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FORMULATION OF A PRODUCT CONTAINING THE MULTIFUNCTIONAL CORROSION INHIBITOR SYSTEM DNBM

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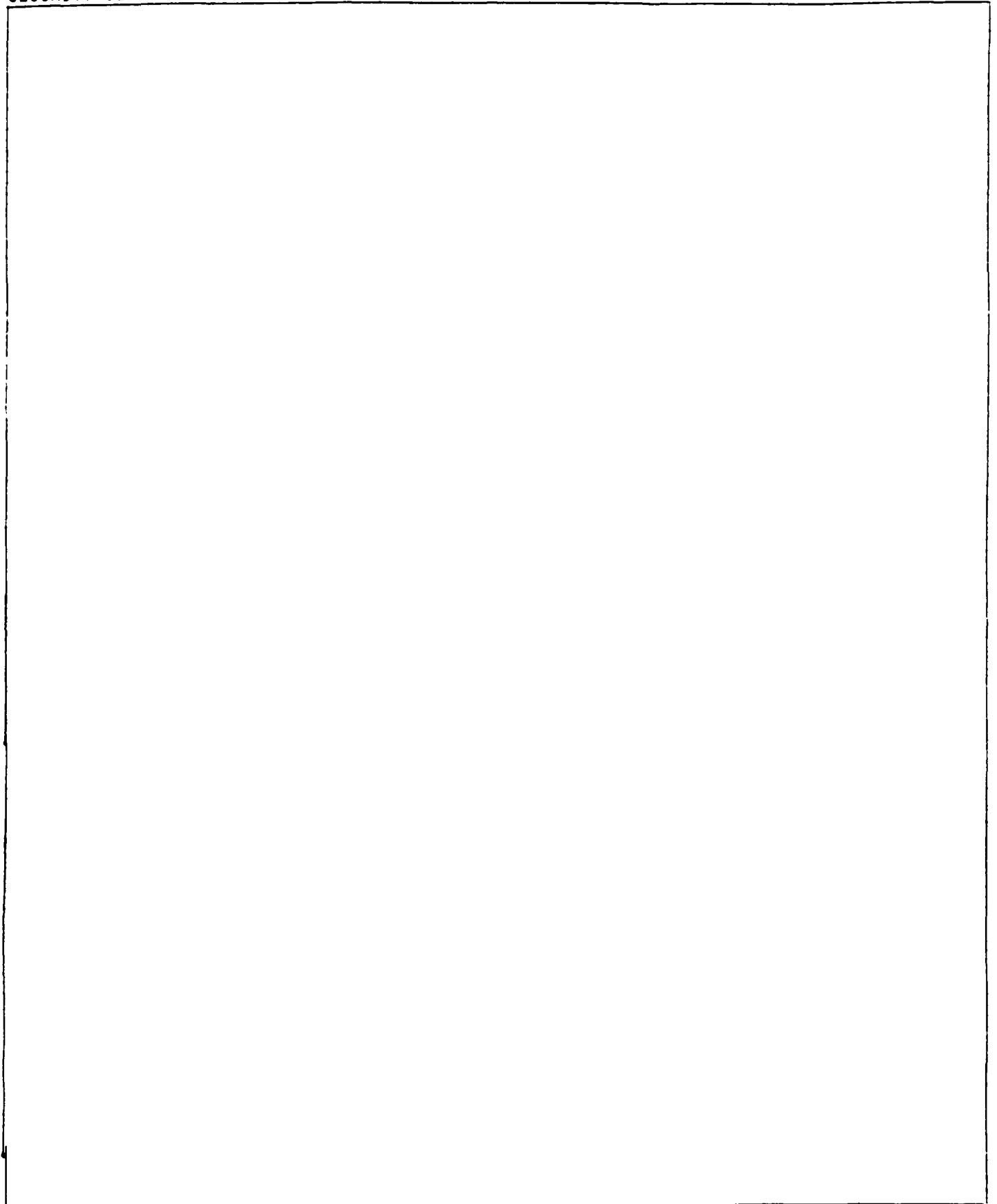
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19 ABSTRACT (Continue on reverse if necessary and identify by block number) Four quaternary ammonium salt inhibitors—DNBM (dichromate, nitrite, borate, and molybdate)—based on the quaternary ammonium chloride phase-change catalyst Adogen 464 were synthesized by double displacement reactions in the laboratory. The DNB product in kilogram quantities was prepared from the equivalent methylsulfate salt to minimize chloride in the final mixture. The mixture was microencapsulated by means of emulsifying the salts in aqueous methylcellulose, followed by spray drying to remove the water phase. To render the microcapsule shells impermeable to solvents in the epoxy-polyamide test primer formulation during cure, an organosilane was applied by vapor deposition. Fumed silica was added after spray drying and before silanizing to change the form of the microcapsules from flocculated to free-flowing. The microcapsules were in the 5- to 50- μ m particle size range, with some 100- μ m particles observed. The basic capsules contained up to 78% DNB core (payload). The inhibitor, DNB, was developed to retard corrosion fatigue and stress corrosion cracking in high-strength steels and aluminum alloys. General corrosion test results were highly favorable with regard to the absence of lifting and rusting of epoxy-coated steel panels at or near the test scribes, in comparison with control coatings.					
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SUMMARY

The principal objective of this investigation was to develop a product that contains the multifunctional corrosion inhibitor designated DNBM [for quaternary ammonium dichromate (D), nitrite (N), borate (B), and molybdate (M)]. When applied to high-strength steel and aluminum alloys, the product will arrest or retard corrosion fatigue and stress corrosion cracking, as well as general corrosion, on these alloys. The product is applicable in coating systems used on naval aircraft. The properties of the product are devised such that the inhibitors will be released when the paint system fails as the result of environmental damage.

Four quaternary ammonium salt inhibitors, D, N, B, and M, based on the quaternary ammonium chloride phase-change catalyst Adogen 464 were synthesized in the laboratory by double displacement reactions. Scaleup to kilogram quantities utilized the methylsulfate salt equivalent, $\text{CH}_3(\text{C}_8\text{-C}_{10})_3\text{N}^+\text{CH}_3\text{SO}_4^-$, as starting material in order to avoid introduction of chloride that might be carried over from the original commodity. The process performed by the supplier was successful for the D, N, and M salts, but not for the borate (B), because of low yields. A developmental quaternary ammonium borate was obtained and characterized for use as the B salt. To prepare a uniform mixture, the four individual salts were dissolved in toluene, which was followed by solvent removal at moderate temperatures under low vacuum.

The mixed DNBM product was microencapsulated by microemulsifying the quaternary ammonium salts in the form of an oil-in-water dispersion in aqueous methylcellulose, followed by spray drying to remove the water phase. To render the microcapsule shells impermeable to the solvents present in the epoxy-polyamide test primer formulations during cure, an organosilane, methyltrimethoxysilane, was applied by vapor deposition. Fumed silica was added following the spray-dry process to change the form of the microcapsules from a strongly flocculated agglomeration to a free-flowing, dispersed powder.

The microcapsules produced had particle sizes principally from 5 to 50 μm , with some 100- μm particles present. The capsules contained up to 78% DNBM core (payload), excluding the silane and fumed-silica addition.

The effectiveness of DNBM as a general corrosion inhibitor was established by depositing 100% DNBM directly onto 1010 steel surfaces, followed by deposition of MIL-P-23377 epoxy-polyamide primer coatings, and testing in a standard ASTM B-117 salt spray. Microencapsulated DNBM (silanized) was formulated in epoxy-polyamide primer formulations that contained no strontium chromate inhibitor. Resistance to lifting and rusting was clearly evident at and near the test scribes in comparison with the control coatings.

A separate demonstration program is recommended to formulate gallon quantities of the DNBM-containing anticorrosion primers or paints for test and evaluation on U. S. Navy aircraft/weapon systems; 5 lb of DNBM microcapsules would be prepared for Navy use in other coatings and polymer formulations.

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Section 1
INTRODUCTION

The development of DNBM as a multifunctional corrosion inhibitor system began as part of an independent research program at Naval Air Development Center, Warminster. The inhibitor was in the form of an aprotic solvent solution and was applied directly to cracks in high-strength steel and aluminum alloys. The successful inhibition of stress corrosion cracking and corrosion fatigue in high humidity and chloride-containing environments (Refs. 1 and 2) has been attributed to several functional properties of the inhibitor that include:

- Inhibition of moisture at a crack tip
- Modification of the interfacial chemistry, wherein atomic hydrogen is removed rapidly, thereby impeding its entry into the metal
- Creation of a chemical barrier (passive film) at the crack surface
- Maintenance of a uniform pH at the crack tip by means of buffer reactions

The term DNBM is an acronym for a mixture of four quaternary ammonium inhibitor salts that were prepared using a phase-change catalyst in double exchange (displacement) reactions of methyltrialkyl(C_8 - C_{10}) ammonium chloride (Adogen 464*) with alkali metal dichromate (D), nitrite (N), borate (B), and molybdate (M) salts.

For the initial applications, the DNBM ammonium salts remained in the aprotic solvent, toluene. In the program described herein, a number of methods were investigated for solubilizing the salts in organic solvents. These included (1) preparation of the quaternary ammonium DNBM salts and separation from the solvents used in synthesis and (2) direct dissolution of inorganic alkali metal salts in varied organic solvents. The purpose of the approaches was to determine the feasibility of formulating the materials into products that could be applied to a paint or primer system without dilution or loss of inhibitor functionality.

Means to achieve these objectives involved:

1. Microencapsulation of the inhibitor salts
2. Formulation of a microemulsion for application as a primer
3. Development of a polymer containing the inhibitors either linked directly or located in intramolecular spaces

The development of these materials and concomitant evaluations in a salt-spray environment are the principal topics discussed in this report.

* Trade-name identifications are given in Appendix A.

Section 2

DEVELOPMENT OF DNBM CORROSION INHIBITORS

The two methods investigated for the solubilization of salts in organic systems were:

1. Preparation of pure, solvent-free, quaternary ammonium DNBM salts via double displacement reactions with a phase-change catalyst
2. Direct dissolution of inorganic alkali metal salts in organic complexing solvents

Method 1 was successful, and is described in this section.

Method 2 was not successful, because of salt interactions with the solvents and high light sensitivities of the resultant solutions. It was also concluded later in the program, via consultation with microencapsulation-service suppliers, that the projected solvent-containing microcapsules, although theoretically feasible with regard to formation, would not retain their necessary long-term stability either as free-standing particles or when formulated in a paint, because of the inevitable diffusion of the contained solvents through the polymer shells of the capsules.

The work involved to develop Method 2 is recorded in Appendix B. Additional toxicity and safety characteristics necessary to assess the practicality of the solvent systems are given in Appendix C. Theoretical dissolution parameters for the solvents and formation of coordination complexes are discussed in Appendix D and were used to explain several of the variations found in the experimental data.

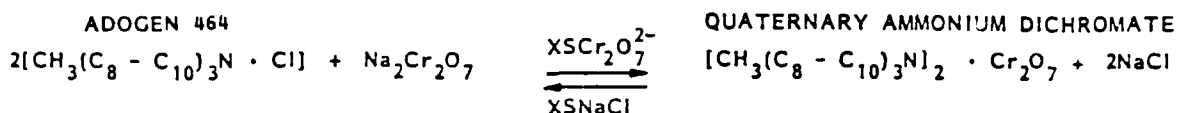
Preparation of Quaternary Ammonium DNBM Component Salts

The preparation method used an exchange or double displacement reaction in which an inorganic salt, e.g., sodium dichromate, reacted with a commercial quaternary ammonium salt (Adogen 464) starting material, $\text{CH}_3(\text{C}_8\text{-C}_{10})_3\text{N}^+\text{Cl}^-$. The quaternary salts D, N, and M were synthesized by this process. The B salt was obtained from a separate source. The starting material has been classified as a phase-transfer catalyst, since it permits the inorganic anion to be transferred from an aqueous to an organic (nonaqueous) medium or phase by its application to the system (Ref. 3).

Quaternary Ammonium Dichromate (D). The basic exchange reaction for synthesis is shown in Fig. 1 and includes the means by which the salts were purified. Table 1 lists some of the salts prepared by the principal supplier, Sherex Chemical Co., with corroborative synthesis at Lockheed Missiles & Space Company, Inc. (LMSC). The analytical data were obtained at LMSC. During the preparative work, Sherex synthesized a candidate made from the methyl sulfate starting material to minimize residual chloride in the quaternary salts produced by the exchange method. These data are also given in Table 1.

The steps to prepare the Adogen 464 dichromate salts were as follows: Adogen 464 was converted to the dichromate by anion exchange with aqueous sodium dichromate. This was accomplished in a toluene-water system using a large excess of sodium dichromate. The recovered product, a dark brown oil, was shown to have a Na:Cr atomic ratio of 1:26. The procedure is: 1.63 g (5.47 mmols) of sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, was dissolved in 5 cm³ water. To this was added a solution of 0.51 g (1.26 mmols) of Adogen 464 in 15 cm³ of toluene. The vial was thoroughly shaken for several minutes and left to separate into layers. The organic layer became brown in color. The layer was separated and dried over magnesium sulfate. Evaporation of the dry toluene solution in a rotary evaporator yielded a high-viscosity, dark-brown oil.

• BASIC EXCHANGE EQUILIBRIA



• PROCESS

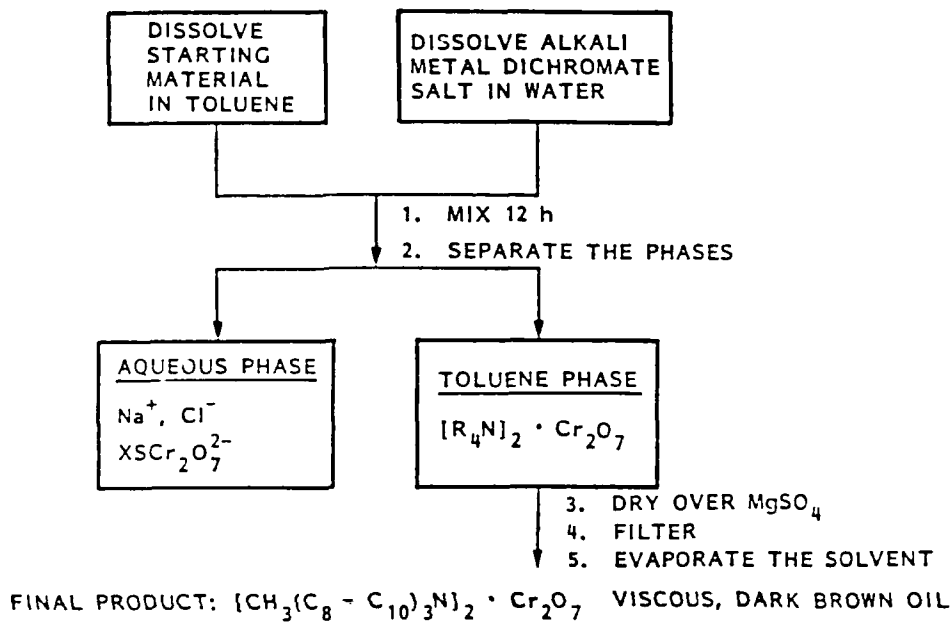


Fig. 1 Synthesis of Quaternary Ammonium Dichromate (D)

The following observations were made:

1. The product was insoluble in distilled (ion-free) water.
2. Addition of Adogen 464 did not effect solubilization.
3. Shaking with sodium chloride solution caused an orange color to develop in the aqueous layer.

This was taken as evidence of reversibility and integrity of the quaternary functionality.

As a result of this investigation, 100 g of the dichromate salt was prepared. Analysis yielded the following data:

Preparation No. 150-148, 100 g

Cr (VI)	9.4%
Chloride impurity	33 ppm
Sulfate impurity	0.74%

A yield of 92.5% is based on the 10.16% Cr content for the completely converted salt.

A 1-kg batch of the same salt was prepared by Sherex, Lot No. 150-149. Analysis indicated that the chloride impurity was 47 ppm, essentially the same as for No. 150-148. The Cr(VI) content was 9.28%;

Table 1 ANALYSIS OF QUATERNARY AMMONIUM DICHROMATE (D)

SAMPLE CODE	STARTING MATERIALS		% TOTAL Cr IODOMETRY	% Cr*(VI) POLAROG- RAPHY	% TOTAL Cr AS Cr(VI)	ppm Cl MICROCOU- LOMETRY	% TOTAL Cr THEORETICAL
	QUATERNARY AMINE	DICHROMATE					
EP-SC-97-103(I), 1982	ADOGEN 464 (Cl ⁻ ANION)	Na ₂ Cr ₂ O ₇ · 2H ₂ O	10.13	9.29	91.4	371	10.16
EP-SC-97-103(II), 1985	ADOGEN 464 (CH ₃ SO ₄ ⁻ ANION)	Na ₂ Cr ₂ O ₇ · 2H ₂ O	8.95	8.54	84.1	88	10.16
LMSC 10990-74	ADOGEN 464 (Cl ⁻)	Na ₂ Cr ₂ O ₇ · 2H ₂ O	—	9.3	91.5	0.1%	10.16
ADOGEN 464 CONTROL 85% SOLIDS, 15% IPA	ADOGEN 464 (Cl ⁻)	NONE	—	—	—	6.9% THEORETI- CAL 6.87%	—

*Cr(VI) DETECTION LIMIT 0.1%

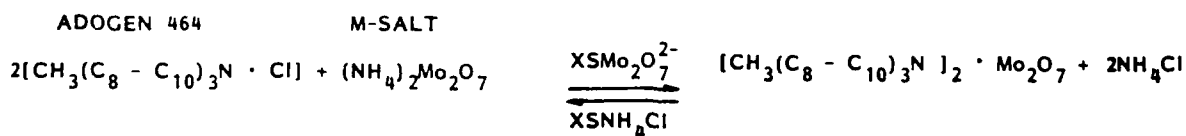
yield, 91.3%. The procedure for this 1-kg batch was adopted for all following quaternary ammonium dichromate salt preparations.

Quaternary Ammonium Molybdate(M). The second salt synthesized was the molybdate. Three inorganic molybdate candidates were evaluated as starting materials, since no previous preparations had been reported in the literature.

- Sodium molybdate, Na₂MoO₄ 39.7% Mo
- Ammonium paramolybdate, (NH₄)₆Mo₇O₂₄·4H₂O 54.3% Mo
- Ammonium dimolybdate, (NH₄)₂Mo₂O₇ 56.4% Mo

The basic exchange process is shown in Fig. 2 for the reaction of Adogen 464 with ammonium dimolybdate. Table 2 contains the analytical data.

• BASIC EXCHANGE REACTION



• OTHER MOLYBDATE SALTS TESTED

SODIUM MOLYBDATE Na₂MoO₄ · 2H₂O

AMMONIUM PARAMOLYBDATE (NH₄)₆Mo₇O₂₄ · 4H₂O

Fig. 2 Synthesis of Quaternary Ammonium Molybdate (M).

Table 2 ANALYSIS OF QUATERNARY AMMONIUM MOLYBDATE (M)

SAMPLE CODE	STARTING MATERIALS		% TOTAL Mo	% SO ₄	% Cl	% TOTAL Mo	NOTES
	QUATERNARY AMMONIUM SALT	MOLYBDATE	POLAROGRAPHY	ION CHROMATOGRAPHY	MICROCOLUMETRY	THEORETICAL	
LMSC 10990-37	ADOGEN 464 (Cl ⁻ ANION)	Na ₂ MoO ₄ · 2H ₂ O	1.6	—	6.3	9.92	YI. VISCOUS OIL
LMSC 10990-38	ADOGEN 464 (Cl ⁻ ANION)	(NH ₄) ₆ Mo ₇ O ₂₄ · 4H ₂ O	28.4	—	0.14	19.3	LT GREEN POWDER
LMSC 10990-45	ADOGEN 464 (Cl ⁻ ANION)	(NH ₄) ₂ Mo ₂ O ₇	13.0	—	6.5	17.2	YI. GREEN OIL
LMSC 10990-47	ADOGEN 464 (Cl ⁻ ANION)	(NH ₄) ₂ Mo ₂ O ₇	21.0	—	2.3	17.2	GLASSY GREEN SOLID
EP-SC-150-120	ADOGEN 464 (Cl ⁻ ANION)	(NH ₄) ₆ Mo ₇ O ₂₄ · 4H ₂ O	11.4	—	2.7	19.3	LT GREEN GLOSSY SOLID APPROX 60% YIELD
EP-SC-150-121	ADOGEN 464 (CH ₃ SO ₃ ⁻)	(NH ₄) ₂ Mo ₂ O ₇	—	5.3	274 ppm	17.2	GREEN GLASSY WAX
EP-SC-150-134	ADOGEN 464 (CH ₃ SO ₃ ⁻)	(NH ₄) ₆ Mo ₇ O ₂₄ · 4H ₂ O	—	3.4	68 ppm	19.3	YI. GREEN HIGH VISCOSITY OIL
EP-SC-150-125	ADOGEN 464 (CH ₃ SO ₃ ⁻)	(NH ₄) ₂ Mo ₂ O ₇	16.8	0.01	52 ppm	17.2	GREEN TAFFY-LIKE SOLID, COMPLETE REACTION
ADOGEN 464 CONTROL	ADOGEN 464 (CH ₃ SO ₃ ⁻)	NONE		THEORETICAL 18.6	—	—	HIGH VISCOSITY FLUID OR WAX

Synthesis of the molybdate quaternary salts indicated that the quaternary ammonium dimolybdate salt appeared to be the most likely candidate for obtaining uniformly high yields. Consequently, Sherex prepared a 1-kg batch, with the following results:

Lot No. 150-151

Molybdenum (VI)	24.9%
Chloride (impurity)	37 ppm
Sulfate (impurity)	0.64%

The high percentage of molybdenum(VI) indicated that the material was probably a monosubstituted salt: [(CH₃(C₈-C₁₀)₃N) · NH₄Mo₂O₇

The conversion of 94.4% is based on a theoretical 26.37% Mo for the monosubstituted quaternary. The material dissolves completely in toluene and all common laboratory solvents. The only difference in solubility between the Mo and Cr quaternaries was that the Cr salt was soluble in petroleum ether (low-molecular-weight aliphatic hydrocarbons), whereas the Mo salt was not.

Quaternary Ammonium Borate (B). The third salt, B, was investigated as follows. An initial reaction of Adogen 464 with sodium tetraborate performed by Sherex yielded a conversion of less than 20%. This was attributed to the relatively low solubility of the Na₂B₄O₇ · 10H₂O starting material in water at room temperature, i.e., low relative to the solubilities of the chromium and molybdenum starting materials under similar conditions. Additional trials using sodium metaborate, NaBO₂ · 4H₂O, also yielded poor yields.

As a consequence of the difficulty of preparing the borate salt in high yield, two developmental quaternary ammonium borates, RD 5444A and RD 6009, manufactured as developmental chemicals by Akzo Chemical Co., were evaluated as alternative salts. RD 5444A was found to be insoluble in deionized water, but yielded a pH of 9 to 10 when mixed with artificial salt water initially at pH7. The salt water resulted in dissociation of the borate quaternary to form the quaternary ammonium cation and boric acid, a weak acid. The resultant pH was alkaline.

The RD 5444A commodity ordinarily contains 10% isopropyl alcohol (IPA) as carrier solvent; however, in the sample analyzed (gas chromatography) 4.3% by weight IPA was found. Approximately 3% by weight free amine was estimated by gas chromatography to be present as an impurity. Chloride was 22 ppm. NMR analysis indicated that the borate is a methyl trialkyl (C_{12} - C_{14}) ammonium salt. Approximately 6% of the carbons in the alkyl chains were alkene carbons. Total nitrogen (titratable) was 1.89%. Total boron was 1.36%. In addition, about 2% ethylene glycol was present, according to the manufacturer. Therefore, it is possible that in the presence of the dichromate quaternary, some components would be oxidized, yielding thereby a concomitant decrease in Cr(VI). Consequently, mixtures of the DNBM salts were analyzed during this period of the program. The IPA was removed without difficulty by vacuum heating at 100°C.

The alternative quaternary ammonium borate, RD 6009, was a 100% solids polyol borate that was slowly soluble/dispersible in water. There was no change in pH when the commodity was mixed with seawater, indicating little dissociation or hydrolysis. Thus, only the RD 5444A, which dissociated fairly readily, was considered as an appropriate candidate for the B quaternary salt: $CH_3(C_{12}-C_{14})_3N \cdot H_2BO_3$.

Quaternary Ammonium Nitrite (N). Using sodium nitrite as starting material, synthetic Adogen 464 nitrite candidates were prepared by Sherex. Analysis indicated reasonable levels of conversion, up to 87% (see Table 3). The high chloride levels probably resulted from the large excess of $NaNO_2$ required for efficient exchange, since up to 50 ppm Cl is normally present in C.P. (analytical grade) sodium nitrite. However, the final chloride value will be reduced when the nitrite quaternary is diluted with the dichromate, borate, and molybdate quaternaries, which contain significantly less chloride in each component.

Table 3 ANALYSIS OF QUATERNARY AMMONIUM NITRITE (N)



Sample Code	% NO_2^-	ppm Cl^-	% SO_4^{2-}	% Conversion Based on Theoretical 10.23% NO_2
150-143	6.5	153	3.8	63.5
150-147	7.0	97	3.4	68.4
150-157	6.7	680	—	65.5
150-159	8.9	258	—	87.0
150-160	7.8	213	—	76.2

As an alternative, quaternary ammonium nitrite, AC 1349, from Akzo Chemical was tested for the required hydrolysis using artificial seawater. No change in pH was observed. Since nitrous acid is a moderately weak acid, if the AC 1349 had hydrolyzed on mixing, some change (increase) in pH would have occurred.

Preparation of Mixed Quaternary Ammonium DNBM Salts

Preliminary Laboratory Investigations. The viscosities of the four salts differed markedly, and therefore it was not feasible to combine the materials directly to obtain uniform distribution in the mixture. The nitrite is

a low-viscosity oil, the dichromate is a high-viscosity liquid, the molybdate is a taffy-like solid, and the borate is a slow-flowing liquid. The salts were therefore dissolved in toluene, and most of the toluene was removed by rotary vacuum evaporation. The remaining solvent was removed at 70 to 90°C over a 4-h period in a vacuum oven at 10 to 50 torr.

In the case of overnight exposures (> 16 h) to laboratory light, the DNBM-toluene solution, or a solution of D in toluene, showed evidence of reduction via changes to a green color, Cr (III), from the original brown Cr(VI). It was determined by gas chromatography-mass spectrometry (GC-MS) that benzoic acid, benzaldehyde, and benzyl alcohol, were present in the green DNBM solutions. As a result, aluminum foil was used to prevent excess exposure of the in-process materials. Using the initial 1-kg batches of dichromate, nitrite, and molybdate quaternaries from Sherex, and the RD5444A from Akzo, several mixtures were prepared. The toluene solvent used to dissolve the salts was, as above, removed by rotary evaporation and vacuum-oven heating.

In each formulation, there were equal numbers of Cr and Mo atoms, and the same (equal) number of nitrite and borate anions. In the first formulations, the borate quaternary was added in single and double amounts to determine its effect on pH in natural seawater.

pH of DNBM Quaternary Ammonium Salt Mixtures in Seawater. The principal mechanism for corrosion inhibition by the DNBM salts is the release of the inorganic inhibitor anions in the presence of salt water, which, under adverse conditions, will make its way through the coatings to the substrates that are to be protected. Thus, an additional requirement for the resultant salt water-DNBM quaternary ammonium mixtures was pH of 6 to 8 for the aluminum alloys and a somewhat higher pH for the high-strength steels.

Natural seawater was used for the tests. The pH readings were determined after mild stirring for 3 and 15 min. Two levels, excess quaternary salt and excess seawater, were selected as conditions that could occur at the surface of a metal in contact with a paint or primer that was in the process of failure. The mixture was stirred slowly in order to maintain continued contact during the two time periods (see Table 4). The borate salt apparently had less effect than anticipated, the result possibly of a rate effect not detected in the time intervals used for the tests.

Scaleup of Mixed DNBM Quaternary Ammonium Salts. Four batches of mixed salts were prepared. During the intervals, several changes in processing were made, which are summarized below.

1. Remove the isopropyl alcohol present in the RD5444A borate commodity to prevent reduction of the Cr(VI) in the DNBM mixture.
2. Remove toluene solvent at a lower temperature than that used initially (70 to 75°C, rather than 70 to 90°C) to avoid potential oxidation of the salts, while maintaining the vacuum at 10 to 100 torr.
3. Use a liquid-nitrogen trap between the mechanical pump and the DNBM-toluene mixture to minimize backstreaming contamination from the silicone oils used in the pump.

Listings for the four mixtures are given in Table 5. In the second batch, too low an amount of Mo quaternary appears to have been added, as can be seen by calculating $2.61\% \text{ Cr} \times \text{Mo/Cr} = \% \text{ Mo}$ to give an equal number of atoms of Mo and Cr. The percent Mo calculated was 4.82%; however only 3.46% was found. In the third batch, the Mo content calculated was 4.26%. The result of 4.83% analyzed appears to have resulted from using too low a solvent figure for the Mo quaternary. Both solvent and Mo content need to be confirmed, therefore, before mixing.

Inspection of the Cr(III) data from Batch 3 shows that some reduction of Cr(VI) may have occurred. This possibility will be examined for long-term storage of DNBM "neat", as well as in microcapsule form, should the reduction be verified. The separation of the Cr quaternary D from the N, B, and M quaternaries may be required later when the salts are microencapsulated. Retained samples of Batches 2 and 3 will be

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Table 4 pH OF MIXTURES OF DNBm QUATERNARY AMMONIUM SALTS AND NATURAL SEAWATER AFTER MILD STIRRING

Mixture	Material (g)				pH Meter Readings			
	Dichromate Quaternary	Nitrite Quaternary	Borate Quaternary	Molybdate Quaternary	Excess Quaternary		Excess Sea water	
	#150-149	#150-160	RD 5444A (Isopropyl alcohol removed by vacuum)	#150-151 (61% solids, 39% toluene)	(10-g mixture, 1 g H ₂ O)		(3.5-g mixture, 10 g H ₂ O)	
					3 min	15 min	3 min	15 min
10990-89	29.01	41.41	31.67	32.89	6.59	6.77	6.20	6.26
10990-92	29.95	42.18	78.03	34.64	7.04	7.06	6.54	6.60
10990-98	59.70	85.67	0	68.65	6.04	5.90	5.25	5.33
RD5444A	—	—	100%	—	10.40	—	9.16	9.21
Natural Seawater (Half Moon Bay, CA) 5/26/86, Filtered	—	—	—	—	7.86	—	—	—

reanalyzed precisely for Cr(VI) and Cr(III) at that time. Notwithstanding the possibility for a 20 to 30% Cr(VI) reduction to Cr(III), all the DNBm batches were used without modification in the microcapsule investigations discussed in the next section.

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Table 5 SCALEUP OF MIXED DNBM QUATERNARY AMMONIUM SALT PREPARATIONS

Batch 1, No. 10990-101, 10/86
 Total weight = 749 g

Salt	Wt. in Mixture (g)	Calculated (%)	Found (%)			
			Polarography	AA	Iodometry	Micro-coulometry
D Dichromate	123	Cr (VI) 1.55 Cr (III) 0	2.0 <0.1 (ND)	1.6	1.9	—
N Nitrite	176	NO ₂ ⁻ 1.76	2.1	—	—	—
B Borate (isopropyl alcohol removed)	312	H ₂ BO ₃ ⁻ 3.19	—	—	—	—
M Molybdate (toluene removed)	138	Mo (VI) 2.81	—	3.4	—	—
Chloride impurity	—	Cl 48 ppm	—	—	—	36 ppm

Batch 2, No. 10990-112, 2/87
 Total weight = 894 g

Salt	Wt. in Mixture (g)	Calculated (%)	Found (%)			
			Polarography	AA	Iodometry	Micro-coulometry
D Dichromate	262	Cr (VI) 2.61 Cr (III) 0	2.60 0.3	2.58	—	—
N Nitrite	194	NO ₂ ⁻ 1.02	1.0	—	—	—
B Borate (isopropyl alcohol removed)	318	H ₂ BO ₃ ⁻ —	—	—	—	—
M Molybdate (toluene removed)	120	Mo (VI) 4.82	—	3.46	—	—
Chloride impurity	—	—	—	—	—	50 ppm

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Table 5 SCALEUP OF MIXED DNBM QUATERNARY AMMONIUM SALT PREPARATIONS (Cont.)

Batch 3, No. 10990-117, 6/87
 Total weight = 1342 g

Salt	Wt. in Mixture (g)	Calculated (%)	Found (%)			
			Polarography	AA	Iodometry	Micro-coulometry
D Dichromate	349	Cr (VI) 2.31 Cr (III) 0	2.1 ± 0.5 0.7 ± 0.3	2.24	—	—
N Nitrite	296	NO ₂ ⁻ 1.03	—	0.93	—	—
B Borate (isopropyl alcohol removed)	480	—	—	—	—	—
M Molybdate (toluene removed)	217	Mo (VI) 4.26	—	4.83	—	—
Chloride impurity	—	—	—	—	—	16 ppm

Batch 4, No. 11048-26, 11/88
 Total weight = 1210 g

Salt	Wt. in Mixture (g)	Calculated (%)	Found (%)	
			Total Cr	Total Mo
D Dichromate	301	Cr 2.48	2.44	
N Nitrite	238	—	—	
B Borate (isopropyl alcohol removed)	394	—	—	
M Molybdate (toluene removed)	277	Mo 4.24	—	4.19

Section 3

MICROENCAPSULATION AND RELATED STUDIES

A principal objective of the program—to develop a product that can be applied in a paint system—requires that no changes occur in the functional properties of the corrosion inhibitors contained in the product. In this regard, the inhibitor release occurs when the paint or primer fails as the result of environmental damage to the coating. Microencapsulation technology was chosen as the means most likely to successfully contain the DNBM mixture in a paint system. The capsule shell of the microcapsule is required to protect the DNBM core from contact with the solvents, polymers, catalysts, fillers, or other components of the paint into which or next to which the DNBM is placed. The criteria for selecting DNBM protective polymers for use as shell materials are as follows:

- Nonreactive with coating or primer components
- Controlled release of DNBM on contact with water-laden salt air or seawater
- Amenable to commercial formulation and production with DNBM components/complexes, etc.
- Well-established polymer properties

The encapsulant polymer must resist all the components that are present in, for example, the epoxy-polyamide and polyurethane topcoat formulations. It is to be expected that some microcapsules will be present at the interface between the primer and topcoat as the result of migration during cure. Therefore, the polymer will have to remain reasonably water-soluble as well as isocyanate-resistant during the period of cure, even if the microcapsules are added to the primer only.

The solvents and mixtures that the candidate polymers must resist are given in MIL-T(thinners)-812772 B, MIL-P(epoxy primers)-23377E, and MIL-C(polyurethane coating)-83286. Included are the general solvents: methylethylketone, isopropyl alcohol, isobutyl alcohol, butylcellosolve, and cellosolve acetate. The epoxy diluent contains MEK, MIBK, and ethylene glycol monoethylether or propylene glycol monomethylether. The polyurethane solvents include several of the above, plus toluene and xylene, up to a maximum of 20 vol %.

Two mechanisms were considered applicable for the release of the DNBM inhibitors. These are (1) dissolution of the polymer film surrounding the DNBM by the water-laden salt air or seawater (splash) in contact with the film and (2) passage of water through the polymer film acting as a semipermeable membrane. In Mechanism 1, the film dissolves directly at a controlled rate during water ingress, releasing the DNBM mixture. In Mechanism 2, only salt water penetrates the polymer, thereby hydrolyzing the DNBM and allowing the solute to pass back through the film to reach the area of corrosive attack.

The polymers selected for the first mechanism were the polysaccharide ethers derived from cellulose: methyl cellulose, hydroxypropyl methyl cellulose, guar gum, and other nonionic polymer candidates. The commercial sodium salts of alginic acid and carboxy methylcellulose were discarded when it was determined that these materials caused instability of the quaternary ammonium salt upon mixing to form the water emulsion required in the microencapsulation process. Likewise, salt impurities in impure cellulose ether commodities were detrimental to the stability of the emulsions; this was readily observed when the quaternary ammonium dichromate salt reacted prematurely with the salts present to produce yellow solutions of Cr(VI). Similar reactions occurred for all polyvinyl alcohol candidates (obtained from hydrolyzed polyvinyl acetate).

For the second mechanism, silicones and polyimides were considered as reasonable, water-insoluble shell/membrane candidates that conceivably would permit passage of the DNBM components when contact with salt water was made.

The initial goal for the size of the microcapsules was 25 to 30 μm . A somewhat lower size restriction is given for the strontium chromate inhibitor epoxy-polyamide primer coating, MIL-P-23377, which is 15 to 23 μm according to the specification. After consideration of the reason(s) for this restriction on the SrCrO_4 -filled primer, it became apparent that a coating of somewhat greater thickness for the microcapsule-pigmented coating could be accepted. The reasons involve (1) a higher density for SrCrO_4 than that of the DNBM microcapsules, 3.9 g/cm^3 versus 1.2 to 1.4 estimated for the capsules, and (2) a reasonable probability that less DNBM would be used in the microcapsule-filled coating, thereby resulting in a lower level of brittleness than in the SrCrO_4 coating.

Preliminary Laboratory Investigations

The initial procedure for preparing microcapsules for the first mechanism used dextran polysaccharide as a coprecipitant for methyl cellulose dispersed in deionized water. To the dextran-methyl cellulose dispersion was added the quaternary ammonium dichromate component with vigorous stirring. Following the dispersing action, the system was heated to 55 to 60°C to coprecipitate the cellulose. Dextran is classified as a complementary polymer which aids in precipitating the microcapsules, thereby facilitating the methyl cellulose separation from the aqueous phase (Ref. 4). Only poor capsules were formed, however, and those could not be isolated because of tackiness of the cellulosic coating.

The second method involved the formation of silicone resin capsules using ultraviolet (UV) light polymerization (Ref. 5). Five samples of microcapsules were obtained that were between 400- and 1600- μm particle size. The samples were evaluated by immersion in Type II epoxy thinner (50% MEK, 20% MIBK, 30% Cellosolve). This mixture is used to dilute epoxy-polyamide coating formulations before spray application, and, as such, constitutes a severe test medium because of its low viscosity and high penetrability. The five samples were permeable to the thinner solvents, thereby releasing the dichromate salt in the organic solvent in 1 to 2 s—a negative result. After several solvent washings, the nonsoluble residues—still containing the Cr(VI) salts as seen by their dark brown colorations—were tested for reaction in artificial seawater (Ref. 6). The results were negative after 48 h; i.e., there was no disassociation to produce yellow colored Cr(VI) anions. Thus, irrespective of particle size, the solution chemistry of the washed products was opposite to that required, which is stability in Type II diluent (no dissolution) and positive reaction in seawater to produce the corrosion inhibitor ions "on demand."

Microemulsification of D Salts

While the preliminary trials on microencapsulation were being run, other approaches were explored. One alternative was direct emulsification in a water-reducible epoxy primer formulation. The D salt was used in these trials, because any hydrolysis or dissociation changes could be readily observed via formation of a yellow solution.

The quaternary ammonium dichromate salt was dispersed in a water-reducible formulation, 44-GN-7, manufactured by Deft Corporation, Irvine, California. This coating is controlled by MIL-P-85582. Three volumes part A (barium chromate pigmented epoxy component), 1 volume part B (clear catalyst), and 8 volumes deionized water were mixed to form the specification coating formulation. To this was added approximately 0.1 volume quaternary ammonium dichromate with vigorous agitation. Dispersion was observed in less than 5 min, with emulsion stability evident for about 1 h in a closed container. However, in 2 to 3 h, when stored in an open shallow cup, significant changes were observed, possibly the result of evaporation of solvents, including water. At this time, the dichromate salt appeared to dissolve in the formulation rather than remain in emulsion form. Separation and curdling of the mixture became obvious, with attendant failure to cure to a hard finish. Further work on this approach was therefore terminated because of retardation of cure.

A test was run next to determine the compatibility of the D salt with the methylcellulose polymer and the epoxy-polyamide binder components in which the D (and DNBM salts) would be formulated. Several

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emulsions were prepared in which varied levels of D were dispersed in 5% methyl cellulose (MC) or hydroxypropyl methylcellulose (HPMC) aqueous colloidal solutions of low molecular weight. The emulsions were prepared in a commercial Oster blender at 18,000 rpm. The resultant emulsions, approximately 500 cm³, were centrifuged to separate the foam produced. Thin, 1- to 2-mil MC or HPMC coatings containing the emulsified dichromate salt were deposited by drawdown blade on glass slides. After drying, the slides were immersed in epoxy diluent to determine any development of a yellow color indicative of chromate leaching. In addition, freshly prepared Mil Spec-P-23377 epoxy polyamide and Mil C-83286 linear aliphatic polyurethane coating formulations were drop cast directly onto the D-filled MC and HPMC coated slides which had passed the immersion test. After 1-week cure, the coated systems were removed from the slides and cross sectioned.

The results of these tests indicated that both MC and HPMC cellulose ethers were nonreactive in contact with the epoxy-polyamide and linear aliphatic polyurethane formulations (which included the respective Type II and I diluents as part of the formulations) during cure. This was a significant result. The maximum level of D-quaternary that could be "loaded" into the coating was 28 to 30% (based on total solids), before immersion in type II diluent began to show a yellow leachate within a 2-h period. No significant change in the cure times was observed. Figures 3 and 4 show (1) the interfaces between the polyurethane-D filled methylcellulose and the epoxy polyamide-D filled methylcellulose coatings and (2) the apparent wetting – but no reactivity – between the coating materials. Inspection indicated no apparent differences between coated and noncoated surfaces. Therefore, in coating form, both MC and HPMC appeared acceptable as shell polymers for the microcapsules. The actual behavior would of course require testing of the material in capsule form to determine the level(s) of correspondence.

In connection with this work, the emulsions that were prepared were observed to retain their stability over 2 to 3 months; i.e., no settling or separation occurred. The absence of any interfacial deterioration, cure rate aberrations, etc., that would be caused by the quaternary salt or the cellulose ether is considered as strong evidence for the protection of the D-salt by both binder candidates.

Microencapsulation by Spray Drying of D and DNBM Cellulose Ether Emulsions, Including Surface Treatment with Silanes

Spray drying as a valid means for removing water from the emulsions was evaluated next. South West Research Institute, San Antonio, Texas (SWRI), performed the laboratory and larger scale spray-drying procedures using this technology.

The laboratory/bench-top system was a Buchi Model 190 mini spray dryer. Five preliminary emulsions were prepared at the Lockheed Palo Alto Research Laboratory (LPARL). These contained 28 to 29% quaternary ammonium dichromate Adogen 464 salt derivatives in 5% methylcellulose and hydroxypropyl methylcellulose in deionized water, and they were spray dried using conditions that bracketed the capability of the Buchi units (see Table 6). The D salt concentration was 28 to 29% based on total solids (methylcellulose plus quaternary D salt). Examination at LPARL indicated that the intrinsic particle size was essentially the same as in the emulsion, 5 to 15 μ m, but significant agglomeration was observed in the dry state. The powder products were readily dispersed in microscope immersion oil (hydrocarbons), and the individual cores were easily seen at 100 $\times$ to 400 $\times$. Inspections indicated that the shells were very thin – sufficient to coat the spheres, but inadequate to prevent leaching by the Type II epoxy diluent.

As the result of the borderline adequacy of the shell material, the application of organosilane monomers to the encapsulated powders was evaluated. Silane monomers were chosen principally because of their insolubility, when polymerized, in the epoxy and polyurethane formulation thinners of the Mil-P-23377 epoxy. The silanes evaluated were: (1) hexamethyldisilazane, (2) methyltrimethoxysilane, (3) phenyltriethoxysilane, and (4) diphenyldimethoxysilane.

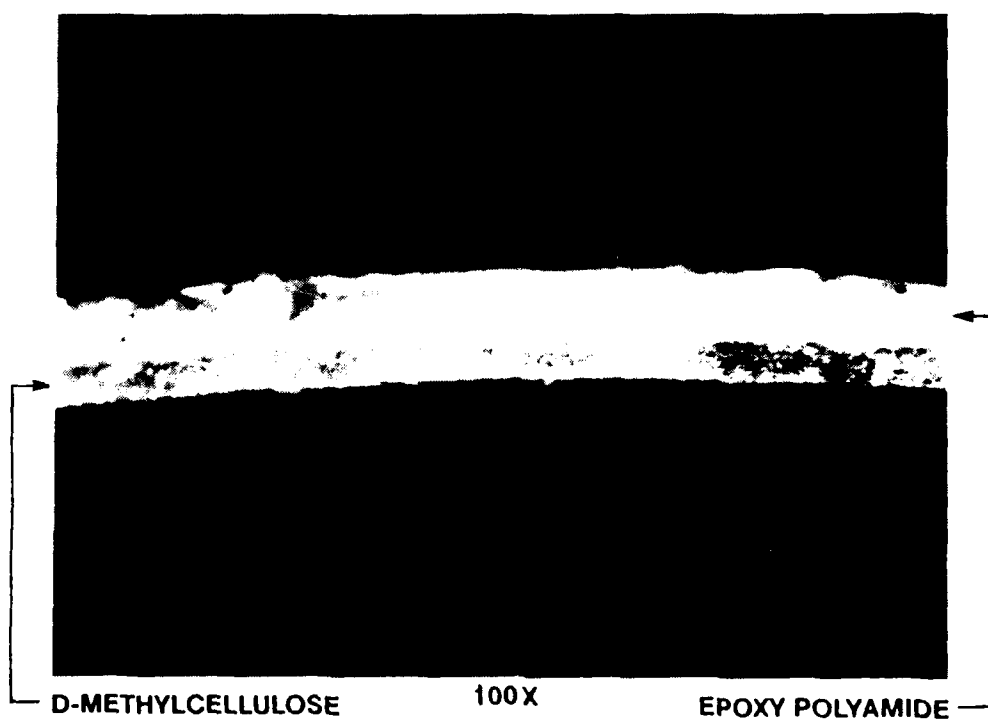


Fig. 3 Cross Section of MIL P-23377 Epoxy-Polyamide/D-Methylcellulose Interface

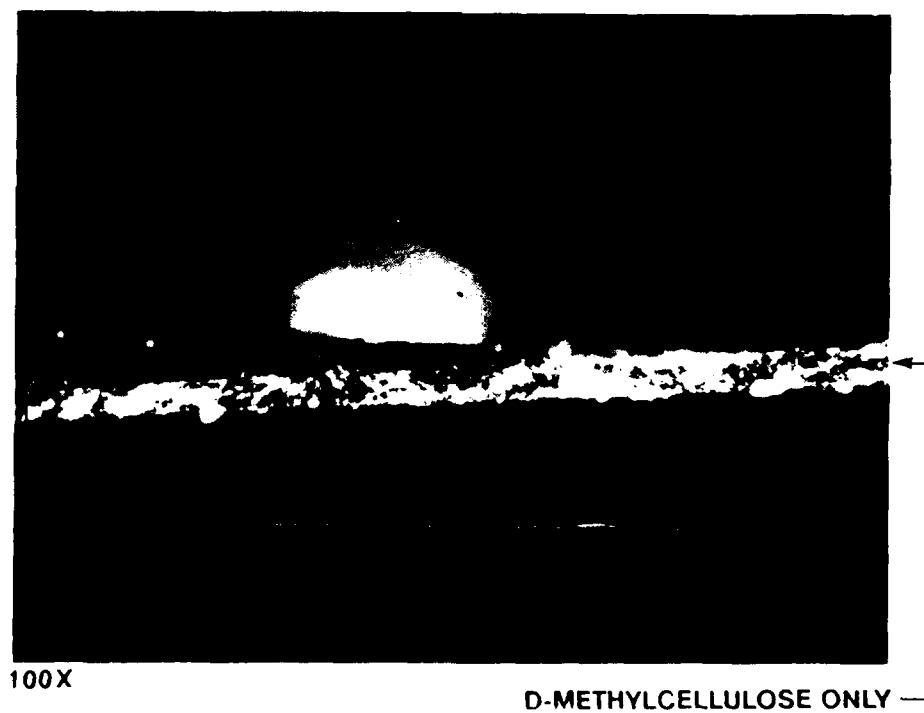
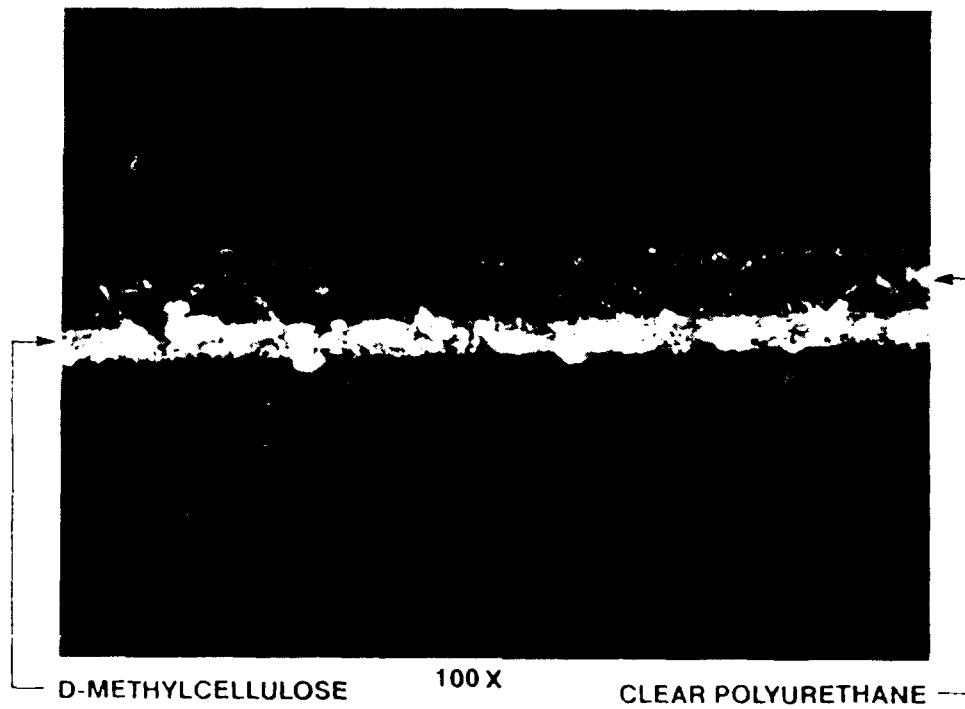


Fig 4 Cross Section of MIL C-83286 Polyurethane/D-Methylcellulose Interface

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Table 6 SPRAY-DRYING CONDITIONS FOR TREATMENT OF AQUEOUS METHYLCELLULOSE-QUATERNARY AMMONIUM DICHROMATE EMULSIONS

Sample Number	Inlet Temp. (°C)	Outlet Temp. (°C)	Atomizing Air Setting	Feed Rate (g/min)	Weight of Emulsion Dried (g)	Amount Recovered (g)
7-902	111	64	700	5.67	51.0	1.0
7-903	110	64	550	5.62	50.6	0.6
7-904	110	68	650	3.85	50.1	1.1
7-905	110	58	700	8.73	50.2	0.8
7-906	110	69	800	3.85	50.1	1.15

The method for the exploratory evaluation was to add the encapsulated powder to the 100% liquid silanes, followed by either simple evaporation in a fume hood for the high-volatility candidates, Nos. 1 and 2, or vacuum removal for the higher boiling fluids, Nos. 3 and 4.

Silanes 1 and 2 were successful in producing surfaces with good holdout of the Mil-T-81772 Type II thinner. Hexamethyldisilazane achieved a holdout for 3 to 4 h, whereas the methyltrimethoxysilane-coated powder gave a holdout for approximately 8 h. The two latter silanes turned green (reduction of the chromate to Cr (III) during evaporation in laboratory light).

It was of interest to observe the stability of the methylcellulose shell-dichromate quaternary core in the silane candidates. No dissolution of core material was observed during the applications, an indication of efficient microencapsulation, since the core materials are otherwise rapidly soluble in the silane monomer liquids. Following the drying/evaporation step, it was necessary to break up the silane-coated powders utilizing a soft grinding action with a metal spatula. Observation of the No. 2 silane-coated system showed no light sensitivity over a 4-week period for the dried powder when the core materials were the single dichromate quaternary, D, or the full mixture, DNBM. Dissolution of the coated candidates in salt water was also tested. This was found to take approximately 0.25 h following immersion.

Microencapsulation Scaleup. To prepare sufficient quantities of the microencapsulated powders, scaleup operations were performed at SWRI. The preparation of 749 g of DNBM mixture was described previously. A preliminary emulsification run was carried out using the D salt as a model compound plus 5% methylcellulose solution. SWRI used a laboratory-size "Sonicator" that utilized ultrasound for dispersion and produced no foam. SWRI applied this method, spray-dried the resultant emulsion, and shipped the powder to LMSC for test. It was determined that a significant amount of the D quaternary was "outside" the methylcellulose shell. This was based on visual inspection of the liquid-silane-plus-powder mixture, which showed obvious dissolution of the chromate salt. Either the emulsification process was inefficient, or some other factor, such as impurities introduced during the dispersion, had come into play.

It was postulated subsequently that the cause was contamination in the Sonicator laboratory ultrasound homogenizer. Since this unit was not scalable to higher output levels, i.e., 500 to 1000 g, the process was not repeated. Further processing utilized a Gifford-Wood(G-F) homogenizer, Model 1-L, and included a laboratory/pilot Anhydro spray dryer. The work performed with these units is described as follows.

Using the G-F homogenizer, which had been thoroughly cleaned and rinsed with 1-m Ω deionized water, 61 g of DNBM, Batch No. 1, was emulsified in 3 L of 5% methylcellulose, also prepared in high-purity deionized water. The percent DNBM added was 29 based on total solids. Approximately 20 min of mixing

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time was required to achieve an emulsion with particles in the 1- to 10- μ m range. Two samples of the emulsion were spray dried using the Buchi 190 laboratory spray drier: the first immediately following preparation of the emulsion; the second after standing overnight to test emulsion stability. Drying conditions were as follows:

Sample No. 7-953 (both samples)

Inlet Temperature	105°C
Outlet Temperature	64°C
Atomizing Air	700 setting on flow meter
Feed Rate	5.5 g/min
Aspirator Air	100%

Testing the two microencapsulated powders that were silanized at LMSC indicated that the process was successful, since immersion in Type II epoxy thinner yielded no extraction of yellow Cr(VI) over 4 h.

Using the G-F homogenizer, 215 g of DNBM, Batch No. 1, was emulsified in 11 L of 5% methylcellulose solution prepared using 1-m Ω H₂O. Approximately 45 min of mixing time was required for preparation. The emulsion was spray dried using the Anhydro dryer (see Fig. 5). The percent DNBM added was 28. The drying conditions were as follows:

Sample No. 7-968

Inlet Temperature	180°C
Outlet Temperature	60°C
Feed Rate	70 g/min
Atomizing Air	25 psi

Recovery was 145 g of dried product. The remainder was lost when large chunks of material came loose from the drying chamber and contaminated the product in the collection vessel. Estimated recovery was about 50%.

After organosilane surface deactivation, the powder was tested for epoxy diluent/solvent compatibility. The recovered material indicated significantly better solvent resistance than any of the previous Buchi 190 laboratory-dried samples. The microencapsulated powder (before silane treatment) was dispersed in oil, and optical micrographs were made at 200 $\times$. For comparison with the microencapsulated D in methylcellulose, sample 7-864 was also photographed. This sample had been spray dried in the Buchi unit, and the emulsion had been prepared at LMSC. (See Figs. 6 and 7, which show dark and bright field illumination photomicrographs of the particles dispersed in immersion oil.) The Anhydro-dried DNBM microparticles were somewhat larger than the Buchi-dried particles. A smaller nozzle and a slightly lower feed rate to reduce the particle size to 10 to 20 μ m or smaller were used in later runs.

To increase the core content/payload above the 28 to 29% levels, two 250-cm³ emulsions were prepared at LMSC, such that in the 5% methyl-cellulose solutions, the core levels based on total solids were 55 and 70% by weight. The emulsions were spray dried in the Buchi unit. The process conditions were as follows:

Inlet Temperature	100°C
Outlet Temperature	60°C
Atomizing Air	800 on flow meter
Aspirator Air	100%
Feed Rate	6 g/min

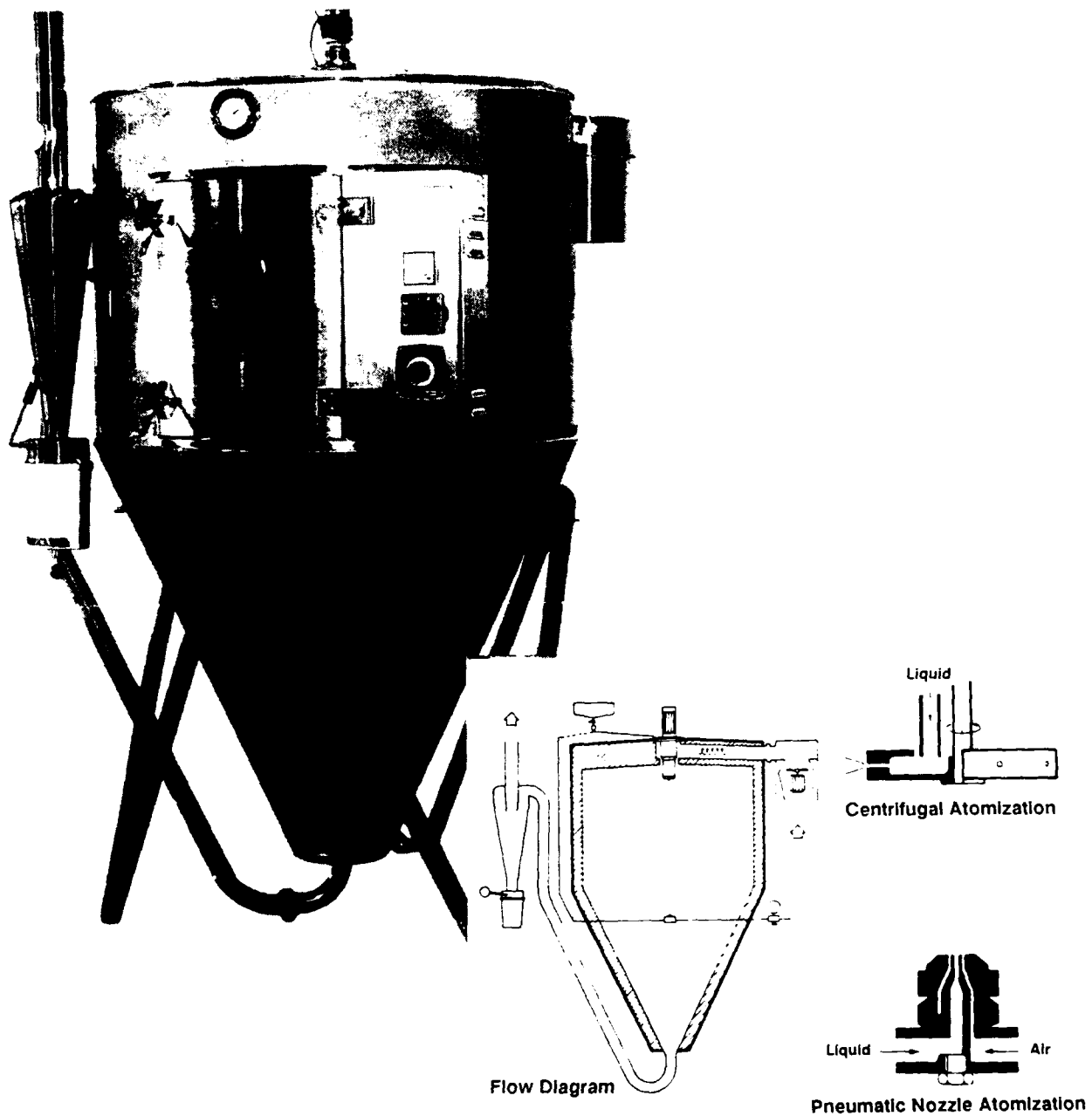


Fig. 5 Anhydro Spray Dryer Photo and Schematic

200X OPTICAL MICROGRAPH, SAMPLE NO. 7-864

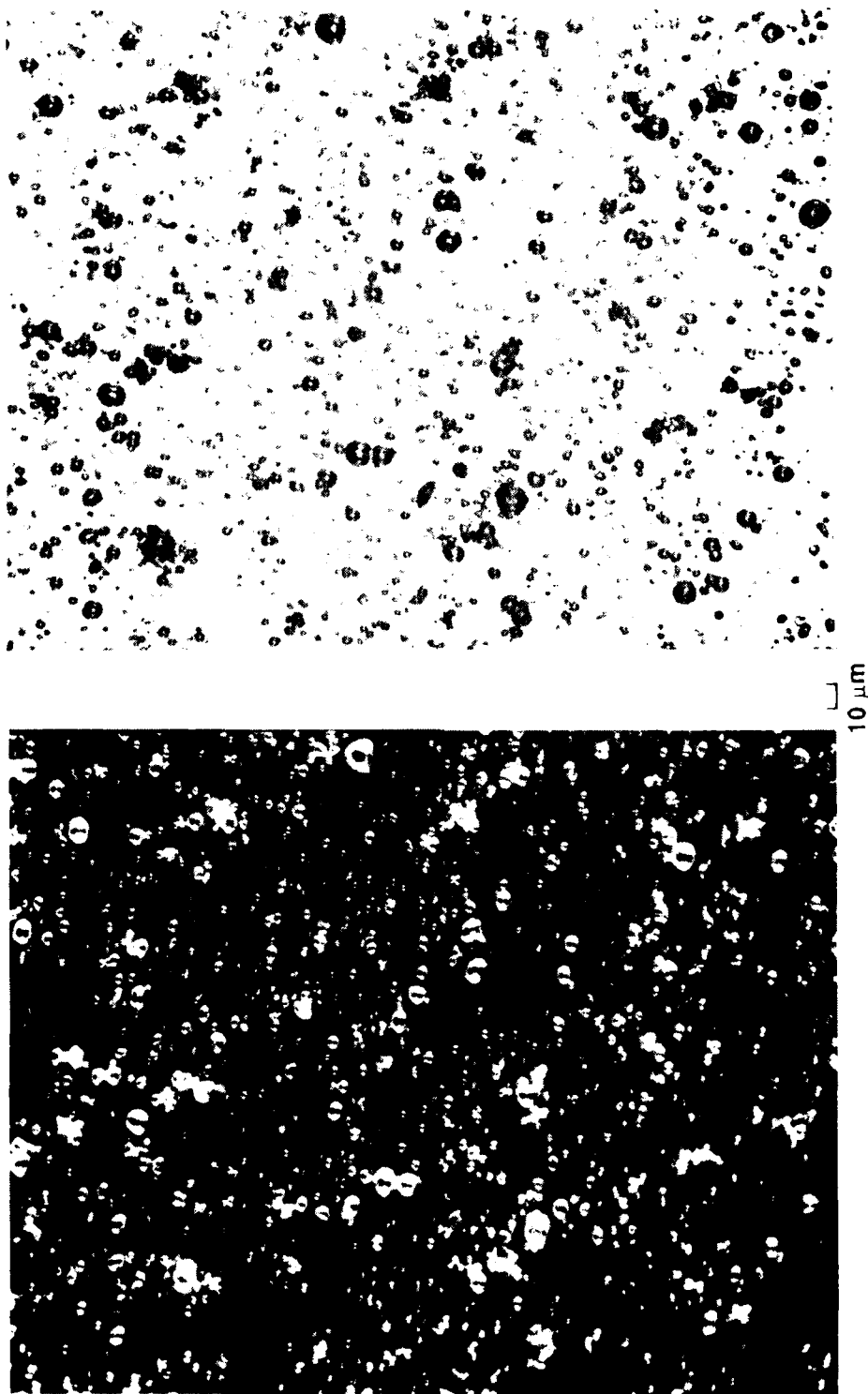


Fig. 6 29% D (Dichromate) Microencapsulated in Methylcellulose (Buchi Dryer)

200X OPTICAL MICROGRAPH, SAMPLE NO. 7-968

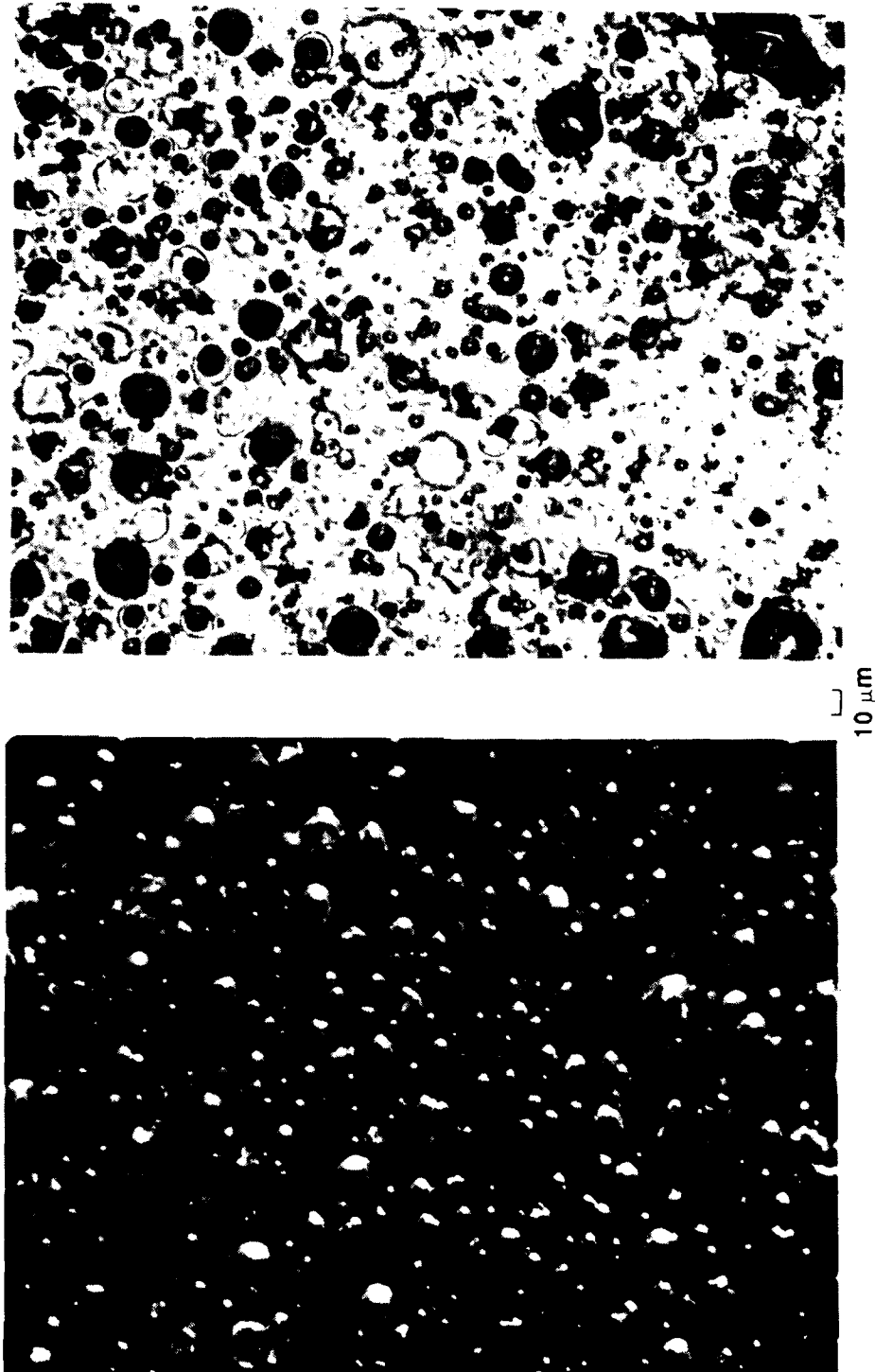


Fig. 7 Initial 28% DNBM Microencapsulation Scaleup (Anhydro Dryer)

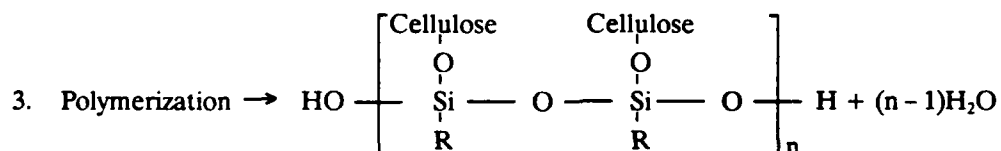
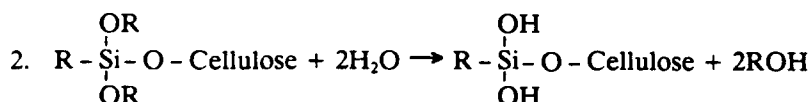
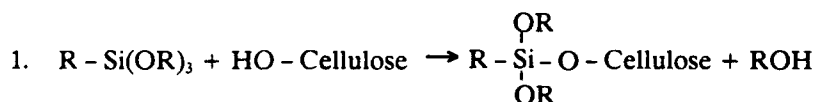
The resultant powders, after silane treatment, did not pass the epoxy diluent test, indicating that part of the payload may not have been completely encapsulated, or, as later postulated following calculations of shell thickness, the coatings were too thin to hold out the diluent.

Silane Deactivation Process and Evaluation. The first silane depositions on the methyl cellulose shells were made by immersion of the microcapsules in liquid alkoxy silanes, followed by evaporation of the excess liquid in a fume hood. Whereas the silanized 30% core (20 to 30-mm capsules) resisted penetration and subsequent leaching of the D-salt for more than 4 h, neither the 55 nor 70% core silanized microcapsules held out the epoxy-polyamide Type II (B) diluent for more than a few minutes.

At this point, a vapor infiltration system was used to attempt to improve the deposition process on the methyl cellulose shell. The following steps illustrate the process.

1. Place 120-mesh microcapsule powder on screen in vacuum oven
2. At 29-in. Hg vacuum, raise temperature to 100°C
3. Inject silane fluid and allow to equilibrate for 2 to 4 h
4. Remove powder, expose to air for several hours, and store in amber glass bottle or Al-foil-covered container

At the specified conditions of the process, the silane is absorbed/adsorbed onto the cellulose surface. After vacuum release, the moisture in the air hydrolyzes the alkoxy bonds to Si-OH, followed by polymerization, to produce hydrophobicity and shell pore blockage. The associated reactions may be written as follows:



Following the hydrolysis reaction in air, approximately 4 h, the Type IIB solvent immersion test was run by dropping approx. 0.1 g of product into 20 cm³ of solvent. For the 30% core microcapsule, complete holdout was achieved for 18 h with no sign of yellow Cr (VI) solution. As before, for the 55 and 70% cores, the Cr (VI) color became apparent in 1 to 5 min and intense within 1 h. Without the silane treatment, the leaching reaction occurred immediately on contact with the diluent solvent.

Calculations of wall thickness (Ref. 7) for a 15-μm-diameter microcapsule containing 70% DNBM (density = 1.0) and 30% methylcellulose (d = 1.2) gave 0.8 μm. At 25 μm, the capsule will have a 1.5-μm shell, probably adequate for absorbing a sufficient quantity of silane for development of solvent holdout. The 15-μm capsule is postulated to have too thin a shell. This is, in part, a rationale for preparing capsules with diameters above 25 μm. The formulas used for the calculations are:

$$W = r_1 - r_2$$

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where W = wall thickness, τ_1 = capsule radius, τ_2 = radius of encapsulate.

$$W = \sqrt[3]{\frac{3V_1}{4\pi}} - \sqrt[3]{\frac{100 - \%wall}{100} \left(\frac{3V_1}{4\pi} \right)}$$

where V_1 = volume of capsule.

Microencapsulation and Silanization Development. Investigations in processing were continued to attempt optimization of particle size. At this point, all emulsions were prepared at SWRI. Using the second batch of DNBM, three microencapsulation runs were completed: 30, 55, and 70%, using the Gifford-Wood homogenizer and the Anhydro spray dryer. The data for the processing are given in Table 7. The amount of material collected represented 30 to 35% of the starting material.

The vapor infiltration method was used to silanize the 55 and 70% core microcapsules. Initially, the batch sizes were 1 to 10 g, in which the powders were spread evenly in a single layer on a screen support in the vacuum oven. The initial reactions were run at 100°C, which was acceptable for the 30 and 55% core microcapsules. At 110°, however, the 70% core migrated through the cellulose shell, as indicated by an obvious color change in the capsule wall to dark brown. DNBM was also found on the chamber walls.

Material from the first 30% core microencapsulation scaleup was silanized first; the batch size was increased to 30 to 40 g. Coating efficiency was so high that the silanized capsules could be immersed in the test solvent and in seawater for > 72 h without any leaching of the Cr values, indicating an excess of the siloxane polymerization. Another silanization reaction involved the second pilot-scale spray dried lot, No. 8-082, 55% core, which held out the test solvent and seawater only moderately. Next, two sieve screens full of 55% core microcapsules, total weight 130 g, were treated. The temperature was lowered to 65 and 85°C, and the same material was exposed three times for a total of 14 h. Deactivation was not achieved beyond 15-min contact time in either solvent or salt water. It was hypothesized that the poor reaction was the result of excessive particle-to-particle contact in the bulk of the powder, thereby

Table 7 SECOND SERIES OF PROCESSING CONDITIONS FOR DNBM MICROCAPSULES
(Gifford Wood homogenizer, Anhydro spray dryer)

Lot No. Payload	8-081 30%	8-082 55%	8-083 70%
<u>Drying Conditions:</u>			
Inlet Temperature	180°C	175°C	175°C
Outlet Temperature	65-70°C	65-70°C	65-70°C
Atomizing Air	65 psi	45 psi	60 psi
Feed Rate	55 g/min	45-55 g/min	55 g/min
<u>Product</u>			
Particle size	Most 10-25, some larger	Most 15-40, some larger	Most 15-50, some larger
Weight Recovered	170 g	165 g	130 g

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preventing diffusion of the silane gas to all sites on the powder surfaces, rather than the 110° versus 85°C difference in reaction temperatures in the vacuum oven. Table 8 summarizes the silane reaction data.

Photomicrographs of the 55 and 70% core microcapsules that were silanized are shown in Fig. 8 and 9, respectively. To disperse (separate) the particles in order to photograph the individual microcapsules, it was necessary to use a dispersion oil. In both photos, but more obviously in Fig. 9, the penetration of the 1- to 10- μ m capsules by the oils, which is a hydrocarbon base, occurred and extracted the DNBM from the smaller spheres (see empty skeletal formations) but not from the larger, 20- to 40- μ m, spheres, after 1- to 2-h standing. This indicated that it would be possible to silanize both the 55% and more desirable 70% cores by changing the spray-drying conditions to minimize the presence of the detrimental 1- to 10- μ m microcapsules. As a result, the following was investigated to increase the diameter of the capsules and minimize the presence of the 1- to 10- μ m particles:

1. Varied nozzle sizes
2. Varied feed rates using the most promising nozzle from 1
3. Varied atomizing air pressures using the most promising system from 2
4. Varied methylcellulose concentrations

Optimization of Microencapsulation Process. The nozzle size, feed rate, atomizing air pressure, and methyl cellulose concentration were varied using a simulant (significantly less expensive material) for the

Table 8 SILANE REACTIONS ON DNBM CORE METHYLCELLULOSE SHELLS

Code	Core (%)	Amount (g)	Silane (cm ³)	Oven Temp (°C)	Contact Time (h)	Resistance to Solvents	Comments
2-133	30	<5	20	110	1	Excellent	Discoloration of cellulose shell to yellow tan, all 110°C reactions
2-136	70	<5	20	110	1	Poor	
2-137A	70	5-10	30	110	2	Poor	
2-137B	55	5-10	30	110	2 1/4	Poor	
2-143	30	33	30	110	6	Excellent	First spray-dry scaleup First silanize scaleup
2-148	30	37	10	110	2	Excellent	Second spray-dry scaleup DNBM migration through shell when silanized at 110°C
3-15	55	35	5	110	2	Moderate	
3-16	70	35	5	110	2	Poor	
3-17	70	35	10	55	2	Poor	Golden yellow color
3-18	70	35	10	65	4	Poor	Rerun of 3-17
3-20	70	35	10	65	2	Poor	Rerun of 3-17
3-31	55	130	20	65	4	Poor	Golden yellow
3-34	55	130	20	65	6	Poor	Rerun of 3-31
3-36	55	130	20	85	4	Poor	Rerun of 3-34

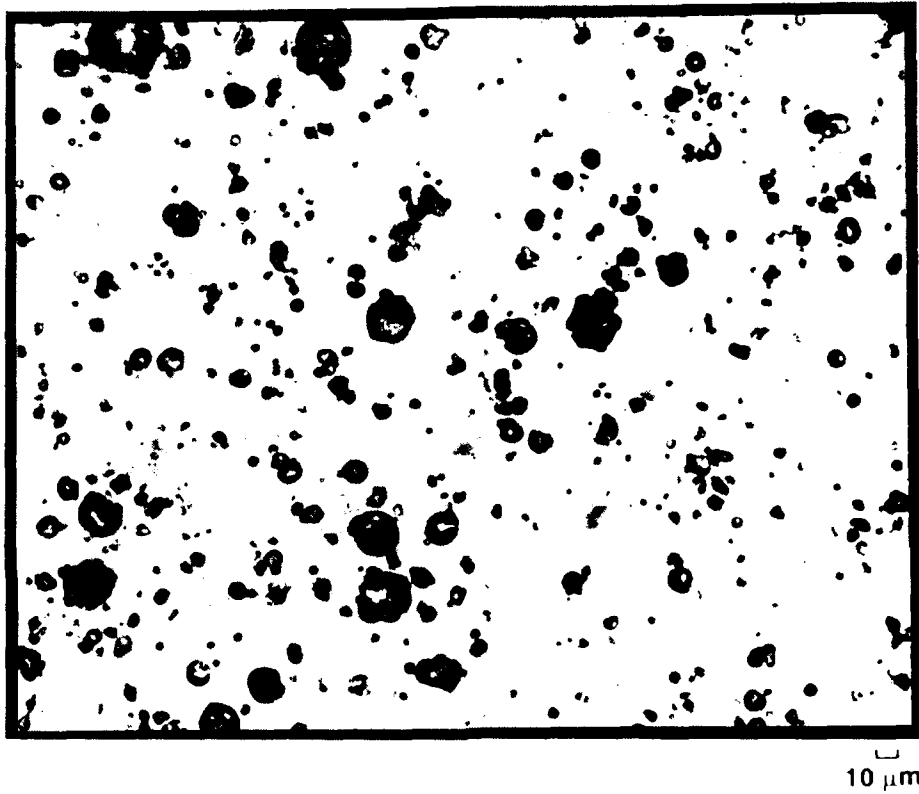


Fig. 8 DNBM Microencapsulation Scaleup, 55% Core, Spray Dried,
Silanized, 200 $\times$ Photomicrograph

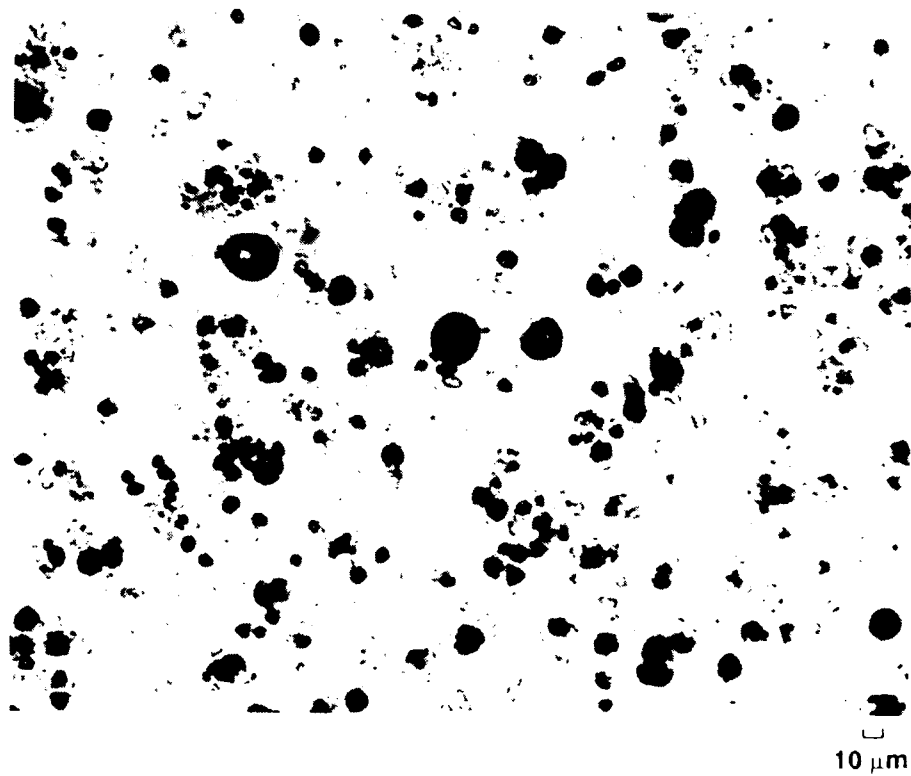


Fig. 9 DNBM Microencapsulation Scaleup, 70% Core, Spray Dried, Silanized, 200 $\times$ Photomicrograph

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DNBM material. This was Adogen 464, $\text{CH}_3(\text{C}_8\text{-C}_{10})_3\text{N}^+\text{Cl}^-$, the starting material used to prepare the DNBM mixture. The results of the optimization are:

Nozzle Size	0.45 to 0.064
Feed Rate	50 g/min
Atomizing Air	20 psi
Counter Air	15 psi
Inlet Temp.	180°C
Outlet Temp.	75°C
Payload (core)	55% Adogen 464
Recovery	49% (based on total solids in Anhydro dryer)

The nozzle was placed in cocurrent position in the dryer—same direction as air flow. The counter air was used to keep the product from building up on the nozzle unit. Feed rates were varied at 37, 67, 77, and 91 g/min with the higher rates producing more shell fragments and less recovered product. Different nozzle sizes were varied at 20 to 30 psi. The shell polymer concentration was reduced from 5 to 4%. This produced a less viscous solution which appeared to atomize more readily.

A sample of the optimized, spray-dried sample dispersed in a high-viscosity immersion oil was inspected at 200 $\times$. Results of inspection of two dispersions indicated the following:

First field	{ most 30 to 40 μm some 10 to 20 very few greater than 40
Second field	{ most 30 to 40 μm many 10 to 20 very few greater than 40

There were significantly fewer particles in the low 10- to 20- μm range than in previous runs. As a result, the third DNBM scaleup batch, 10990-117, was microencapsulated using the conditions derived above.

In this series, approximately 1100 g of DNBM was microencapsulated in methylcellulose under the following conditions.

Nozzle size	0.046 to 0.064 in.
Feed rate	30 to 50 g/min
Atomizing air	20 psi
Counter air	15 psi
Inlet temp	185 to 180°C
Outlet temp	85 to 75°C
Payload (core)	55% DNBM
Recovery	66%

Particle size was measured using high-viscosity immersion oil to prepare the dispersions. The resultant capsules were mostly in the range 20 to 40 μm , some were from 50 to 70 μm , and a few were below 20 μm . Large clumps of DNBM-methylcellulose wall material were observed as had occurred previously, the apparent result of the length of the sequences.

Chemical analysis was performed to evaluate the 55% core levels of the microcapsules. Samples were dried overnight at 80°C, followed by dissolution in concentrated H_2SO_4 , dilution to volume, and analysis by atomic absorption spectroscopy. Percent total Cr(VI) found was as follows:

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Sample	% Cr in Microcapsules	% Cr in DNBM	% Core Level*
8-154A	1.223	2.24	54.6
8-154B	1.328	2.24	59.3

* % core level = 100 (% Cr in microcapsules/% Cr in DNBM)

The vapor silanization process was applied to the optimized microcapsules described above. However, the treated capsules uniformly failed the epoxy diluent test. The 55% core also was unstable, i.e., leached out, when immersed in methyltrimethoxy silane fluid, in contrast to 30% core materials when similarly immersed. It was hypothesized that the capsule shells were defective, or too thin, or that the vapor silanization process was inadequate. Scanning electron microscopy (SEM) photos were taken to more closely assess the morphology of the capsules. Figure 10 shows the poor homogeneity of the samples.

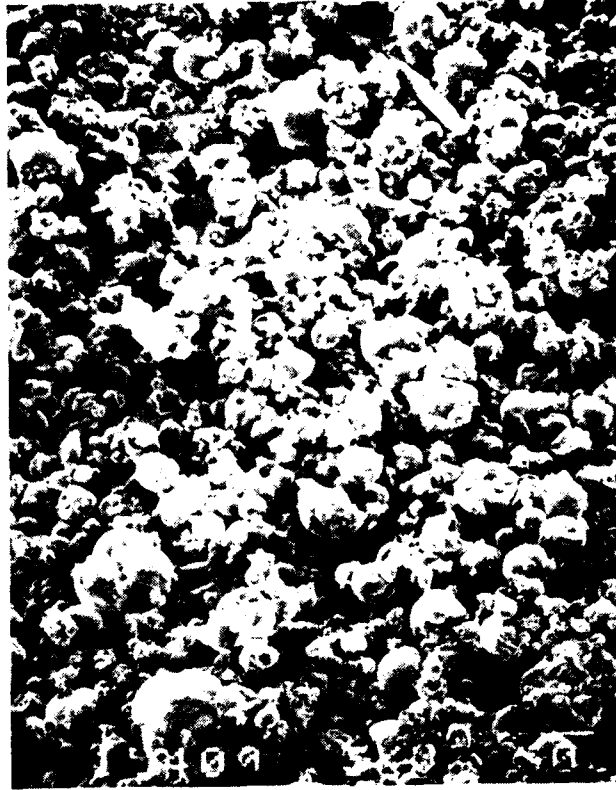
An encapsulation was also carried out using a higher molecular weight methylcellulose powder. The latter MC polymer gave a viscosity of 1500 cps for a 2% solution, whereas previous MC polymers gave 25 cps for a 2% solution. Since the polymer was higher in viscosity, a lower concentration was necessary, 1.75% instead of 4% used for the lower viscosity MC. The temperature required to dry the product was slightly higher than that required for previous samples. Following conventional silanization processing, there was no significant difference in response to the Type II B epoxy diluent holdout.

As a result of the failures, a modified procedure was developed to improve the silanization process in order to minimize the Cr(VI) extracted by the epoxy diluent. The process involved the vacuum exhausting of methyltrimethoxysilane vapors through 10- to 15-g microcapsules to be coated that were placed on a 4-in.-diameter 140-mesh stainless steel screen in a vacuum chamber. Pressure was approximately 10 torr. The liquid silane was located below the screen in a Petri dish reservoir and the excess silane was trapped beyond the particles in a liquid nitrogen-cooled Dewar flask in front of the mechanical vacuum pump. After maintaining the vapors in contact with the powder for 2 h at room temperature, the vacuum chamber was opened to air slowly and held for 6 h. This was followed by sieving through a 240-mesh screen to break down large agglomerates. Testing in the epoxy diluent showed a significant improvement after the process was repeated twice. There was some initial Cr(VI) extraction, but after the first yellow supernatant solution was poured off, there was no further extraction for 24 h when fresh diluent was added to and mixed with the microcapsules.

A final microencapsulation sequence was performed to prepare sufficient microcapsules for formulation with MIL-P-23377 epoxy-polyamide primer (minus SrCrO_4). Five hundred grams of DNBM mixture was microemulsified and spray dried yielding a microcapsule weight of 380 g. The spray dry processing was performed under the following conditions:

Nozzle size	0.060 to 0.120 in.
Feed rate	65 g/min
Atomizing air	40 psi
Inlet temperature	190 to 200°C
Outlet temperature	100 to 110°C
Recovery	53%

200X



50 μm

1000X



5 μm

1000X



5 μm

Fig. 10 SEM Photographs of Microcapsule Lot 154A

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Analysis of microcapsule morphology was carried out using SEM. The elemental analysis of Cr and Mo was performed for comparison with the starting DNBM material data. Percent moisture in the capsule shell material was determined by heating at 80°C overnight. Calculation gives the actual percent core values.

Sample No.	Identification	%Cr (AA, Total)	%Mo (AA, Total)	%H ₂ O
11048-29	DNBM	2.44	4.19	—
8-530	DNBM Microcapsules	1.76	3.08	7.32

Calculate core content:

a. using Cr data

1.76% in microcapsules $\times 100 = 72.1\%$

2.44% in neat DNBM

$72.1/0.9268 = 77.8\%$ core (dry wt)

b. using Mo data

3.08% in microcapsules $\times 100 = 73.5\%$

4.19% in neat DNBM

$73.5/0.9268 = 79.3\%$ core (dry wt)

Averaging the dry weight values yields 78.5% payload

This was the highest core level prepared. Figure 11 shows the microcapsule size distributions as determined by SEM. The improvements in uniformity and sphericity were obvious, although many 1- to 10- μ m particles were present.

Fumed-Silica Treatment and Silanization of Microcapsules

A method for deflocculation of the DNBM microcapsules that utilizes commercially available fumed silicas was developed at LPARL. By adding to, and three-dimensionally mixing, 15-25% by weight of fumed silica with microcapsule Lot 8-530, the properties of the capsules were changed from a strongly flocculated to a dispersed state. The addition resulted in a radical, fluid-like change in flow properties such that the powder could be air-classified with minimum concern regarding the presence of agglomerates. The materials evaluated included Cabot M-5 and Tullanox 500 fumed silicas (Fig. 12).

Both treated powders were then silane treated and hydrolyzed in laboratory air (Fig. 13). Tests for resistance to penetration by epoxy diluent were positive (favorable), although complete resistance was not achieved.

The ability to disperse the flocculated solids from the spray dryer has made the process suitable for reactions in a twin-shell blender or other means to keep the particles in suspension during the silanization reaction sequences. In addition, should air classification be required to remove over- and/or undersize microcapsules, the dispersion process described will permit a high probability for success in this operation.

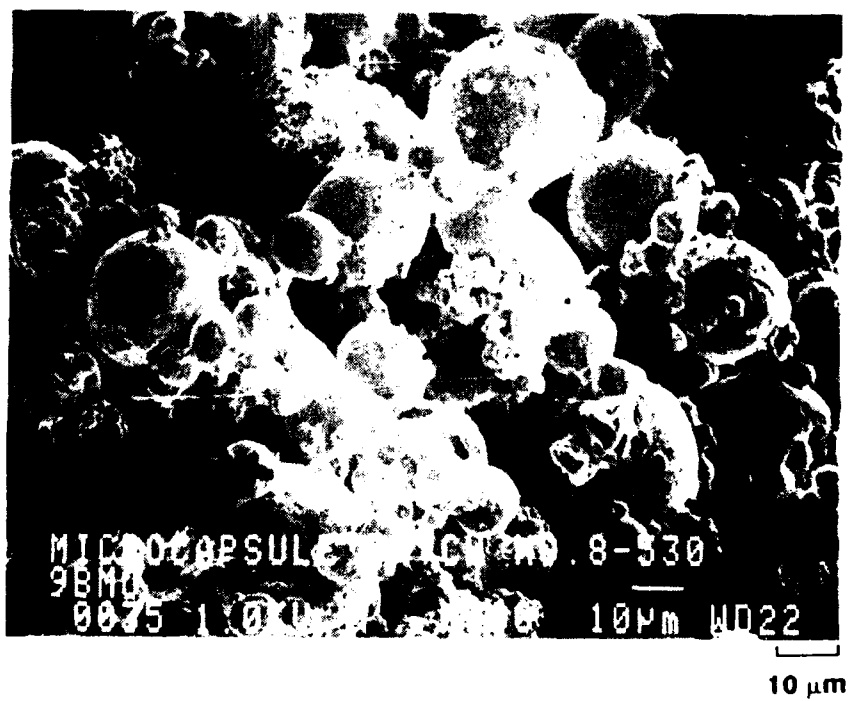
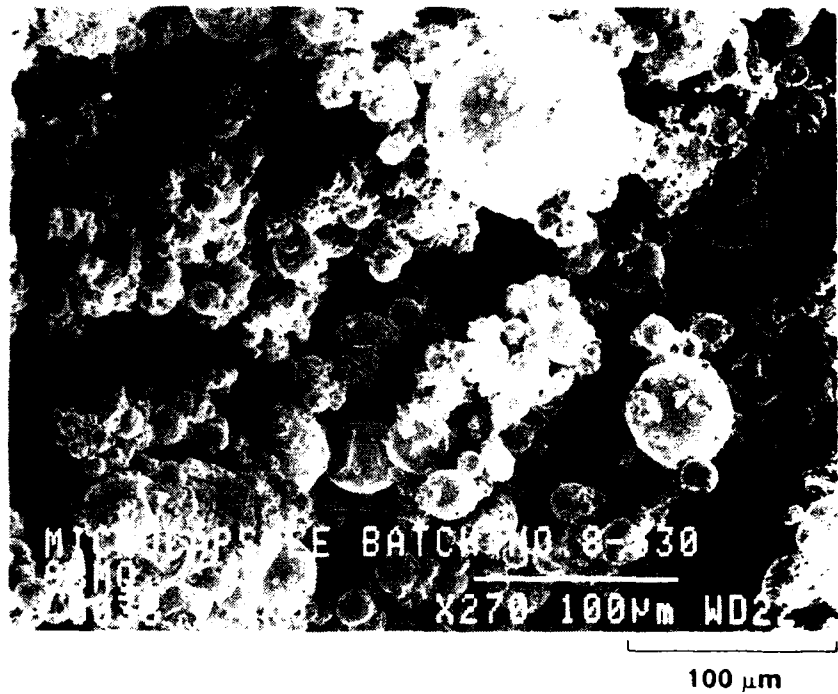


Fig. 11 SEM Photographs of Microcapsule Lot 8-530, Untreated



10 µm



10 µm



10 µm

Fig. 12 SEM Photographs of Microcapsules Containing 78% DNBM, Lot 8-530, Silanized, No Fumed Silica

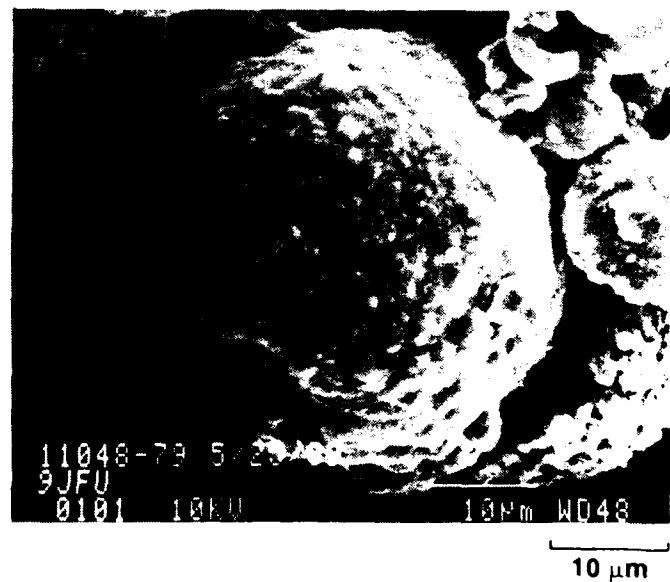
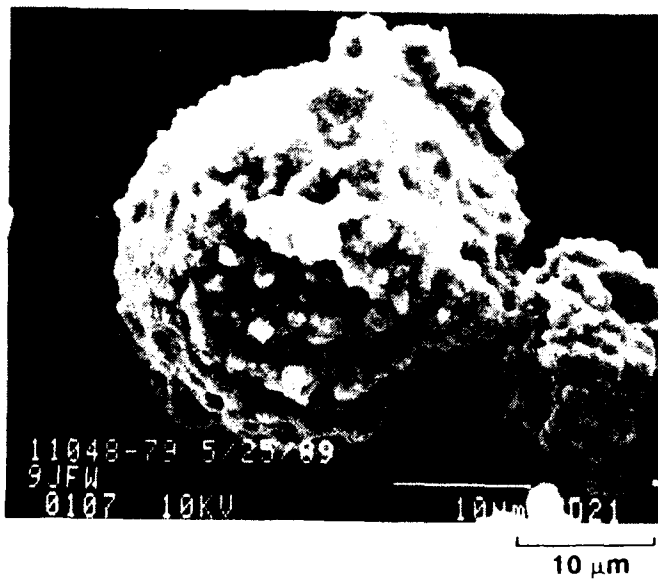
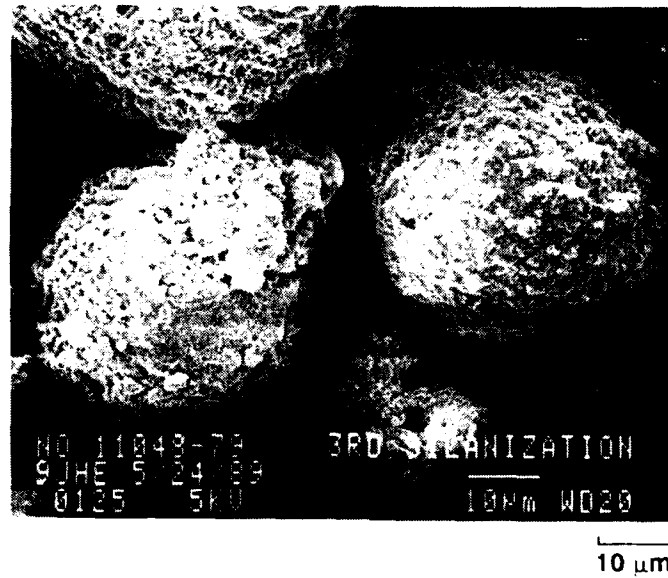


Fig. 13 SEM Photographs of Microcapsules Containing 78% DNBM, Lot 8-530, Fumed Silica Addition, Silanized

Section 4

TEST AND EVALUATION OF DNBM AND DNBM MICROCAPSULES IN EPOXY-POLYAMIDE COATINGS

DNBM (100%) as a Subcoat Under Epoxy-Polyamide Coatings

Preliminary to establishing the effectiveness of the DNBM microcapsules in an epoxy-polyamide primer formulation, a baseline test was designed using 100% DNBM applied directly to steel surfaces. The successes that were obtained with the preliminary form of DNBM that mitigated corrosion fatigue and stress corrosion cracking in 7075-T6 high-strength aluminum, AISI 4340, and 300M steel alloys may be recalled at this point (Refs. 1 and 2). In the series described below, the objective was to assess the effectiveness of the DNBM developed on the current program as a general corrosion inhibitor.

To carry out this evaluation, a DNBM mixture was spray applied from a toluene solution onto 1010 steel panels that had been sand blasted to white metal. The calculated weight of DNBM was based on the amount of microcapsules designed to take the place, weight for weight, of the strontium chromate in the MIL-P-23377 epoxy-polyamide primer. For a 4 in. $\times$ 6 in. $\times$ 1/8-in. 1010 steel panel, 0.3 to 0.4 g DNBM was deposited directly onto the bare steel surface, followed, after evaporation of the solvent, by deposition of both chromate-free and chromate-containing epoxy layers. A similar quantity of methyl sulfate quaternary (starting material for the DNBM quaternary salts) was also deposited. Clear epoxy was applied last, since some DNBM was observed to have bled through into the first epoxy layer before cure was complete. Following 7 days of room-temperature cure, diagonal scribe lines were drawn on the panels according to ASTM D-1654 using a vertically positioned tungsten carbide tip, style E, with 1/64-in. nose radius.

The coatings were exposed to an ASTM B-117 salt-spray environment for 1000 h. Salt-spray effects were observed at the scribe lines or within the coatings, depending on the formulation and type of inhibitor. Table 9 lists the observed corrosion results. Photographs of the corrosion areas are shown in Figs. 14 through 16.

The order of anticorrosion effectiveness via the method of time-to-failure was:

- | | |
|-------|--|
| Best | 1. DNBM/Epoxy (No Cr in epoxy) |
| | 2. DNBM/MIL-P-23377 Epoxy (Contains SrCrO_4) |
| | 3. MIL-P-23377 Epoxy (Contains SrCrO_4) |
| | 4. Epoxy (No Cr) |
| | 5. $\text{CH}_3\text{SO}_4\text{Quat}$ /Epoxy (No Cr) |
| Worst | 6. $\text{CH}_3\text{SO}_4\text{Quat}$ /MIL-P-23377 (Contains SrCrO_4) |

The effects of corrosion inhibition by the DNBM materials are clearly evident.

DNBM Microcapsules in Epoxy-Polyamide Primer

Initial Microcapsule-Filled Formulations. Two epoxy-polyamide formulations were prepared using two original 70% core batches that were silane treated. The formulations were made up as follows:

- No. 1 Part A 50.0 g (No SrCrO_4 , all other fillers present)
 Part B 42.6 g
 Microcapsule Lot No. V 15.0 g
 Epoxy diluent 72 cm^3

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Table 9 SALT-SPRAY CORROSION RESISTANCE OF MULTILAYER
 DNBM/EPOXY-POLYAMIDE COATINGS ON 1010 STEEL

Coating Number*	Coating System	Time-To-Failure (h)	Mechanism of Corrosion
74 (4)	DNBM/Epoxy (No Cr)	1000	Blisters
77 (3)	DNBM/Epoxy MIL-P-23377	1000	Blisters, lifting
83 (3)	CH ₃ SO ₄ Quat/ Epoxy (No Cr)	144	Excess small blisters
85 (2)	CH ₃ SO ₄ Quat/ Epoxy (MIL-P-23377)	72	Excess small blisters
88 (2)	Epoxy (No Cr)	240	Large blisters
90 (3)	Epoxy, MIL-P-23377	< 1000	Undercutting, lifting

* Each coating was topcoated with clear, unfilled epoxy.
 (Numbers in parentheses indicate the number of test panels exposed.)

No. 2 Part A 50.0 g (No SrCrO₄, all other fillers present)
 Part B 42.6 g
 Microcapsule Lot No. IV 11.5 g
 Epoxy diluent 60 cm³

Control coatings were standard MIL-P-23377, plus the same formulation minus SrCrO₄. Panels were coated by spray and drawn-down. The formulations were sprayed with a Binks C-gun at 25 psi using nitrogen as the carrier gas. Because both microcapsule formulations resulted in mat finishes, a minimum amount of epoxy-polyamide clear polymer (no fillers) was spray applied to cover the declivities and valleys of the coatings. These flaws could have led to results that were not necessarily related to the efficacy of the capsules as corrosion inhibitors at the cross-hatch marks. The use of the clear epoxy resulted in coatings that more closely resembled both the SrCrO₄ and unpigmented controls.

Because of the limitations in the method of deposition of the siloxane (at the time) on the surface of the capsules, which increases the surface area, much less DNBM could be added to replace the SrCrO₄ without exceeding the binder demand of the pigment. The 1010 steel panels (not shown) were coated with non-SrCrO₄ primer that contained the 5% DNBM in microcapsule form, whereas standard MIL-P-23377 contained 25 to 30% SrCrO₄ inhibitor. The panels were tested in the 5% salt spray chamber for up to 36 days. At 15 and 36 days of exposure, the severity of corrosion and blistering in the scribe region was significantly less for the panels that contained the microcapsules versus the standard MIL-P-23377 panels. Of course, the magnitude of corrosion increased after 36 days. However, the relative performance was the same.

Second Series of Microcapsule-Filled Formulations. A second series of five epoxy-polyamide coatings was formulated in which the test microcapsules contained 78% DNBM. The results are given in Table 10 for a 1000-h salt-spray exposure. Three of the coatings contained microcapsules that had been silane treated, two with and one without fumed-silica treatment. The two controls were MIL-P-23377 with SrCrO₄,

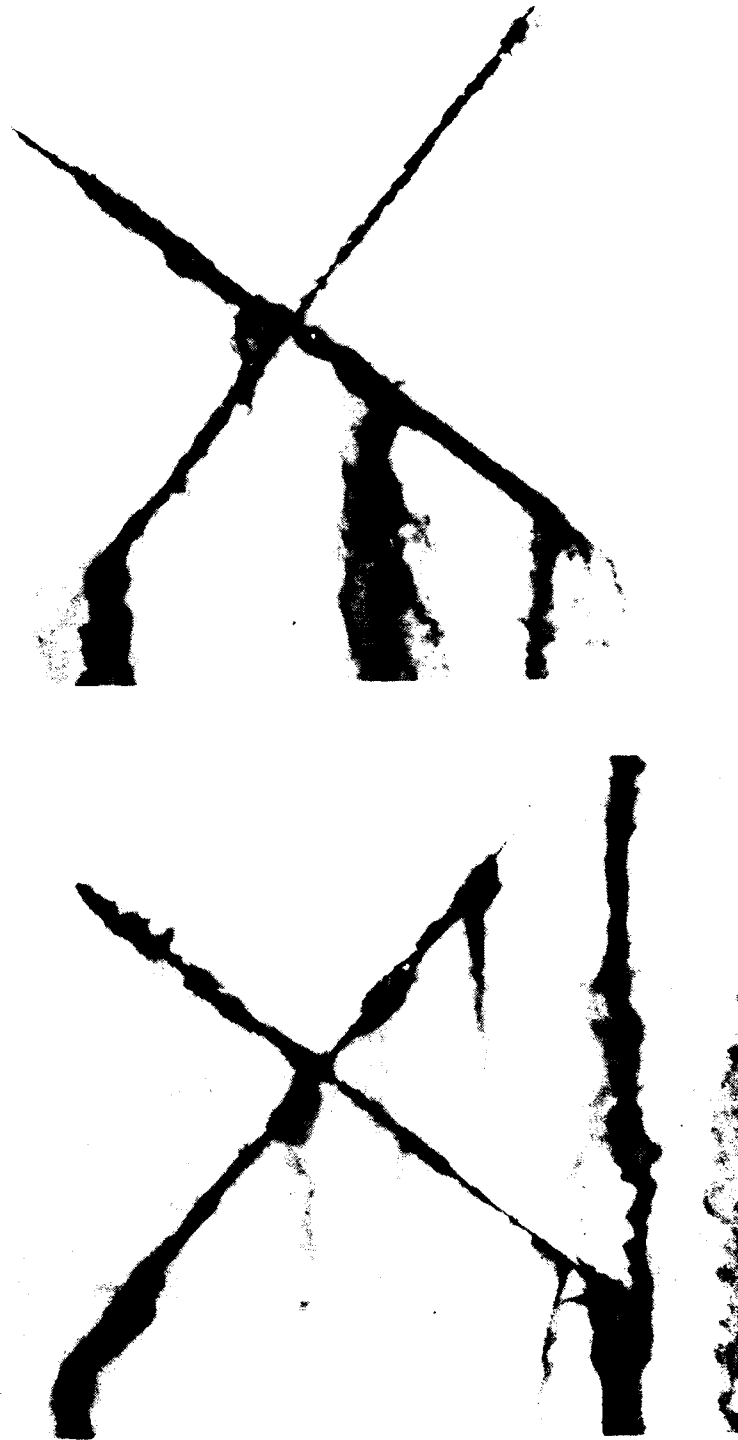


Fig. 14 Salt-Spray Exposure of Multilayer DNBM/Epoxy-Polyamide Coatings
on 1010 Steel (Note DNBM Bleed-Through), No. 74 Top, No. 77 Bottom

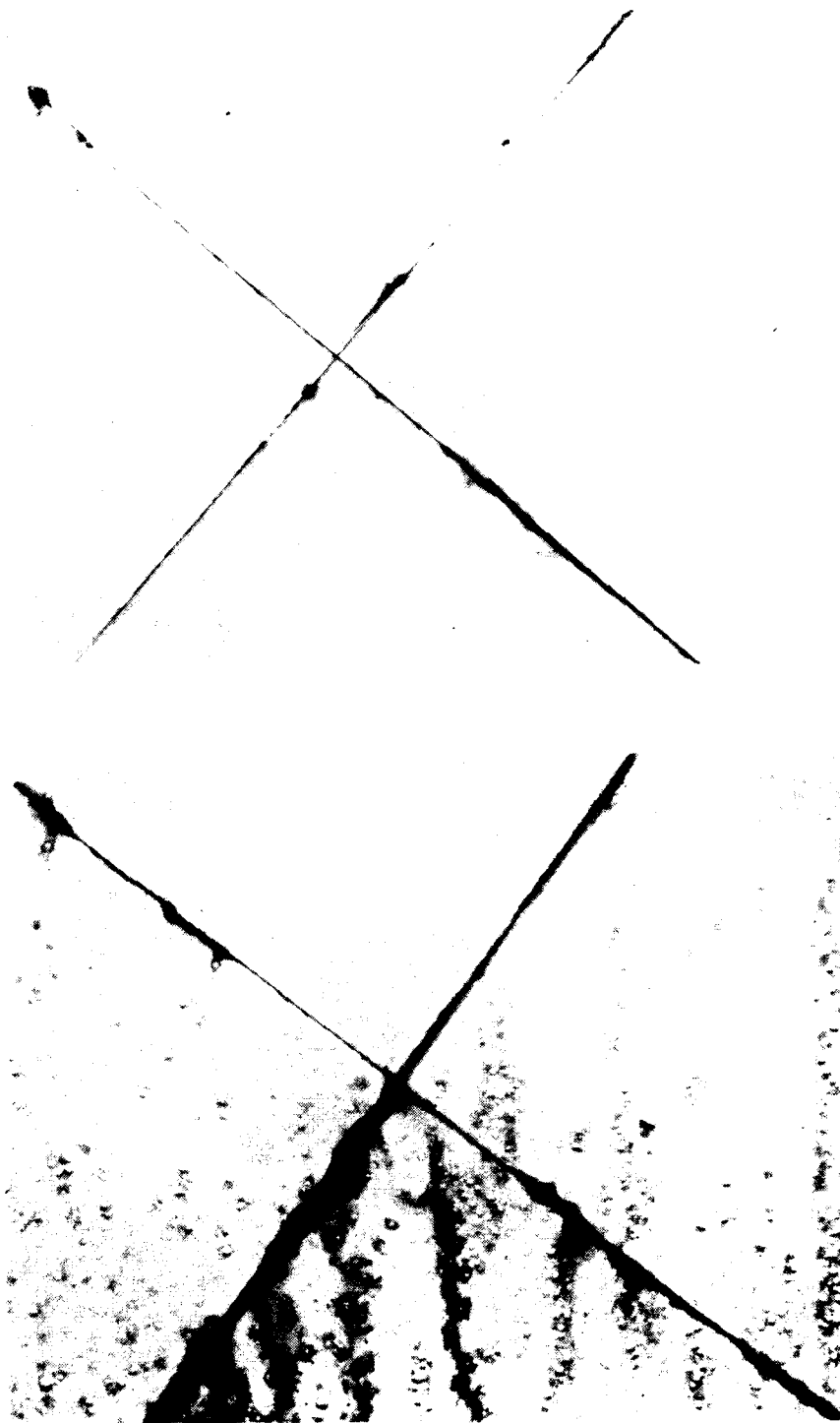


Fig. 15 Salt-Spray Exposure of Methyl Sulfate Quaternary Epoxy-Polyamide Coatings on 1010 Steel (Note Blistering), No. 83 Top, No. 85 Bottom



Fig. 16 Salt-Spray Exposure of Control Epoxy-Polyamide Coating on 1010 Steel, No. 88 Top, No. 90 Bottom

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Table 10 SALT-SPRAY CORROSION RESISTANCE OF DNBM MICROCAPSULE-FILLED EPOXY-POLYAMIDE COATING ON Q-PANELS

Coating Designation (No. of panels in test)	Inhibitor	Hours to Failure or Test Completion	Observations	Comments
20 <u>Base Epoxy.</u> No SrCrO_4 . No other fillers. (4). Dry coat. Exceeded CPVC	Silanized DNBM microcapsules. Incl. fumed silica	336	Rust penetration. Insignificant lifting at X	Poor response to penetration. Excellent response to lifting
27 <u>Base Epoxy.</u> No SrCrO_4 . No other fillers (3). Normal coat	Silanized DNBM microcapsules. Incl. fumed silica	1000	No rust, blisters, or lifting at X	Excellent overall response
36 <u>Base Epoxy.</u> No SrCrO_4 . All other fillers present (6). Brush coat. Not uniform	Silanized DNBM microcapsules. No fumed silica	336-432	Rust penetration. Minimal lifting at X	Poor response to penetration. Good response to lifting
2 <u>MIL-P-23377</u> Standard (4)	SrCrO_4	264-336	Blisters at X. No rust	Poor response at X
49 <u>MIL-P-23377</u> Minus SrCrO_4 . All other fillers present (4)	No SrCrO_4	504-696	Blisters over surface. No rust. Some lifting at X	Moderate corrosion resistance at 500h

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and a second without SrCrO_4 , both of which contained all other fillers, TiO_2 , etc. Ground-finish Q-panels were used as test substrates. Figures 17 and 18 show that at the end of 1000 h, the coatings that contained the silanized, fumed-silica-treated DNBM microcapsules displayed minimal corrosion at the scribe marks, and there were no rust spots or blisters at the coating surface. The standard MIL-P-23377 SrCrO_4 epoxy failed at 264-336 h by forming small blisters near the scribe lines. The second set of controls, MIL-P-23377 minus SrCrO_4 , failed between 504 and 696 h by developing large blisters over the coating surface. All the panels that contained excess microcapsules, i.e., insufficient epoxy binder, failed by rusting through the panels. However, the scribe areas in these otherwise-failed panels showed very little, if any, lifting, blisters, etc. (indeed, these areas were the best in the entire series) because of the presence of the large amount of treated microcapsules at the scribes. Optimization of fillers, binder, and DNBM should result in further improvements and is indicated for continued work.



Fig. 17 Salt-Spray Exposure of Control Epoxy-Polyamide Coatings on Q-Panels,
No. 49 Top, No. 2 Bottom

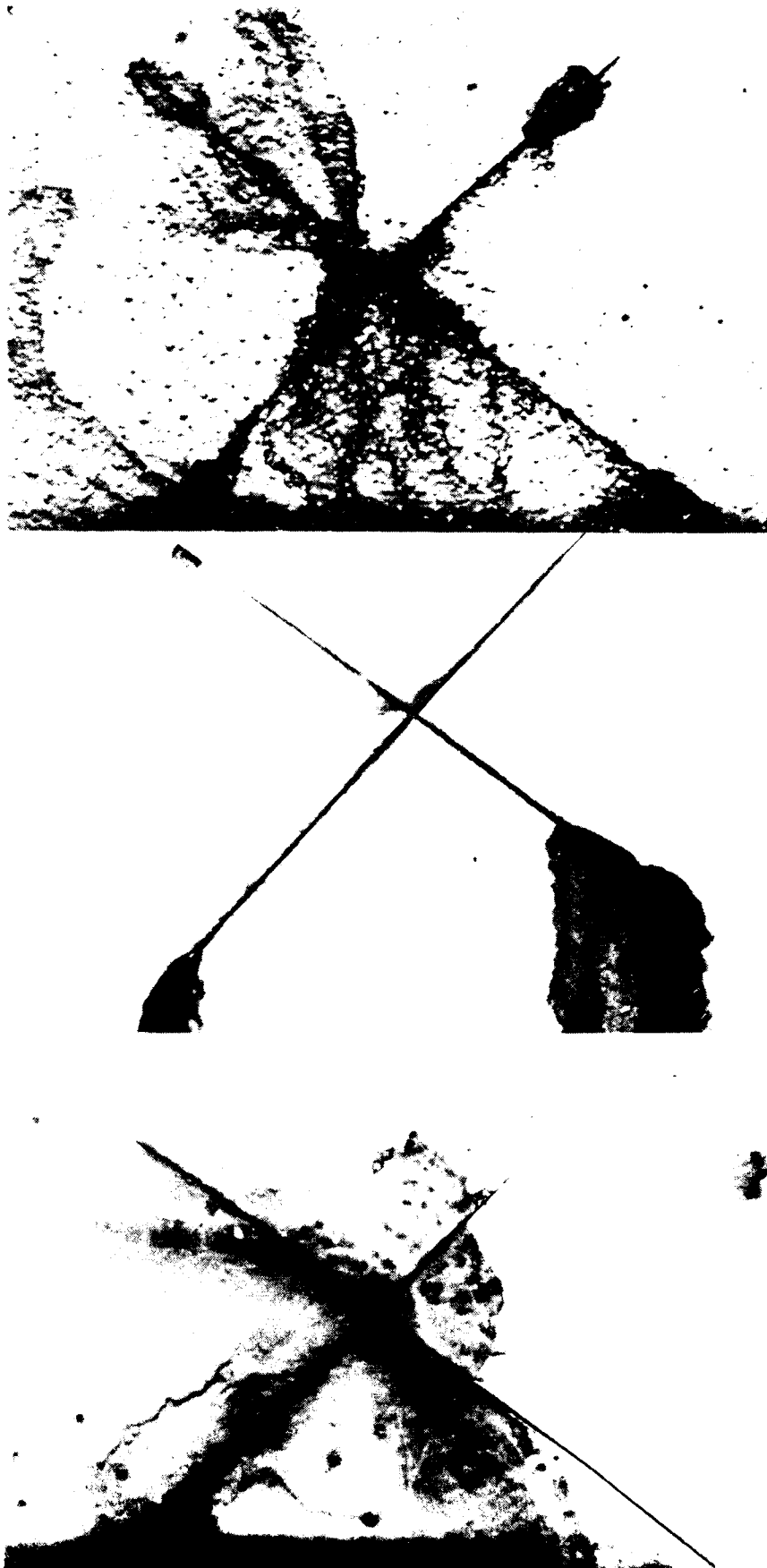


Fig. 18 Salt-Spray Exposure of DNB Microcapsules in Epoxy-Polyamide Coatings
on Q-Panels, No. 20 Top, No. 27 Middle, No. 36 Bottom

Section 5

RECOMMENDATIONS FOR CONTINUED WORK

The principal tasks that need to be performed or improved upon to qualify the DNBM microcapsules for application in primers, paints, and other coatings for Navy use are outlined as follows:

1. Develop the process for uniform application of methyltrimethoxsilane on the spray-dried DNBM microcapsules. The method utilizing a twin-shell dry blender with intensifier bar will maintain the microcapsules in suspension in air under controlled conditions of rotation for the blender and the intensifier. By design, the silane will be introduced via an inert-gas bubbler through the bar, which is hollow, and the excess will be transmitted back and trapped outside of the blender.
2. An adequate quantity of epoxy-polyamide primer formulation, such as 10 gal, should be prepared for test and evaluation of the microcapsules on aircraft/hardware chosen by the Navy. A separate quantity of 5 lb of the microcapsules that are maintained in the powder state should be made available for polymer and other formulation work.
3. The epoxy-polyamide formulation should be tested to a point at which a military specification document can be started, and larger quantities of paints and microcapsules can be formulated.

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Appendix A
TRADE-NAME IDENTIFICATION

	<u>Trade Name or Designation</u>	<u>Source</u>
Adogen 464	Methyltrialkyl (C ₈ -C ₁₀) ammonium chloride	Sherex Chemical
RD5444A	Methyltrialkyl(C ₁₂ -C ₁₄) ammonium dihydroborate	Akzo Chemical
RD6009	Proprietary polyol borate	Akzo Chemical
AC1349	Proprietary quaternary ammonium nitrite	Akzo Chemical
Cabosil M-5	Fumed silica commodity	Cabot
Tullanox 500	Fumed silica commodity, hydrophobic	Tullanox
Methocel A	Methyl cellulose	Dow Chemical
Methocel E	Hydroxypropylmethylcellulose	Dow Chemical
Culminal MC	Methyl cellulose	Henkel
Culminal MHPC	Methylhydroxypropylcellulose	Henkel

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Appendix B

DISSOLUTION OF INORGANIC INHIBITOR SALTS IN ORGANIC SOLVENTS

The direct dissolution of inorganic inhibitor salts in organic solvents was investigated as an alternative approach for the preparation of quaternary ammonium salts. In this instance the D, N, B, and M are the inorganic salt components without the added quaternary ammonium cation. The relative simplicity of direct dissolution appeared to be an advantage initially when compared with the requirement for preparing and characterizing the four individual quaternary salts.

Solubility of Single Inorganic Salts

The solvents included ethanol and several aprotic liquids known for complexation reactions with inorganic compounds. The salts chosen included ammonium, sodium, and potassium dichromates, chromates, molybdates, various borates, nitrites, vanadates, cerates, and nitrates, all of which will manifest corrosion inhibitive properties under varying environments. Nitrates were included because of the possibility for oxidation of dissolved nitrites by Cr(VI) ion, in which case the solubility ratings for nitrates would be needed. The procedure for assessing extent of solubility was as follows: One gram of the candidate salt was added to 50 cm³ of solvent in a reflux flask. The salt was considered soluble (S) if it dissolved at room temperature or required heating to 100°C, and the solute remained in solution on cooling. The salt was considered moderately soluble (MS) when the mixture was heated to the solvent reflux temperature and, following cooling, some, but not all, of the solute remained in solution. The salt was considered insoluble (I) when no dissolution was apparent after extended refluxing and cooling. Table B-1 summarizes the solubility data obtained for these compounds.

Vanadium salts were excluded from further testing because of apparent conversions to V(II) as indicated by the reduction colors of the V(II) solutions in dimethylsulfoxide and N-methyl-2-pyrrolidone. Potassium hexachloropalladium (IV), an initial consideration, was not evaluated principally because of obvious high chloride content and high cost.

Of the six solvent candidates, dimethylformamide (DMF), dimethylsulfoxide (DMSO), and N-methyl-2-pyrrolidone (NMP) showed promise. The remaining three appeared to be limited in scope. Although ethanol dissolved several of the salts, its susceptibility toward oxidation at elevated temperatures (such as can occur on the surface of aircraft) negated further consideration.

Solubility of Combined (Mixed) Inorganic Salts and Sensitivity to Light

The combined solution stabilities were determined as follows: Each of the individual solutions containing 1 g in 50 cm³ of solvent was mixed to give a concentration of 1 g per 200 cm³ for each salt in the final mixture. It was observed soon thereafter that reduction of Cr(VI) to Cr(III) occurred over a period of 1 to 3 days in laboratory light, either fluorescent or incandescent. When stored in the dark, however, the original orange color remained the same over several months.

Notwithstanding the deleterious effects of light, the presence of solids which formed on standing was considered as an important negative result. In the DMF and NMP systems, several solute variations were made to minimize the interactions. Only limited success was achieved. Table B-2 lists the combined systems and the resultant reactions.

The use of LiNO₂·H₂O in the NMP solvent system resulted in an essentially clear solution, but the oxidation state of the NO₂-anion following heating (necessary to dissolve the salt) was unknown. During the light exposures, samples were evaluated for Cr and Mo oxidation states. The data are given in Table B-3 and show the reduction of the chromate salts in both DMSO and NMP. DMF samples were not run principally because of the offensive, probably toxic, odors that developed with time. This would most likely preclude practical use of these systems in normal applications.

Table B-1 SOLUBILITY OF SINGLE INORGANIC INHIBITOR SOLUTES IN NONAQUEOUS SOLVENTS

	SOLUTES/SOLVENTS	DIMETHYL FORMAMIDE	DIMETHYL SULFOXIDE	N-METHYL-2- PYRROLIDONE	GAMMA- BUTYROLACTONE	ACETO- NITRILE	ETHYL ALCOHOL 95%, UNDENATURED
"D"	<u>CHROMATES</u> (NH ₄) ₂ Cr ₂ O ₇ (NH ₄) ₂ CrO ₄ Na ₂ Cr ₂ O ₇ ·2H ₂ O Na ₂ CrO ₄ K ₂ Cr ₂ O ₇ K ₂ CrO ₄	S MS S I MS I	S S S I S I	S MS S I MS I	I I	I I	MS I
"N"	<u>NITRITES</u> LiNO ₂ ·H ₂ O NaNO ₂ KNO ₂	MS MS MS	MS S S	MS MS S	I	I	MS
"B"	<u>BORATES</u> (NH ₄) ₂ B ₁₀ O ₁₆ ·8H ₂ O (NH ₄) ₂ B ₄ O ₇ ·4H ₂ O Na ₂ B ₄ O ₇ ·10H ₂ O Na ₂ B ₄ O ₇ ·5H ₂ O Na ₂ B ₄ O ₇ NaBO ₂ ·4H ₂ O K ₂ B ₁₀ O ₁₆ ·8H ₂ O	MS S I I I I MS	S S I I I I MS	S S I I I I I	I	I	MS S
"M"	<u>MOLYBDATES</u> (NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O (V. Slow pptn) (NH ₄) ₂ Mo ₂ O ₇ Na ₂ MoO ₄ ·2H ₂ O K ₂ MoO ₄ <u>VANADATES</u> NH ₄ VO ₃ NH ₄ Na(VO ₃) ₂ NaVO ₃ KVO ₃	MS I I I - I - -	S S I I I S [REDUCED TO V(II)] I I	MS S I I I S [REDUCED TO V(II)] I I	I	I	I
	<u>CERATES</u> (NH ₄) ₂ Ce(NO ₃) ₆	S	S	S			
	<u>NITRATES</u> NH ₄ NO ₃ NaNO ₃ KNO ₃	S S MS	S S S	S S MS	S	I	S

S = SOLUBLE (see text)

MS = MODERATELY/SPARINGLY SOLUBLE

I = INSOLUBLE

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Table B-2 SOLUBILITY OF COMBINED INORGANIC INHIBITOR SOLUTES IN NONAQUEOUS SOLVENTS

Combined Solutes (a)	Solvent (b)	Concentrations	Color/Reaction	Notes
D) N) B) M)	DMSO	1 g. ea. solute in 200 cm ³ (~5000ppm)	Clear med. orange solution. Turns green in light, 1-3 days	Formation of soluble Cr(III) in DMSO
D) N) B) M)	DMSO	4 g. ea. in 200 cm ³ (~20,000 ppm)	Clear dark orange solution	Dark storage
C) N) B) M-2)	NMP	1 g. ea. in 200 cm ³	Turbid green-brown ppt. in light	Discard
C) N-2) B) M-2)	NMP	1 g. ea. in 200 cm ³	Turbid green-brown ppt. in light	Discard
D) N-4) B-2) M-2)	NMP	1 g. ea. in 200 cm ³	Clear med. orange solution. Sl. sediment from LiNO ₂ ·H ₂ O	In storage
D) N-4) B-2) M-2)	NMP	2 g. ea. in 200 cm ³	Dark orange solution white precipitates	Ksp exceeded
D) N-3) B) M)	DMF	1 g. ea. in 200 cm ³	Clear med. orange solution in dark. Turned to green ppt. in light	Formation of insol. Cr(III) in DMF

(a) D (NH₄)₂Cr₂O₇ N NaNO₂ N-3 KNO₂ B (NH₄)₂B₁₀O₁₆·8H₂O M (NH₄)₆Mo₇O₂₄·4H₂O
 C (NH₄)₂CrO₄ N-2 KNO₃ N-4 LiNO₂·H₂O B-2 (NH₄)₂B₄O₇·4H₂O M-2 (NH₄)₂Mo₂O₇

(b) DMSO Dimethylsulfoxide NMP N-Methyl-2-Pyrrolidone DMF Dimethylformamide

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Table B-3 OXIDATION STATE OF Cr and Mo IN COMBINED SOLUTES IN NONAQUEOUS SOLVENTS

Formulation (a)	Solvent (b)	Laboratory Fluorescent Light Exposure	Cr(VI)	Cr(III)	Mo(VI)
			g/L	g/L	g/L
10990-34-DNBM	DMSO	No	2.0	<0.01	2.4
10990-25-DNBM	DMSO	Yes (2 wks)	1.1	0.7	2.7
10990-25-DNBM	DMSO	Yes (5 wks)	0.8	0.6	2.7
10990-25-DNBM	DMSO	Yes (10 wks)	0.1	0.8	2.5
10990-33-CN2BM2	NMP (obvious ppt formed)	Yes (2 wks)	0.4	0.4	1.2
10990-33-CN2BM2	NMP (obvious ppt formed)	Yes (5 wks)	0.3	0.2	0.8
10990-33-CNBM2	NMP (obvious ppt formed)	Yes (2 wks)	1.7	0.2	1.9
10990-33-CNBM2	NMP (obvious ppt formed)	Yes (5 wks)	1.0	0.4	1.8

Estim. error: ± 0.2 g/L for Cr(VI) and Mo(VI)
 ± 0.1 g/L for Cr(III)

(a) D $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ N NaNO_2 B $(\text{NH}_4)_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}$ M $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$
C $(\text{NH}_4)_2\text{CrO}_4$ N-2 KNO_3 M-2 $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$

(b) DMSO Dimethylsulfoxide NMP N-Methyl-2-Pyrrolidone

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During the solubility study, it was determined that when the combined salt solutions were dissolved in deionized water, 5 cm³ in 95 cm³ H₂O, the pH values were in the 4 to 5 range, somewhat low for contact with aluminum and steel alloys. Several alkaline materials were added to raise the values to pH 6 to 8. These were ammonia gas; crystalline ammonium carbonate, (NH₄)₂CO₃·H₂O; monoethanolamine; and triethylamine. The data for neutralization and the resultant changes in oxidation state are listed in Table B-4. Only triethylamine appeared practical for the DMSO solutions.

Because of the above and the inherent problems associated with the combined DNBM solutes in the presence of light, further work was postponed until a determination could be made regarding the feasibility for microencapsulation.

Additionally, during the course of this study, it was necessary to consider the toxicity and safety characteristics of the solvents. On a theoretical basis, it was also useful to examine the several solvent dissolution parameters used to predict the inorganic salt solubilities. These topics are reported in Appendixes C and D.

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Table B-4 OXIDATION STATE STABILITY AND pH OF INORGANIC SOLUTES IN NON-AQUEOUS SOLUTIONS

Sample Code	Solutes(A)	Solvent	Alkaline Additive	As Prepared g/L	Following Aqueous Dilution, Stored in Dark (10cc ³ diluted to 100cc ³ DI H ₂ O)		
					g/L	pH	Comments
10990-60	DNBH	DMSO	None	Cr(VI) 2.2 Cr(III) <0.01 NO ₂ 4.0 Mo(VI) 4.1	---	4.6	--
10990-63	DNBH	DMSO	Ammonium carbonate, heated to 60°C	Cr(VI) 2.1 Cr(III) <0.01 NO ₂ 2.3 Mo(VI) 4.0	Cr(VI) 2.1 Cr(III) <0.01 NO ₂ 2.4 Mo(VI) 4.0	6.2	Stable. Nitrite partially oxidized during neutralization
10990-65	DNBH	DMSO	Monoethanolamine	Cr(VI) 2.1 Cr(III) 0.4 NO ₂ 3.0 Mo(VI) 4.0	Cr(VI) 1.6 Cr(III) 0.2 NO ₂ 2.2 Mo(VI) 3.7	6.8	Unstable.
10990-67-1	DNBH	DMSO	Triethylamine	Cr(VI) 2.3 Cr(III) <0.01 NO ₂ 2.2 Mo(VI) 4.0	Cr(VI) 2.2 Cr(III) <0.01 NO ₂ 1.8 Mo(VI) 4.1	6.7	Stable. Nitrite partially oxidized on dissolution
10990-64-2	DN(4) B(2) M(2)	NMP	Ammonium carbonate, heated to 60°C	Cr(VI) 2.1 Cr(III) <0.01 NO ₂ 1.9 Mo(VI) 1.9	Cr(VI) 1.9 Cr(III) <0.01 NO ₂ 1.3 Mo(VI) 1.9	6.0	Stable. Nitrite partially oxidized on dissolution
10990-672	DN(4) B(2) M(2)	NMP	Triethylamine	Cr(VI) 1.9 Cr(III) 0.02 NO ₂ 0.03 Mo(VI) 2.3	Cr(III) 1.9 Cr(III) 0.02 NO ₂ 0.03 Mo(VI) 2.4	6.9	Nitrite unstable in as-prepared solution

(A) D - (NH₄)₂Cr₂O₇ N - NaNO₂ N(4) - LiNO₂ B - (NH₄)₂B₁₀O₁₆·8H₂O B(2) - (NH₄)₂B₄O₇·4H₂O
M - (NH₄)₆Mo₇O₂₄·4H₂O M(2) - (NH₄)₂Mo₂O₇

Appendix C

SOLVENT TOXICITY AND SAFETY CHARACTERISTICS

To assess the utility, practicality, and ultimate safety and toxicity of the combined solute systems prepared, a summary of characteristics was collated for the three principal solvents considered as primary candidates. Tables C-1 and C-2 list comparative LD50 toxicity values for some common solvents, including DMSO, NMP, and DMF (Ref. C1).

Dimethyl Sulfoxide (DMSO)

DMSO is reported to present less hazard than many solvents in common use. However, DMSO has the ability to penetrate the skin and carry with it certain chemicals (Ref. C1) with which it is combined under certain conditions. The toxicity will depend on the nature of the chemical used and the degree of penetration. Not all chemicals are carried through the skin, even though the DMSO may penetrate (Ref. C2). Chemicals and reactions to be avoided with DMSO include vigorous, explosive reactions with iodine pentafluoride, periodic acid, potassium permanganate, silver fluoride, and other strong oxidizing agents such as magnesium perchlorate and perchloric acid. No mention, however, has been made of precautions involving dichromates, molybdates, etc. A solution of sodium dichromate and sulfuric acid in DMSO has been used with apparent safety to oxidize primary alcohols to aldehydes and secondary alcohols to ketones. Here, the DMSO acts as a solvent, not as reactant (Ref. C3).

N-Methyl-2-Pyrrolidone (1-Methyl-2-Pyrrolidone) (NMP)

NMP is not a skin irritant and is comparatively nontoxic (Ref. C4), but the eyes should be protected. Since it is a powerful solvent for fats, it removes the protective layer of fat when it comes in contact with the skin, with attendant risk of eczema and other irritants. If NMP is exposed to the atmosphere, oxygen is dissolved, with the result that hydroperoxides are formed on the order of ppm. Autooxidation of NMP is favored by light exposure. If heated to 150 to 160°C, NMP hydroperoxide decomposes, one of the products being N-methyl-succinimide (Ref. C5). No explosive reactions are mentioned by BASF, the principal manufacturer of NMP.

Dimethylformamide (DMF)

DMF as a component of mixtures with certain halocarbons (e.g., carbon tetrachloride, hexachlorobenzene) may decompose violently. Reactions of explosive violence may also occur when dissolving nitrates or in oxidation reactions with chromic acid (Ref. C6). In addition, DMF solutions decompose during dissolution to produce very strong objectionable amine aromas, whereas DMSO and NMP appear to be more stable.

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Table C-1 SINGLE-DOSE TOXICITY (RATS) FOR SOME COMMON SOLVENTS (Ref. C1)

<u>Solvent</u>	<u>LD₅₀, mg/kg</u>	
	<u>Oral</u>	<u>Dermal</u>
Glycerine	31,600	10,000
DMSO	17,400	40,000
Ethanol	13,700	---
Acetone	9,750	---
NMP	7,000	---
Xylene	3,830	10,000
DMF	2,250	442
Sodium laurylsulfate	1,650	10,000

Table C-2 SINGLE-DOSE TOXICITY (MICE) FOR SOME 4 M COMMON SOLVENTS (Ref. C1)

<u>Solvent</u>	<u>LD₅₀, mg/kg</u>	
	<u>Intravenous</u>	<u>Intraperitoneal</u>
<u>DMSO</u>	7,176	14,664
Glycerine	6,164	6,900
<u>DMF</u>	3,650	6,570
<u>NMP</u>	1,980	3,564

Appendix D
SOLVENT DISSOLUTION PARAMETERS

The principal factors utilized to attempt to predict the solubility characteristics of nonaqueous solvents toward inorganic compounds are dipole moment (μ) and relative permittivity (ϵ). The dipole moment tends to determine the orientation of solvent molecules that surround the solute, whereas dissolution of ions is promoted by high relative permittivity (dielectric constant) of the solvent. The electrostatic factor (EF) is defined as the product of e and m , and takes both effects into account, thereby providing a basis for solvent classification (Refs. D1 and D2). See Tables D-1 and D-2. These data are at best approximations to dissolution properties, since the formation of complexes which may be insoluble in the solvents cannot be predicted from individual (separate) solvent-solute parameters. Nevertheless, the factors are valuable for the preliminary selection of candidate solvents. After the fact, it may be seen from Table D-1 that the solubilities of the DNBM compounds in acetonitrile—which might be expected to be high—are indeed low (poor). Since acetonitrile is a poor hydrogen bonding solvent, whereas DMSO, DMF, and NMP have moderate H-bonding capabilities (D3), a requirement for dissolution in organic vehicles may involve this additional property. Further, for DMSO, the high dipole moment of the sulfur-oxygen bond (4.3) and the high dielectric constant (approximately 47) for bulk DMSO suggest its solvating properties and the ability to disperse charged solutes. DMSO is not a hydrogen donor in H-bonding reactions and, as a result, solvates anions poorly except by means of dipolar associations with polarizable anions (Ref. D4).

The solvent dissolution parameters discussed above which result in high electrostatic factors for the three successful solvents also predict a high factor for acetonitrile, which, however, is a very poor solvent for the DNBM 100% inorganic salts. Thus, it is more likely that the ability of the solvent to form complexes

Table D-1 CLASSES OF SOLVENT ACCORDING TO ELECTROSTATIC FACTOR

Class	Solvent Type	10^{30} EF/Cm (SI units)
I	Hydrocarbon	0 - 7
II	Electron donor	7 - 70
III	Hydroxylic	50 - 170
IV	Dipolar aprotic	≥ 170

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Table D-2 ELECTROSTATIC FACTORS OF ORGANIC LIQUIDS (Ref. D1)

Solvents	ϵ_r (20-25°C)	μ (10^{30} /Cm) (Liquids except where noted)	EF (SI units)
<u>Class I Hydrocarbons</u>			
Benzene	2.28	0.00	0.0
Toluene	2.38	1.30	3.1
1-Pen tene	2.10	1.57	3.3
<u>Class II, Electron Donors</u>			
Acetic acid	6.13	2.77	17.0
Diethylether	4.34	4.54	19.7
Chlorobenzene	5.62	5.20	29.3
Tetrahydrofuran	7.61	5.44	41.4
Bromoethane	9.39	6.71	63.0
<u>Class III, Hydroxylic Solvents</u>			
O-Cresol	11.5	4.70	54.1
1-Butanol	17.1	5.61	95.8
Ethanol	24.30	5.61	136.2
Methanol	32.63	5.54	100.7
Water (in this class because of structure)	78.5	6.14	481.9
<u>Class IV, Dipolar Aprotic Solvents</u>			
N-methyl-2-pyrrolidone (NMP)	32	13.6	436.(*)
Nitrobenzene	34.82	13.31	464
N,N-Dimethylformamide (DMF)	36.7	12.74 (vapor)	468
	36.7	13.1	482.(*)
N,N-Dimethylformamide (DMF)	37.8	12.64	478
Acetonitrile	37.5	12.81 (vapor)	480
	37.5	13.0	488
Dimethylsulfoxide (DMSO)	46.6	14.98 (vapor)	698
	46.6	13.14	612 (*)

(*) Calculated from supplier data.

(coordination compounds) with specific salts plays a much more important role than dipole moments and/or dielectric constants. For a discussion of this theory and its use in predicting solvent behavior, the work of Drago and Prucell is referenced (Ref. D5).

Although the electrostatic and coordination model theories do not agree, both contribute to our knowledge of the dissolution of the compounds in question. The electrostatic model should be used with care, therefore, when attempting to predict whether or not a given compound will dissolve in a specific solvent.

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Appendix E

DIFFERENTIAL PULSE POLAROGRAPHY TECHNIQUE

The method used for the analysis of Cr(VI) or Mo(VI) was differential pulse polarography. The technique uses a dropping mercury electrode as a cathode for the potentiostatic reduction of metal ions in solution. When the controlled potential reaches the reduction potential of the analyte in solution, an amount of current flows through an external circuit which is proportional to the concentration of the analyte. Using a standard calibration curve or a standard addition method, the absolute concentration can be determined directly. To reduce the possibility of matrix effects, the sample containing the metal ion is diluted in a very large volume of supporting electrolyte which is chosen to optimize the current response.

The experimental values used for analysis of Cr and Mo are :

	<u>Cr (VI)</u>	<u>Mo (VI)</u>
Initial potential	-0.700 V	-0.100 V
Final potential	-0.950 V	-0.400 V
Peak potential	-0.830 V	-0.220 V
Supporting electrolyte (in CH ₃ CN)	1 M NaOH	0.1 M HCl
Standard curve (SC) or Standard addition (SA)	SA	SC

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