COATING and CHEMICAL LABORATORY

CCL REPORT NO. 159

PAINT STRIPPER FOR USE ON MILD STEEL AND ALUMINUM

BY

JOSEPH T. CROCKETT

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MARYLAND

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U. S. Army Coating and Chemical Laboratory
Aberdeen Proving Ground
Maryland

UNCLASSIFIED

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ABSTRACT

The object is the development of a paint remover suitable for use on any type of organic coating over any metal. This report covers Phase I of this project, to formulate a paint remover that would loosen all paints and related films from mild steels and aluminum.

The second object of Phase I required that the formulated paint remover be quick acting, highly efficient, and that it penetrate multi-layer coatings and small crevices or fissures that are filled with paint. All the objectives of Phase I have been achieved.

It is recommended that test methods be devised to insure procurement of this paint remover and that a procurement specification be written. It is also recommended that modifications be attempted for the purpose of extending this paint remover for use on magnesium.

I. INTRODUCTION

The problem is the removal of all types of paints and related films from all surfaces quickly and efficiently. Industry attempts to solve this problem by providing different paint removers for the different paint systems. For military purposes, a "single" system is needed which will sufficiently loosen all paints and related films from metal surfaces, chiefly mild steel and aluminum, so that the loosened paint may be washed away with a steady stream of water. The problem of finding a formulation that would accomplish this on mild steel and aluminum became Phase I of our project. The investigation began with studies of the several acid type paint strippers on the market today. These studies led to new theories and insights as to why acid type paint removers are effective. From these new theories it was possible to plan a study of related compounds and formulations which would result in a much more efficient and more universally applicable paint remover.

The first formulation derived that would achieve all the objectives presented a new problem of safety in materials handling and waste disposal. To solve this problem, the component causing the difficulties had to be completely eliminated. This was successfully accomplished.

In order to render the formulation non corrosive to the desired metals, further work was done to find a suitable inhibitor. The accomplishment of this purpose led to the final formulation which is non corrosive to mild steels and aluminum even when galvanically coupled.

This final formulation was then retested on all types of paints used for military purposes and found to be highly efficient and achieve all the objectives desired for mild steel and aluminum.

II. TEST METHODS

A. Efficiency

1. Screening Method

Percent efficiency refers to the percent of surface area in contact with the paint stripper that was completely cleaned of paint.

The efficiency of laboratory formulations was screened by placing 6 drops of the formulation, from an eyedropper, on a painted metal panel and covering with a 25 mm watch glass. After 6 minutes, the watch glass was removed and the area washed with a stream of water from a faucet at an impact pressure of 10 psi (gage). An arbitrary six minute time limit was used because initial experiments indicated that was all the time required to completely clean the surface area in contact with the stripper. The percent of the surface area, under the watch glass, completely cleaned of paint was measured by visual observation and reported as percent efficiency.

2. Epoxy Paint System

Although the remover formulations are not applicable for use on magnesium because of attack on the metal, because of the extreme difficulty of paint removal an "ethylene diamine cured epoxy baked for 20 minutes at 300°F. at 1 mil thickness over MIL-M 45202, Type I Class C treated magnesium" was used for test purposes.

If no marked paint removal was noted in six minutes, the test was rerun leaving the watch glass on and recording the time required to reach 100% efficiency.

To substantiate the first efficiency rating, a 3/8" X 3" strip from the same panel was immersed in the formulation being tested. After 6 minutes it was removed and washed by a stream of water from a faucet at an impact pressure of 10 psig. Efficiency here was reported, based on the percent of the total surface area of the strip that was completely cleaned of paint. For substantiation, the efficiency had to be equal or better than that of the first test. Again, if no stripping was exhibited in six minutes, the test was rerun, recording time required to reach 100% efficiency.

B. Penetration

In order to test the ability of the final formulation to penetrate cracks or small preforations that have been painted over, a 21 pitch, diamond knurl was put on a .032 inch, cold rolled, SAE 1010 steel panel and this panel phosphate treated according to Federal Specification TT-C-490, Type I. The panel was then coated with an epoxy type coating, ethylene diamine cured, and baked 20 minutes at 300°F. The panel was then submerged for 6 minutes in the formulation being tested and then was flushed with water at an impact pressure of 10 psig.

C. Corrosion

Specimens were made by cutting ½ inch X 3 inch strips from .032 inch SAE 1010 steel and No. 2002 aluminum panels. A 1/32 inch hole was drilled at each end of each strip to facilitate handling. Each strip was then given 100 strokes on each surface with No. 6/0 (silicon carbide) sand paper. A galvanically coupled specimen was made by tieing an aluminum and steel strip together with a short cotton thread.

For each formulation tested, three specimens were used; steel, aluminum and a steel-aluminum galvanic couple. Each specimen was submerged for 2 hours in the formulation and then removed and inspected visually for discoloration, pitting or other signs of corrosion.

D. Military Application

Military application of the final formulation was tested using the same method for testing efficiency with the exception that the paints and coatings had been aged 18 months and were representative of those used throughout the Army on mild steel and aluminum and described by Federal or Military Specifications. Fourteen specification coatings were studied (see Table VIII).

III. DISCUSSION

The most efficient commercial paint removers tested were formic acid types which contained cresylics. It appears that use of cresylics in commercial acid strippers, to date, has been as an activator. It was theorized that the presence of water in formulations containing formic acid would increase the activity of the formic acid causing rapid disintegration of the paint or coating and better penetration of the stripper. It was further theorized that these disintregration products would become hydrogen bonded to the cresylic acid or its homologue with the resultant bonding products being soluble in the vehicle, methylene chloride. The removal of the reaction products by the methylene chloride would make it possible for further attack by the formic acid.

The difficulty was the incorporation of sufficient water in a predominantly methylene chloride solution. A solublizer was required. It was discovered that phenol in the proper concentration would act both as an emulsifier for the water and as a substitute for the cresylic acid. A series of tests were run to determine stripping time and efficiency of formulations having various concentrations. The results are shown in Table I.

Since phenol, in cleaners, is new and could present novel waste disposal problems and since indications were that there might be difficulties in manufacturing the paint stripper, it was desired to eliminate the phenol. Phenol is shown in Table I, example 6 to have an optimum concentration of 23.3 weight percent.

In eliminating phenol, cresylic acid again became necessary to the formulation. Since cresylic acid will not incorporate water and methylene chloride, numerous surface active agents were tested for this purpose and found non-suitable (Table II). It was found however, that dodecyl benzene sulfonic acid would emulsify enough water to activate the formic acid.

A study was made to determine the effect of varying the concentrations of the components on stripping time in order to find optimum ranges of dodecyl benzene sulfonic acid, m-cresol, 90% formic acid and water (see Tables III, IV, V, VI) (Graphs 1,2,3,4).

As can be seen from Graph 4 the percent by weight of water can be greatly increased, but there is a corresponding decrease in efficiency. The optimum range" is between 4.8 and 6.0 wt. percent.

The problem of corrosion of steel and aluminum was next investigated with the object of finding an inhibitor for the formulation to prevent attack on ferrous metals, aluminum, and ferrous-aluminum galvanic couples (Table VII). It was found that dibutylthiourea was highly effective in the prevention of the corrosion otherwise caused by the paint remover formulation.

A final evaluation of the developed formulation was made by testing it on the paints and related coatings used by the Army and described by Military or Federal Specifications (Table VIII), Graphs 5,6,7,8.

IV CONCLUSION

The developed formulation evolving from the investigation is:

Methylene chloride	67.85	Wt. %
m-cresol	12.0	Wt. %
90% formic acid	8.	Wt. %
Dodecylbenzene sulfonic acid	6.5	Wt. %
Water	5.0	Wt. %
Dibutylthiourea	.65	Wt. %

This formulation is very efficient, rapid in its action and does not contain ingredients that would present novel problems in either manufacture or in the field.

The above formulation will not cause corrosion of mild steel or aluminum even if galvanically coupled.

V. RECOMMENDATIONS

It is recommended that requisite test methods be developed and a specification be issued for the purpose of making the above formulation available to all military installations.

It is further recommended that investigation be continued for the purpose of attempting to modify the above formulation so that it may be applied in removing paint from magnesium surfaces without corroding magnesium.

APPENDICES

APPENDIX A

Tables

TABLE I

EXPERIMENTAL COMPOSITIONS, REMOVAL EFFICIENCY STRIPPING TIMES

Basic Components: Phenol, water, 90% formic acid, methylene chloride

Paint System Tested: Ethylene diamine cured epoxy resin baked 20 minutes at 300°F. at 1 mil thickness over MIL-M-45202, Type I, Class C treated magnesium panel.

EXAMPLES

	1		2		3		4	
	Wt gm	Wt %	Wt gm	Wt %	Wt gm	Wt %	Wt gm	Wt %
Methylene chloride	0	0	2.672	21.5	4.008	32.2	5.344	42.7
Phenol	5	32.3	7	56.2	6	48.3	5	39.9
Formic acid* calculated as anhydrous	.434	2.8	1.073	8.6	1.073	0.6	1.073	8.6
Total water	10.048	64.9	1.708	13.7	1.358	10.9	1.108	8.8
Time	6 min		6 min		6 min		6 min	
Efficiency	0%		0%		35%		45%	

EXAMPLES

	5		6		7		8	
	Wt gm	Wt %	Wt gm	Wt %	Wt gm	Wt %	Wt gm	Wt %
Methylene chloride	6.680	52.6	8.016	62.1	9.352	72.3	10.688	82.1
Phenol	4	31.5	3	23.3	2	15.5	1	7.7
Formic acid* calculated as anhydrous	1.073	8.4	1.073	8.3	1.073	8.3	1.073	8.2
Total water	.958	7.5	.808	6.3	.508	3.9	.258	2.0
Time	6 min		6 min		6 min		6 min	
Efficiency	90%		99%		94%		90%	

TABLE I (CONTINUED)

	EXAMPLES							
	9		10		11		12	
	Wt gm	Wt %	Wt gm	Wt %	Wt gm	Wt %	Wt gm	Wt %
Methylene chloride	6.680	93.3	0	0	2.672	24.6	4.008	35.8
Phenol	0	0	5	91.2	7	64.5	6	53.6
Formic acid* calculated as anhydrous	.434	6.0	.434	7.9	1.073	9.8	1.073	9.6
Total water	.048	.7	.048	.9	.108	1.1	.108	1 0
Time	6 min		6 min		6 min		6 min	
Efficiency	0%		0%		0%		0%	

	EXAMPLES							
	13		14		15		16	
	Wt gm	Wt %	Wt gm	Wt %	Wt gm	Wt %	Wt gm	Wt %
Methylene chloride	5.344	46.4	12.024	69.9	8.016	65.7	9.352	74.6
Phenol	5	43.4	4	23.3	3	24.6	2	16.0
Formic acid* calculated as anhydrous	1.073	9.3	1.073	6.2	1.073	8.8	1.073	8.6
Total water	.108	.9	.108	.6	.108	.9	.108	.9
Time	6 min		6 min		6 min		6 min	
Efficiency	0%		0%		5%		20%	

TABLE I (CONTINUED)

	EXAMPLES							
	17		18		19		20	
	Wt gm	Wt %	Wt gm	Wt %	Wt gm	Wt %	Wt gm	Wt %
Methylene chloride	10.688	83.1	8.016	68.4	6.680	52.6	8.016	57.7
Phenol	1	7.8	3	25.6	2	15.8	3	21.6
Formic acid* calculated as anhydrous	1.073	8.3	0	0	3.252	25.6	1.951	14.1
Total Water	.108	.8	.700	6.0	.761	6.0	.917	6.0
Time	6 min		6 min		6 min		6 min	
Efficiency	20%		0%		18%		72%	

* Any concentration of Formic acid may be used as long as the total water is as shown above.

TABLE II

ABILITY OF SURFACE ACTIVE AGENTS TO CONVERT THE TWO PHASE (LIQUID-LIQUID) SOLVENT SYSTEM TO A ONE PHASE (LIQUID) SYSTEM

Solvent System:

Methylene Chloride	---------------	60 Wt. %
m-Cresol	------------------------	20 Wt. %
Formic Acid (90%)	----------------	10 Wt. %
Water	----------------------------	10 Wt. %

Surface Active Agent	No. of Liquid Phases After Use
Substituted oxazoline	2
Manide monooleate	2
Sorbitan sesquioleate	2
Glycerol sorbitan laurate	2
Polyoxyethylene sorbitol oleate	2
Polyoxyethylene sorbitol laurate	2
Polyoxyethylene sorbitol stearate	2
1-hydroxy 2-heptadecyl imidazoline	2
Polyethylene glycol laurate	2
Polyethylene glycol oleate	2
Polyethylene glycol stearate	2
Nonylphenoxypoly (ethylene oxy) ethanol	2
Diethanol amide of mixed fatty esters	2
Polyhydric alcohol sulfonic acid derivative	2
Polyoxyethylated tridecyl alcohol	2
Sulfonated oils	2
Complex amine salts of arylsulfonates	2
Mixed esters of free acid phosphates	2
Metallic salts of alkyl aryl sulfonic acids	2
Dodecylbenzene sulfonic acid	1

TABLE III

EXPERIMENTAL COMPOSITIONS, STRIPPING TIME TO REACH 100% EFFICIENCY

Solvent System:
- m-Cresol ---------------------- 20 Wt. %
- Methylene Chloride ----------- 64 Wt. %
- Water ------------------------ 7 Wt. %
- Formic Acid (90%) ------------ 9 Wt. %

Variable Parameter: Dodecylbenzene sulfonic acid.

Paint System Tested: Ethylene diamine cured epoxy resin, baked 20 minutes at 300°F. at 1 mil thickness over a MIL-M-45202, Type I, Class C treated magnesium panel.

Solvent System (Wt. %)	100	96	95.5	95	94.5	94	93.5	92.0	90.0
Dodecylbenzene sulfonic acid (Wt. %)	0	4	4.5	5.0	5.5	6.0	6.5	8.0	10.0
Stripping time to reach 100% efficiency (min.)	60	6.5	6.0	5.5	5.5	5.5	6.0	7.0	8.5

TABLE IV

EXPERIMENTAL COMPOSITIONS, STRIPPING TIME TO REACH 100% EFFICIENCY

Solvent System:
- Methylene Chloride --------------- 77.5 Wt. %
- Water ---------------------------- 7.0 Wt. %
- Formic Acid (90%) ---------------- 9.0 Wt. %
- Dodecylbenzene Sulfonic Acid ----- 6.5 Wt. %

Variable Parameter: m-Cresol

Paint System Tested: Ethylene diamine cured epoxy resin, baked 20 minutes at 300°F. at 1 mil thickness over a MIL-M-45202, Type I, Class C treated magnesium panel.

Solvent System (Wt. %)	100	95	92	90	85	80	75	70	65
m-Cresol (Wt. %)	0	5	8	10	15	20	25	30	35
Stripping time to reach 100% efficiency (min.)	60	8	5	4.5	5	6	6	6.5	8

TABLE V

EXPERIMENTAL COMPOSITIONS, STRIPPING TIME TO REACH 100% EFFICIENCY

Solvent System:
- Methylene Chloride ---------------- 74.5 Wt. %
- Dodecylbenzene Sulfonic Acid ------- 6.5 Wt. %
- Water ---------------------------- 7.0 Wt. %
- m-Cresol ------------------------- 12.0 Wt. %

Variable Parameter: Formic Acid (90%)

Paint System Tested: Ethylene diamine cured epoxy resin, baked 20 minutes at 300°F. at 1 mil thickness over a MIL-M-45202, Type I, Class C treated magnesium panel.

Solvent System (Wt. %)	100	99	98	96	94	92	90	88	86
Formic Acid (90%) (Wt. %)	0	1	2	4	6	8	10	12	14
Stripping time to reach 100% efficiency (min.).	00	>60	20	13	6	4.5	5	5.75	6.5

TABLE VI

EXPERIMENTAL COMPOSITIONS, STRIPPING TIME TO REACH 100% EFFICIENCY

Solvent System:
- Dodecylbenzene Sulfonic Acid ------------ 6.5 Wt. %
- m-Cresol ------------------------------- 12.0 Wt. %
- Formic Acid (90%) ---------------------- 8.0 Wt. %
- Methylene Chloride --------------------- 73.5 Wt. %

Variable Parameter: Water

Paint System Tested: Ethylene diamine cured epoxy resin, baked 20 minutes at 300°F. at 1 mil thickness over a MIL-M-45202, Type I, Class C treated magnesium panel.

Solvent System (Wt. %)	100	99.5	99	98	95	94	90	80	73.5	70	65	61
Water (Wt. %)	0	0.5	1.0	2.0	5.0	6.0	10	20	26.5	30	35	39
Stripping time to reach 100% efficiency (min.).	>60	>60	28	11	5	5	8	8.5	9.5	10.5	12	12.8

TABLE VII

CORROSION INHIBITORS, DEGREE OF CORROSION
MILD STEEL, ALUMINUM, MILD STEEL-ALUMINUM GALVANIC COUPLE

Basic Composition of Corrosive Formulation:

Methylene Chloride	68.5 Wt. %
m-Cresol	12.0 Wt. %
Formic Acid (90%)	8 0 Wt. %
Dodecylbenzene Sulfonic Acid	6.5 Wt. %
Water	5.0 Wt. %

Inhibitor	Degree of Corrosion: Steel	Degree of Corrosion: Aluminum	Galvanic Couple: Steel	Galvanic Couple: Aluminum
None	Blackened, pitting	Grey discoloration, no pitting	Blackened, some pitting.	Grey discoloration, no pitting
Formaldehyde (formed a resin, rapidly, in the formulation)	Brownish discoloration, no pitting	Very slight grey discoloration, no pitting	Brownish discoloration, no pitting	Very slight grey discoloration, no pitting
Tricresyl Phosphate	Blackened, no pitting	Dark grey, no pitting	Blackened, no pitting	Dark grey, no pitting
Dibutylthiourea	No discoloration, no pitting.	No discoloration, no pitting	No discoloration, no pitting.	No discoloration, no pitting

TABLE VIII

STRIPPING TIME REQUIRED FOR THE PREFERRED PAINT STRIPPER FORMULATION TO BE 100% EFFICIENT ON PAINT SYSTEMS DESCRIBED BY MILITARY AND FEDERAL SPECIFICATIONS

Paint Systems (1 mil thick)	Stripping time for 100% efficiency (MM)
MIL-E-10687, Enamel, Lustreless, Quick Drying	1.0
MIL-E-52227, Enamel, Semi-Gloss, Quick Drying	0.5
MIL-L-11195, Lacquer, Lustreless, Hot Spray	6.0
MIL-E-13515, Enamel, Vinly-Alkyd, Semi-Gloss Rust Inhibiting	11.9
TT-E-529, Enamel, Alkyd, Semi-Gloss	1.75
TT-E-489, Enamel, Alkyd, Gloss	1.5
MIL-L-12277, Lacquer, Automotive, Hot Spray	12.0
TT-E-527, Enamel, Alkyd, Lustreless	5.5
TT-E-485, Type II, Enamel, Semi-Gloss, Rust Inhibiting	4.0
TT-E-485, Type IV, Enamel, Semi-Gloss, Rust Inhibiting	3.5
MIL-L-19537, Lacquer, Acrylic-Nitrocellulose, Gloss	23
MIL-P-52192, Primer Coating Epoxy	6
MIL-P-23377A, Primer, Epoxy-Polyamide, Chemical and Solvent Resistant	3.5
MIL-C-23236, Paint Coating Systems, Steel Ship Tank, Fuel and Salt Water Ballast (7 mils thick on sandblasted steel) (Class I epoxy for ships ballast tanks)	36

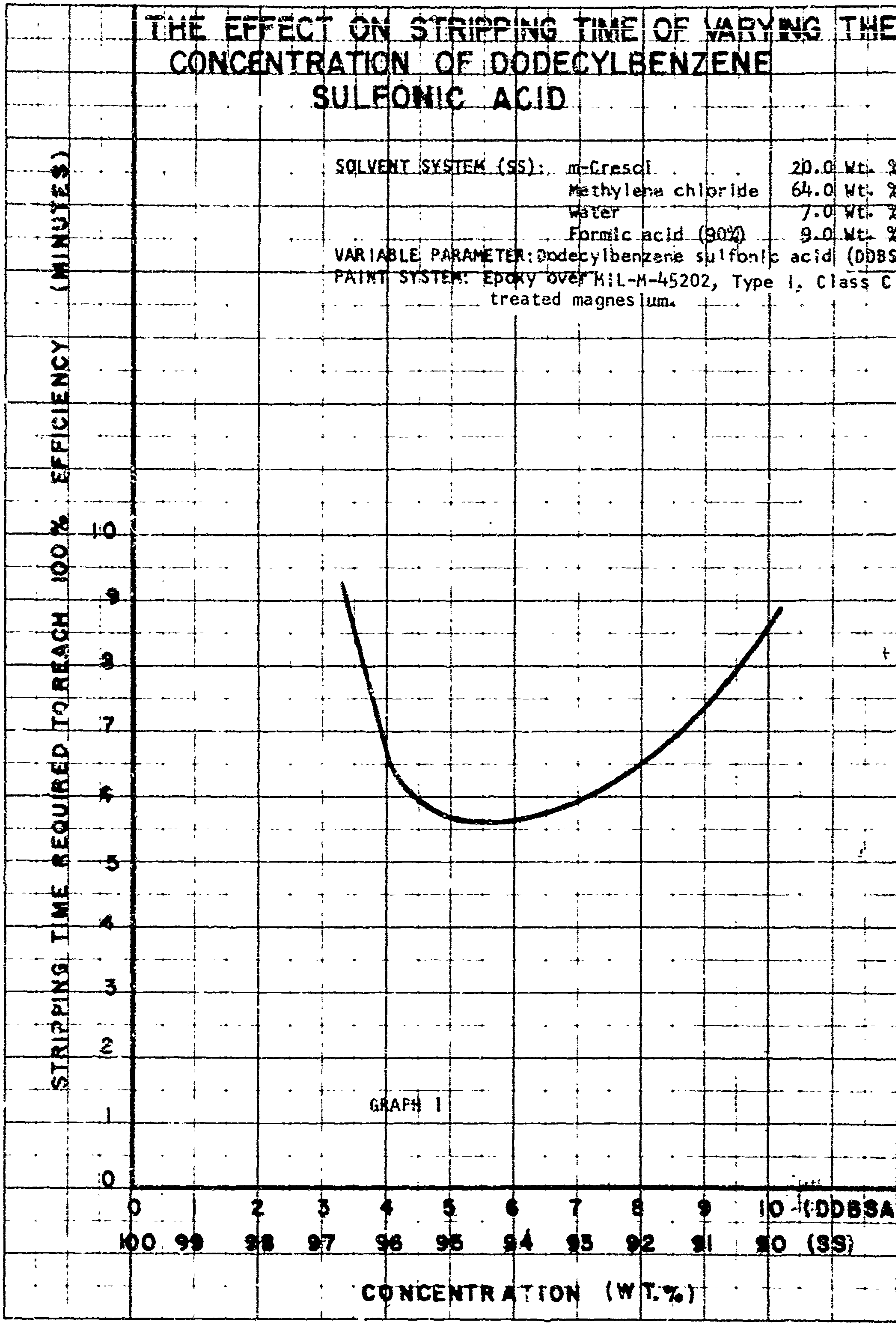
TABLE IX

RECOMMENDED PAINT STRIPPER FORMULATION

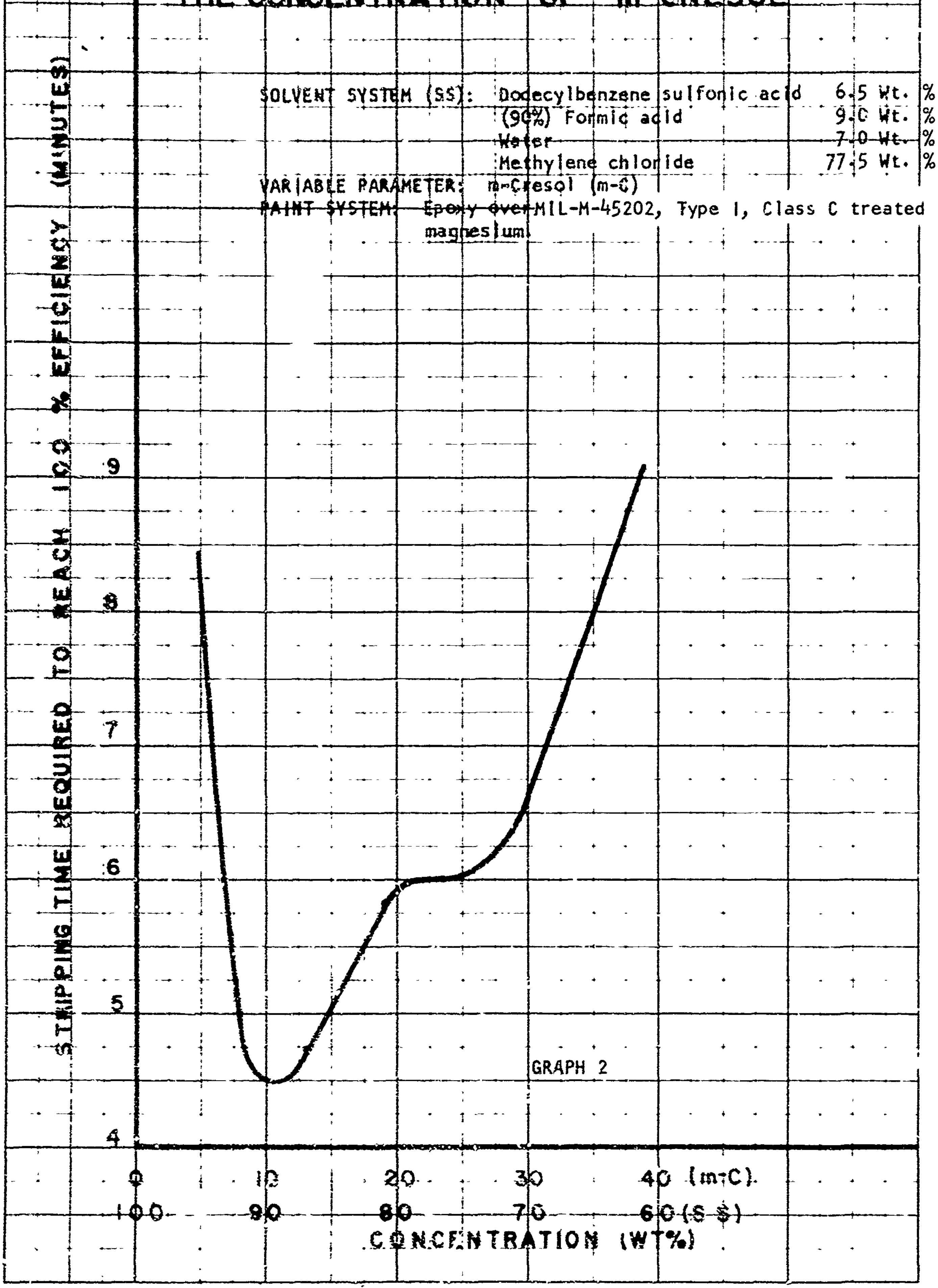
Methylene Chloride	67.85 Wt. %
m Cresol	12.0 Wt. %
Formic Acid (90%)	8.0 Wt. %
Dodecylbenzene Sulfonic Acid	6.5 Wt. %
Water	5.0 Wt. %
Dibutylthiourea	.65 Wt. %

APPENDIX 9

Graphs


THE EFFECT ON STRIPPING TIME OF VARYING THE CONCENTRATION OF DODECYLBENZENE SULFONIC ACID
SOLVENT SYSTEM (SS): m-Cresol 20.0 Wt. %
Methylene chloride 64.0 Wt. %
Water 7.0 Wt. %
Formic acid (90%) 9.0 Wt. %
VARIABLE PARAMETER: Dodecylbenzene sulfonic acid (DDBSA)
PAINT SYSTEM: Epoxy over MIL-M-45202, Type I, Class C treated magnesium.
STRIPPING TIME REQUIRED TO REACH 100% EFFICIENCY (MINUTES)
0
1
2
3
4
5
6
7
8
9
10
GRAPH I
0 1 2 3 4 5 6 7 8 9 10 (DDBSA)
100 99 98 97 96 95 94 93 92 91 90 (SS)
CONCENTRATION (WT.%)

THE EFFECT ON STRIPPING TIME OF VARYING THE CONCENTRATION OF m-CRESOL

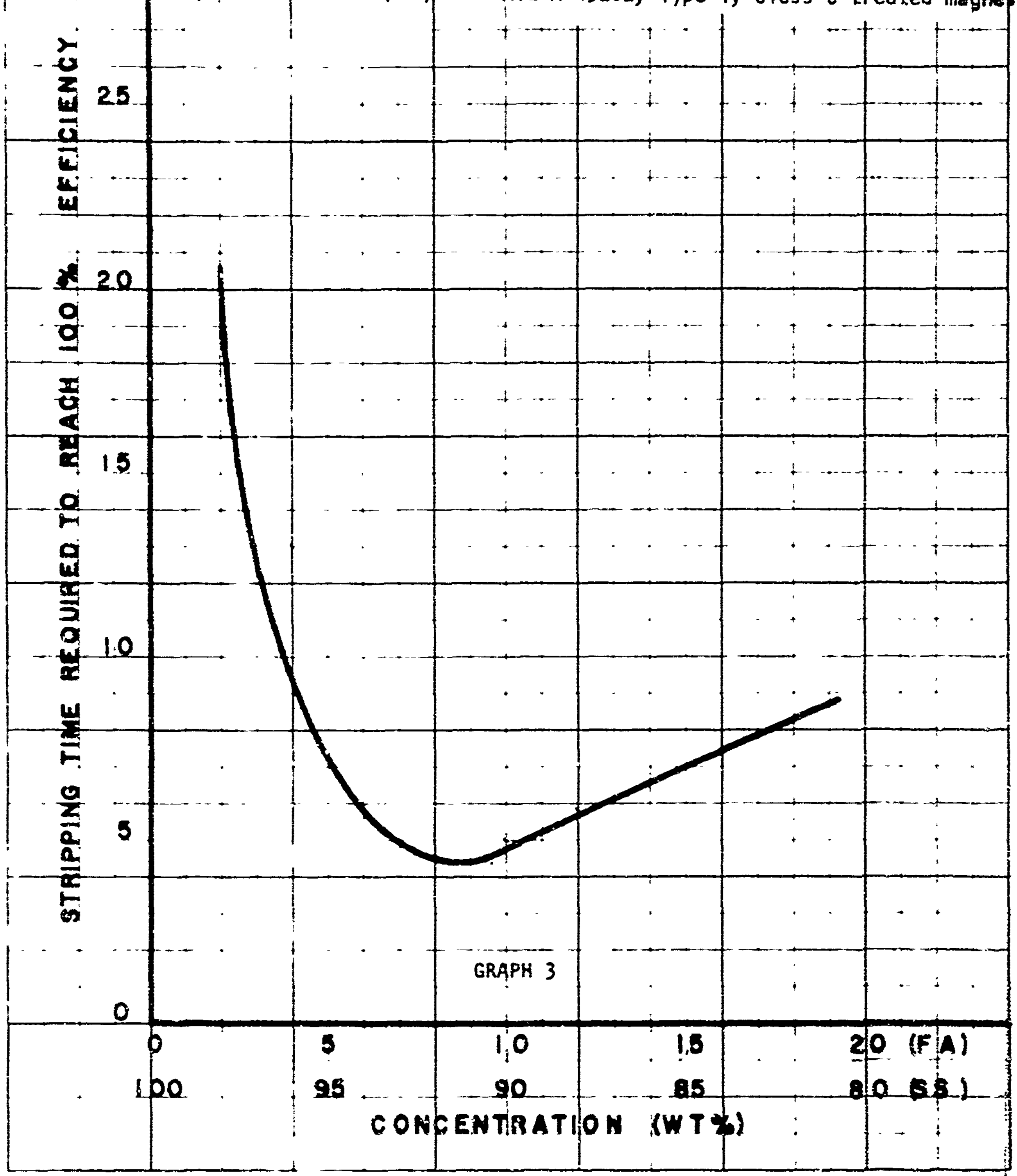


THE EFFECT ON STRIPPING TIME OF VARYING THE CONCENTRATION OF FORMIC ACID

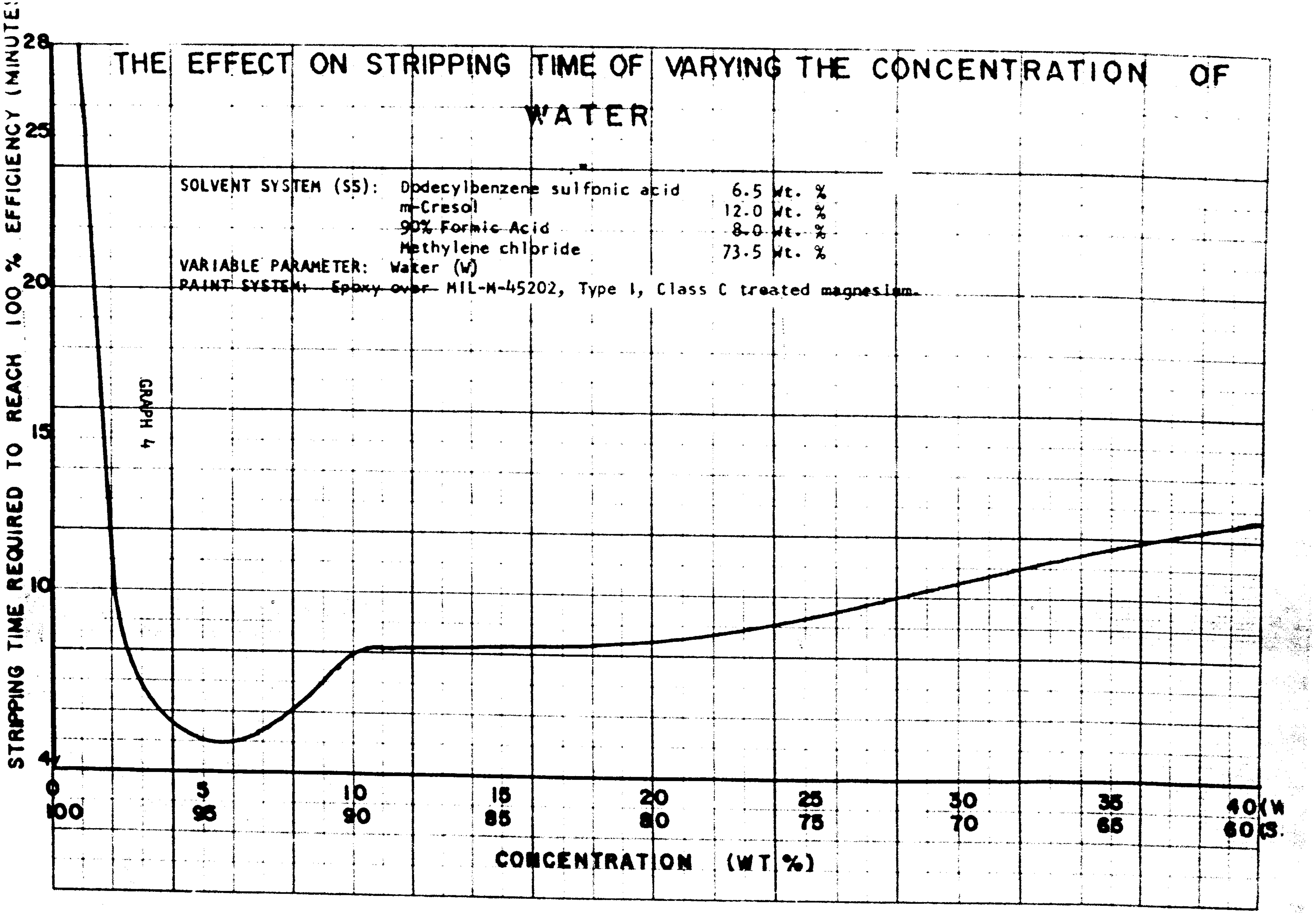
SOLVENT SYSTEM (SS):	Dodecylbenzene sulfonic acid	6.5 Wt. %
	m-Cresol	12.0 Wt. %
	~~Methylene chloride~~	74.5 Wt. %
	Water	7.0 Wt. %

VARIABLE PARAMETER: 90% Formic acid (FA)

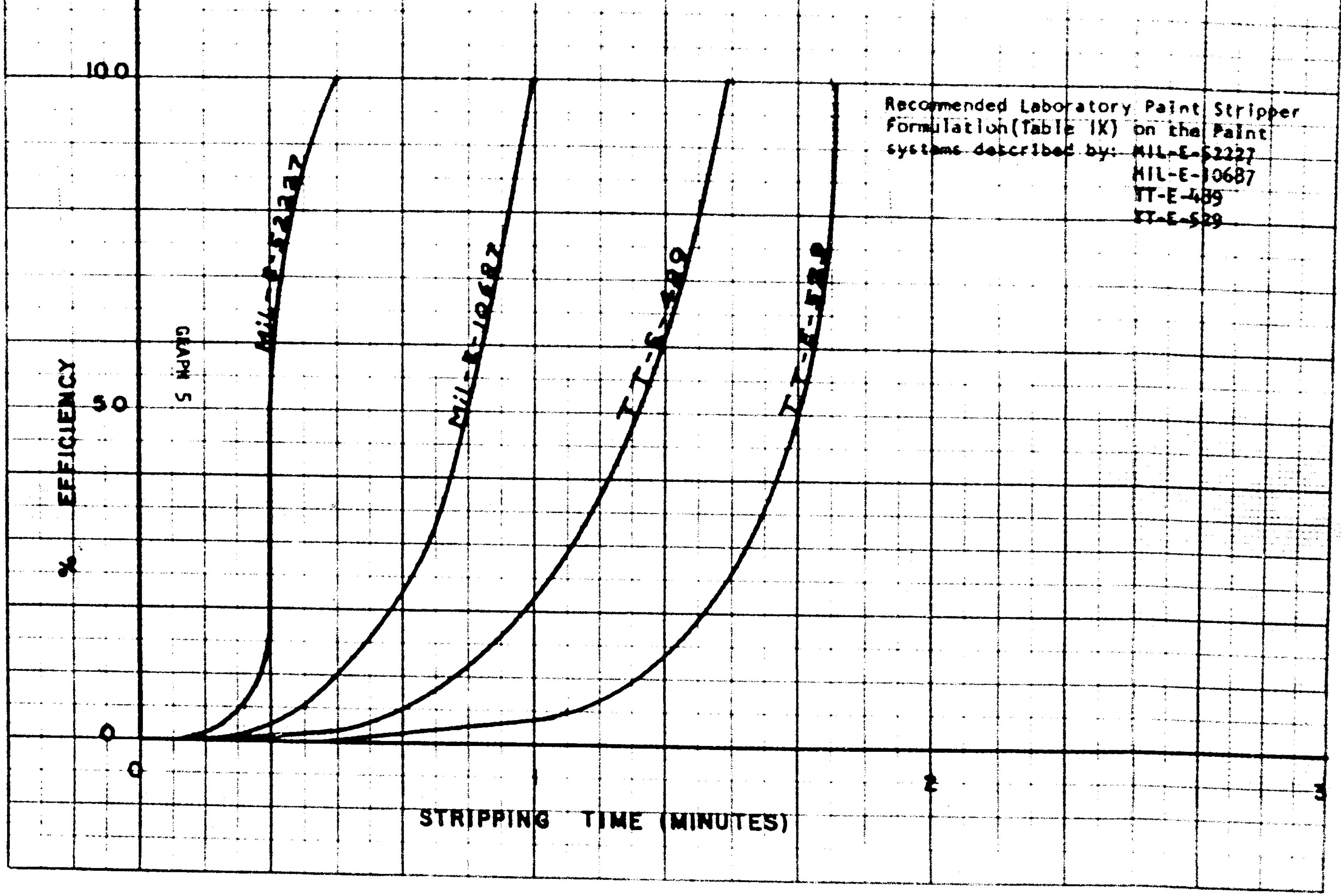
PAINT SYSTEM: Epoxy over MIL-M-45202, Type I, Class C treated magnesium.



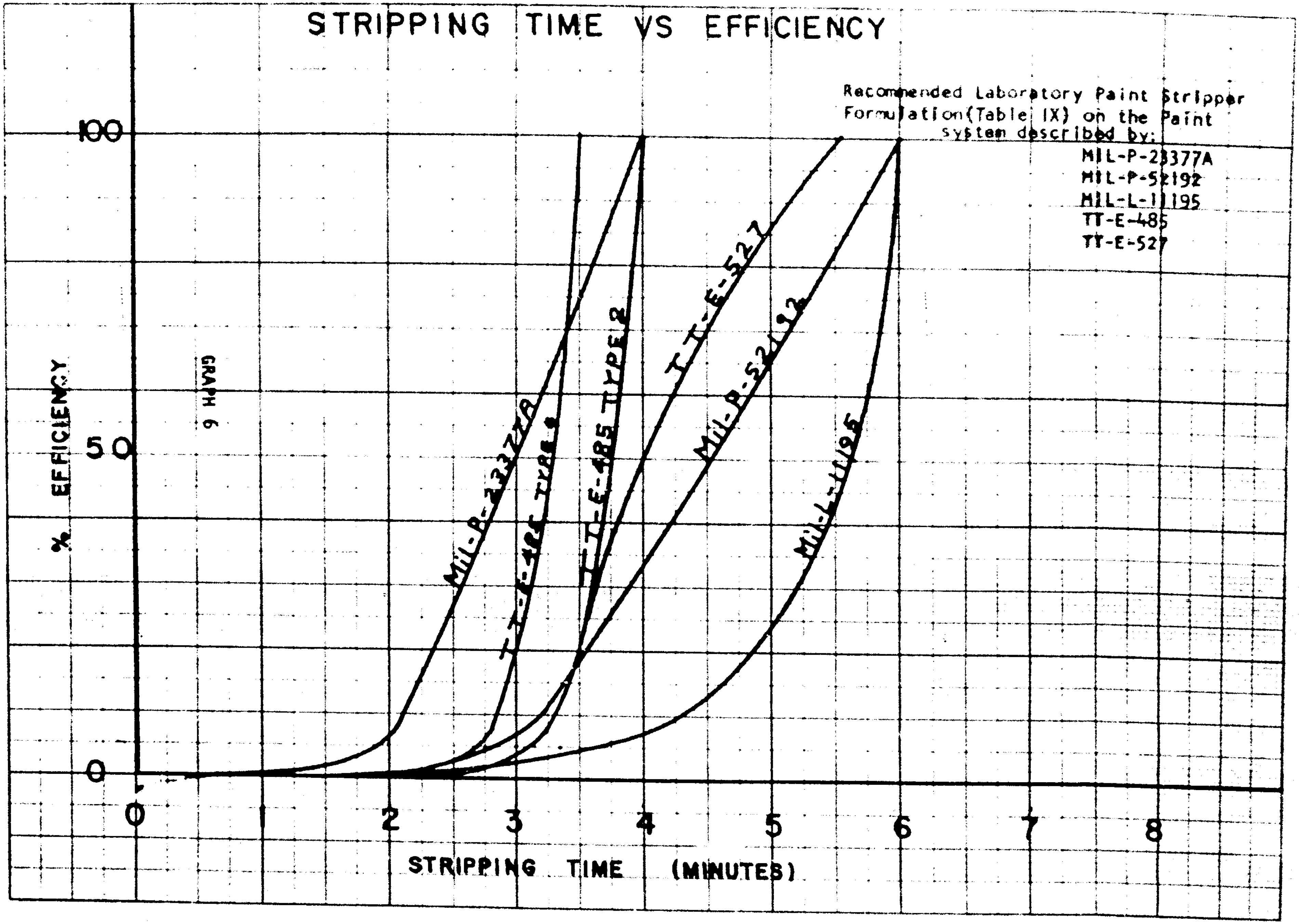
GRAPH 3

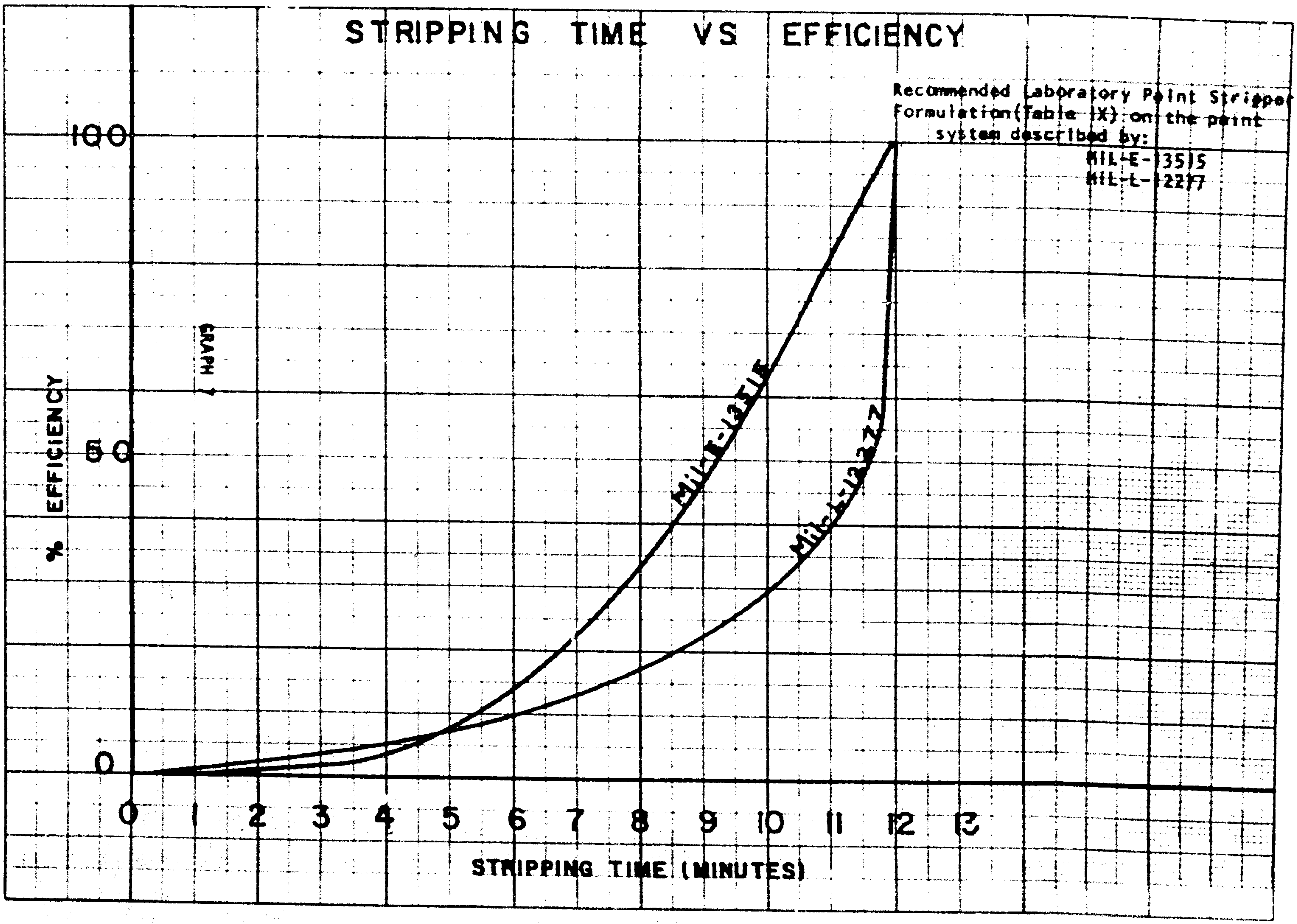

THE EFFECT ON STRIPPING TIME OF VARYING THE CONCENTRATION OF WATER
SOLVENT SYSTEM (SS): Dodecylbenzene sulfonic acid 6.5 Wt. %
m-Cresol 12.0 Wt. %
90% Formic Acid 8.0 Wt. %
Methylene chloride 73.5 Wt. %
VARIABLE PARAMETER: Water (W)
PAINT SYSTEM: Epoxy over MIL-M-45202, Type I, Class C treated magnesium
GRAPH 4
STRIPPING TIME REQUIRED TO REACH 100 % EFFICIENCY (MINUTES)
28
25
20
15
10
4
0 100
5 95
10 90
15 85
20 80
25 75
30 70
35 65
40 (W) 60 (S)
CONCENTRATION (WT %)

STRIPPING TIME VS EFFICIENCY

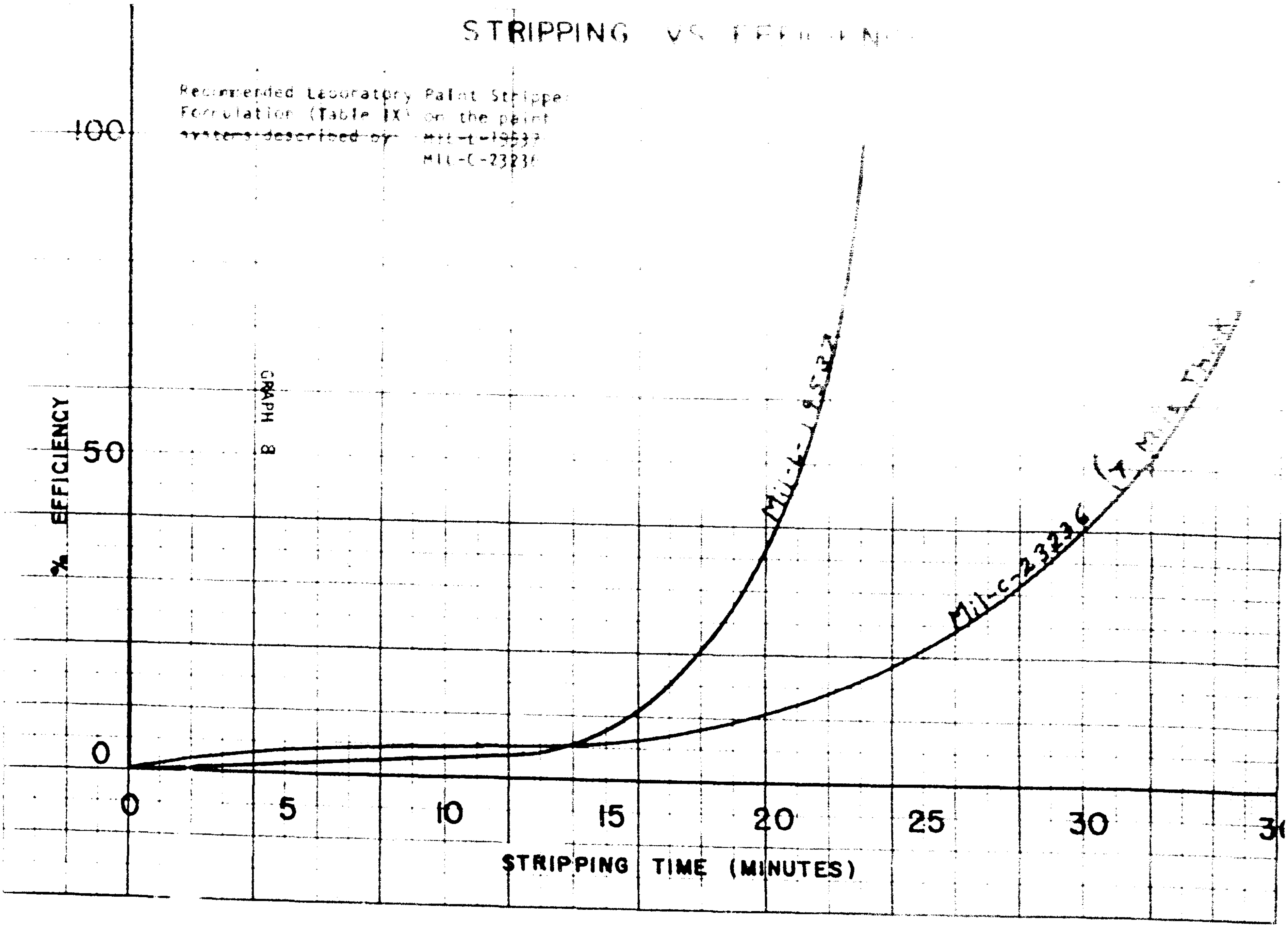


GRAPH 5


STRIPPING TIME VS EFFICIENCY
Recommended Laboratory Paint Stripper Formulation (Table IX) on the Paint System described by:
MIL-P-23377A
MIL-P-52192
MIL-L-11195
TT-E-485
TT-E-527
GRAPH 6
% EFFICIENCY
100
50
0
0
1
2
3
4
5
6
7
8
STRIPPING TIME (MINUTES)
Mil-P-23377A
TT-E-485 TYPE 1
TT-E-485 TYPE 2
TT-E-527
Mil-P-52192
Mil-L-11195



STRIPPING TIME VS EFFICIENCY
Recommended Laboratory Paint Stripper Formulation (Table IX) on the paint system described by:
MIL-E-13515
MIL-L-12277
100
50
0
% EFFICIENCY
GRAPH 7
MIL-E-13515
MIL-L-12277
0 1 2 3 4 5 6 7 8 9 10 11 12 13
STRIPPING TIME (MINUTES)


STRIPPING VS
Recommended Laboratory Paint Stripper
Formulation (Table IX) on the paint
systems described by
MIL-C-23236
GRAPH 8
100
50
0
% EFFICIENCY
0
5
10
15
20
25
30
STRIPPING TIME (MINUTES)
Mil-C-23236