QUANTITATION OF BURIED CONTAMINATION BY USE OF SOLVENTS

Semi-Annual Report

for

Jan. 1, 1973 through June 30, 1973

Supported by

NASA Grant NGR 35-001-012
Supplement No. 2

Submitted to the

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

by the

Department of Polymers and Coatings
North Dakota State University
Fargo, North Dakota 58102

Investigators: S. Peter Pappas, Paul Hsiao, and Loren W. Hill

Introduction

The objectives of the overall project are (1) to develop nonsporicidal methods for solvent degradation of cured polymeric resins that are used in spacecraft, and (2) to determine whether reaction conditions during resin cure cause decontamination of the component that is being fabricated. The previous reports described (1) the application of solubility parameter methods to the degradation of amine cured epoxy resins,[1] (2) the solubilization of cured silicone resins in amine solvents,[2] (3) spore viability studies on exposure to amine solvents, which demonstrated that reduced viability reflected a sporostatic effect which could be eliminated by removing the amine solvent during the plating process[2] or by utilizing higher dilution techniques,[3] and (4) recovery studies on a silicone potting compound (RTV 41) that is used in spacecraft, which demonstrated that (a) spores remain viable during chemical cure of this potting compound, and (b) greater than 90% of the spore population is recoverable by amine dissolution and proper plating techniques.[3] Thus, the results to date directly relate to our objectives. That is, we have developed a nonsporocidal method with which high spore recoveries are achievable from silicone coatings and potting compounds, and (2) we have demonstrated that spores remain viable during cure of a silicone potting compound. The present report describes an extension of these studies to silicone potting compound RTV 60, as well as our attempts to provide a sound statistical

basis for the results by extensive sampling. In addition, we report the results of our studies on viscosity changes following amine solubilization of various silicones, as well as cross-linking density changes following evaporation of amine solvents. Such studies have provided both mechanistic and practical information about the amine solubilization phenomenon.

Results and Discussion

As noted in the previous report, extension of the viability studies to cured silicone potting compounds required the use of an organic solvent for dilution. The cured silicone rubber was dissolved in n-butylamine and recovery was determined by the plate counting technique with series dilution in benzene. Of course, it was not possible to dilute the butylamine-silicone rubber solution with water because the silicone precipitated. Benzene was selected because it has been reported to be less toxic to spores than many other organic solvents[4] and because it is a good solvent for the silicone rubbers. The use of benzene for series dilution necessitated control experiments in the absence of silicone rubber or curing agents. The results of spore viability studies on (1) exposure to n-butylamine followed by dilution with water or benzene, (2) exposure to water followed by dilution with water, and (3) exposure to benzene followed by dilution with benzene are presented in Table 1. The data is plotted in Figure 1 as log of mean spore counts *versus* days of exposure. The numbers in the table and the points on the graph

represent the mean of colony counts from 20 plates, derived from 4 duplicates of 5 samples. The most salient feature is the surprisingly high and stable recovery on exposure to n-butylamine followed by dilution with benzene. These results are currently under investigation both at NDSU and the University of Minnesota under Dr. Pflug's direction.

The results of studies on spore recovery from inoculated silicone potting compound RTV 60 following curing, dissolution in n-butylamine, and series dilution with benzene are presented in Table II. As previously determined for RTV 41, the data illustrate that (1) decontamination does not occur on curing, and (2) the method is effective for spore recovery.

The results of viscosity studies on n-butylamine solutions of silicone oil (DC 200), silicone prepolymer (DC 840), and cured silicone polymer (cured DC 840) are provided in Figure II. Only in the case of the cured DC 840 solution does a substantial decrease in viscosity occur with time which levels off at the viscosity of the prepolymer. These results indicate that the cured resin is degraded and suggest that cleavage occurs primarily at the centers at which cross-linking takes place in the curing process. Based on the mechanism for amine solubilization presented in an earlier report (see p. 8, scheme II of ref. 2), it was anticipated that a significant number of these cross-linking sites would reform on evaporation of the amine solvent. In support of this hypothesis, it was determined by extraction techniques that 70% of the original cross-linked

sites were regenerated when the amine was removed under vacuum at room temperature. These findings have suggested exciting new possibilities for (1) the recovery of silicone molds and, (2) the silicone coating of heat-sensitive materials. A report describing these findings has been submitted for patent consideration to the appropriate NASA office (Mr. J. Warden, Code GP).

References

1. A. E. Rheineck and R. A. Heskin, "Quantitation of Buried Contamination by the Use of Solvents", First Interim Report, Part I, NASA Grant No. NGR-001-012, February, 1972.

2. S. P. Pappas, P. Hsiao, and L. W. Hill, "Quantitation of Buried Contamination by the Use of Solvents", Semi-Annual report, NASA Grant No. NGR-001-012, January 1 to June 30, 1972.

3. Idem, July 1 to December 31, 1972.

4. "Microbial Cell Recovery from Solid Materials", Final Summary Report, NASA Contract No. 950740, The Jet Propulsion Laboratory, Pasadena, Calif., May, 1968, p. 88.

Table I No. of colony counts of *Bacillus subtilis* spores after exposure to solvents and diluents for varying periods of days.

Mean* \ Treatment	Exposed to *n*-butylamine & diluted with		Exposed to Water & dil.	Exposed to Benzene & dil.
Days	Benzene	Water	with Water	with Benzene
0	205.0 (2.3118)**	94.20 (1.9714)	147.17 (2.1679)	12.83 (1.1082)
1	251.95 (2.4010)	45.30 (1.6561)	84.50 (1.9269)	10.33 (1.0139)
2	252.40 (2.4021)	45.20 (1.6551)	60.75 (1.7836)	12.50 (1.0969)
3	252.40 (2.4021)	31.45 (1.4976)	50.75 (1.6996)	6.83 (0.7841)
4	217.75 (2.3375)	23.65 (1.3738)	37.83 (1.5777)	3.03 (0.4836)
5	202.25 (2.3060)	32.05 (1.5058)		
6	213.10 (2.3286)	13.80 (1.1399)		
7	193.15 (2.2860)	10.95 (1.0039)		

* Means of the No. of colony counted from 20 plates (five samples, each sample has four dublicate)

**Common logarithm of the means of the number of colony counted

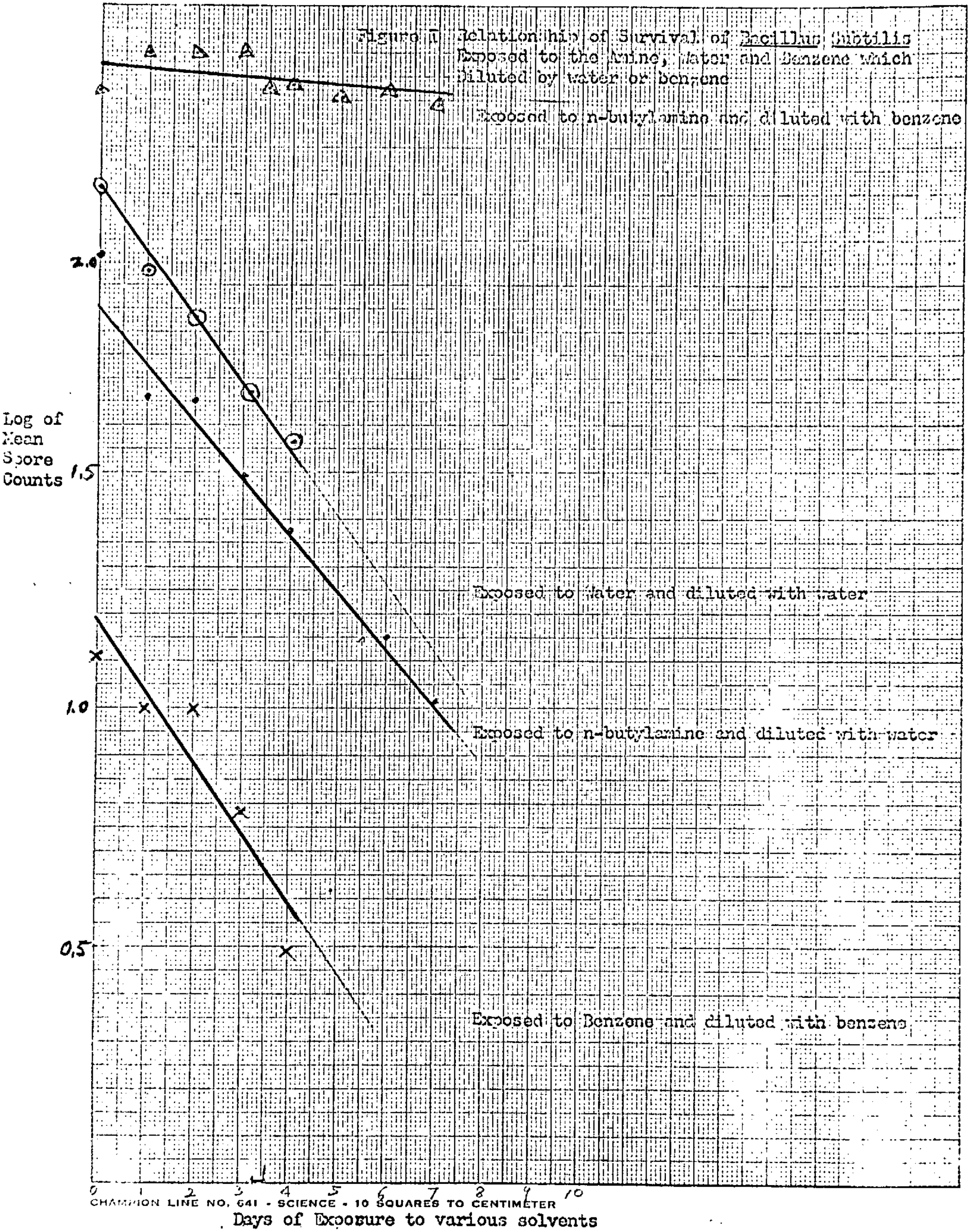


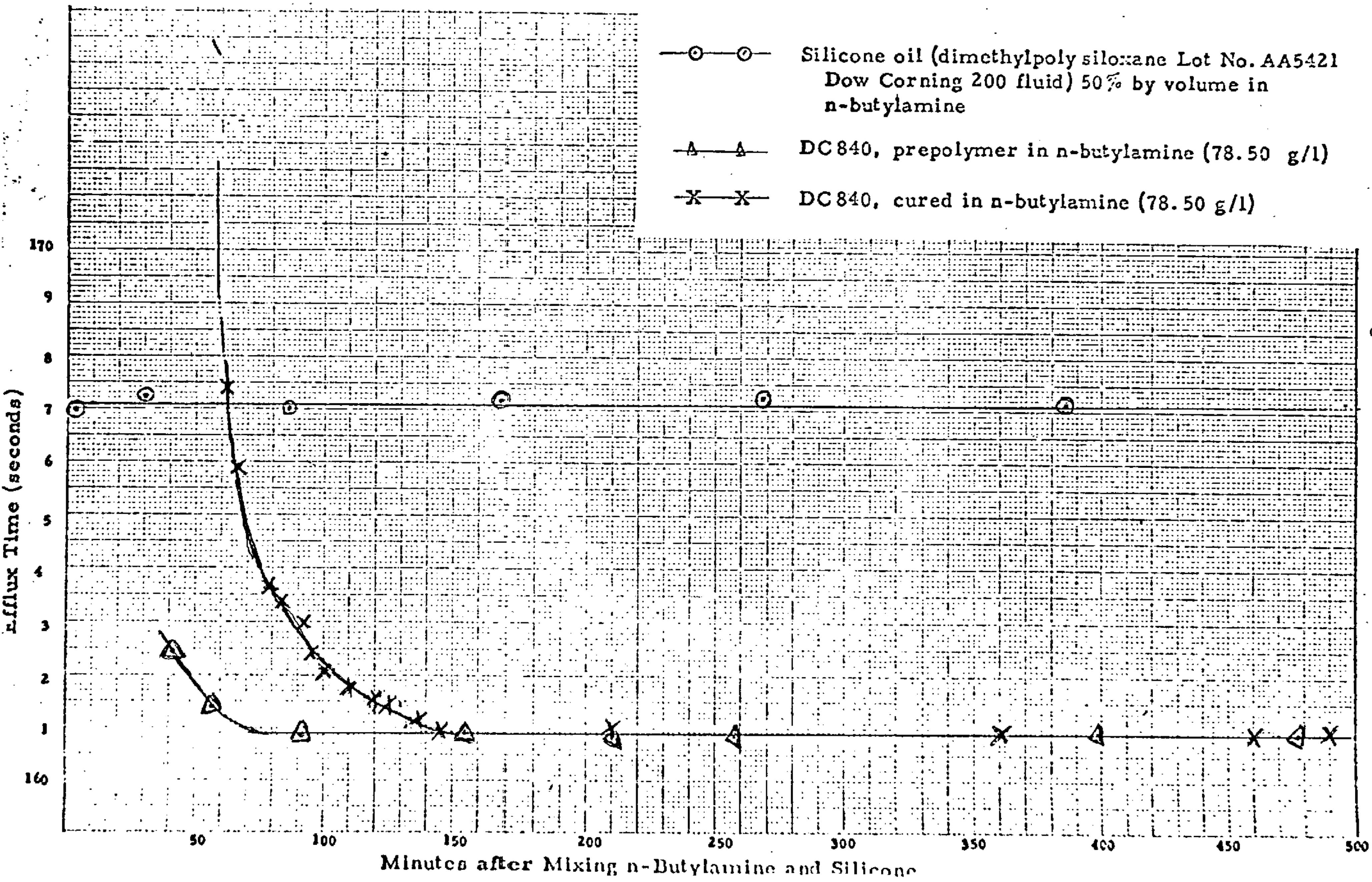
Figure II Relationship of Survival of Bacillus Subtilis Exposed to the Amine, Water and Benzene Which Diluted by water or benzene

Table II Colony Counts Obtained from n-Butylamine Solution of Inoculated Silicone Potting Compound, RTV 60, Using Series Dilution in Benzene; Dilution Factor = 10^6

Experiment Number	Time*	Number of Colonies				Average
I	0	288	290	286	278	285.5
	1	327	288	259	283	281.3
	2	264	277	245	251	259.3
	3	256	268	248	261	258.9
	4	267	274	254	248	260.8
	7	245	256	238	251	247.5
	10	276	245	221	242	246.0
II	0	280	281	276	310	286.8
	1	277	265	281	288	278.0
	2	287	284	276	310	289.3
	3	292	287	281	254	278.5
	4	269	286	263	246	266.0
	7	246	255	231	258	247.4
	10	247	257	251	258	253.3
III (control)	0 to 10	no colony was observed				

* days

Figure 11 Variation in Viscosity with Time for a Silicone Oil, a Silicone Prepolymer (DC 840), and a Cured Silicone Resin (cured DC 840) in n-Butylamine Solution. Cannon Viscometer, 50-1711 at 45°C.



QUANTITATION OF BURIED CONTAMINATION

BY USE OF SOLVENTS

Semi-Annual Report

for

Jan. 1, 1973 through June 30, 1973

Supported by

NASA Grant NGR 35-001-012
Supplement No. 2

Submitted to the

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

by the

Department of Polymers and Coatings
North Dakota State University
Fargo, North Dakota 58102

Investigators: S. Peter Pappas, Paul Hsiao, and Loren W. Hill

Introduction

The objectives of the overall project are (1) to develop nonsporicidal methods for solvent degradation of cured polymeric resins that are used in spacecraft, and (2) to determine whether reaction conditions during resin cure cause decontamination of the component that is being fabricated. The previous reports described (1) the application of solubility parameter methods to the degradation of amine cured epoxy resins,[1] (2) the solubilization of cured silicone resins in amine solvents,[2] (3) spore viability studies on exposure to amine solvents, which demonstrated that reduced viability reflected a sporostatic effect which could be eliminated by removing the amine solvent during the plating process[2] or by utilizing higher dilution techniques,[3] and (4) recovery studies on a silicone potting compound (RTV 41) that is used in spacecraft, which demonstrated that (a) spores remain viable during chemical cure of this potting compound, and (b) greater than 90% of the spore population is recoverable by amine dissolution and proper plating techniques.[3] Thus, the results to date directly relate to our objectives. That is, we have developed a nonsporocidal method with which high spore recoveries are achievable from silicone coatings and potting compounds, and (2) we have demonstrated that spores remain viable during cure of a silicone potting compound. The present report describes an extension of these studies to silicone potting compound RTV 60, as well as our attempts to provide a sound statistical

basis for the results by extensive sampling. In addition, we report the results of our studies on viscosity changes following amine solubilization of various silicones, as well as cross-linking density changes following evaporation of amine solvents. Such studies have provided both mechanistic and practical information about the amine solubilization phenomenon.

Results and Discussion

As noted in the previous report, extension of the viability studies to cured silicone potting compounds required the use of an organic solvent for dilution. The cured silicone rubber was dissolved in n-butylamine and recovery was determined by the plate counting technique with series dilution in benzene. Of course, it was not possible to dilute the butylamine-silicone rubber solution with water because the silicone precipitated. Benzene was selected because it has been reported to be less toxic to spores than many other organic solvents[4] and because it is a good solvent for the silicone rubbers. The use of benzene for series dilution necessitated control experiments in the absence of silicone rubber or curing agents. The results of spore viability studies on (1) exposure to n-butylamine followed by dilution with water or benzene, (2) exposure to water followed by dilution with water, and (3) exposure to benzene followed by dilution with benzene are presented in Table 1. The data is plotted in Figure 1 as log of mean spore counts *versus* days of exposure. The numbers in the table and the points on the graph

represent the mean of colony counts from 20 plates, derived from 4 duplicates of 5 samples. The most salient feature is the surprisingly high and stable recovery on exposure to n-butylamine followed by dilution with benzene. These results are currently under investigation both at NDSU and the University of Minnesota under Dr. Pflug's direction.

The results of studies on spore recovery from inoculated silicone potting compound RTV 60 following curing, dissolution in n-butylamine, and series dilution with benzene are presented in Table II. As previously determined for RTV 41, the data illustrate that (1) decontamination does not occur on curing, and (2) the method is effective for spore recovery.

The results of viscosity studies on n-butylamine solutions of silicone oil (DC 200), silicone prepolymer (DC 840), and cured silicone polymer (cured DC 840) are provided in Figure II. Only in the case of the cured DC 840 solution does a substantial decrease in viscosity occur with time which levels off at the viscosity of the prepolymer. These results indicate that the cured resin is degraded and suggest that cleavage occurs primarily at the centers at which cross-linking takes place in the curing process. Based on the mechanism for amine solubilization presented in an earlier report (see p. 8, scheme II of ref. 2), it was anticipated that a significant number of these cross-linking sites would reform on evaporation of the amine solvent. In support of this hypothesis, it was determined by extraction techniques that 70% of the original cross-linked

sites were regenerated when the amine was removed under vacuum at room temperature. These findings have suggested exciting new possibilities for (1) the recovery of silicone molds and, (2) the silicone coating of heat-sensitive materials. A report describing these findings has been submitted for patent consideration to the appropriate NASA office (Mr. J. Warden, Code GP).

References

1. A. E. Rheineck and R. A. Heskin, "Quantitation of Buried Contamination by the Use of Solvents", First Interim Report, Part I, NASA Grant No. NGR-001-012, February, 1972.

2. S. P. Pappas, P. Hsiao, and L. W. Hill, "Quantitation of Buried Contamination by the Use of Solvents", Semi-Annual report, NASA Grant No. NGR-001-012, January 1 to June 30, 1972.

3. Idem, July 1 to December 31, 1972.

4. "Microbial Cell Recovery from Solid Materials", Final Summary Report, NASA Contract No. 950740, The Jet Propulsion Laboratory, Pasadena, Calif., May, 1968, p. 88.

Table I No. of colony counts of Bacillus subtilis spores after exposure to solvents and diluents for varying periods of days.

Treatment / Mean* / Days	Exposed to n-butylamine & diluted with: Benzene	Exposed to n-butylamine & diluted with: Water	Exposed to Water & dil. with Water	Exposed to Benzene & dil. with Benzene
0	205.0 (2.3118)**	94.20 (1.9714)	147.17 (2.1679)	12.83 (1.1082)
1	251.95 (2.4010)	45.30 (1.6561)	84.50 (1.9269)	10.33 (1.0139)
2	252.40 (2.4021)	45.20 (1.6551)	60.75 (1.7836)	12.50 (1.0969)
3	252.40 (2.4021)	31.45 (1.4976)	50.75 (1.6996)	6.83 (0.7841)
4	217.75 (2.3375)	23.65 (1.3738)	37.83 (1.5777)	3.03 (0.4836)
5	202.25 (2.3060)	32.05 (1.5058)		
6	213.10 (2.3286)	13.80 (1.1399)		
7	193.15 (2.2860)	10.95 (1.0039)		

* Means of the No. of colony counted from 20 plates (five samples, each sample has four dublicate)

**Common logarithm of the means of the number of colony counted

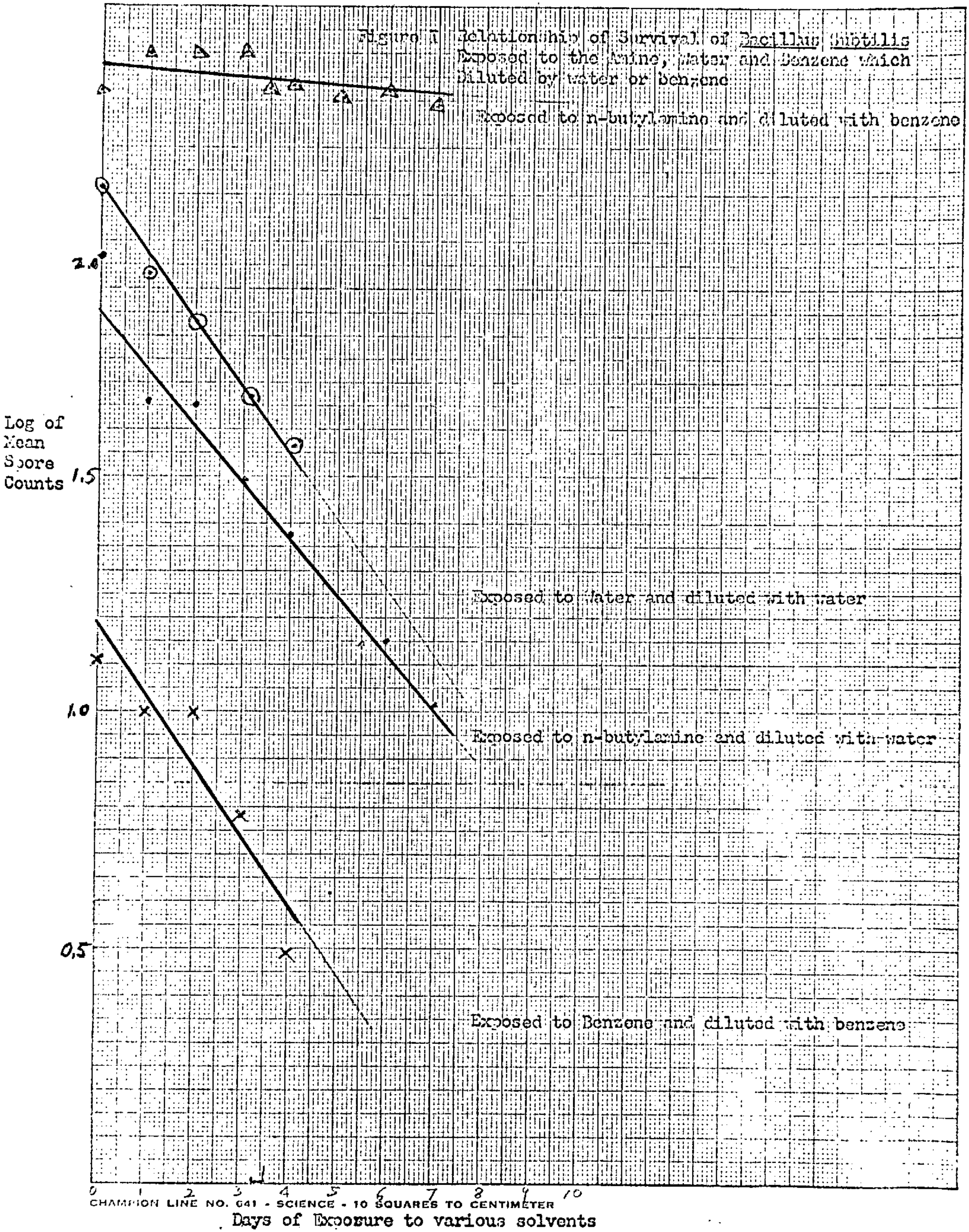


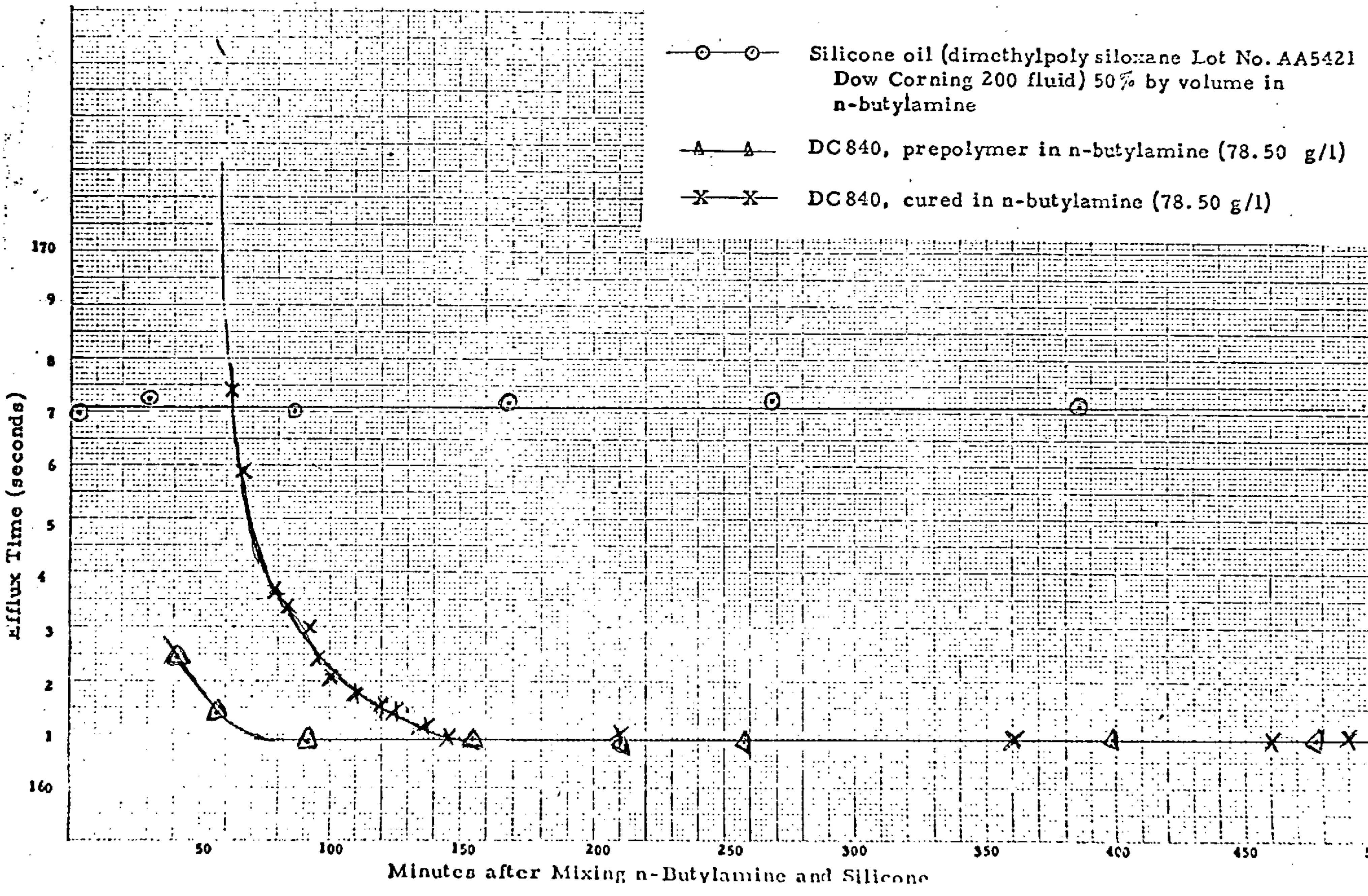
Figure I Relationship of Survival of Bacillus Subtilis
Exposed to the Amine, Water and Benzene which
Diluted by water or benzene
Exposed to n-butylamine and diluted with benzene
Exposed to Water and diluted with water
Exposed to n-butylamine and diluted with water
Exposed to Benzene and diluted with benzene
Log of Mean Spore Counts
2.0
1.5
1.0
0.5
0
1
2
3
4
5
6
7
8
9
10
CHAMPION LINE NO. 641 - SCIENCE - 10 SQUARES TO CENTIMETER
Days of Exposure to various solvents

Table II Colony Counts Obtained from n-Butylamine Solution of Inoculated Silicone Potting Compound, RTV 60, Using Series Dilution in Benzene; Dilution Factor = 10^6

Experiment Number	Time*	Number of Colonies				Average
I	0	288	290	286	278	285.5
	1	327	288	259	283	281.3
	2	264	277	245	251	259.3
	3	256	268	248	261	258.9
	4	267	274	254	248	260.8
	7	245	256	238	251	247.5
	10	276	245	221	242	246.0
II	0	280	281	276	310	286.8
	1	277	265	281	288	278.0
	2	287	284	276	310	289.3
	3	292	287	281	254	278.5
	4	269	286	263	246	266.0
	7	246	255	231	258	247.4
	10	247	257	251	258	253.3
III (control)	0 to 10	no colony was observed				

* days

Figure 11 Variation in Viscosity with Time for a Silicone Oil, a Silicone Prepolymer (DC 840), and a Cured Silicone Resin (cured DC 840) in n-Butylamine Solution. Cannon Viscometer, 50-1711 at 45°C.



QUANTITATION OF BURIED CONTAMINATION

BY USE OF SOLVENTS

Semi-Annual Report

for

Jan. 1, 1973 through June 30, 1973

Supported by

NASA Grant NGR 35-001-012
Supplement No. 2

Submitted to the

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

by the

Department of Polymers and Coatings
North Dakota State University
Fargo, North Dakota 58102

Investigators: S. Peter Pappas, Paul Hsiao, and Loren W. Hill

Introduction

The objectives of the overall project are (1) to develop nonsporicidal methods for solvent degradation of cured polymeric resins that are used in spacecraft, and (2) to determine whether reaction conditions during resin cure cause decontamination of the component that is being fabricated. The previous reports described (1) the application of solubility parameter methods to the degradation of amine cured epoxy resins,[1] (2) the solubilization of cured silicone resins in amine solvents,[2] (3) spore viability studies on exposure to amine solvents, which demonstrated that reduced viability reflected a sporostatic effect which could be eliminated by removing the amine solvent during the plating process[2] or by utilizing higher dilution techniques,[3] and (4) recovery studies on a silicone potting compound (RTV 41) that is used in spacecraft, which demonstrated that (a) spores remain viable during chemical cure of this potting compound, and (b) greater than 90% of the spore population is recoverable by amine dissolution and proper plating techniques.[3] Thus, the results to date directly relate to our objectives. That is, we have developed a nonsporocidal method with which high spore recoveries are achievable from silicone coatings and potting compounds, and (2) we have demonstrated that spores remain viable during cure of a silicone potting compound. The present report describes an extension of these studies to silicone potting compound RTV 60, as well as our attempts to provide a sound statistical

basis for the results by extensive sampling. In addition, we report the results of our studies on viscosity changes following amine solubilization of various silicones, as well as cross-linking density changes following evaporation of amine solvents. Such studies have provided both mechanistic and practical information about the amine solubilization phenomenon.

Results and Discussion

As noted in the previous report, extension of the viability studies to cured silicone potting compounds required the use of an organic solvent for dilution. The cured silicone rubber was dissolved in n-butylamine and recovery was determined by the plate counting technique with series dilution in benzene. Of course, it was not possible to dilute the butylamine-silicone rubber solution with water because the silicone precipitated. Benzene was selected because it has been reported to be less toxic to spores than many other organic solvents[4] and because it is a good solvent for the silicone rubbers. The use of benzene for series dilution necessitated control experiments in the absence of silicone rubber or curing agents. The results of spore viability studies on (1) exposure to n-butylamine followed by dilution with water or benzene, (2) exposure to water followed by dilution with water, and (3) exposure to benzene followed by dilution with benzene are presented in Table 1. The data is plotted in Figure 1 as log of mean spore counts *versus* days of exposure. The numbers in the table and the points on the graph

represent the mean of colony counts from 20 plates, derived from 4 duplicates of 5 samples. The most salient feature is the surprisingly high and stable recovery on exposure to n-butylamine followed by dilution with benzene. These results are currently under investigation both at NDSU and the University of Minnesota under Dr. Pflug's direction.

The results of studies on spore recovery from inoculated silicone potting compound RTV 60 following curing, dissolution in n-butylamine, and series dilution with benzene are presented in Table II. As previously determined for RTV 41, the data illustrate that (1) decontamination does not occur on curing, and (2) the method is effective for spore recovery.

The results of viscosity studies on n-butylamine solutions of silicone oil (DC 200), silicone prepolymer (DC 840), and cured silicone polymer (cured DC 840) are provided in Figure II. Only in the case of the cured DC 840 solution does a substantial decrease in viscosity occur with time which levels off at the viscosity of the prepolymer. These results indicate that the cured resin is degraded and suggest that cleavage occurs primarily at the centers at which cross-linking takes place in the curing process. Based on the mechanism for amine solubilization presented in an earlier report (see p. 8, scheme II of ref. 2), it was anticipated that a significant number of these cross-linking sites would reform on evaporation of the amine solvent. In support of this hypothesis, it was determined by extraction techniques that 70% of the original cross-linked

sites were regenerated when the amine was removed under vacuum at room temperature. These findings have suggested exciting new possibilities for (1) the recovery of silicone molds and, (2) the silicone coating of heat-sensitive materials. A report describing these findings has been submitted for patent consideration to the appropriate NASA office (Mr. J. Warden, Code GP).

References

1. A. E. Rheineck and R. A. Heskin, "Quantitation of Buried Contamination by the Use of Solvents", First Interim Report, Part I, NASA Grant No. NGR-001-012, February, 1972.

2. S. P. Pappas, P. Hsiao, and L. W. Hill, "Quantitation of Buried Contamination by the Use of Solvents", Semi-Annual report, NASA Grant No. NGR-001-012, January 1 to June 30, 1972.

3. Idem, July 1 to December 31, 1972.

4. "Microbial Cell Recovery from Solid Materials", Final Summary Report, NASA Contract No. 950740, The Jet Propulsion Laboratory, Pasadena, Calif., May, 1968, p. 88.

Table I No. of colony counts of Bacillus subtilis spores after exposure to solvents and diluents for varying periods of days.

* Treatment / Mean / Days	Exposed to n-butylamine & diluted with Benzene	Exposed to n-butylamine & diluted with Water	Exposed to Water & dil. with Water	Exposed to Benzene & dil. with Benzene
0	205.0 (2.3118)**	94.20 (1.9714)	147.17 (2.1679)	12.83 (1.1082)
1	251.95 (2.4010)	45.30 (1.6561)	84.50 (1.9269)	10.33 (1.0139)
2	252.40 (2.4021)	45.20 (1.6551)	60.75 (1.7836)	12.50 (1.0969)
3	252.40 (2.4021)	31.45 (1.4976)	50.75 (1.6996)	6.83 (0.7841)
4	217.75 (2.3375)	23.65 (1.3738)	37.83 (1.5777)	3.03 (0.4836)
5	202.25 (2.3060)	32.05 (1.5058)		
6	213.10 (2.3286)	13.80 (1.1399)		
7	193.15 (2.2860)	10.95 (1.0039)		

* Means of the No. of colony counted from 20 plates (five samples, each sample has four dublicate)

**Common logarithm of the means of the number of colony counted

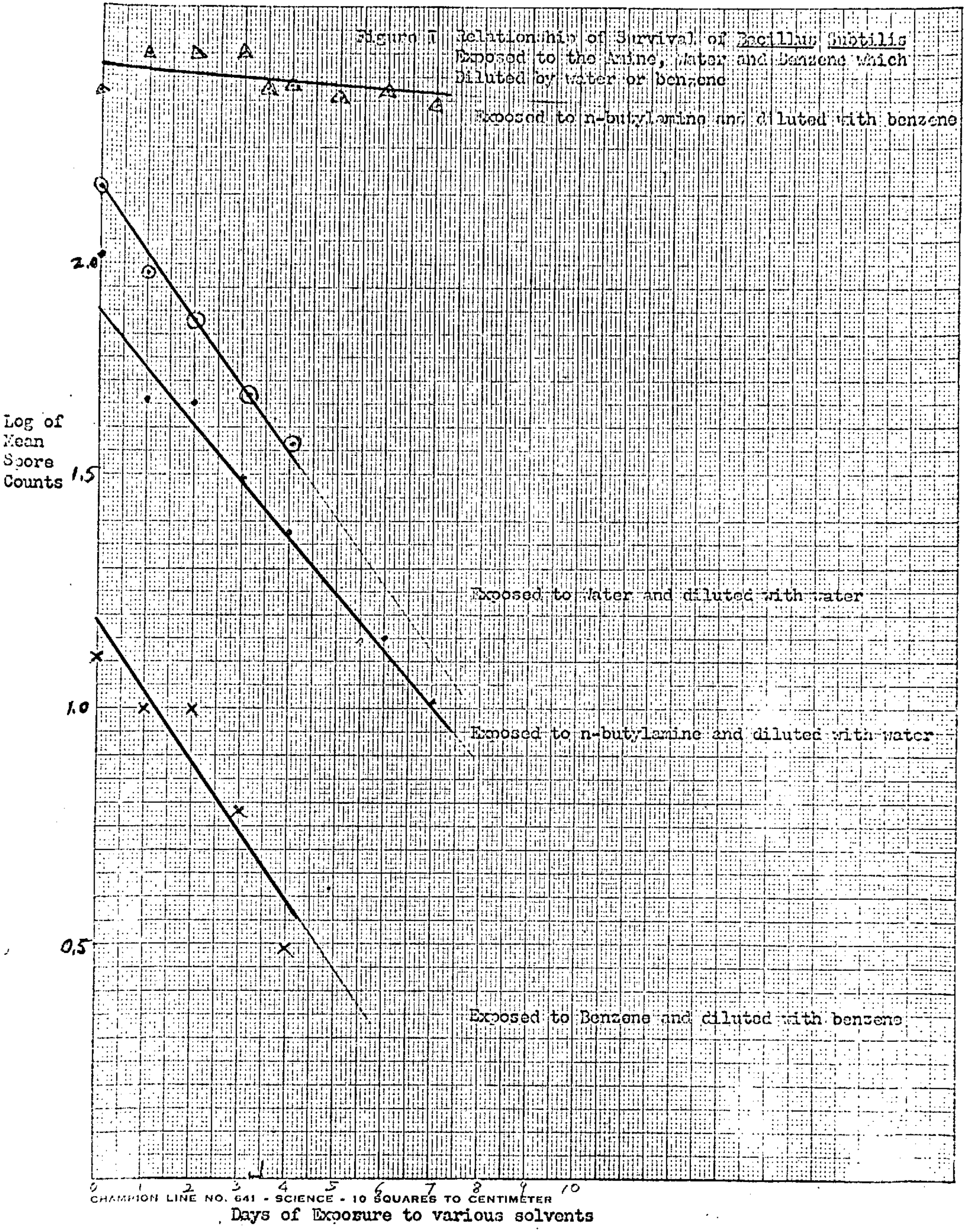


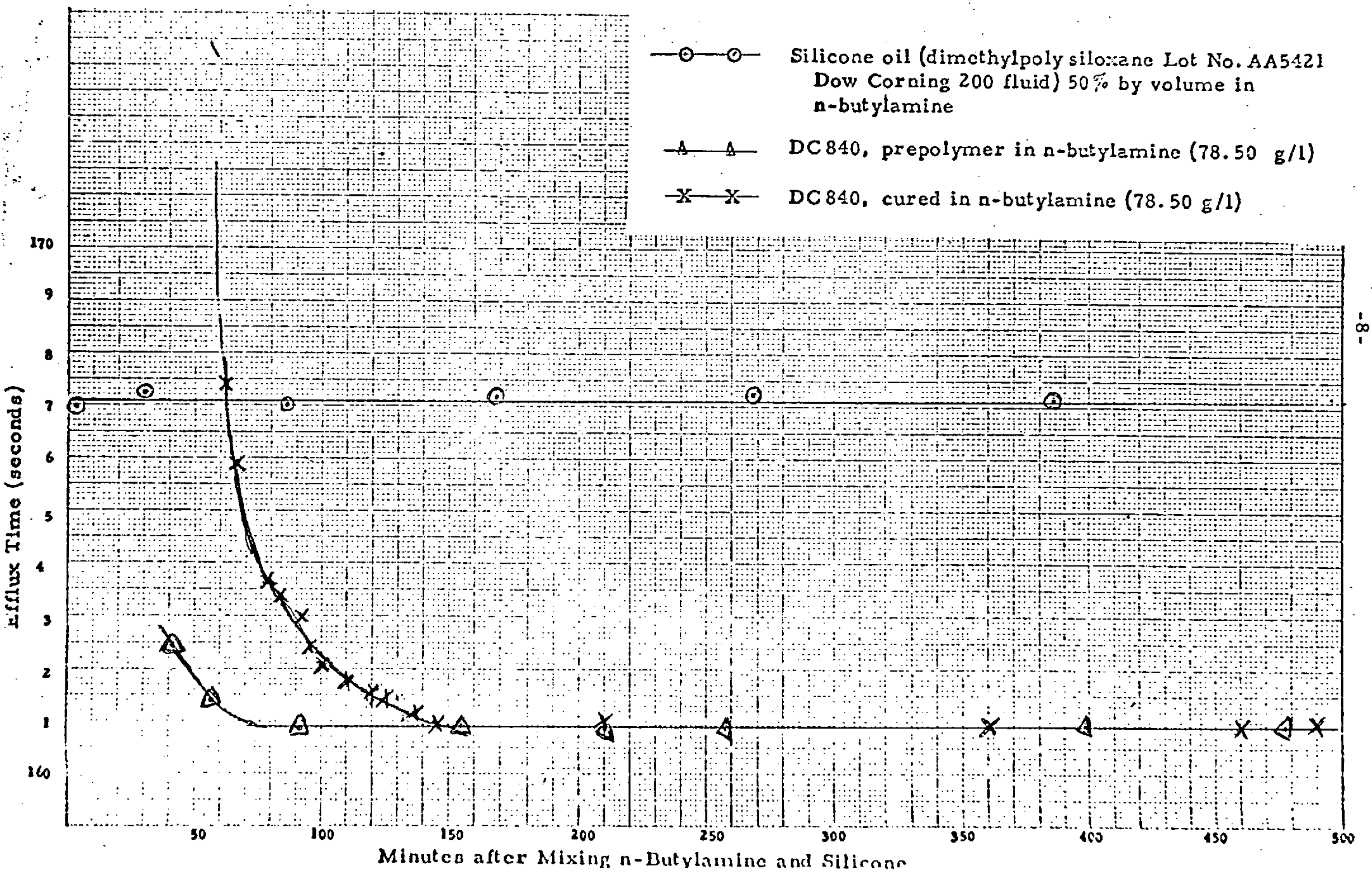
Figure I Relationship of Survival of *Bacillus Subtilis* Exposed to the Amine, Water and Benzene which Diluted by water or benzene

Table II Colony Counts Obtained from n-Butylamine Solution of Inoculated Silicone Potting Compound, RTV 60, Using Series Dilution in Benzene; Dilution Factor = 10^6

Experiment Number	Time*	Number of Colonies				Average
I	0	288	290	286	278	285.5
	1	327	288	259	283	281.3
	2	264	277	245	251	259.3
	3	256	268	248	261	258.9
	4	267	274	254	248	260.8
	7	245	256	238	251	247.5
	10	276	245	221	242	246.0
II	0	280	281	276	310	286.8
	1	277	265	281	288	278.0
	2	287	284	276	310	289.3
	3	292	287	281	254	278.5
	4	269	286	263	246	266.0
	7	246	255	231	258	247.4
	10	247	257	251	258	253.3
III (control)	0 to 10	no colony was observed				

* days

Figure 11 Variation in Viscosity with Time for a Silicone Oil, a Silicone Prepolymer (DC 840), and a Cured Silicone Resin (cured DC 840) in n-Butylamine Solution. Cannon Viscometer, 50-1711 at 45°C.



QUANTITATION OF BURIED CONTAMINATION

BY USE OF SOLVENTS

Semi-Annual Report

for

Jan. 1, 1973 through June 30, 1973

Supported by

NASA Grant NGR 35-001-012
Supplement No. 2

Submitted to the

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

by the

Department of Polymers and Coatings
North Dakota State University
Fargo, North Dakota 58102

Investigators: S. Peter Pappas, Paul Hsiao, and Loren W. Hill

Introduction

The objectives of the overall project are (1) to develop nonsporicidal methods for solvent degradation of cured polymeric resins that are used in spacecraft, and (2) to determine whether reaction conditions during resin cure cause decontamination of the component that is being fabricated. The previous reports described (1) the application of solubility parameter methods to the degradation of amine cured epoxy resins,[1] (2) the solubilization of cured silicone resins in amine solvents,[2] (3) spore viability studies on exposure to amine solvents, which demonstrated that reduced viability reflected a sporostatic effect which could be eliminated by removing the amine solvent during the plating process[2] or by utilizing higher dilution techniques,[3] and (4) recovery studies on a silicone potting compound (RTV 41) that is used in spacecraft, which demonstrated that (a) spores remain viable during chemical cure of this potting compound, and (b) greater than 90% of the spore population is recoverable by amine dissolution and proper plating techniques.[3] Thus, the results to date directly relate to our objectives. That is, we have developed a nonsporocidal method with which high spore recoveries are achievable from silicone coatings and potting compounds, and (2) we have demonstrated that spores remain viable during cure of a silicone potting compound. The present report describes an extension of these studies to silicone potting compound RTV 60, as well as our attempts to provide a sound statistical

basis for the results by extensive sampling. In addition, we report the results of our studies on viscosity changes following amine solubilization of various silicones, as well as cross-linking density changes following evaporation of amine solvents. Such studies have provided both mechanistic and practical information about the amine solubilization phenomenon.

Results and Discussion

As noted in the previous report, extension of the viability studies to cured silicone potting compounds required the use of an organic solvent for dilution. The cured silicone rubber was dissolved in n-butylamine and recovery was determined by the plate counting technique with series dilution in benzene. Of course, it was not possible to dilute the butylamine-silicone rubber solution with water because the silicone precipitated. Benzene was selected because it has been reported to be less toxic to spores than many other organic solvents[4] and because it is a good solvent for the silicone rubbers. The use of benzene for series dilution necessitated control experiments in the absence of silicone rubber or curing agents. The results of spore viability studies on (1) exposure to n-butylamine followed by dilution with water or benzene, (2) exposure to water followed by dilution with water, and (3) exposure to benzene followed by dilution with benzene are presented in Table 1. The data is plotted in Figure 1 as log of mean spore counts *versus* days of exposure. The numbers in the table and the points on the graph

represent the mean of colony counts from 20 plates, derived from 4 duplicates of 5 samples. The most salient feature is the surprisingly high and stable recovery on exposure to n-butylamine followed by dilution with benzene. These results are currently under investigation both at NDSU and the University of Minnesota under Dr. Pflug's direction.

The results of studies on spore recovery from inoculated silicone potting compound RTV 60 following curing, dissolution in n-butylamine, and series dilution with benzene are presented in Table II. As previously determined for RTV 41, the data illustrate that (1) decontamination does not occur on curing, and (2) the method is effective for spore recovery.

The results of viscosity studies on n-butylamine solutions of silicone oil (DC 200), silicone prepolymer (DC 840), and cured silicone polymer (cured DC 840) are provided in Figure II. Only in the case of the cured DC 840 solution does a substantial decrease in viscosity occur with time which levels off at the viscosity of the prepolymer. These results indicate that the cured resin is degraded and suggest that cleavage occurs primarily at the centers at which cross-linking takes place in the curing process. Based on the mechanism for amine solubilization presented in an earlier report (see p. 8, scheme II of ref. 2), it was anticipated that a significant number of these cross-linking sites would reform on evaporation of the amine solvent. In support of this hypothesis, it was determined by extraction techniques that 70% of the original cross-linked

sites were regenerated when the amine was removed under vacuum at room temperature. These findings have suggested exciting new possibilities for (1) the recovery of silicone molds and, (2) the silicone coating of heat-sensitive materials. A report describing these findings has been submitted for patent consideration to the appropriate NASA office (Mr. J. Warden, Code GP).

References

1. A. E. Rheineck and R. A. Heskin, "Quantitation of Buried Contamination by the Use of Solvents", First Interim Report, Part I, NASA Grant No. NGR-001-012, February, 1972.

2. S. P. Pappas, P. Hsiao, and L. W. Hill, "Quantitation of Buried Contamination by the Use of Solvents", Semi-Annual report, NASA Grant No. NGR-001-012, January 1 to June 30, 1972.

3. Idem, July 1 to December 31, 1972.

4. "Microbial Cell Recovery from Solid Materials", Final Summary Report, NASA Contract No. 950740, The Jet Propulsion Laboratory, Pasadena, Calif., May, 1968, p. 88.

Table I No. of colony counts of Bacillus subtilis spores after exposure to solvents and diluents for varying periods of days.

Treatment / Mean* / Days	Exposed to n-butylamine & diluted with Benzene	Exposed to n-butylamine & diluted with Water	Exposed to Water & dil. with Water	Exposed to Benzene & dil. with Benzene
0	205.0 (2.3118)**	94.20 (1.9714)	147.17 (2.1679)	12.83 (1.1082)
1	251.95 (2.4010)	45.30 (1.6561)	84.50 (1.9269)	10.33 (1.0139)
2	252.40 (2.4021)	45.20 (1.6551)	60.75 (1.7836)	12.50 (1.0969)
3	252.40 (2.4021)	31.45 (1.4976)	50.75 (1.6996)	6.83 (0.7841)
4	217.75 (2.3375)	23.65 (1.3738)	37.83 (1.5777)	3.03 (0.4836)
5	202.25 (2.3060)	32.05 (1.5058)		
6	213.10 (2.3286)	13.80 (1.1399)		
7	193.15 (2.2860)	10.95 (1.0039)		

* Means of the No. of colony counted from 20 plates (five samples, each sample has four dublicate)

**Common logarithm of the means of the number of colony counted

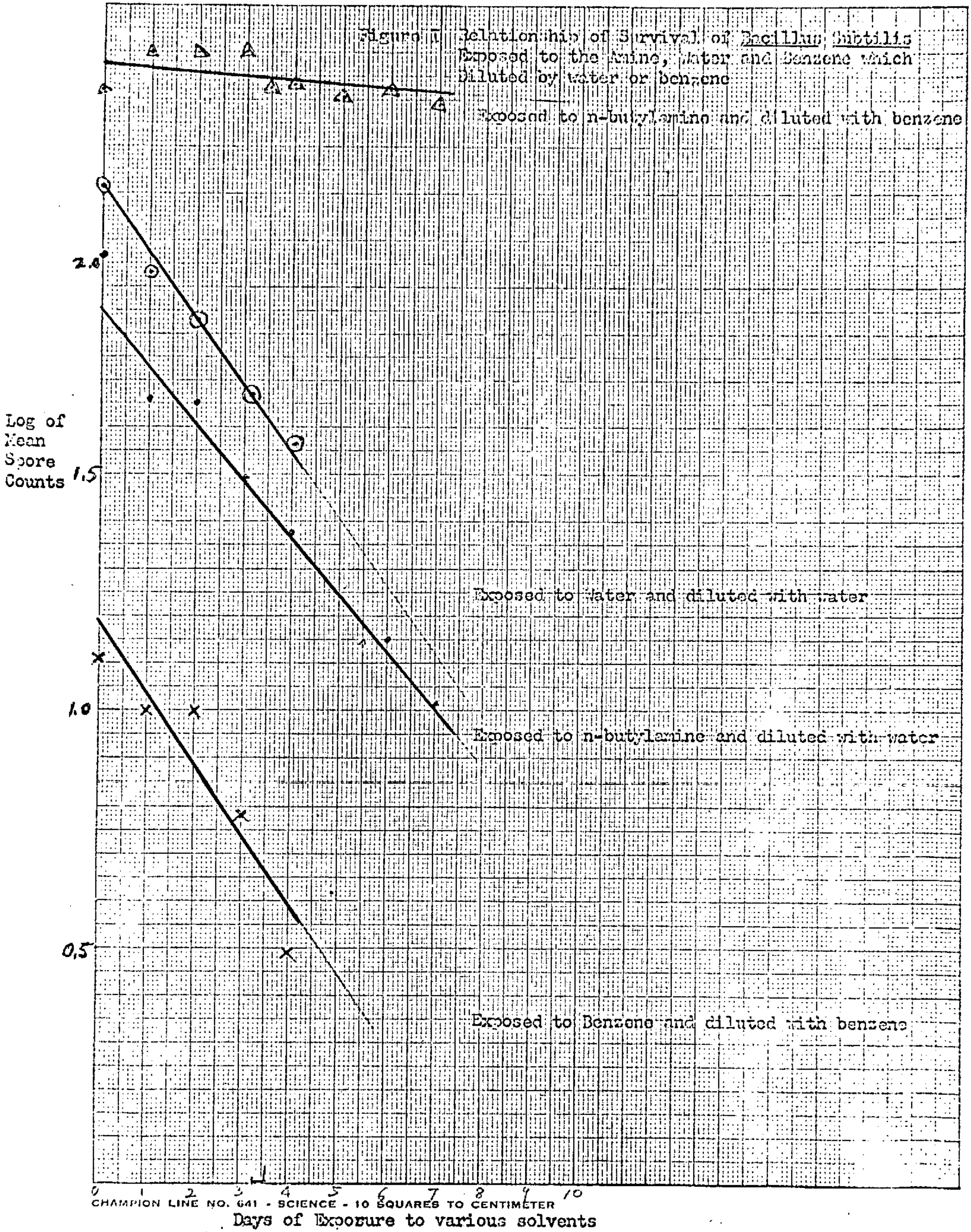


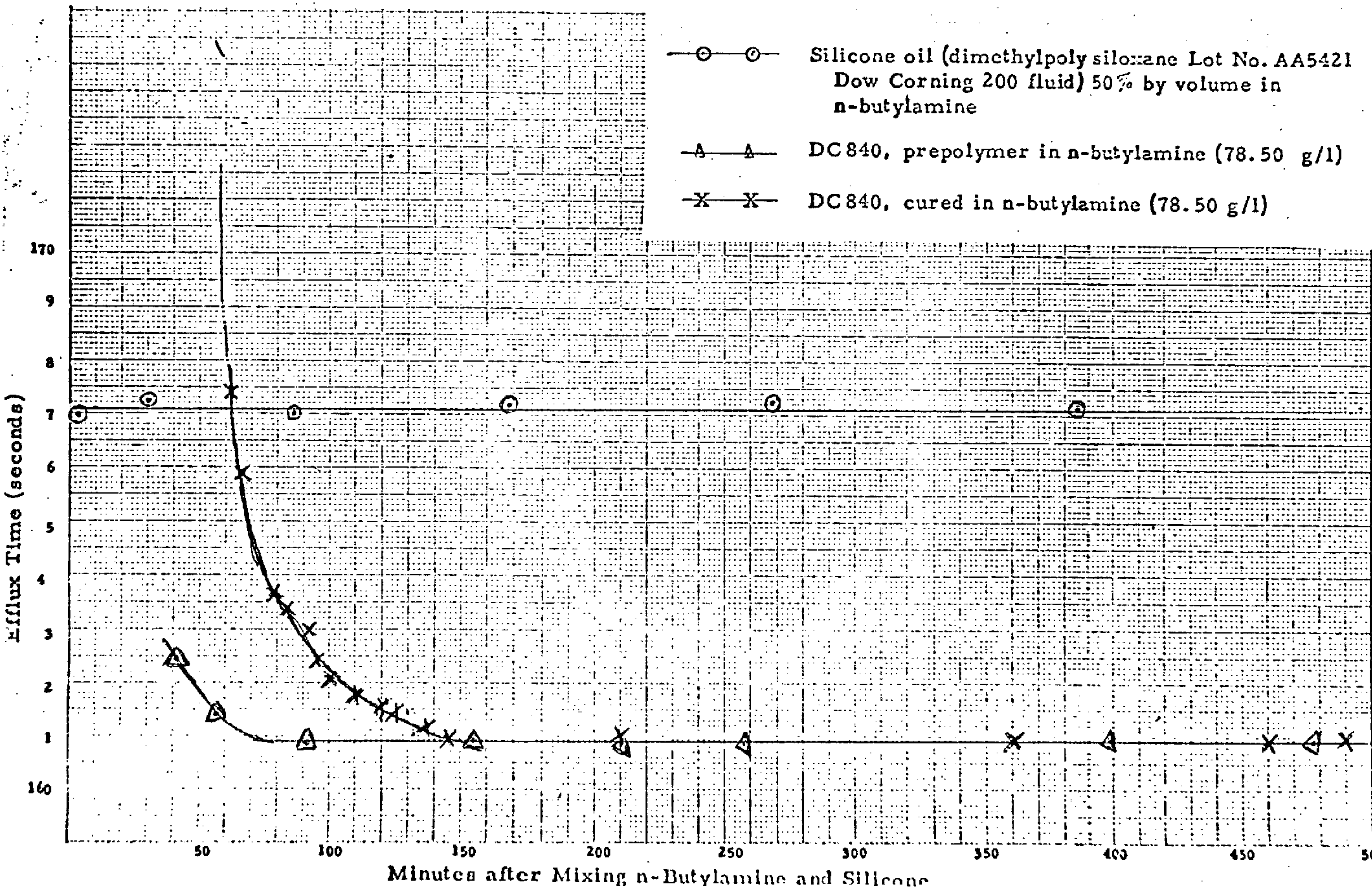
Figure I Relationship of Survival of *Bacillus Subtilis* Exposed to the Amine, Water and Benzene which Diluted by water or benzene

Table II Colony Counts Obtained from n-Butylamine Solution of Inoculated Silicone Potting Compound, RTV 60, Using Series Dilution in Benzene; Dilution Factor = 10^6

Experiment Number	Time*	Number of Colonies				Average
I	0	288	290	286	278	285.5
	1	327	288	259	283	281.3
	2	264	277	245	251	259.3
	3	256	268	248	261	258.9
	4	267	274	254	248	260.8
	7	245	256	238	251	247.5
	10	276	245	221	242	246.0
II	0	280	281	276	310	286.8
	1	277	265	281	288	278.0
	2	287	284	276	310	289.3
	3	292	287	281	254	278.5
	4	269	286	263	246	266.0
	7	246	255	231	258	247.4
	10	247	257	251	258	253.3
III (control)	0 to 10	no colony was observed				

* days

Figure 11 Variation in Viscosity with Time for a Silicone Oil, a Silicone Prepolymer (DC 840), and a Cured Silicone Resin (cured DC 840) in n-Butylamine Solution. Cannon Viscometer, 50-1711 at 45°C.



QUANTITATION OF BURIED CONTAMINATION
BY USE OF SOLVENTS

Semi-Annual Report

for

Jan. 1, 1973 through June 30, 1973

Supported by

NASA Grant NGR 35-001-012
Supplement No. 2

Submitted to the

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

by the

Department of Polymers and Coatings
North Dakota State University
Fargo, North Dakota 58102

Investigators: S. Peter Pappas, Paul Hsiao, and Loren W. Hill

Introduction

The objectives of the overall project are (1) to develop nonsporicidal methods for solvent degradation of cured polymeric resins that are used in spacecraft, and (2) to determine whether reaction conditions during resin cure cause decontamination of the component that is being fabricated. The previous reports described (1) the application of solubility parameter methods to the degradation of amine cured epoxy resins,[1] (2) the solubilization of cured silicone resins in amine solvents,[2] (3) spore viability studies on exposure to amine solvents, which demonstrated that reduced viability reflected a sporostatic effect which could be eliminated by removing the amine solvent during the plating process[2] or by utilizing higher dilution techniques,[3] and (4) recovery studies on a silicone potting compound (RTV 41) that is used in spacecraft, which demonstrated that (a) spores remain viable during chemical cure of this potting compound, and (b) greater than 90% of the spore population is recoverable by amine dissolution and proper plating techniques.[3] Thus, the results to date directly relate to our objectives. That is, we have developed a nonsporocidal method with which high spore recoveries are achievable from silicone coatings and potting compounds, and (2) we have demonstrated that spores remain viable during cure of a silicone potting compound. The present report describes an extension of these studies to silicone potting compound RTV 60, as well as our attempts to provide a sound statistical

basis for the results by extensive sampling. In addition, we report the results of our studies on viscosity changes following amine solubilization of various silicones, as well as cross-linking density changes following evaporation of amine solvents. Such studies have provided both mechanistic and practical information about the amine solubilization phenomenon.

Results and Discussion

As noted in the previous report, extension of the viability studies to cured silicone potting compounds required the use of an organic solvent for dilution. The cured silicone rubber was dissolved in n-butylamine and recovery was determined by the plate counting technique with series dilution in benzene. Of course, it was not possible to dilute the butylamine-silicone rubber solution with water because the silicone precipitated. Benzene was selected because it has been reported to be less toxic to spores than many other organic solvents[4] and because it is a good solvent for the silicone rubbers. The use of benzene for series dilution necessitated control experiments in the absence of silicone rubber or curing agents. The results of spore viability studies on (1) exposure to n-butylamine followed by dilution with water or benzene, (2) exposure to water followed by dilution with water, and (3) exposure to benzene followed by dilution with benzene are presented in Table 1. The data is plotted in Figure 1 as log of mean spore counts versus days of exposure. The numbers in the table and the points on the graph represent the mean of colony counts from 20 plates, derived from 4 duplicates of 5 samples. The most salient feature is the surprisingly high and stable recovery on exposure to _n_-butylamine followed by dilution with benzene. These results are currently under investigation both at NDSU and the University of Minnesota under Dr. Pflug's direction.

The results of studies on spore recovery from inoculated silicone potting compound RTV 60 following curing, dissolution in _n_-butylamine, and series dilution with benzene are presented in Table II. As previously determined for RTV 41, the data illustrate that (1) decontamination does not occur on curing, and (2) the method is effective for spore recovery.

The results of viscosity studies on _n_-butylamine solutions of silicone oil (DC 200), silicone prepolymer (DC 840), and cured silicone polymer (cured DC 840) are provided in Figure II. Only in the case of the cured DC 840 solution does a substantial decrease in viscosity occur with time which levels off at the viscosity of the prepolymer. These results indicate that the cured resin is degraded and suggest that cleavage occurs primarily at the centers at which cross-linking takes place in the curing process. Based on the mechanism for amine solubilization presented in an earlier report (see p. 8, scheme II of ref. 2), it was anticipated that a significant number of these cross-linking sites would reform on evaporation of the amine solvent. In support of this hypothesis, it was determined by extraction techniques that 70% of the original cross-linked

sites were regenerated when the amine was removed under vacuum at room temperature. These findings have suggested exciting new possibilities for (1) the recovery of silicone molds and, (2) the silicone coating of heat-sensitive materials. A report describing these findings has been submitted for patent consideration to the appropriate NASA office (Mr. J. Warden, Code GP).

References

1. A. E. Rheineck and R. A. Heskin, "Quantitation of Buried Contamination by the Use of Solvents", First Interim Report, Part I, NASA Grant No. NGR-001-012, February, 1972.

2. S. P. Pappas, P. Hsiao, and L. W. Hill, "Quantitation of Buried Contamination by the Use of Solvents", Semi-Annual report, NASA Grant No. NGR-001-012, January 1 to June 30, 1972.

3. Idem, July 1 to December 31, 1972.

4. "Microbial Cell Recovery from Solid Materials", Final Summary Report, NASA Contract No. 950740, The Jet Propulsion Laboratory, Pasadena, Calif., May, 1968, p. 88.

Table I No. of colony counts of Bacillus subtilis spores after exposure to solvents and diluents for varying periods of days.

Mean* / Treatment / Days	Exposed to n-butylamine & diluted with Benzene	Exposed to n-butylamine & diluted with Water	Exposed to Water & dil. with Water	Exposed to Benzene & dil. with Benzene
0	205.0 (2.3118)**	94.20 (1.9714)	147.17 (2.1679)	12.83 (1.1082)
1	251.95 (2.4010)	45.30 (1.6561)	84.50 (1.9269)	10.33 (1.0139)
2	252.40 (2.4021)	45.20 (1.6551)	60.75 (1.7836)	12.50 (1.0969)
3	252.40 (2.4021)	31.45 (1.4976)	50.75 (1.6996)	6.83 (0.7841)
4	217.75 (2.3375)	23.65 (1.3738)	37.83 (1.5777)	3.08 (0.4886)
5	202.25 (2.3060)	32.05 (1.5058)		
6	213.10 (2.3286)	13.80 (1.1399)		
7	193.15 (2.2860)	10.95 (1.0039)		

* Means of the No. of colony counted from 20 plates (five samples, each sample has four dublicate)

**Common logarithm of the means of the number of colony counted

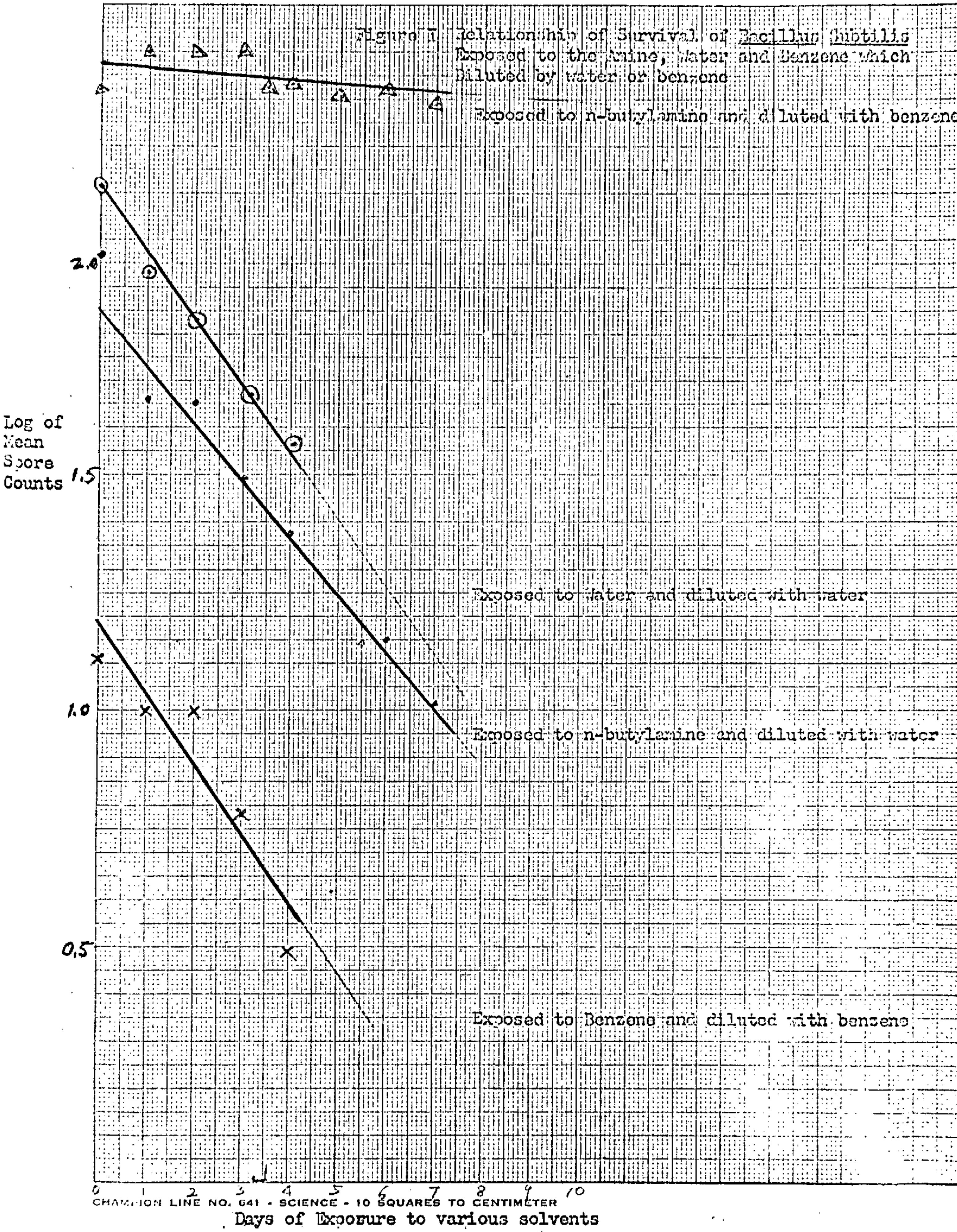


Figure I Relationship of Survival of Bacillus Subtilis Exposed to the Amine, Water and Benzene which Diluted by water or benzene

Table II Colony Counts Obtained from n-Butylamine Solution of Inoculated Silicone Potting Compound, RTV 60, Using Series Dilution in Benzene; Dilution Factor = 10^6

Experiment Number	Time*	Number of Colonies				Average
I	0	288	290	286	278	285.5
	1	327	288	259	283	281.8
	2	264	277	245	251	259.3
	3	256	268	248	261	258.9
	4	267	274	254	248	260.8
	7	245	256	238	251	247.5
	10	276	245	221	242	246.0
II	0	280	281	276	310	286.8
	1	277	265	281	288	278.0
	2	287	284	276	310	289.3
	3	292	287	281	254	278.5
	4	269	286	263	246	266.0
	7	246	255	231	258	247.4
	10	247	257	251	258	253.3
III (control)	0 to 10	no colony was observed				

* days

Figure 11 Variation in Viscosity with Time for a Silicone Oil, a Silicone Prepolymer (DC 840), and a Cured Silicone Resin (cured DC 840) in n-Butylamine Solution. Cannon Viscometer, 50-1711 at 45°C.