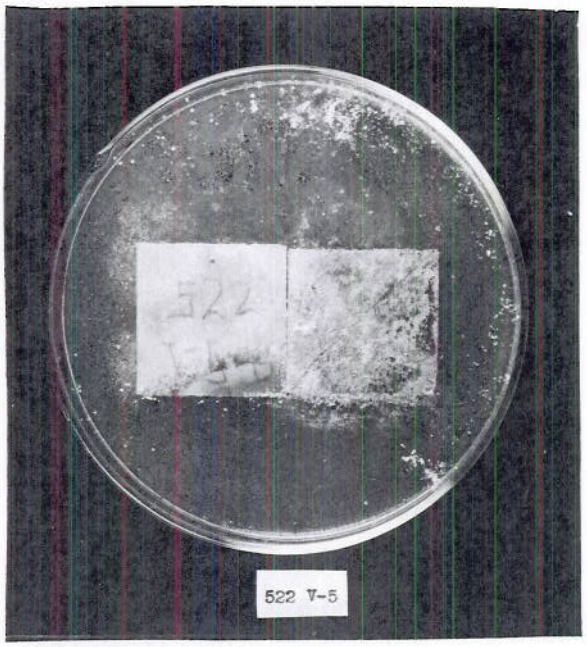


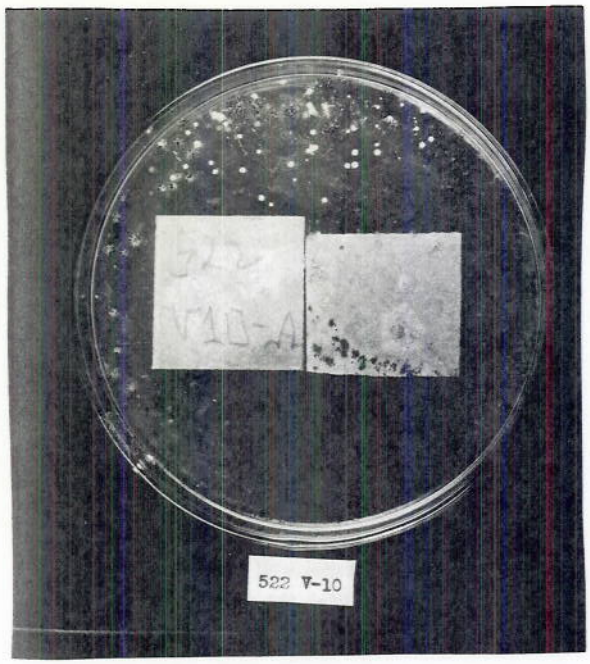


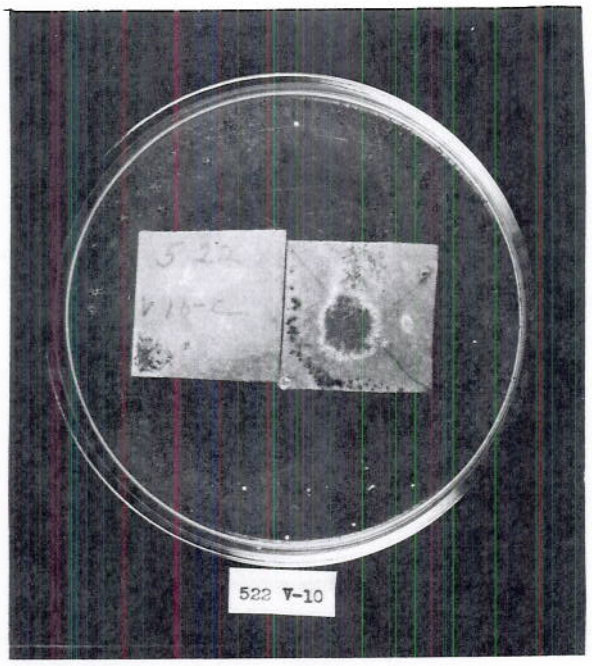


FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 7

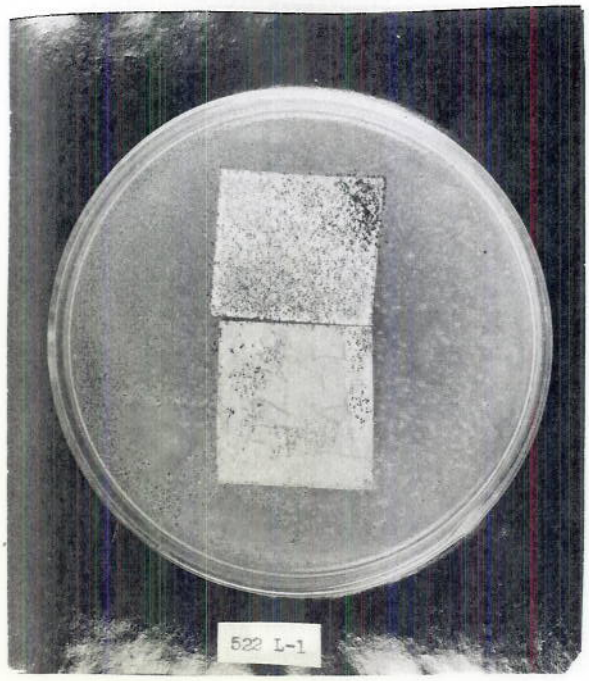


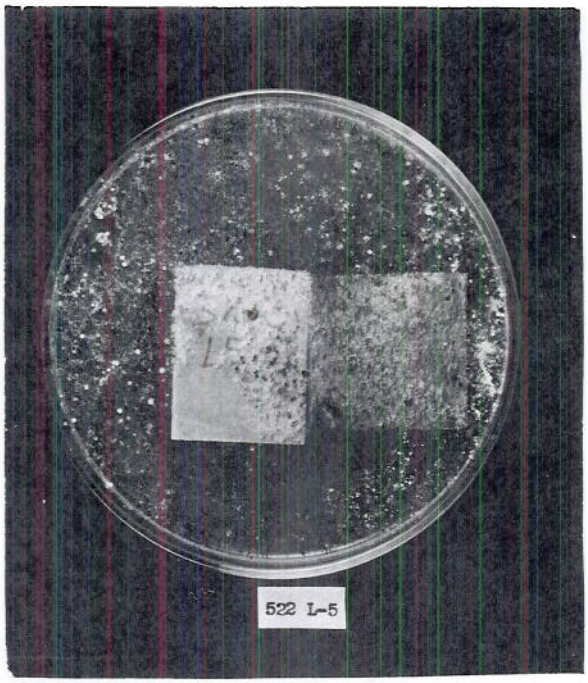


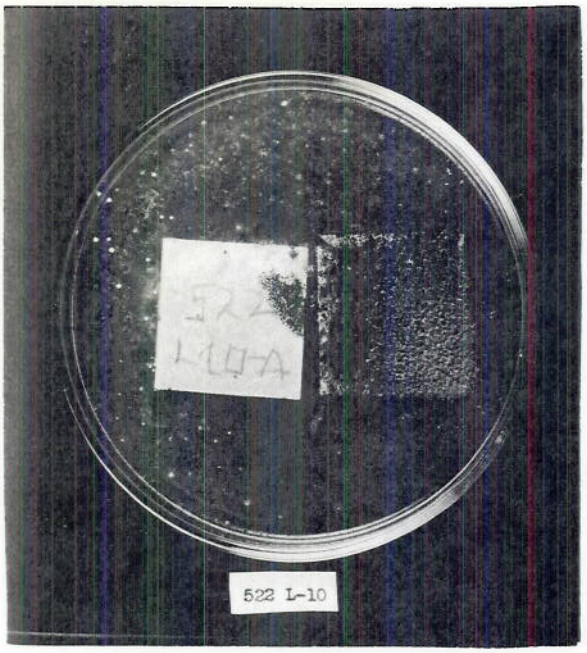


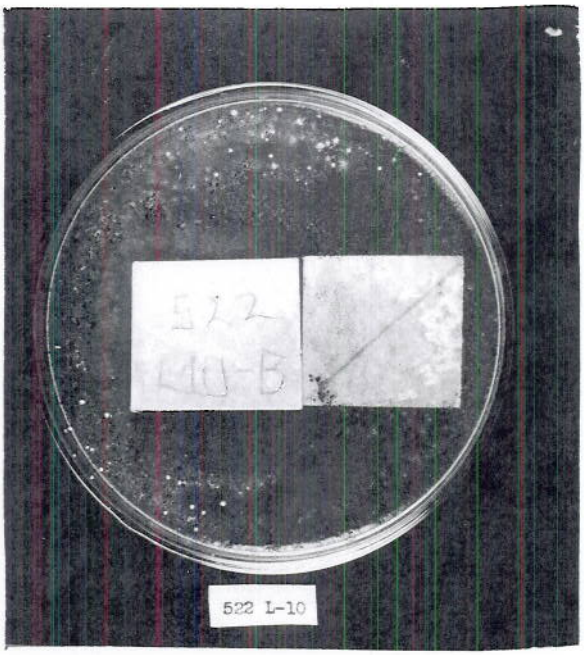
FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 8



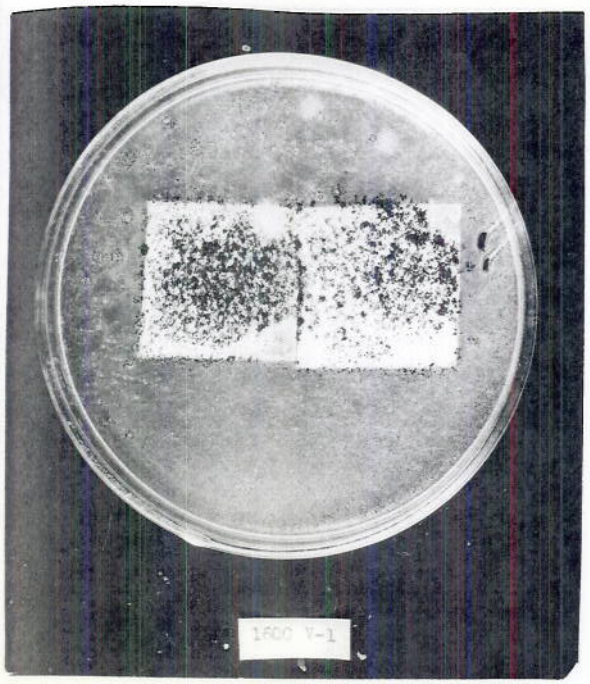


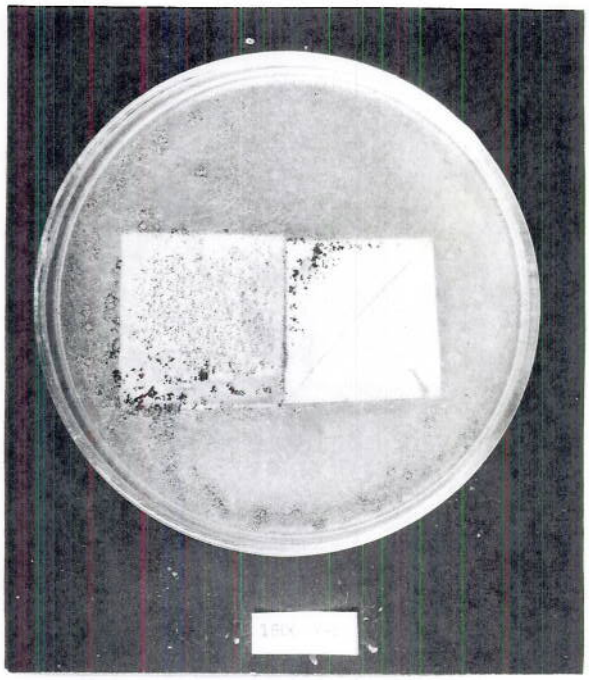


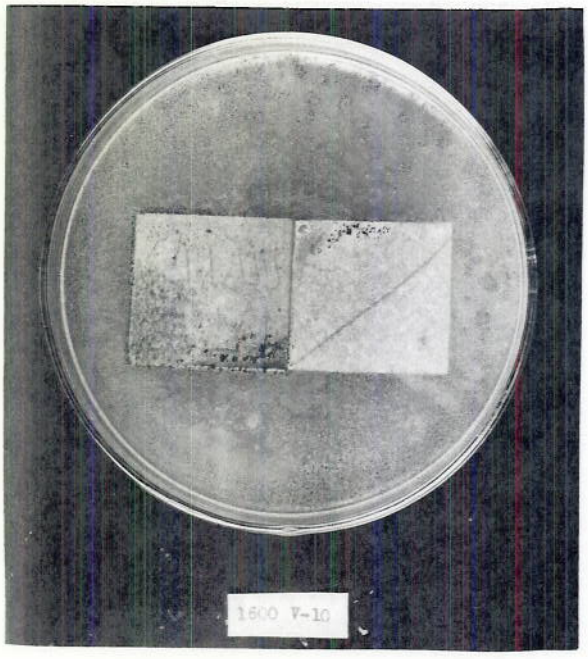


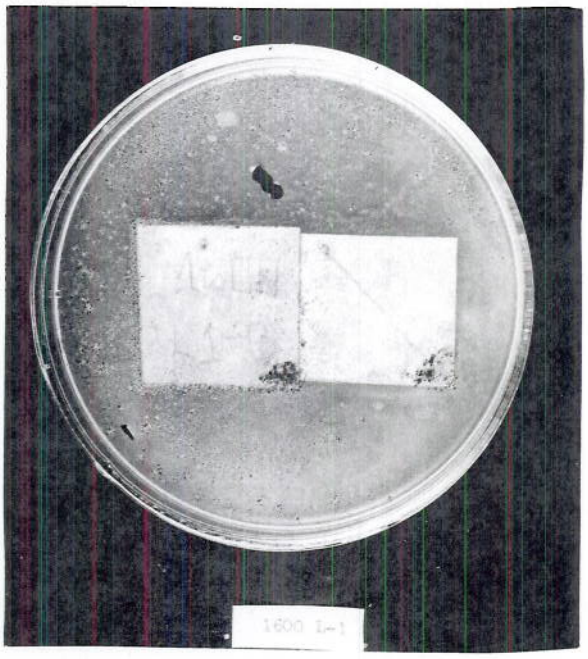
FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 9



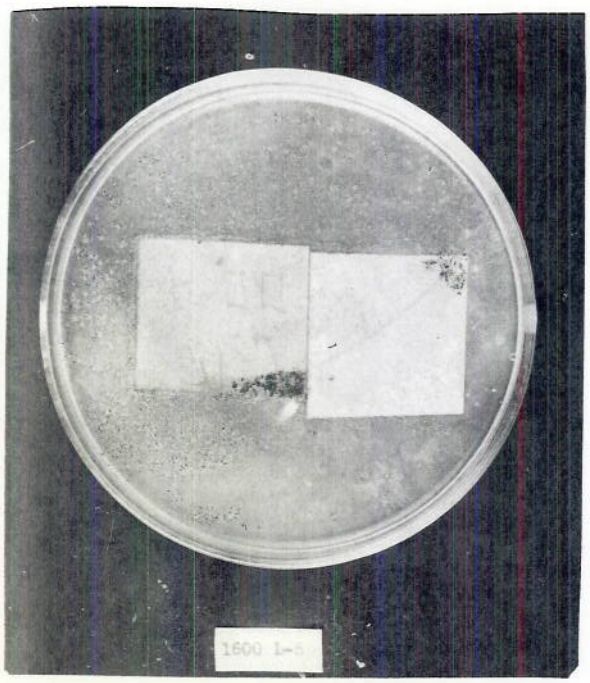


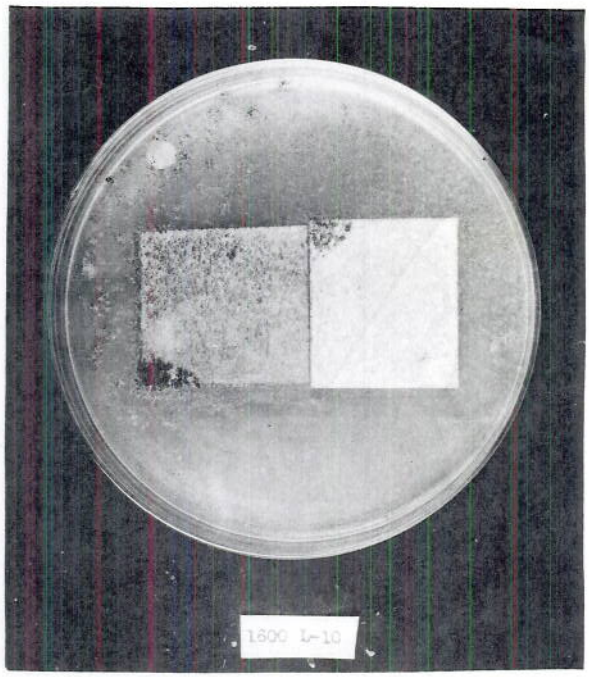


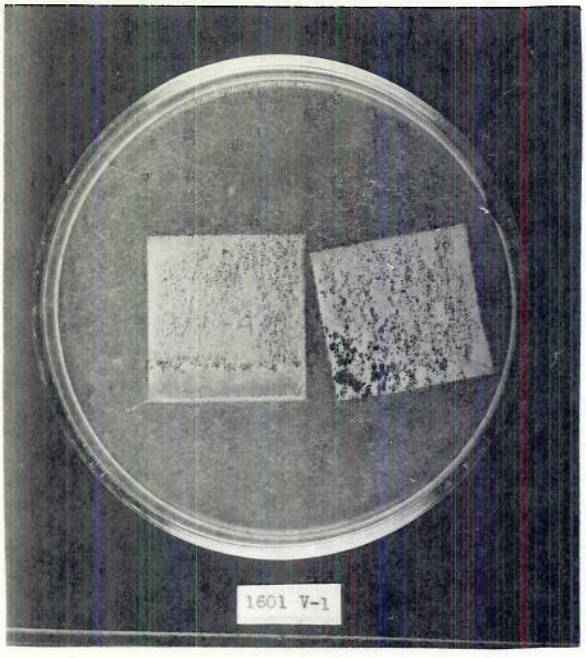


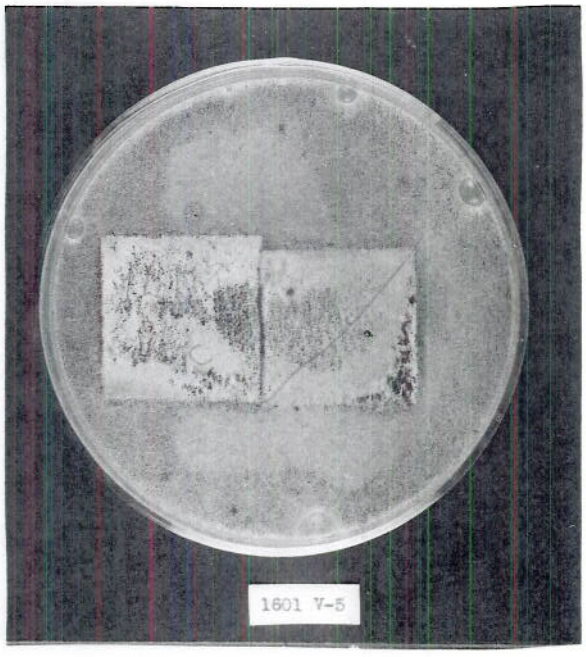
FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 10



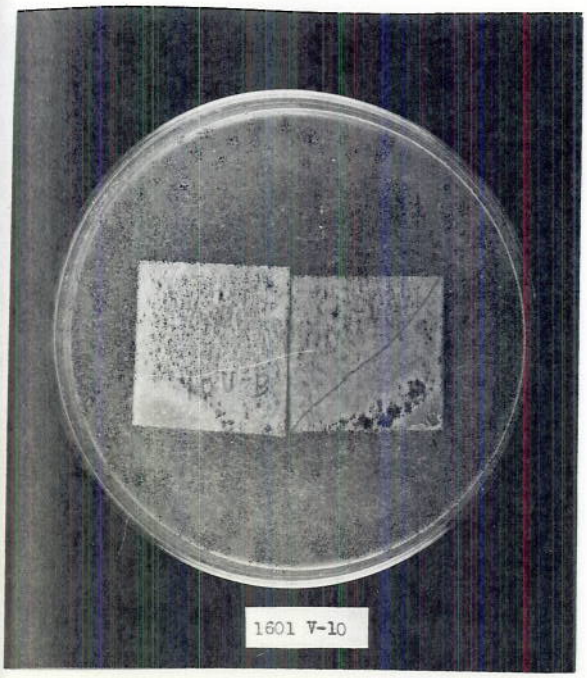


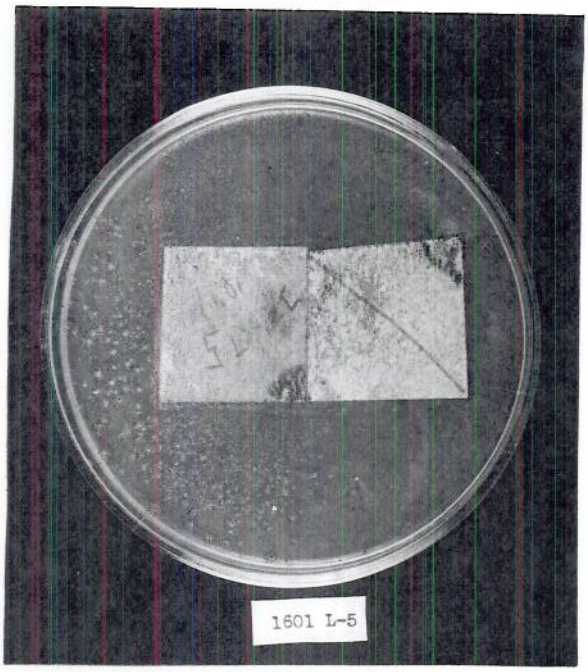


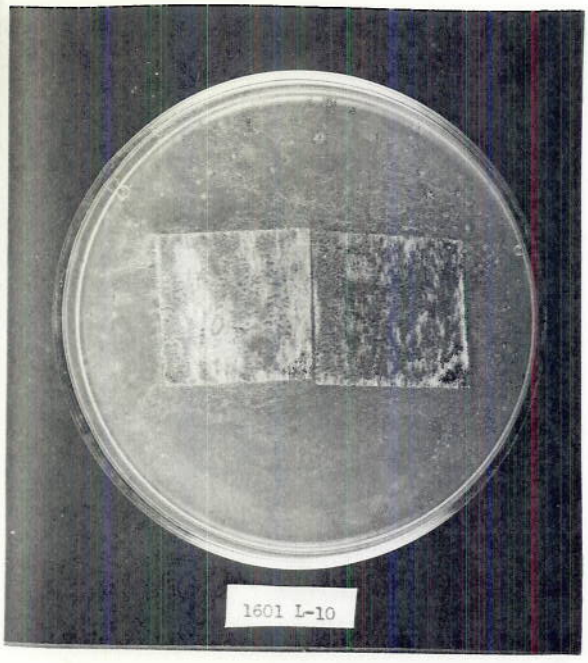


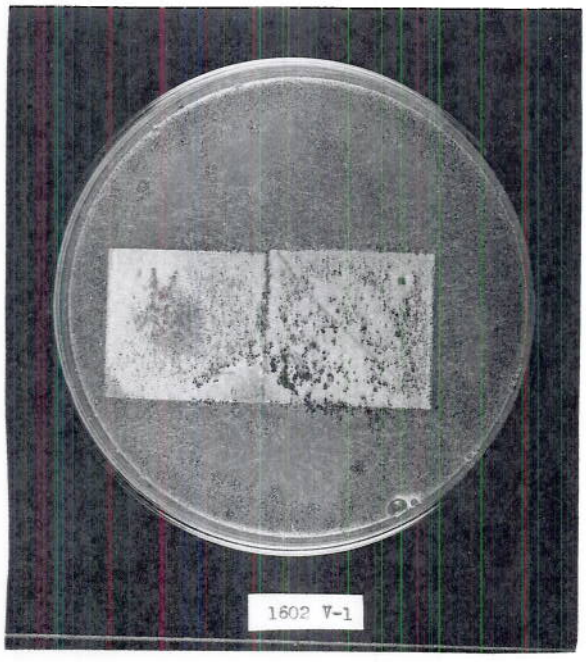
FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE II



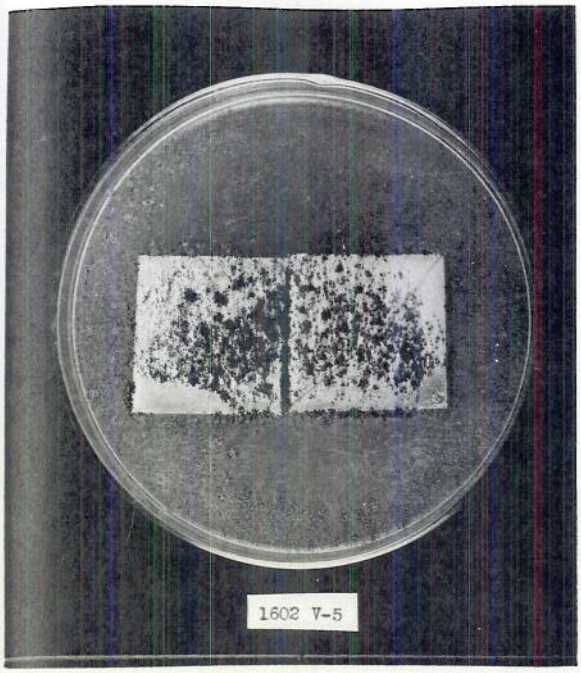


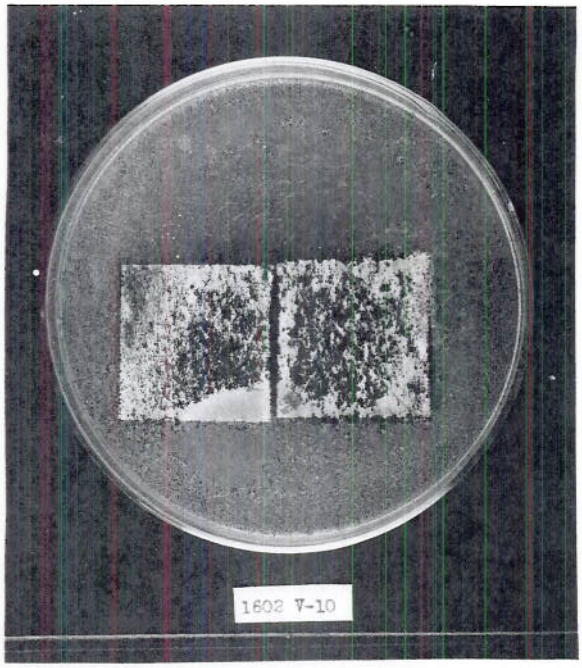


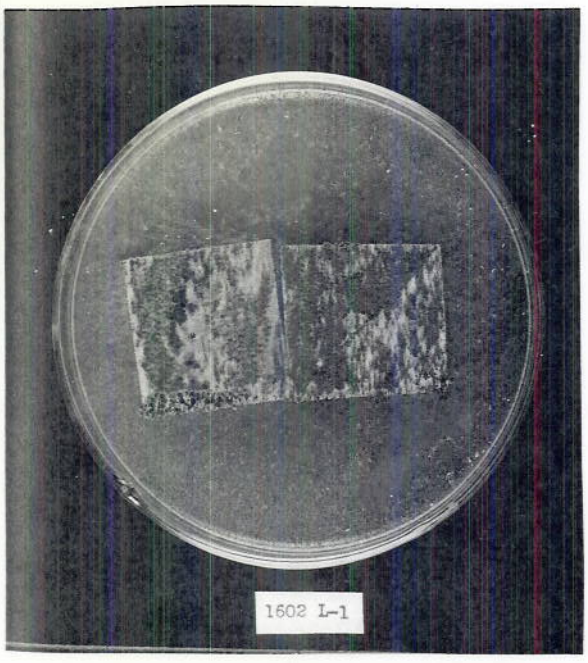


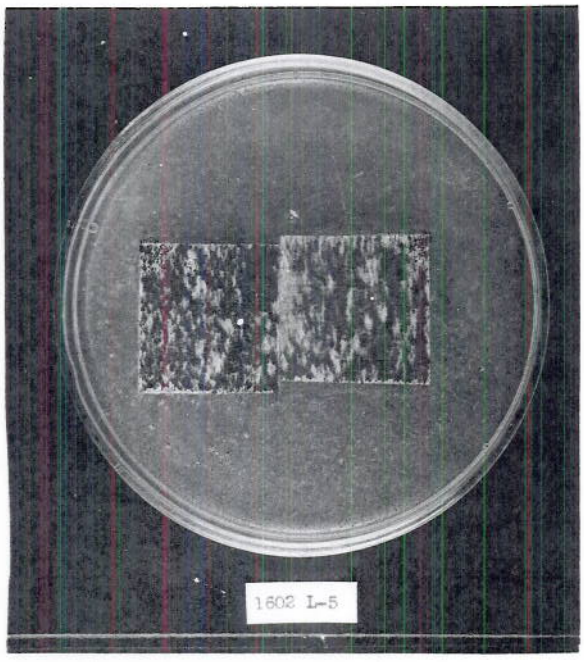
FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 12



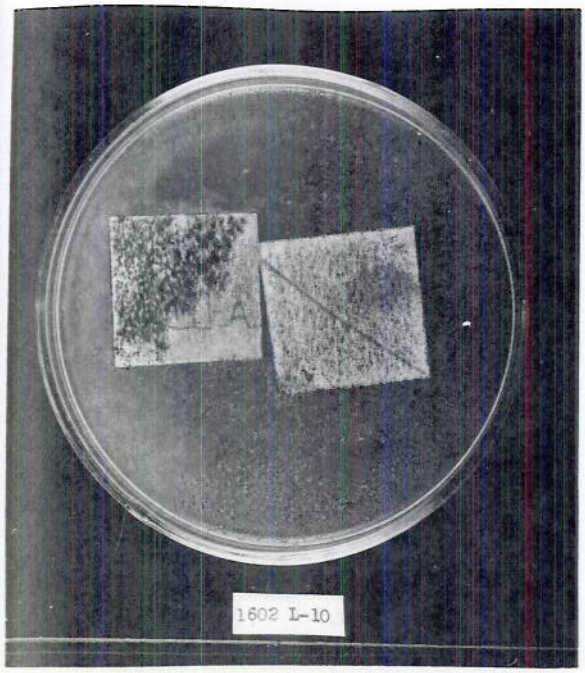


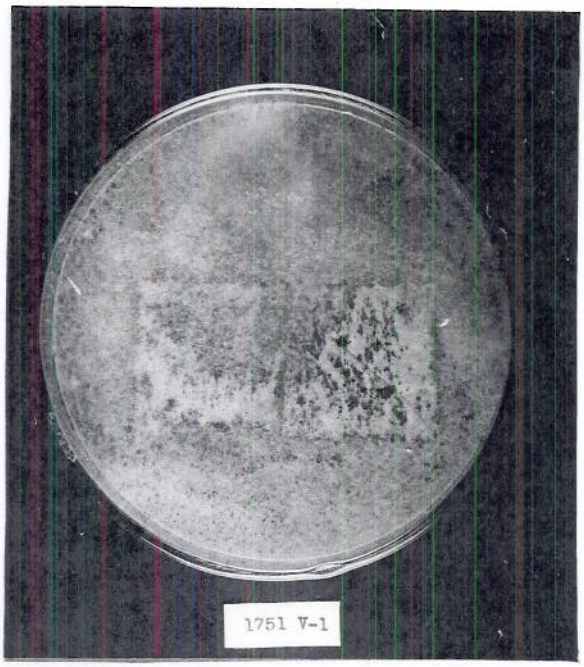


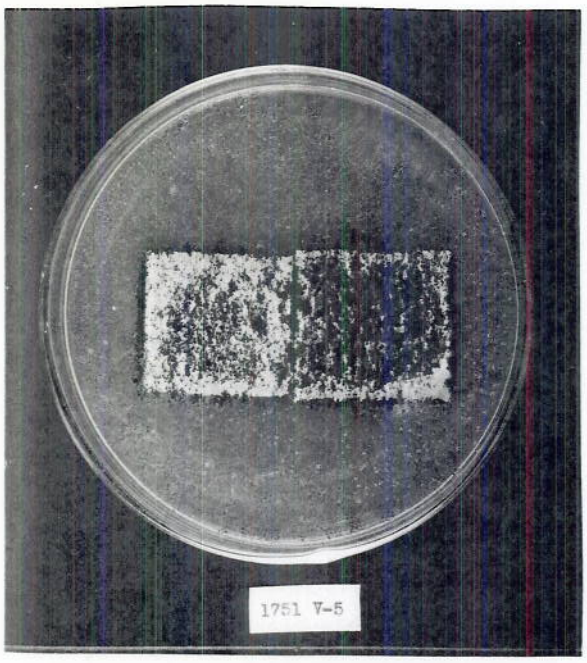


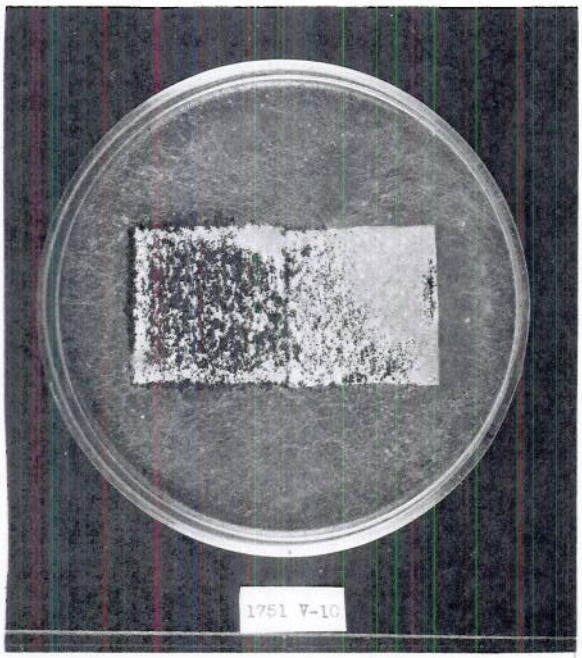
FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 13



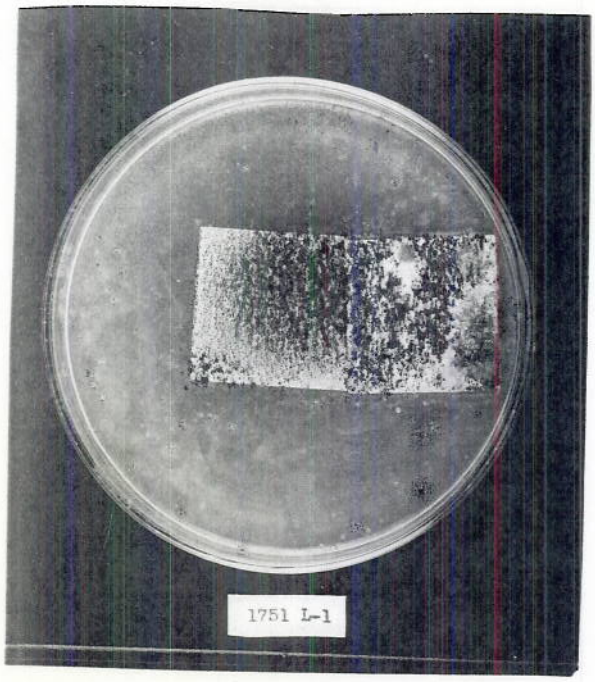


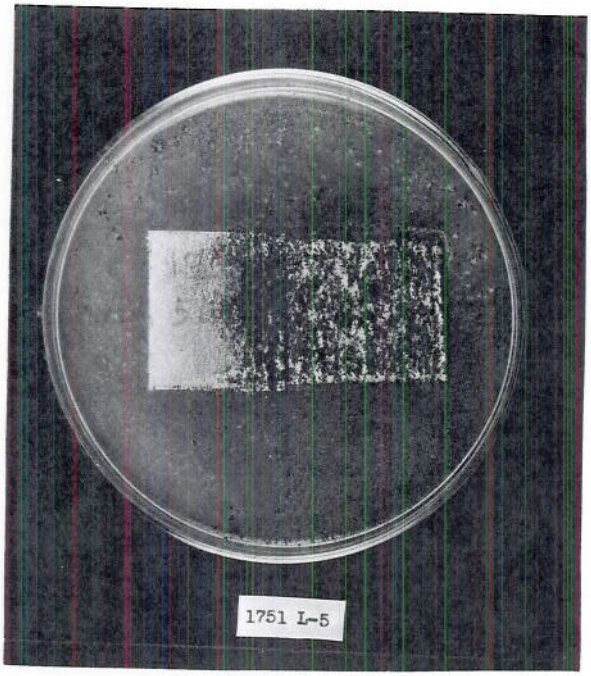


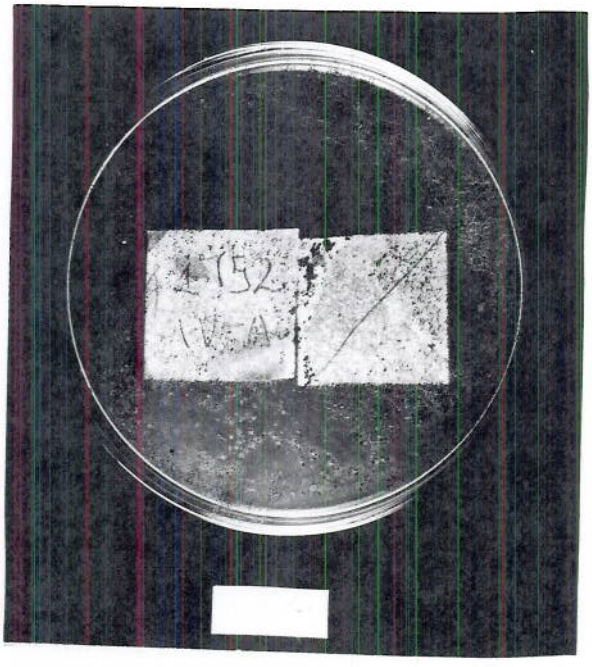


FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 14

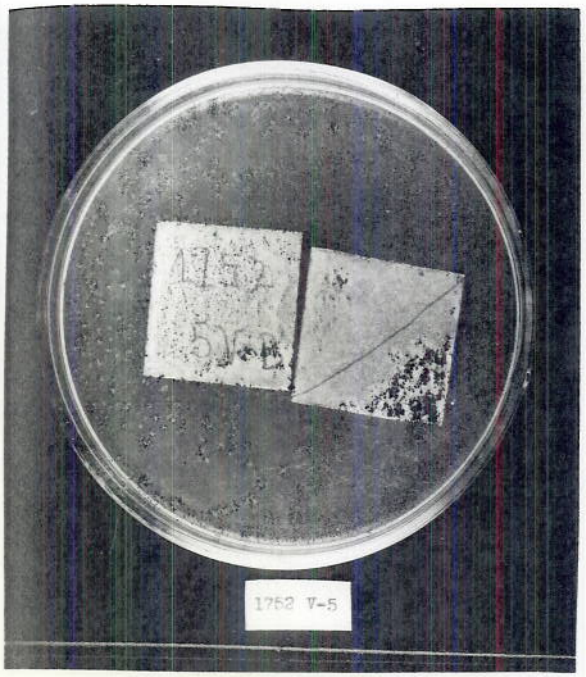


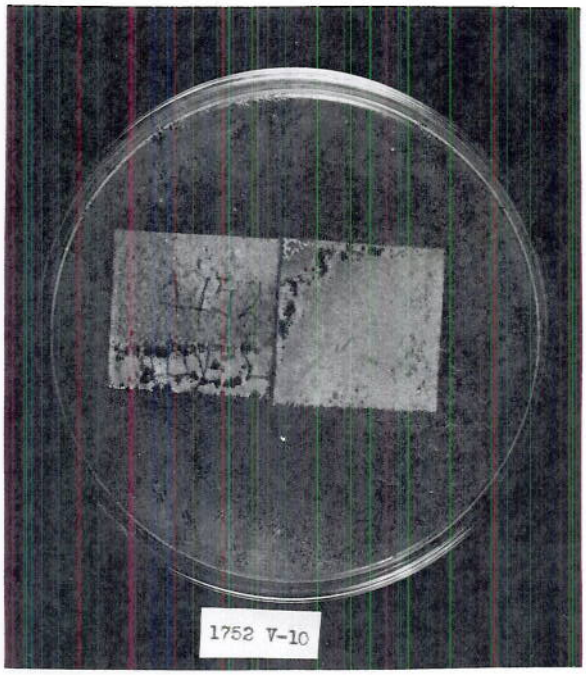


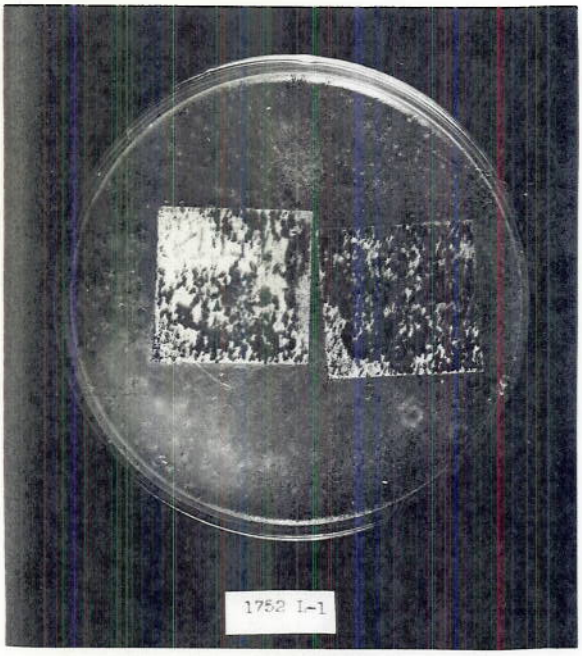


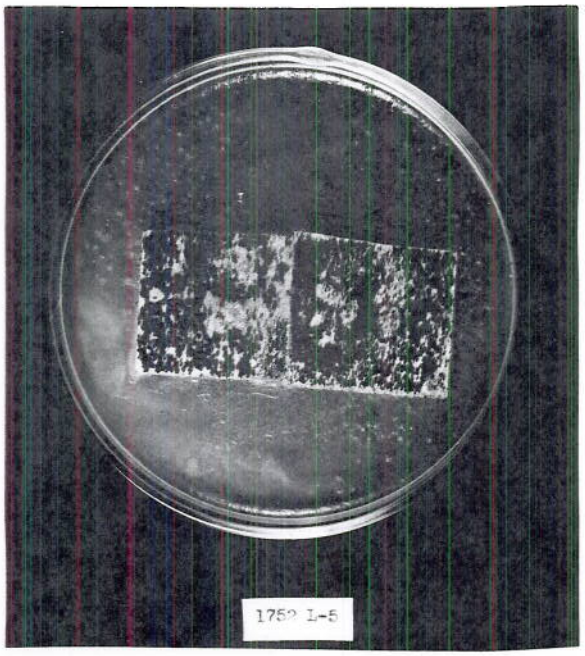
FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 15



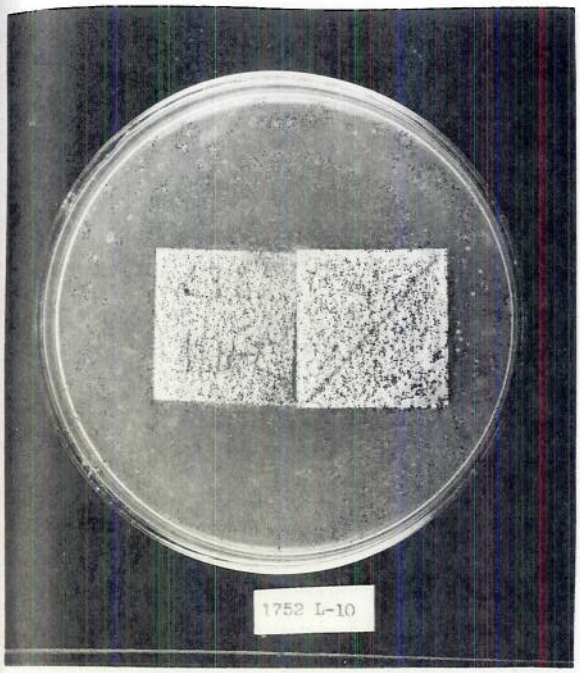


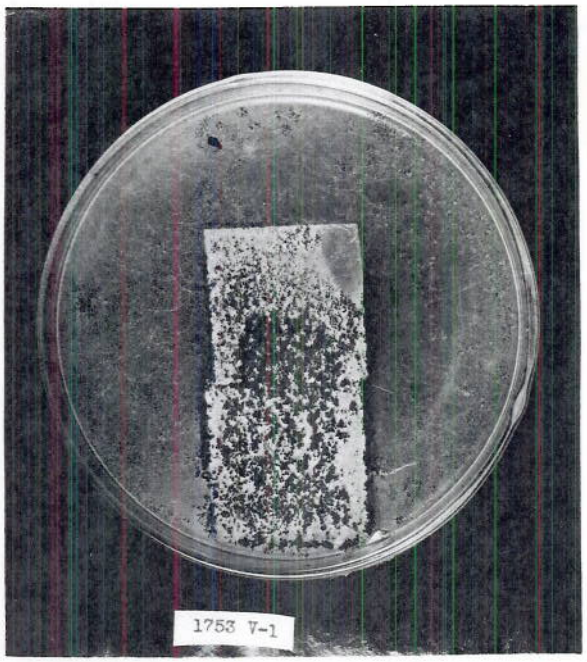


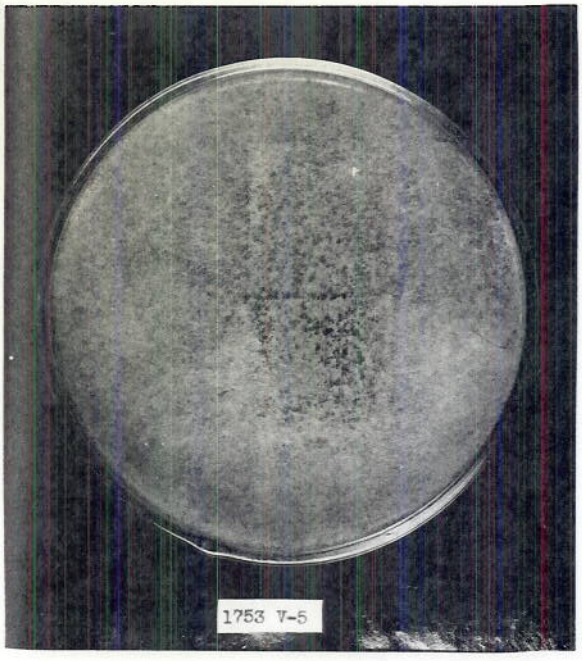


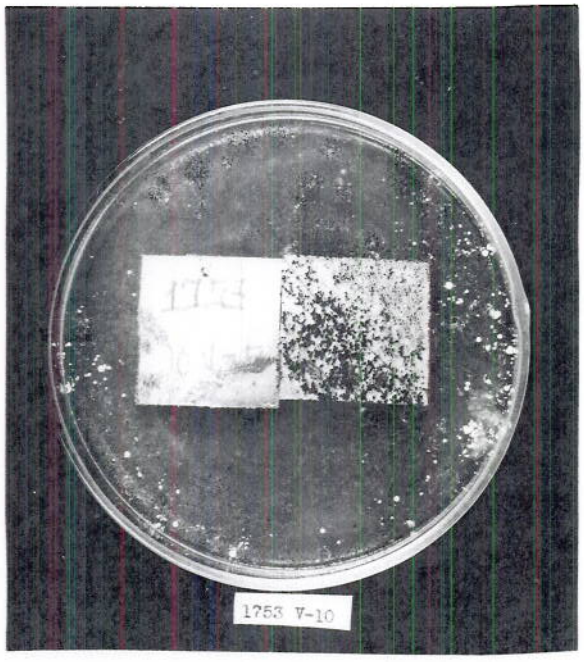
FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 16



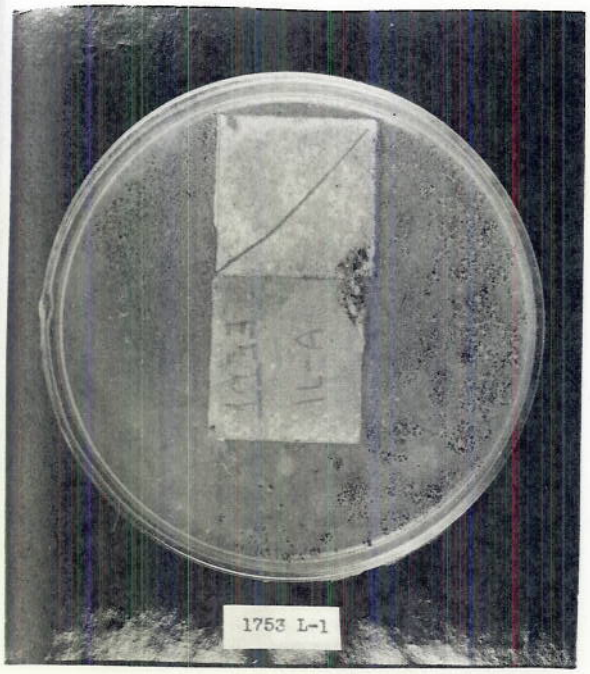


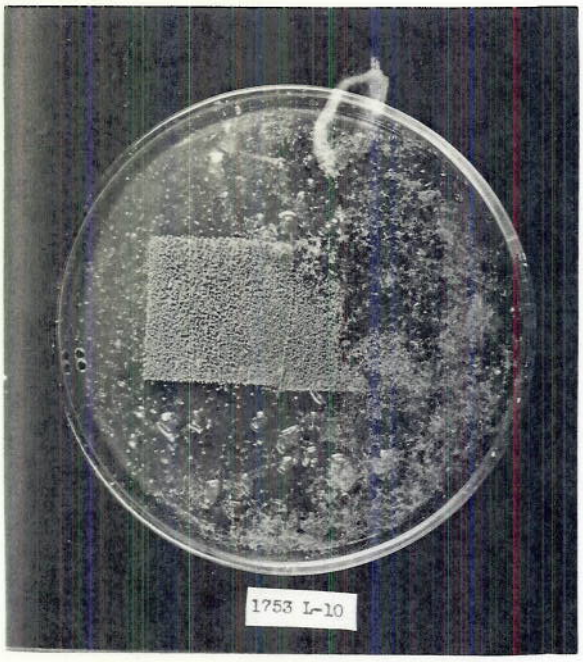


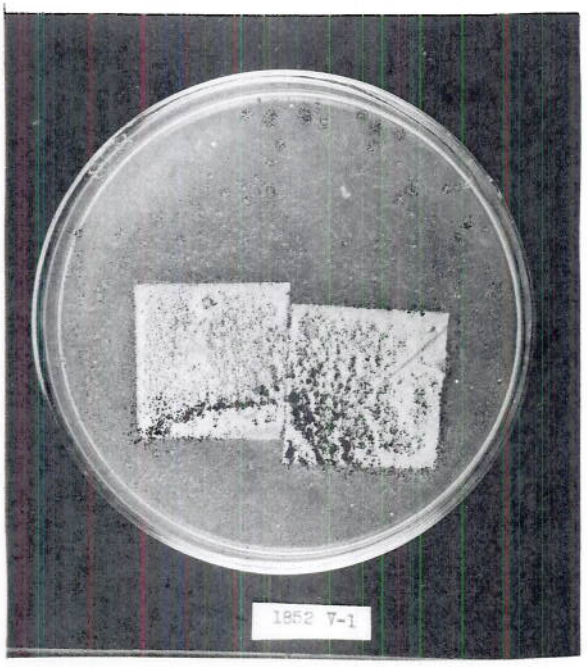


FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 17

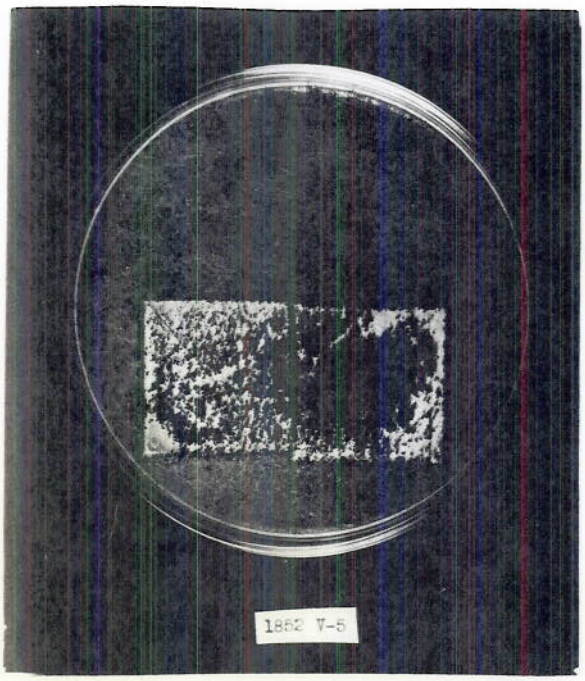


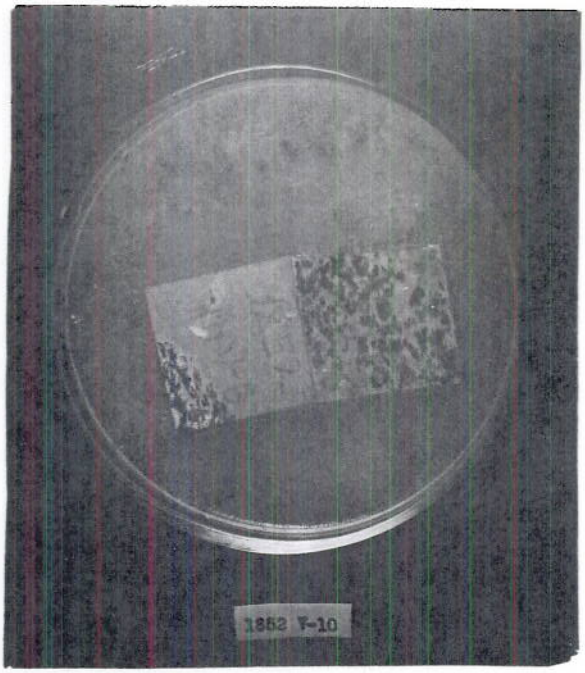


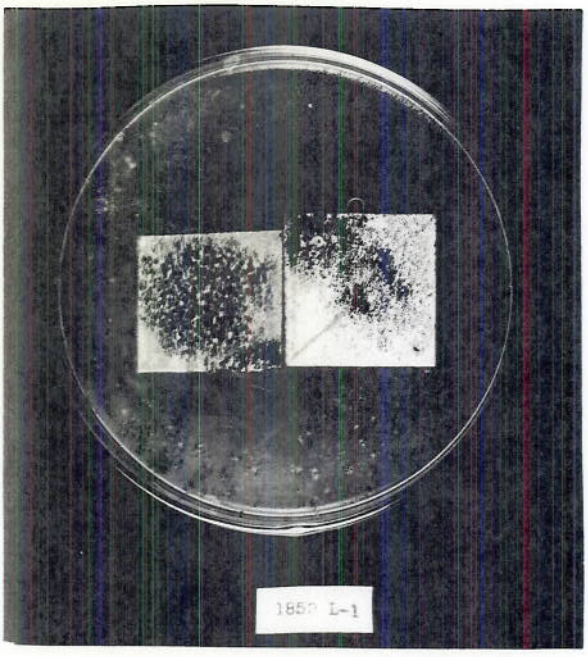


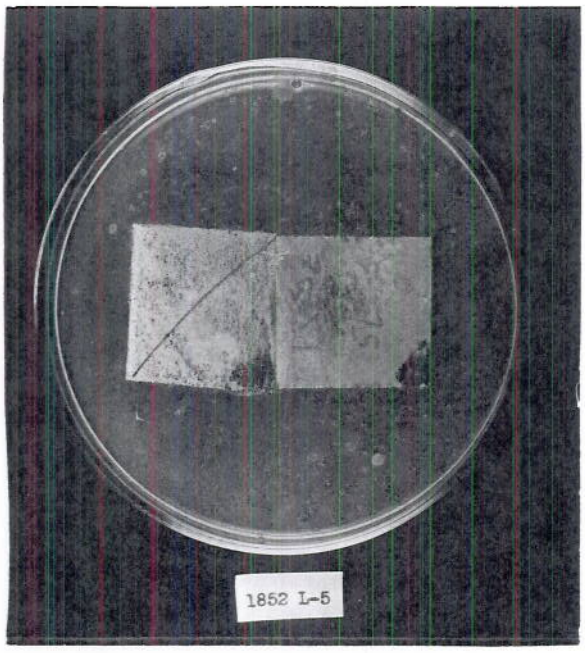
FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 18



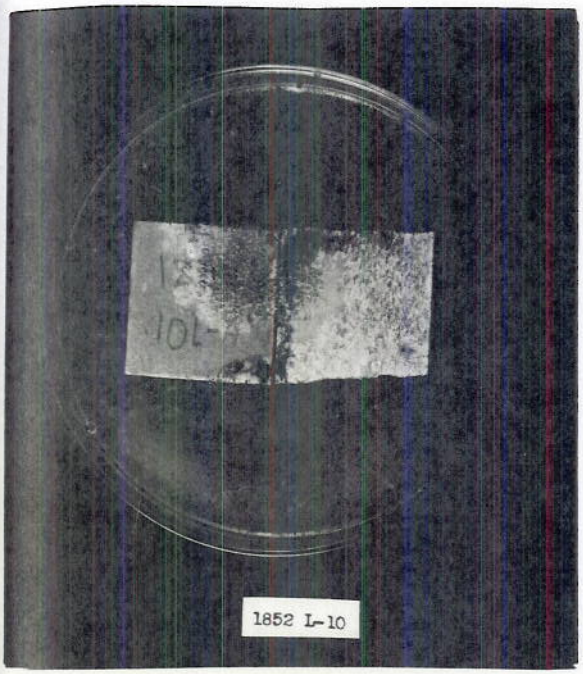


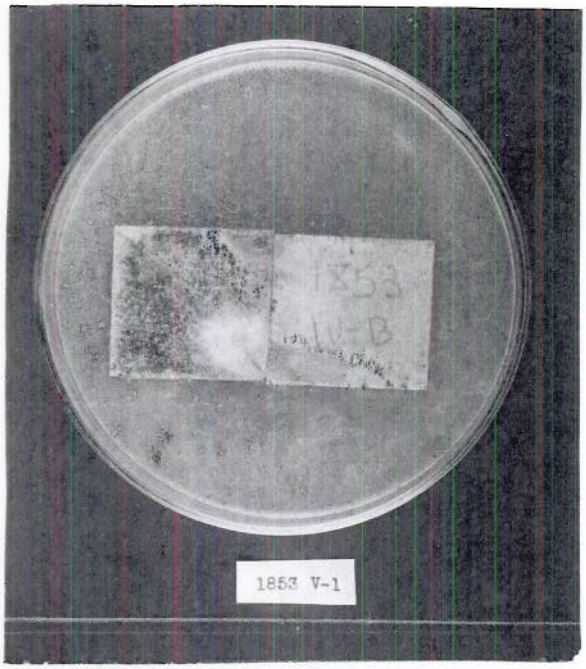


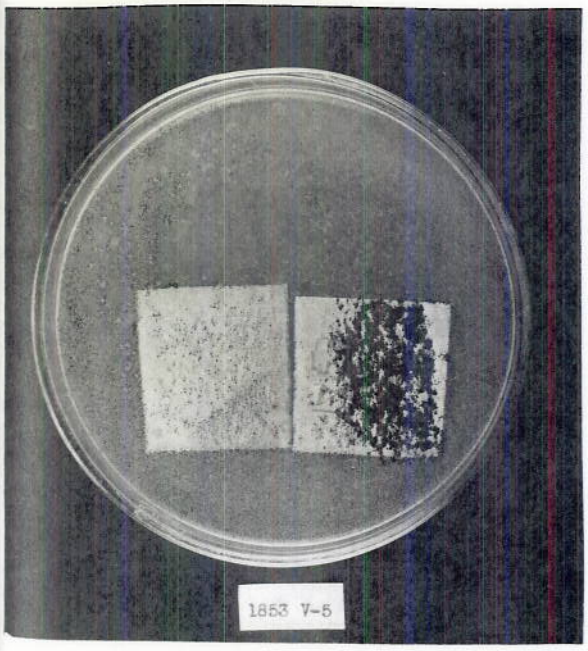


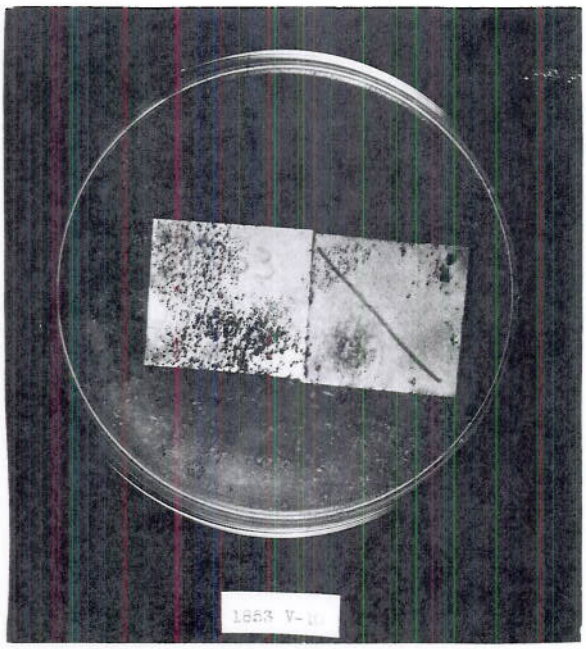
FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 19



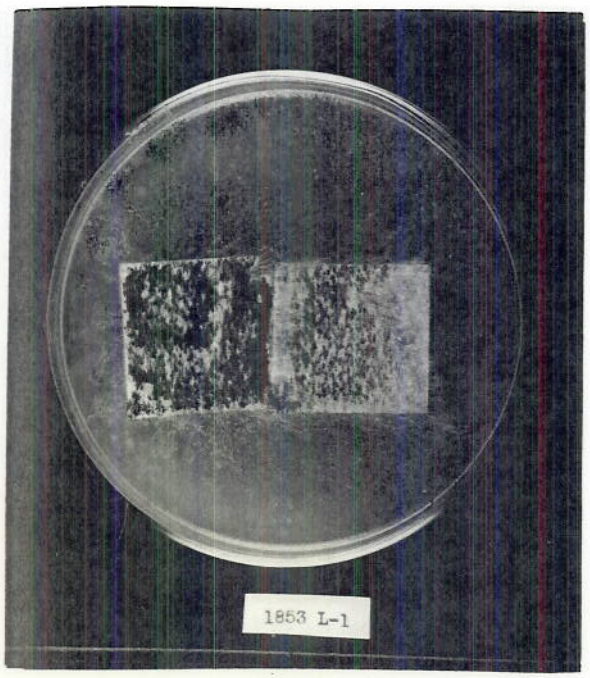


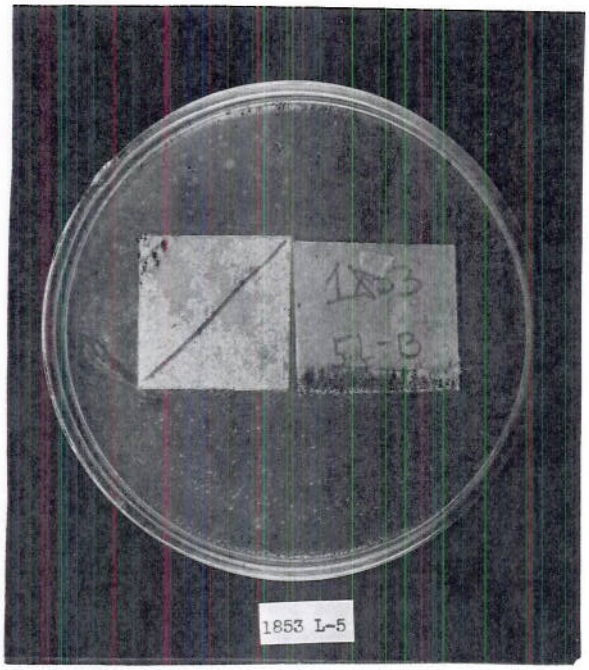


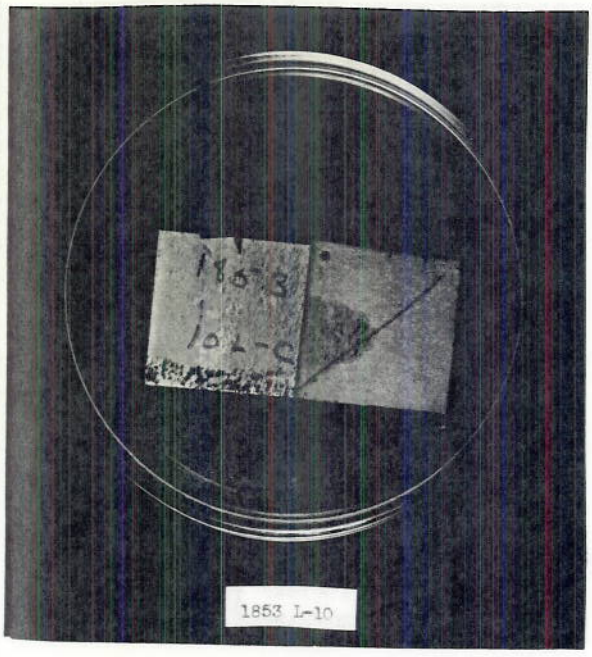


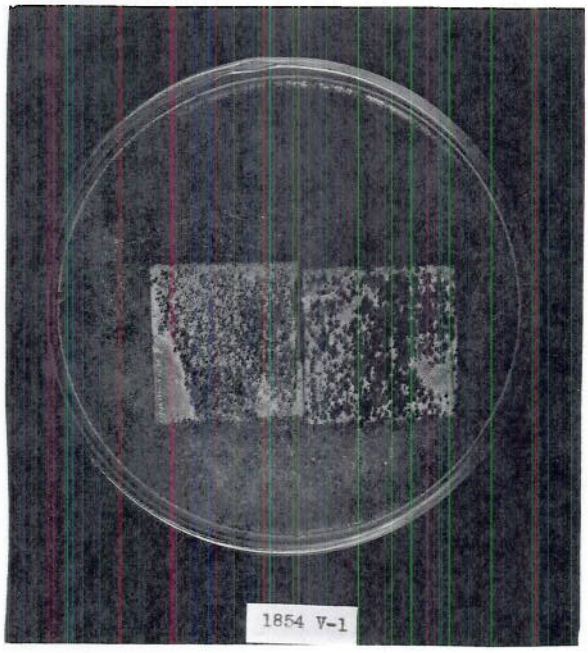
FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 20



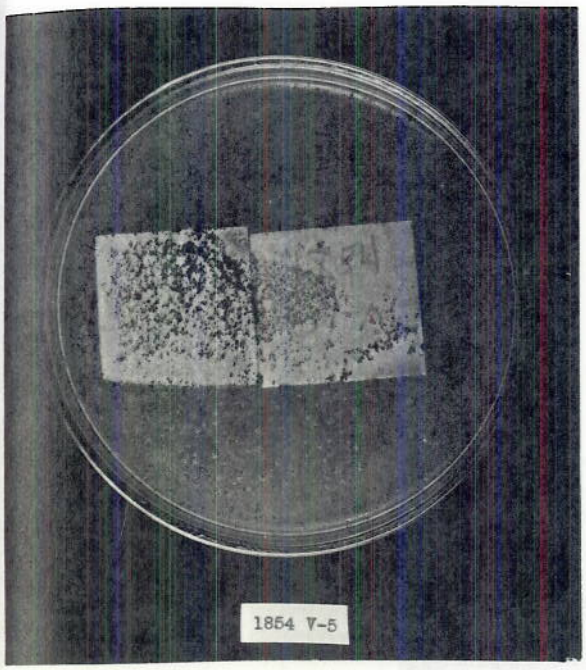


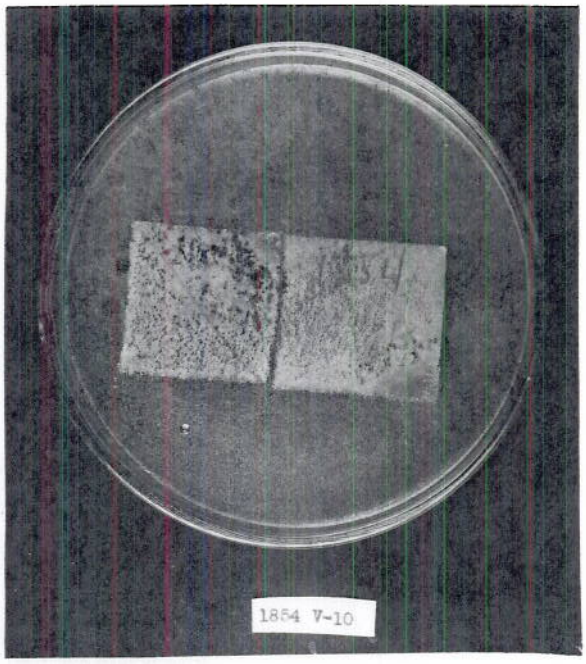


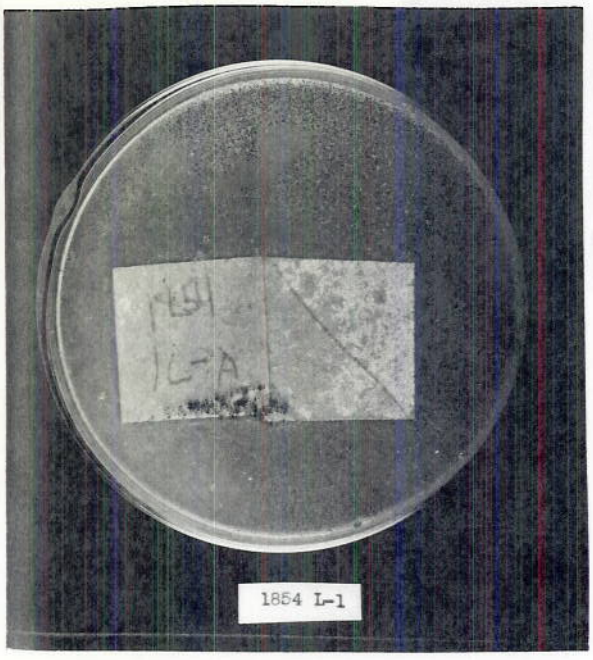


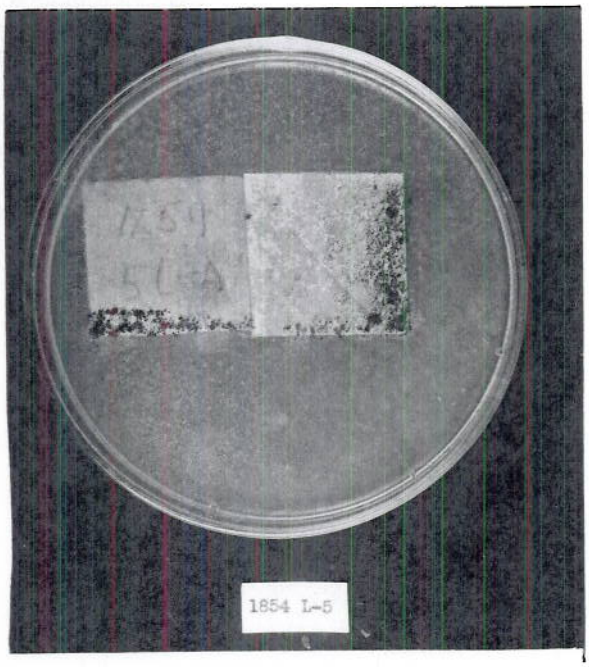
FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 21



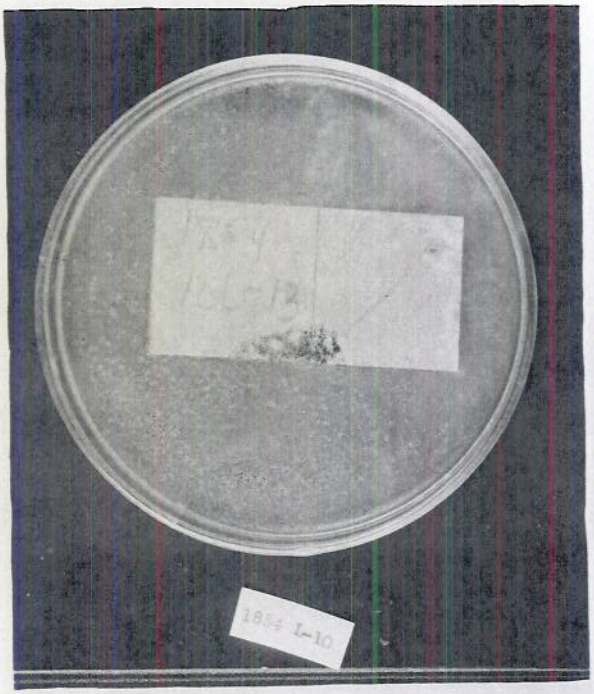






FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 22



FUNGICIDAL ACTIVITY OF COATING MATERIALS

PLATE 23

DISTRIBUTION

BuShips (25)
OR&I (2)