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DEMONSTRATION OF MULTIFUNCTIONAL DNBM CORROSION INHIBITORS IN PROTECTIVE COATINGS FOR NAVAL AIR/WEAPON SYSTEMS

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The corrosion protective properties of multifunctional DNBM salts (quaternary ammonium dichromate, nitrate, borate, and molybdate) have been demonstrated on high-strength steel and aluminum alloys found in prototype aerospace weapon systems. The 100% DNBM mixture added to MIL-P-23377 epoxy-polyamide, minus strontium chromate inhibitor, on bare 7075-T6 aluminum alloy resisted 1000 h ASTM B-117 salt spray. However, the coatings were not resistant to hydraulic fluid immersion at the higher concentrations required for the corrosion inhibition. Microencapsulation of the reactive DNBM mixture was adopted as a means to prevent this susceptibility, as well as the destructive oxidation of the hydroxyl groups in the epoxy resin during cure.

In the scale-up operation, approximately 20 gallons of DNBM weighing 64 kg (141 lb) was prepared from the four starting quarternary salts synthesized in a chemical process pilot plant. The salts were mixed by dissolving in toluene. Following removal of solvent, the resultant dark-brown liquid, approximating molasses in viscosity, was microencapsulated by the following method:

The DNBM was dispersed to form an oil-in-water emulsion in an aqueous colloidal solution of low-viscosity, high-purity methyl cellulose using a Gifford-Wood homogenizer, followed by spray drying in an Anhydro spray dryer. The maximum practicable payload was 75% DNBM. After spray drying, the capsules

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were treated with methyltrimethox[illegible]e that was vaporized in a Patterson Industries 10-quart twin-shell blender with intensifier bar. Prelim[illegible]o this treatment, the capsules were mixed with 20% hydrophobic fumed silica to change the form of the microcapsules from flocculated to free-flowing. ESCA/XPA analysis of the silanized product indicated that some of the capsules were incompletely silanized: this was the result of DNBM found on the surface and within the shell of the methyl cellulose capsules. Consequently, the silanized capsules were washed free of surface DNBM using Mil-T-8772B Type II epoxy thinner. After removal of solvent at ~40°C, the dried capsules were sieved through a 250 mesh screen (Tyler rating) to remove particles greater than 63 µm. Air classification was then applied to produce particles in the 10–50µm range for use in room-temperature cure paints, primers, and other formulations. The payloads contained 50–60% of the original Cr values. Nineteen pounds of microcapsules were produced. Samples were formulated in epoxy-polyamide primer, minus $SrCrO_4$, and deposited on bare 1010 steel Q-panels. Salt-spray fog testing showed the expected resistance to blistering and undercutting at the diagonally scribed lines during the 500-h test exposure.

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SUMMARY

The objective of this program was to demonstrate the corrosion protective and crack retarding qualities of multifunctional DNBM corrosion inhibitors for high-strength steel and aluminum alloys used in naval aerospace weapon systems.

Nineteen (19) pounds (8.6 kg) of surface-treated DNBM microcapsules were prepared from the four quaternary ammonium starting materials: dichromate, nitrite, borate, and molybdate, by blending in toluene, followed by vacuum removal of the solvent. Twenty kilograms of each salt were prepared in the pilot plant operations. The total weight of the mixed DNBM product was 64 kg (141 pounds) to produce a volume of ~20 gallons.

The microencapsulation process, required to protect the resin system from oxidation by the Cr (VI) in the DNBM, consisted of forming an oil-in-water emulsion of DNBM in an aqueous dispersion of low-viscosity high-purity methyl cellulose. The emulsion was spray dried to form microcapsules with the DNBM as core and methyl cellulose as shell. Because some DNBM was detected by ESCA (Electron Spectroscopy for Chemical Analysis) on the surface of the shells, interfering thereby with the surface silanization process used to form a solvent barrier on the microcapsules, it was necessary to remove the DNBM by washing the silanized capsules with epoxy thinner. Residual solvent was removed at moderate temperatures in an air-circulating oven. The microcapsules were then sieved to break up soft agglomerates and to remove capsules greater than 63 μm. Air classification was then carried out to separate particles larger than 45 μm.

Both 100% DNBM and treated microcapsules were formulated in epoxy-polyamide primer, Mil-Spec-P-23377, minus the strontium chromate corrosion inhibitor ordinarily used in this formulation. The "neat" DNBM was added at several levels, and those that passed 1000-h salt spray when the primer was deposited on 7075-T6 aluminum alloy were susceptible to hydraulic fluid exposure. The microcapsules of DNBM were also added to epoxy-polyamide and were deposited on bare 1010 steel Q-panels. These coatings showed no blistering or lifting at the scribe marks formed diagonally across the panels in the 500-h salt-fog exposure. Hydraulic fluid exposure was not a problem.

Improved oil-in-water dispersion technology is needed to obviate the presence of DNBM core material on the surface and within the shell zone of the microcapsules. A simple means of testing beyond ESCA is also needed and should be investigated pending continuation or further scale-up of microcapsule manufacturing. This would result in deletion of the solvent wash and waste removal steps, as well as reduced loss of the DNBM values resulting from dissolution by the solvent.

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INTRODUCTION

Research performed by Naval Air Warfare Center Aircraft Division, Warminster(1) has demonstrated that multifunctional corrosion inhibitors based on dichromate, nitrite, borate, and molybdate anions (DNBM) are especially suited for application to naval weapon systems. The term DNBM is an acronym for a mixture of four quaternary ammonium salts that are prepared using a phase-change catalyst in double exchange (displacement) reactions of methyltrialkyl (C_8-C_{10}) ammonium chloride (Adogen 464(2)) with the four alkali metal inhibitor anions.

The successful inhibition of stress corrosion cracking and corrosion fatigue in high humidity and chloride-containing environments has been attributed to the functional properties of the inhibitor mixture, as elucidated in the literature (References 1 and 2). The development of DNBM for use in coatings by Lockheed Missiles & Space Company, Inc. (LMSC),(3) is *described in Reference* 3. As a result of this successful development, a demonstration program, the subject of this report, was performed to expand the preparation and microencapsulation of these systems.

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(1) Air Vehicle and Crew Systems Technology Department, Code 6062.
(2) Trade-name identifications are given in Appendix A.
(3) Lockheed Palo Alto Research Laboratory, Palo Alto, California.

Section 2

PILOT SCALE-UP OF DNBM

In order to prepare an adequate quantity of DNBM for preparation of the finished microcapsules, as well as for testing and evaluation, 20 kg each of the four quaternary ammonium salts were produced. The D, N, and M salts were made by Sherex Chemical Co., Columbus, Ohio, and the B salt was made by Akzo Chemical Co., Chicago, Illinois, at their respective pilot plants. The following analytical data are listed for the four components. Data on Sherex R&D laboratory samples made on this program prior to the pilot runs are given in Appendix B.

2.1 QUATERNARY AMMONIUM DICHROMATE (D)

The 20-kg pilot lot of D salt, $[CH_3(C_8-C_{10})_3N]_2 \cdot Cr_2O_7$, prepared by Sherex Chemical, yielded the following results.

Total Cr, atomic absorption spectroscopy (AAS):	8.3, 8.5, ave. 8.4%
Cr (VI), polarography:	7.0, 7.2, 7.2, ave. 7.1%
Cr (III), by difference:	1.3%
Cr (III), in total Cr:	15.5%
Cl^-, Dohrmann method:	25 ppm

Percent yield of dichromate quaternary was based on 10.2% Cr calculated for the 100% converted salt, or $(8.4/10.2) \times 100 = 82.4\%$.

The principal physical difference between the pilot run and past laboratory runs was viscosity. The pilot run was reddish-brown, semihard, and nonflowing, and the laboratory runs were dark brown and molasses-like in viscosity. The high nonflowing viscosity was attributed to low water content. Karl Fischer analysis gave 0.04% H_2O for the pilot run and 0.7% H_2O in a retained R&D preparation. Water was introduced, therefore, during the DNBM mixing sequence, which increased the free-flowing property of the quaternary salts significantly.

2.2 QUATERNARY AMMONIUM NITRITE (N)

Sherex Chemical prepared $CH_3(C_8-C_{10})_3N \cdot NO_2$, by a new, proprietary method, first in their R&D laboratory, then by scale-up in their pilot plant. Data for the pilot material are as follows:

Total NO_2^-, ion chromatography (IC):	9.35%
Cl^-, Dohrmann:	79 ppm
SO_4^{2-}, IC:	580 ppm

Icn chromatography was used for the analysis, except for Cl^-, which was by Dohrmann. The amount of nitrate caused by oxidation of nitrite during the pilot process was less than 290 ppm. Based on a theoretical maximum of 10.28% NO_2, the pilot lot conversion was $(9.35/10.28) \times 100 = 91.0\%$. The new method appears to be an improvement over the double displacement reaction with regard to yield and impurity content.

2.3 QUATERNARY AMMONIUM BORATE ($\underline{B}$)

The 20-kg lot from Akzo Chemical was made using toluene rather than isopropyl alcohol to avoid oxidation of the alcohol by the chromium salt in the DNBM mixture (with a resultant decrease in Cr (VI) values). The analytical data for RD5444AT are as follows.

Volatiles: toluene:	10.4%
Boron:	1.34%
Cl^-, Dohrmann:	22 ppm

On a dry-weight basis, %B = 1.49, ppm Cl^- = 25. The lot of RD5444A analyzed during the DNBM development program yielded 1.36% B; ppm Cl was 22, showing good reproducibility. The formula for the $\underline{B}$ quaternary has been estimated to be $(CH_3)(C_{12}H_{25})_3N \cdot H_2BO_3$. [The $\underline{B}$ is underlined to distinguish the symbol from that of B for elemental boron.]

2.4 QUATERNARY AMMONIUM MOLYBDATE (M)

The Sherex 20-kg pilot lot yielded the following data for the product as shipped.

Solvent: toluene:	6.9%
Molybdenum, inductively coupled plasma (ICP):	17.7, 17.8, ave. 17.75%, 19.07% dry wt
Cl^-, Dohrmann:	295 ppm

The %Mo value was low when compared to the Sherex R&D laboratory preparation, which yielded 26.8%. This figure was similar to the 24.9%Mo value obtained in the development program and was assumed to be the monosubstituted salt, $CH_3(C_8\text{-}C_{10})_3N \cdot NH_4Mo_2O_7$, theoretical Mo = 26.52%. The 19.07% Mo value reported for the pilot lot resembles the 17.33% theoretical value for Mo in a disubstituted salt, $[CH_3(C_8\text{-}C_{10})_3N]_2 \cdot Mo_2O_7$, and was assumed to be so by the manufacturer. Later analysis indicated the material to be the monosalt accompanied by a relatively large quantity of unreacted quaternary ammonium methylsulfate starting material.

2.5 DNBM PREPILOT MIXING TRIALS

A trial 1-kg mixture of the four DNBM salts was prepared in the Sherex R&D laboratory preliminary to mixing in the Sherex pilot plant. For each mixture, equal numbers of Cr and Mo atoms were specified, plus the same number of nitrite and borate anions. The four salts were dissolved in analytical reagent-grade toluene. After mixing, the solvent was removed by evaporation under mild heat and vacuum.

A sample calculation is given below. The percentages are derived from analysis of the four salts.

(1) D Start with 300 g D salt
Multiply by percent Cr: 8.4% × 300 = 25.2 g Cr

(2) N Multiply by NO_2^-/Cr: (46.005/51.996) 25.2 g = 22.3 g NO_2^-
(wt. NO_2^-/%NO_2^- in quat. salt): 22.3/0.0935 = 238 g N salt

(3) $\underline{B}$ Multiply by B/Cr: (10.811/51.996) × 25.2 g = 5.24 g B
(wt. B/%B in commodity): 5.24/0.0134 = 391 g (with solvent); 350 g (no solvent)

(4) M Multiply by Mo/Cr: (95.94/51.996) × 25.2 g = 46.5 g Mo
(wt. Mo/%Mo in commodity): 46.5 g/0.1775 = 262 g (with solvent); 244 g (no solvent)

Adding the four components:
300 g D + 238 g N + 350 g $\underline{B}$ + 244 g M
Total: 1132 g DNBM (100% solids)
For the larger, several-kilogram mixtures, simple ratio calculations give the proportions required.

Analysis of the Sherex laboratory DNBM sample gave the following results:

Total Cr, AAS:	2.5%
Cr (VI), polarography:	1.6%
Cr (III), by difference:	0.9%
Cl^-, Dohrmann:	53 ppm

The 36% decrease in Cr (VI) was higher than expected and was surmised to have resulted from heating the mixture above 60°C during removal of the toluene solvent.

A second trial mix was prepared at the Sherex pilot plant. Analytical data are as follows:

Total Cr, AAS:	2.6%
Cr (VI), polarography:	2.1%
Cr (III), by difference:	0.5%
Mo, ICP:	4.46%

The Cr (VI) content decreased 19%, significantly less than the previous batch.

Other tests applied to the two sets of DNBM were time of stability in high-purity deionized water, not less than 2 h without color change, and hydrolysis/dissociation in salt/seawater to give yellow Cr (VI) in less than 1/2 h. Both mixtures passed these tests.

The pH range for 10% DNBM in seawater was 7.0 ± 0.4. The second pilot trial mixture gave a pH of 6.6; the seawater pH was 8.1.

To test the physical mixing process, the ratio of theoretical %Mo/%Cr should equal 95.94/51.996 = 1.845. For the second pilot trial, 4.46/2.6 = 1.72. This figure was not considered excessively low in comparison with ratios for mixtures of similar size prepared at LMSC (Reference 3, p. 9).

2.6 DNBM PILOT MIXTURE AND ANALYSIS

Sherex Chemical, Mapleton, Illinois, performed the pilot four-component mixing operation. An in-process sample was removed and submitted for analysis after removal of toluene. The data are as follows:

Total Cr, AAS:	2.4%
Cr (VI), polarography:	1.6%
Cr (III), by difference:	0.8%
NO_2^-, IC:	2.5%
B, ICP:	0.44%
Mo, ICP:	4.57%
SO_4^{2-}, IC:	1.5%
Cl^-, Dohrmann:	<100 ppm

There was a 1/3 loss in Cr (VI), and the value for sulfate was higher than expected. The analysis of the four components for the sulfate impurity revealed that the quaternary ammonium molybdate was the principal contributor, giving 5.13% SO_4^{2-}. Although there were significantly lower contributions to total sulfate by the D, N, and B components, the original assumption that the diquaternary salt had been formed apparently was not correct. The salt reaction product was the incompletely converted monoquaternary ammonium molybdate that contained a relatively large quantity of quaternary ammonium methylsulfate starting material. Details of the calculations are given in Appendix C. The effect of sulfate on the corrosion inhibitor activity of pilot DNBM is discussed in Section 5.

The quantity of DNBM was 64 kg (141 pounds), producing a volume of approximately 20 gallons, packaged in four 5-gallon unlined steel cans.

Section 3

MICROENCAPSULATION OF DNBM

The purpose of microencapsulation was to separate the DNBM corrosion inhibitor materials from the reactive epoxy-polyamide components subject to oxidation by Cr (VI). The objective was to encapsulate the DNBM as core using a colloidal dispersion of methyl cellulose (MC) as shell material. The maximum size of the capsule was limited to less than 50 μm for use in 2-mil coatings.

The process consisted of forming an oil-in-water emulsion of DNBM in an aqueous dispersion of low-viscosity, high-purity methyl cellulose. The emulsion was spray-dried to form the microcapsules. Because DNBM was detected by ESCA on the surface of the shells and interfered with the surface silanization process used to form a solvent barrier on the microcapsules, it was necessary to remove the residual DNBM by washing the silanized capsules with epoxy thinner. The residual solvent was removed at 45°C in an air-circulation oven. The microcapsules were than sieved through a 250 mesh screen using light shear to break up soft agglomerates and remove capsules greater than 63 μm. Air classification was then carried out to remove most particles larger than 45 μm. The microencapsulation was carried out by Southwest Research Institute (SWRI), San Antonio, Texas.

3.1 EVALUATION OF INCREASED PAYLOADS

Four evaluation samples were prepared having payload levels from 70 to 85% (70, 75, 80, 85%) to maximize the core values. The DNBM was a grab sample from the Sherex pilot run at Mapleton, Illinois. Inspection of the shell surfaces by SEM at LMSC indicated incomplete coverage of the core contents. However, large holes in the capsules could be seen readily in all the runs. This was attributed to the changes in processing required to increase the yield as well as the higher core content levels. All runs were conducted using a Gifford-Wood high-shear mixer to reduce the introduction of air into the mixture.

The methyl cellulose solution was made up in Milli-Q high-purity water. The spray-drying process was conducted using an Anhydro spray dryer under the following conditions at SWRI:

Inlet temperature:	~190–220°C
Outlet temperature:	~98–105°C
Feed rate:	~37–39 g/min
Atomizing air:	~10–12 psi
Nozzle size:	0.033 in. (inner diameter) 0.068 in. (outer diameter)

Table 1 presents microencapsulation data on the four products obtained.

SEM photomicrographs of the four runs were taken at LMSC. A 270X photo of set 9-147 is shown in Fig. 1. Magnification of a hole area at 6,000X shows details of the aberration.

For comparison, the spray conditions applied to SWRI Sample No. 8-530, the final scale-up spray-dry run in the NADC development program (Reference 3, p. 27) are stated below. Few holes were seen, although some spots were visible on close inspection.

SWRI Sample No. 8-530	
Inlet temperature:	190–220°C
Outlet temperature:	100–110°C
Feed rate:	65 g/min
Atomizing air:	40 psi
Nozzle size:	0.060 to 0.120 in.

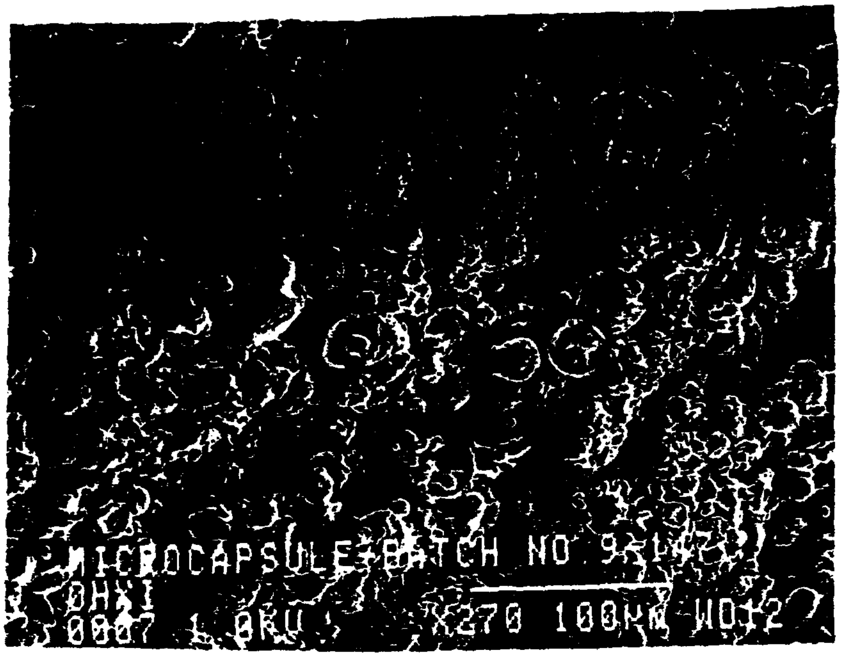
The principal differences were feed rate and atomizing air pressure. On this basis, SWRI prepared additional microcapsule samples. The compositions were 70% DNBM core, and 30% methyl cellulose shell. The pH of the slurry was measured at 6–6.5. The three sample runs were conducted using the Anhydro spray dryer with a nozzle size of 0.60 to 0.120 in. Data for the samples are given in Table 2.

Sample 9-195 was best, i.e., showed few holes, with samples 9-196 and 9-197 having many of the holes shown in the previous series. Recoveries were low, however, at 20%, 11%, and 55%, respectively. A SEM photo of sample 9-195 is shown in Fig. 2.

Conclusions drawn by SWRI included the need for a lower viscosity methyl cellulose, i.e., lower than that used to date, to increase the solids content of the feed slurry, thereby improving yield and minimizing hole formation. Dow Methocel A15-LV, premium grade, was

Table 1 PARTICLE SIZE AND CALCULATED PAYLOADS FOR DNBM MICROCAPSULES

SWRI Sample No.	Fill	Shell	Calculated Payload (%)	Approximate Size Range (μm)		Sample Wt (g)
				Most	Up to 70	
9-145	Pilot DNBM (Container 2)	2.25% Methyl cellulose 97.75% Milli-Q-H_2O	70	5-50	Up to 70	~61
9-146	Pilot DNBM (Container 2)	2.25% Methyl cellulose 97.75% Milli-Q-H_2O	80	5-50	Up to 70	~65
9-147	Pilot DNBM (Container 2)	2.25% Methyl cellulose 97.75% Milli-Q-H_2O	85	5-50	Up to 70	~62
9-148	Pilot DNBM (Container 2)	2.25% Methyl cellulose 97.75% Milli-Q-H_2O	75	5-50	Up to 70	~62



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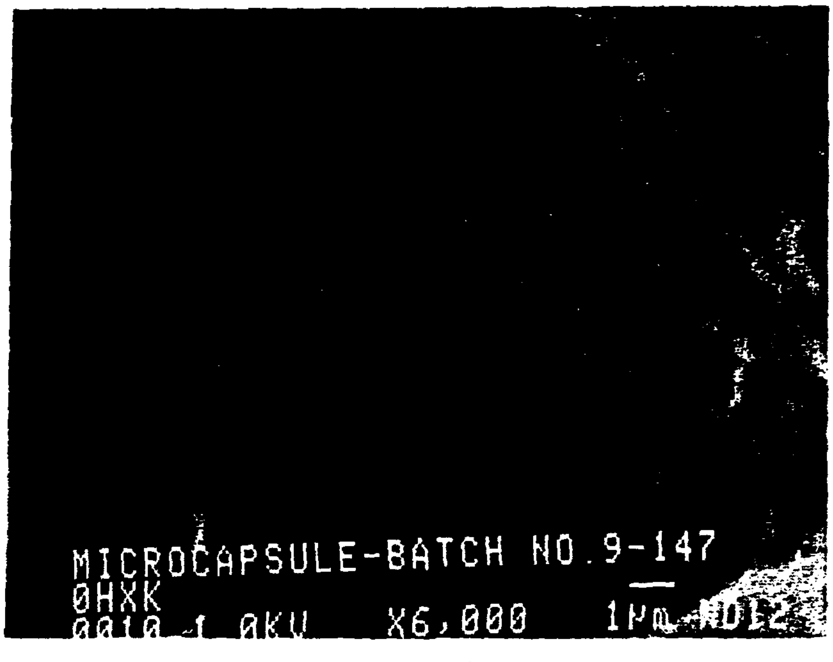


6,000X

Fig. 1 SEM Photomicrographs of 85% DNBM Microcapsules

Table 2 EXPERIMENTAL CONDITIONS FOR HOLE-FREE MICROCAPSULES AT 70% PAYLOAD

SWRI Sample No.	Feed Rate (g/min)	Atomizing Air (psi)	Inlet Temperature (°C)	Outlet Temperature (°C)	Recovery (%)	Sample Weight (g)
9-195	~60-65	40	190-200	100-110	20.0	27
9-196	~60-65	40	195-210	96-105	11.5	8
9-197	~40	15	195-215	110-115	54.7	41

Sample 9-195 was prepared using 4% methyl cellulose.
Samples 9-196 and 9-197 were prepared using 2.25% methyl cellulose.

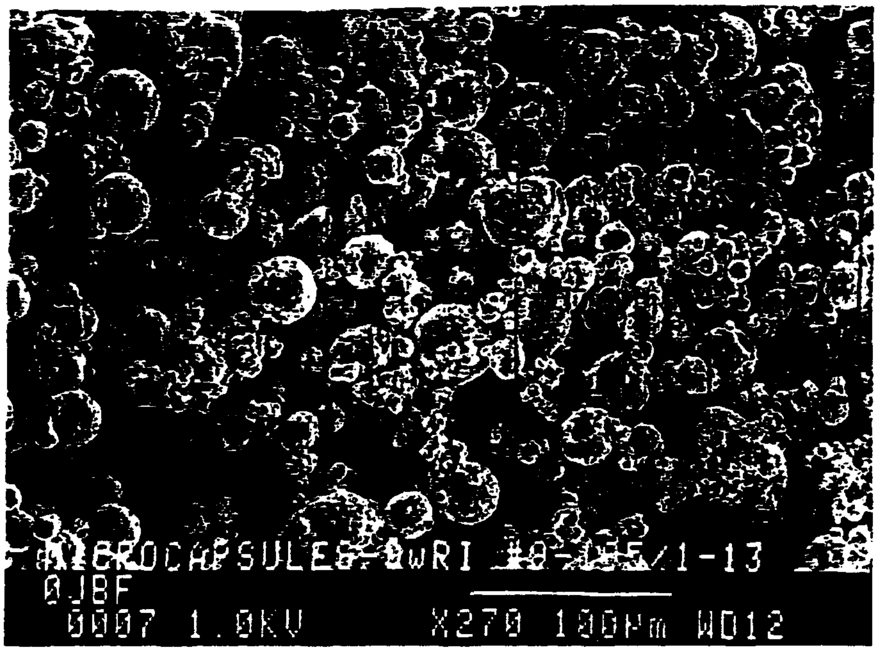


Fig. 2 SEM Photomicrograph of Improved SWRI Sample No. 9-195, 270X

chosen as the new candidate. The original Henkel material, Culminal 25S, had been found to be very low in NaCl, which was the principal reason for its selection. Test results indicated that the A15-LV lot selected had a satisfactorily low chloride level, as illustrated by no sign of yellow Cr (VI) coloration from the DNBM dispersion in the A15-VL solution. As analyzed by LMSC, percent Cl^- was 0.39% (0.64% NaCl). The original Henkel lot was 0.097% Cl^- (0.16% NaCl), markedly higher in purity. The availability of lower viscosity lots from Henkel was problematic, however, according to the importer. Three 50-pounds bags of the selected Dow lot were therefore shipped to SWRI.

3.2 MICROENCAPSULATION SCALE-UP OF PILOT DNBM

Using Dow A15-LV methyl cellulose as shell material and the pilot DNBM prepared at Mapleton, 75% payload microcapsules were prepared by the standardized practice of emulsification using the Gifford-Wood homogenizer and spray drying by Anhydro spray dryer. SEM photos (Fig. 3) indicated successful coating, with particle dimensions the same as those obtained previously (Reference 3, p. 30). However, the sample color was a more intense yellow-brown than observed on previous batches. Although this was attributed to the new DNBM, based on the same results with the original MC, later ESCA analysis indicated that the darker color was caused by the presence of DNBM on the shell exterior and within the shell layer.

For the preparation of microcapsules, using two 5-gallon cans of Sherex pilot DNBM, SW produced 40 pounds (18kg) of the encapsulated product. Average conditions for the spray-drying operation were as follows:

Inlet temperature: 180–190°C
Outlet temperature: 80°C
Feed rate: 32 g/min
Atomizing air: 30 psi
Nozzle size: 0.028-in. inner (liquid)
0.064-in. outer (air)

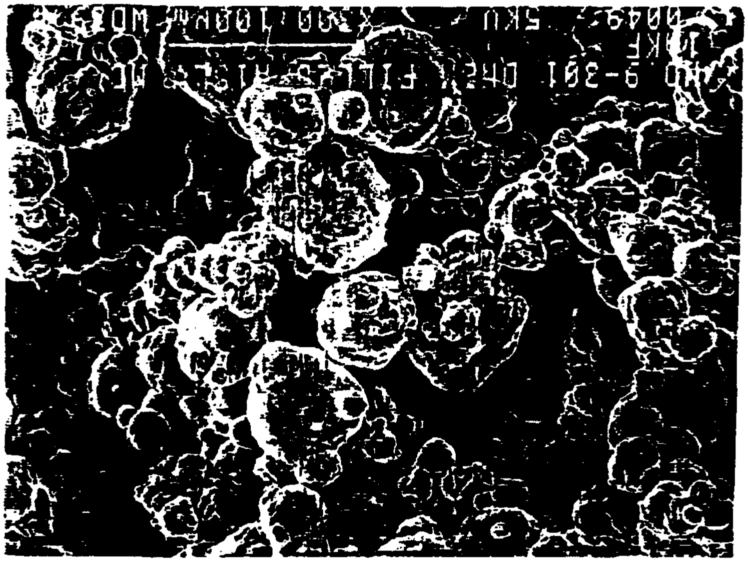


Fig. 3 SEM photomicrograph of Microencapsulated DNBM, Scale-up Run, SWRI No. 9-301, 300X

Section 4

SURFACE TREATMENT OF MICROCAPSULES

The purpose of the surface treatment is to obtain solvent hold-out when the microcapsules are formulated in a primer or paint mixture. The silane chosen (Reference 3, pp. 13, 21), methyltrimetho-xysilane, reacts with the surface water on the methyl cellulose shell and produces hydrophobic siloxane as a barrier to the solvents. Preliminary to the silanization process, fumed silica is added to the microcapsules which are highly flocculated when exiting the spray dryer.

4.1 FUMED SILICA ADDITIONS TO MICROCAPSULES

Three hydrophobic commercial fumed silica commodities were evaluated by three-dimensionally mixing 25% silica by weight with 75% microcapsules in a Red Devil Mixer for 15 min. The grades evaluated were:

(1) Cabot TS530 (equivalent to Tullanox 500, Reference 3, p. 29), silane treated with hexamethyldisilazane

(2) Cabot TS720, treated with dimethylsilicone

(3) Degussa R805, treated with trimethyloctylsilane

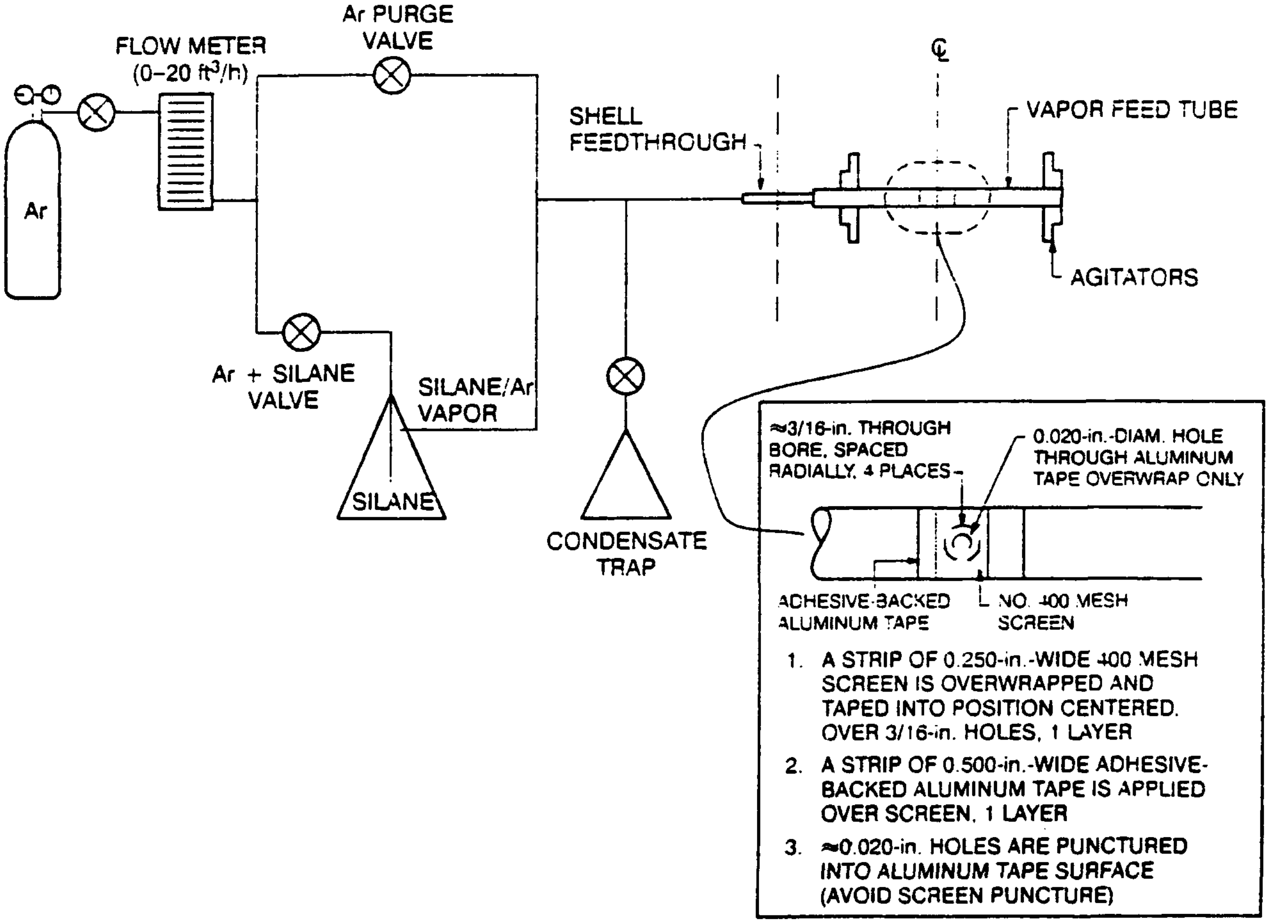
Silica No. 3 left some free silica clumps in the mixture. No. 2 was satisfactory, but it was precluded since it could not not be used in water-base or water-dispersible paint systems because of potential adhesion problems. Silica No. 1 was best, and it was selected for the continuing development. Cabot M-5 hydrophilic silica was retained for trial based on previous dispersion results. At a 50% level (50% TS530, 50% microcapsules), it was thought that the use of the Red Devil Mixer would produce a permanent hydrophobic characteristic. However, after contact with deionized water, the mixture wetted in less than 1/2 h.

In contact with epoxy diluent (MEK, MIBK, and MEPG), the solvent mixture wetted the 50/50 silica/microcapsule mixture in less than 5 min. Further evaluations with TS530 indicated that a lower percentage, 20% fumed silica, could be formulated which could retain the dispersed state of the microcapsules.

4.2 SILANIZATION OF MICROCAPSULES

The process was carried out successfully in a Patterson Twin-Shell Blender. Argon gas was bubbled through liquid methyltrimethoxysilane at room temperature. The mixture passed through an intensifier bar rotating at moderate speed (400 rpm) to avoid disrupting the capsules during the mixing/reaction process. Excess silane was trapped in liquid nitrogen or passed through a water trap and vented to air. Figure 4 is a line drawing illustrating the feed system for the argon/silane mixture. Figures 5 through 7 are photographs of the feed and reaction systems. Details of the process were developed at LMSC in a 3-quart twin-shell for technology transfer to SWRI. Approximately 200-g microcapsules mixed with fumed silica were treated. For scale-up of the process at SWRI, a 10-quart twin-shell holding approximately 1 kg was used. Procedural notes are given in Appendix D.

It was necessary to add water vapor to the silane-treated capsules to hydrolyze completely the adsorbed silane molecules to form the siloxane coating on the microcapsule surface. This was carried out in an environment of constant humidity (80-90% RH), at room temperature, remaining overnight. At completion of the exposure, no further aroma or smell of the silane



1. A STRIP OF 0.250-in.-WIDE 400 MESH SCREEN IS OVERWRAPPED AND TAPED INTO POSITION CENTERED. OVER 3/16-in. HOLES, 1 LAYER
2. A STRIP OF 0.500-in.-WIDE ADHESIVE-BACKED ALUMINUM TAPE IS APPLIED OVER SCREEN, 1 LAYER
3. ≈0.020-in. HOLES ARE PUNCTURED INTO ALUMINUM TAPE SURFACE (AVOID SCREEN PUNCTURE)

Fig. 4 Silane/Argon Vapor Feed System: Line Diagram for Interface to Twin-Shell Blender

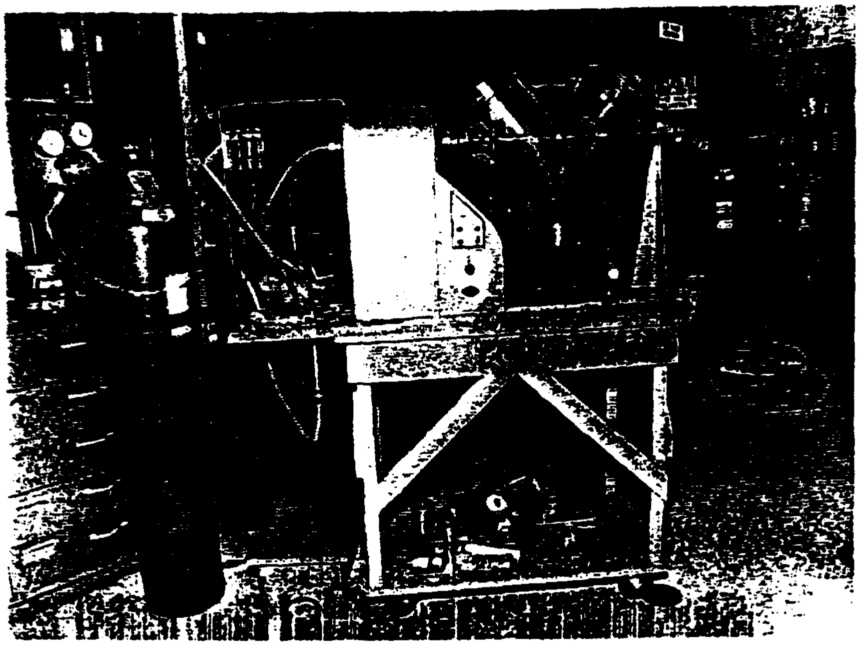


Fig. 5 Twin-Shell Blender Silanization System

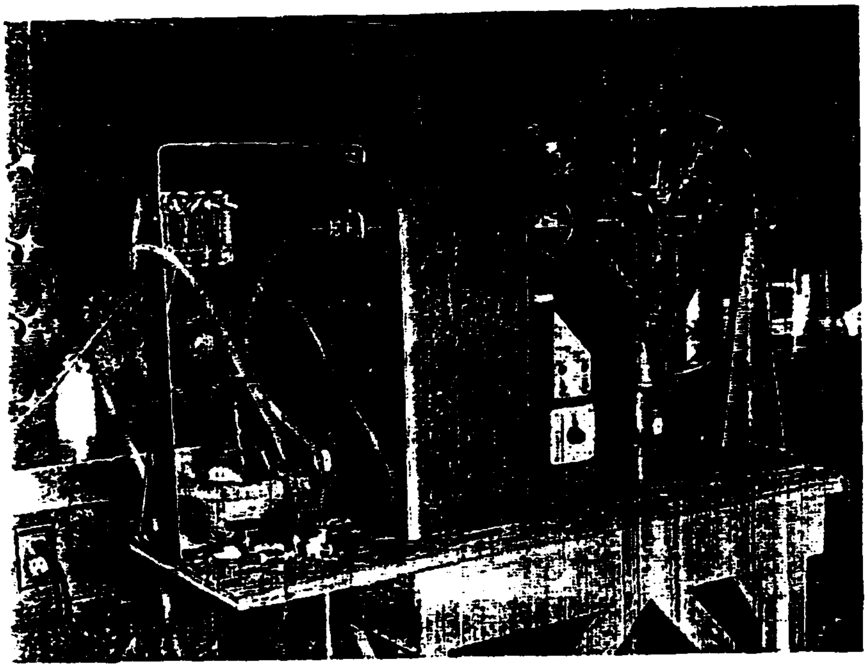


Fig. 6 Closeup of Silane Feed, Twin-Shell Blender

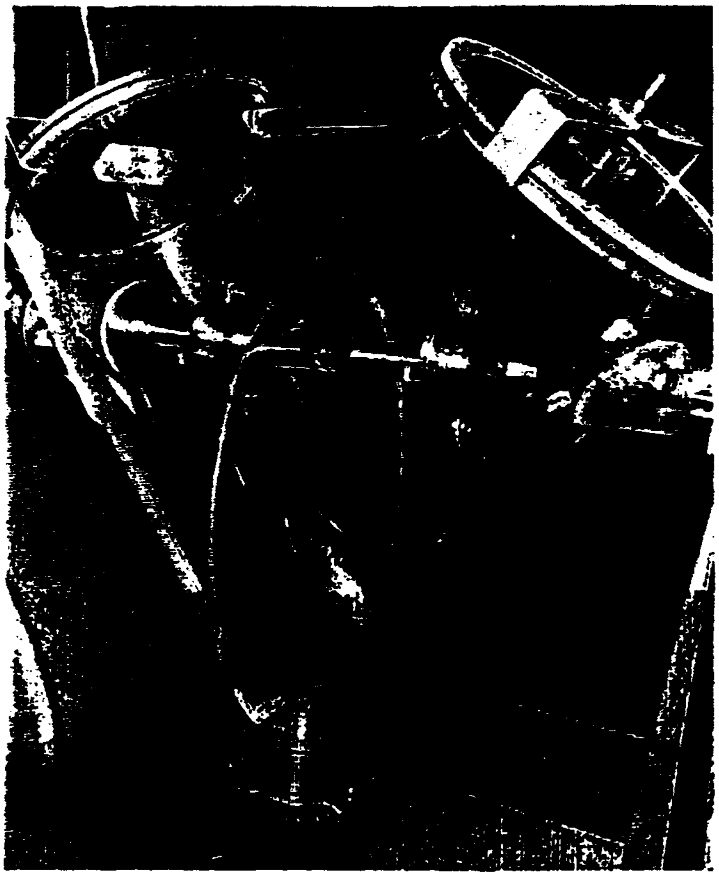


Fig. 7 Closeup of Twin-Shell Blender Intensifier-Bar

(sweet/pungent) was detected. The powder was then crushed with minimum force and passed through a 250 mesh (Tyler) screen.

During the development, Cabot M-5 silica (hydrophilic) and TS530 (hydrophobic) were added to the microcapsules for corroborative trials. Methyltrimethoxysilane and the silane used on TS530, hexamethyldisilazene, were evaluated. Table 3 lists the combinations tested for relative solvent holdout—the principal test to determine the efficiency of the siloxane coverage. The solvent test consisted of adding ~2 g of treated microcapsules to 30 cm^3 epoxy thinner Mil-T-81772B (II) with stirring for 1–2 min. After settling 2-3 min, the yellow-green supernatent liquid is decanted, and more thinner is added. In a fully silanized sample, there is significant (deep) yellow color remaining in the dried capsules, with little or no color in the supernatent liquid after the initial decanting. The difficulty in silanizing the entire shell surface was found to be related to the presence of DNBM on the surface of the methyl cellulose shell material.

Table 3 RESULTS OF SILANE REACTIONS ON DNBM CAPSULE/FUMED-SILICA MIXTURES

Run	SWRI Lot	Fumed Silica (Cabot Corp. Supplier)	Silane	Relative Solvent Holdout
11056-104	9-786	25% TS-530	MTMS(1)	Good
11056-105B	9-786	20% M-5(3)	MTMS	Good
11056-106	9-786	20% TS-530	MTMS	Good
11056-107	9-786	20% TS-530	HMDS(2)	Poor
11056-108	9-737	20% TS-530	MTMS	Good
11056-110B	9-773	20% TS-530	MTMS	Good

(1) Methyltrimethoxysilane.
(2) Hexamethyldisilazane.
(3) Silanized twice.

4.3 ANALYSIS OF DNBM ON MICROCAPSULE SURFACES

The dark yellow-brown color of the capsules made from the first scaled-up lot of DNBM was a hint that some aberration had occurred during the microencapsulation process that caused these capsules to differ from the original microcapsule preparations described in Reference 3. In a fully silanized capsule, there should be little or no color to the supernatent liquid during the initial extraction. The presence of some DNBM on the surfaces of the capsules and in the cross-section of the shell interiors was detected by ESCA techniques, including argon ion etching.

To perform the analysis, three lots of varying yellowness were selected. The microcapsules were spread on contact-adhesive tabs and evaluated for molybdenum and chromium, with carbon and oxygen included. The percentages given in Table 4 are surface percents, since only the top 50 Å were analyzed. Argon ions penetrated the capsules still further, but because of the inhomogeneities of the surface, the depths could not be measured exactly.

Conversion of the Mo% on the surface (down to 50 Å thickness) yields $(CH_3(C_8\text{-}C_{10})_3N \cdot NH_4Mo_2O_7/2\ Mo) \times 100 = (723.73/191.9) \times 0.9\% = 3.8\%$ Mo quaternary. Similar calculations apply to Cr, NO_2^-, and B; and 10% or more DNBM is present both on and in the methyl cellulose shell. During the silane process, the surface DNBM prevents the silane from reacting with the water on the methyl cellulose shell. The silane wets the DNBM but does not form the siloxane polymer across the shell surface and therefore does not prevent the solvent/thinner from dissolving the DNBM on the surface or from passing through the unprotected shell. From these data and resultant calculations, it is likely that the Cr and Mo quaternary salts were not completely emulsified, i.e., all the DNBM particles were not fully formed as complete DNBM cores. As a result, some DNBM remained on the surface of the capsules after the spray-drying process.

Table 4 RELATIVE AREAS OF Mo AND Cr ON METHYL CELLULOSE SHELL SURFACES BY ESCA

SWRI Lot	9-145 Darkest (1990)	9-773 Medium (1991)	9-737 Lightest (1991)
As Received			
Carbon	89.30	89.10	90.10
Oxygen	9.00	9.80	8.90
Total CO	98.30	98.90	99.00
Molybdenum	0.90	0.60	0.50
Chromium	0.80	0.50	0.50
Ion Etched			
Carbon	90.00	93.20	92.30
Oxygen	8.70	5.80	7.10
Total CO	98.70	99.00	99.40
Molybdenum	0.80	0.30	0.30
Chromium	0.60	0.60	0.30
	Summary	Summary	Summary
As Received			
Molybdenum	0.90	0.60	0.50
Chromium	0.80	0.50	0.50
Ion Etch			
Molybdenum	0.80	0.30	0.30
Chromium	0.60	0.60	0.30

4.4 SOLVENT EXTRACTION OF DNBM FROM MICROCAPSULE SURFACES

Epoxy thinner was used to remove the DNBM impurities from the silanized microcapsules. The method developed for laboratory extraction is as follows: 100 g of silanized microcapsules are placed in a 2-L polypropylene beaker and stirred with 1 L thinner for 3-5 min. The mixture is filtered through a Whatman No. 50 paper in a Buchner funnel using air suction, followed by washing with thinner until the filtrate was colorless. After evaporating in the hood for ~1/2 h, the filter cake was placed in an air-circulation oven at 40-45°C for 1 h or until dry. Table 5 gives extracted and nonextracted Cr and Mo values in the appropriate microcapsules. Analysis was by ICP for Cr and Mo. The organic components were decomposed with H_2SO_4/HNO_3 in the usual manner, and HF was used to remove the siloxane silica before the ICP runs.

The %Mo/%Cr ratios were 1.75 and 1.79, reasonably close to the theoretical ratio of 1.85. The percent decrease in Cr for nonextracted capsules was $[(2.40 - 1.28)/2.48] \times 100 = 48.4\%$, and for Mo $[(4.34 - 2.27)/4.34] \times 100 = 47.7\%$, essentially the same, since the Mo and Cr percentages could not actually change in value. The Cr and Mo changes that did occur

Table 5 PERCENT Cr and Mo in SOLVENT-TREATED MICROCAPSULES

Sample	%Cr	%Mo	%Mo/%Cr Ratio	Theoretical Mo/Cr (95.94/51.996)
Pilot DNBM 100% Neat	2.45 2.51 Ave. 2.48	4.34	1.75	1.85
Not Extracted 11056-110B 20% TS530 80% 9-773	1.27 1.29 Ave. 1.28	2.27	1.79	1.85
Solvent Extracted 11056-110B 20% TS530 80% 9-773	0.71 0.75 Ave. 0.73 43% loss	0.47 79% loss	0.64	1.85

resulted from the 20% TS530 dilution and a similar percentage drop caused by the siloxane formations at the capsule surfaces.

The percentage drop for the solvent-extracted capsules was large, as expected. For Cr, it was 100 × (1.28 - 0.73)/1.28 = 43.0%; for Mo, 100 × (2.27 - 0.47)/2.27 = 79.3%. The data indicated a significant decrease in %Mo at the surface relative to %Cr. These data agree with the greenish-yellow color of the solvent leachant (supernatent liquid), since the molybdate quaternary is green in the Mil-T-81772B Type II thinner. Figure 8 shows a sequence of microcapsules, fumed silica plus microcapsules, and solvent-extracted silanized microcapsules of pilot DNBM.

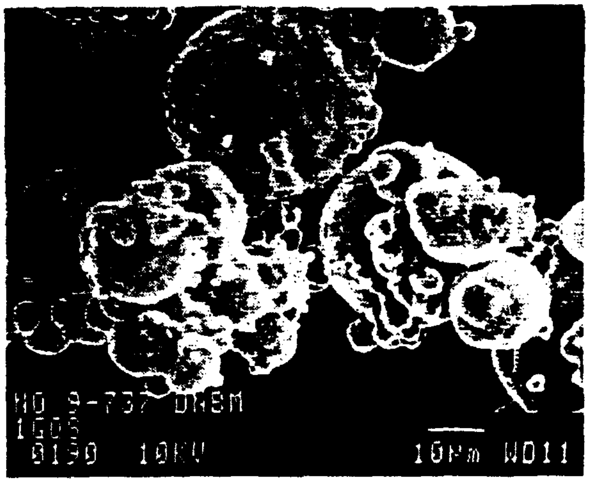
4.5 SIEVING OF SOLVENT-CLEANED MICROCAPSULES

The purpose of the sieving process was to break up soft agglomerates that formed in the drying step following solvent cleaning. Using mild shear from a ceramic pestle, the dry microcapsules were forced through a 12-in.-diameter 250 mesh screen (Tyler, -63 μm). There was little loss of material. The resulting particles were suitable for air classification.

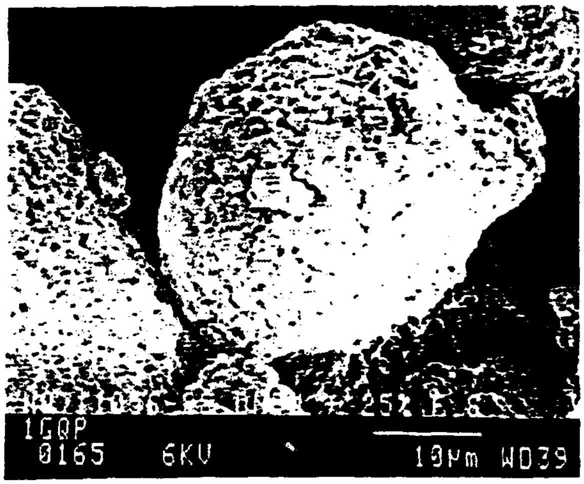
4.6 AIR CLASSIFICATION OF SIEVED MICROCAPSULES

The purpose of the air classification step was to reduce further the particle size of the sieved capsules to 45 μm or less. Work was carried out at Vortec, Inc., Long Beach, California, using a Vortec Particle Classifier, Model C-1.

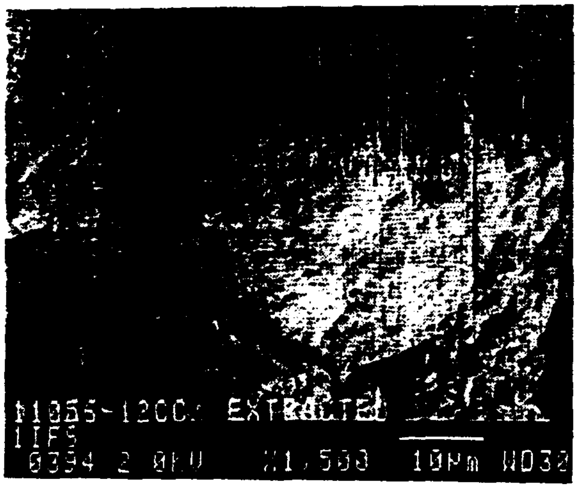
The silane-treated, washed, and sieved microcapsules were air classified to produce 19 pounds of finished microcapsules for use as corrosion inhibitors in room- temperature cure primers, paints, and polymers.



a. Microencapsulated DNBM



b. Fumed-Silica Mixed Microcapsules



c. Solvent-Extracted Silanized Microcapsules

Fig. 8 SEM Photomicrographs of Pilot-DNBM Microcapsules

Section 5

FORMULATION AND TEST OF 100% DNBM AND MICROENCAPSULATED DNBM IN EPOXY-POLYAMIDE PRIMER

At the start of the program, a series of coatings was prepared in which several levels of 100% DNBM were added directly to epoxy formulations, and spray-deposited on bare and chromate conversion-coated 7075 aluminum alloy panels. The DNBM addition levels were 1, 4, 7, 12, 20, and 30%. Using a different catalyst (an amidoamine), 40 and 50% DNBM coatings were formulated and applied. At the program start, there was still a question regarding the necessity for microencapsulation, and these tests were designed to assist in the decision. Testing for hydraulic fluid, lube oil, and solvent resistance were part of the evaluations.

Later in the program, after the microcapsules had been prepared, solvent washed, and sieved, formulations were made and tested to evaluate the microcapsules, including the effect of sulfates and the added steps on resistance to salt spray. This section describes the formulations, properties, and test results for the new coatings.

5.1 100% DNBM FORMULATIONS

Nonmicrocapsule formulations of DNBM were made directly with Mil-P-23377 epoxy-polyamide minus $SrCrO_4$; all other pigments and fillers were present. The test panels were 3-in. × 5-in. × 32 mil 7075-T6 aluminum alloy. Half of the panels were Alodine 600 chromate conversion-coating treated, and half were bare. Several coatings were deposited on 7075-T73 alloy. Before coating and before Alodine coating treatment, the bare surfaces were abraded physically with 3M Scotch-Brite very fine abrasive pads to remove the 10–30% Mg on the surface of the panels.

The base epoxy-polyamide was prepared by Deft Coatings, Irvine, California. The two controls were the base (0% DNBM) and the coating containing $SrCrO_4$. In this series, the A and B components and thinner were mixed and allowed to stand for the prescribed 1/2-h induction period. The DNBM was added with additional thinner to give a sprayable consistency. The panels were given a final rinse/cleaning with thinner before the spray application. Following a 7-day cure in the laboratory, the panels were scribed 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 a ASTM B-117 salt-spray environment for up to 1000 h. Failed coatings were removed as soon as observed. Results are given in Table 6.

Table 6 SALT-SPRAY CORROSION RESISTANCE OF DNBM-FILLED MIL-P-23377F MINUS SrCrO$_4$
Panels were 7075-T6, except where noted, and 3M Scotch-Brite deoxidized.

PANEL NO. (TEMPER)	COATING	SUBSTRATE TREATMENT	OBSERVATIONS					
			1 WK	2 WKS	3 WKS	4 WKS	5 WKS	6 WKS
			168 h	336 h	504 h	672 h	840 h	1008 h
211 (T6)	GRAY EPOXY	BARE	■					
212 (T6)	NO SrCrO$_4$	BARE	■					
276 (T6)	GRAY EPOXY	ALODINE 500	✓	✓	✓	✓(1)	■	
277 (T6)	NO SrCrO$_4$	ALODINE 600	✓	✓	✓	✓	■	
217 (T6)	YI SrCrO$_4$	BARE	✓	✓	✓	✓	✓	✓
219 (T6)	Mil-P-23377	BARE	✓	✓	✓	✓	✓	✓
286 (T6)	YI SrCrO$_4$	ALODINE 600	✓	✓	✓	✓	✓	✓
288 (T6)	Mil-P-23377	ALODINE 600	✓	✓	✓	✓	✓	✓
225 (T6)	1% DNBM	BARE	■					
226 (T6)	1% DNBM	BARE	■					
292 (T6)	1% DNBM	ALODINE 500	✓	✓	✓	✓	✓	✓
295 (T6)	1% DNBM	ALODINE 600	✓	✓	✓	✓	✓	✓
237 (T6)	4% DNBM	BARE	■					
238 (T6)	4% DNBM	BARE	■					
262 (T6)	4% DNBM	ALODINE 500	✓	✓	✓	✓	✓	✓
264 (T6)	4% DNBM	ALODINE 500	✓	✓	✓	✓	✓	✓
242 (T6)	7% DNBM	BARE	✓	✓	■			
244 (T6)	7% DNBM	BARE	✓	✓	✓	✓(1)	✓	■
270 (T6)	7% DNBM	ALODINE 600	✓	✓	✓	✓	✓	✓
274 (T6)	7% DNBM	ALODINE 600	✓	✓	✓	✓	✓	✓
260 (T6)	NONE	ALODINE 600	✓	✓	■			
279 (T6)	NONE	ALODINE 600	✓	✓	■			
285 (T6)	NONE	ALODINE 500	✓	✓	■			
58 (T73)	7% DNBM	BARE	■					
61 (T73)	7% DNBM (DNBM ADDED BEFORE INDUCTION PERIOD)	BARE	■					
305 (T6)	12% DNBM	BARE	■					
306 (T6)	12% DNBM	BARE	■					
309 (T6)	20% DNBM	BARE	✓	✓	✓	✓	✓	✓
311 (T6)	20% DNBM	BARE	✓	■				
313 (T6)	30% DNBM	BARE	✓	✓	✓	✓	✓	✓(1)
314 (T6)	30% DNBM	BARE	✓	✓	✓	✓	✓	✓
76* (T73)	40% DNBM	BARE	✓	✓	✓	✓	✓	✓
79* (T73)	50% DNBM	BARE	✓	✓	✓	✓	✓	✓

■ PANELS REMOVED BECAUSE OF CORROSION FAILURES
✓ NO EVIDENCE OF CORROSION

* EPON 828 AND GENAMID 2000 CATALYST
(1) CORROSION IN SCRIBE. NO LIFTING OR BLISTERS

Table 7 presents fluid-resistance test results. Formulation calculations and other details are tabulated in Appendix F. In Table 6, only those DNBM epoxy coatings that were deposited on the Alodine treated 7075-T6 panels withstood the 1000-h exposure (end of test), whereas the non-SrCrO$_4$ gray-epoxy on Alodine-treated 7075-T6 panels failed at 840 h. The 30% DNBM coating withstood the 1000-h exposure, but the 20% addition level was not conclusive.

The 1-week failures of 7% DNBM coatings on 7075-T73 in which the DNBM was added to the epoxy A plus B components before commencement of the induction period was not obvious. It may have been related to oxidation of the OH groups on the DGEBPA, diglycidyl ether of bisphenol A, resin molecule by the Cr (VI) in the DNBM mixture. This would have occurred

Table 7 SALT-SPRAY CORROSION AND FLUID RESISTANCE OF DNBM-FILLED MIL-P-23377F EPOXY VERSUS CONTROLS
Panels were 7075-T6, except as noted, and 3M Scotch-Brite deoxidized.

PANEL NO. (TEMPER)	COATING	SUBSTRATE TREATMENT	OBSERVATIONS						PANEL	FLUID RESISTANCE	
			1 WK 168 h	2 WKS 336 h	3 WKS 500 h	4 WKS 672 h	5 WKS 840 h	6 WKS 1000 h		LUBE OIL	HYDRAULIC FLUID
211 (T6)	GRAY EPOXY	BARE	■(2)						210,BARE	✓	
212 (T6)	NO $SrCrO_4$	BARE	■(2)						301,B	✓	
276 (T6)	GRAY EPOXY	ALODINE 600	✓	✓	✓	✓(1)	■		302,B		✓
277 (T6)	NO $SrCrO_4$	ALODINE 600	✓	✓	✓	✓(1)	■		287,A600		✓
217 (T6)	YI $SrCrO_4$	BARE	✓	✓	✓	✓	✓	✓	222,B	✓	
219 (T6)	Mil-P-23377	BARE	✓	✓	✓	✓	✓	✓	318,B	✓	
286 (T6)	YI $SrCrO_4$	ALODINE 600	✓	✓	✓	✓	✓	✓	317,B		✓
288 (T6)	Mil-P-23377	ALODINE 600	✓	✓	✓	✓	✓	✓	278,A600		✓
225 (T6)	1% DNBM	BARE	■								
226 (T6)		BARE	■								
292 (T6)	1% DNBM	ALODINE 600	✓	✓	✓	✓	✓	✓	296.A600	✓	
295 (T6)		ALODINE 600	✓	✓	✓	✓	✓	✓	297.A600		✓
237 (T6)	4% DNBM	BARE	■						234.B	✓	
238 (T6)		BARE	■								
262 (T6)	4% DNBM	ALODINE 600	✓	✓	✓	✓	✓(1)	✓	263.A600		✓
264 (T6)		ALODINE 600	✓	✓	✓	✓	✓	✓			
242 (T6)	7% DNBM	BARE	✓	✓	■						
244 (T6)		BARE	✓	✓	✓	✓(1)	✓(1)	■	245.B		✓
270 (T6)	7% DNBM	ALODINE 600	✓	✓	✓	✓	✓	✓	269.A600	✓	
274 (T6)		ALODINE 600	✓	✓	✓	✓	✓	✓	272.A600		✓
275 (T73)	7% DNBM	ALODINE 600	✓	✓	✓	✓	✓	✓			
305 (T6)	12% DNBM	BARE	■						304.B	✓	
306 (T6)		BARE	■						307.B		X
309 (T6)	20% DNBM	BARE	✓	✓	✓	✓	✓	✓	308.B	✓	
311 (T6)		BARE	✓	■					310.B		X
313 (T6)	30% DNBM	BARE	✓	✓	✓	✓	✓	✓	315,B	✓	
314 (T6)		BARE	✓	✓	✓	✓	✓	✓	312,B		X
58 (T73)	7% DNBM	BARE	■(2)						62,T73,B		✓
61 (T73)	(DNBM ADDED BEFORE INDUCTION PERIOD)	BARE	■(2)						248,T6,B		✓

■ PANELS REMOVED BECAUSE OF CORROSION FAILURES
✓ NO EVIDENCE OF CORROSION OR OTHER FAILURE
X COHESIVE FAILURE IN COATING
(1) CORROSION IN SCRIBE LINES, BUT NO LIFTING OR BLISTERING
(2) BLISTERS AT SCRIBE LINES

before the start of the catalytic hardening. When the induction period is observed, i.e., before adding DNBM, the OH groups may be adequately protected, thereby avoiding the loss of Cr (VI) via reduction to Cr (III). A more likely explanation pertains to the high sensitivity to pitting corrosion experienced by 7075-T73 panels relative to 7075-T6, which are relatively nonpitting.

Results indicated the need for large quantities of DNBM on bare panels before corrosion inhibition became obvious. The 40 and 50% DNBM epoxy coatings were prepared following technical consultations with Henkel Polymers Division, La Grange, Illinois. Of the several candidates evaluated in preliminary trials to achieve accelerated cure in the presence of the DNBM quaternary ammonium salt mixture, Genamid 2000, a fast-cure amidoamine catalyst/hardener resin, was selected. It was formulated with Shell Epon 828 epoxy resin.

Others tested qualitatively were Henkel Versamine EH30, Genamid 151, Genamid 2000, and Versamid 150.

Hydraulic fluid and lube oil resistance tests were performed on the DNBM-filled coatings. For the 12, 20, and 30% DNBM coatings shown in Table 7, failures were observed in Mil-H-83282 hydraulic fluid at 66°C over 24 h, but passing results were observed for the oil exposures. The 7% DNBM coatings passed uniformly, irrespective of when the DNBM was added to the epoxy-polyamide component mixture.

The 40% DNBM epoxy showed tack-free behavior overnight, 18 h, whereas the 50% coating required 72 h. However, the 40 and 50% coatings tested were attacked by MEK (methylethylketone) in the Mil-P-23377F solvent wipe test.

5.2 MICROENCAPSULATED DNBM FORMULATIONS AND TEST

Because of the relatively high level of sulfate found in the 141-pound (64-kg) pilot lot of DNBM, the silanized microcapsules made from the lot were tested. Several epoxy-polyamide formulations were prepared. The formulations were deposited on 1010 steel Q-panels for comparison with previously prepared laboratory-scale microcapsules (Reference 3, p. 34). In addition, 10% levels of the pilot DNBM and LMSC laboratory DNBM (no. 11048-26, Reference 3, p. 10), dated 1988, were added to epoxy-polyamide component mixtures that were allowed to stand overnight, 18 h, before adding the DNBM. The samples were added later than usual to minimize the interactions of Cr (VI) with the oxidizable OH^- groups in the part A resin. See Appendix C for calculation of the sulfate content of lot 11048-26.

Two sets of microcapsules were formulated with clear (pigment-free) Deft Coatings Co. epoxy-polyamide. The microcapsule candidates were solvent-leached (in the laboratory) and nonleached (silanized only). The resultant microcapsules were passed through a 250 mesh screen (Tyler rating) to remove aggregates and agglomerates larger than 61 μm, but the capsules were not air classified because of limited quantities.

The microcapsules were formulated in Deft Coatings no. 02X-009 (clear) epoxy-polyamide (no pigments).

37 cm^3 Part A × 0.91 g/cm^3, sp.gr. = 33.67 g
33.26% solids in A × 33.67 g = $\underline{11.20}$ g solids

37 cm Part B × 0.84 g/cm^3, sp.gr. = 31.08 g
22.24% solids in B × 31.08 g = $\underline{6.91}$ g solids

In 74 cm^3 of the two-part epoxy, there are 11.20 g A plus 6.91 g B, a total of 18.11 g. Percentage added microcapsules by weight was [8.5 g/(18.11 + 8.5)] × 100 = 31.9%. The resultant coatings were mat (nonglossy) in appearance. The nonleached microcapsule-filled coatings were light green, indicating some Cr (VI) reduction to Cr (III). The leached microcapsule coatings were yellow.

Results for 500-h salt-fog exposure are in Table 8. Summarizing the salt-fog data, the solvent-extracted silanized microcapsules in epoxy-polyamide passed the ASTM B117

Table 8 SALT-SPRAY CORROSION RESISTANCE OF PILOT DNBM-FILLED MICROCAPSULES AND 100% DNBM FORMULATED IN EPOXY-POLYAMIDE COATINGS ON 7075-T6 ALUMINUM ALLOY

Panel No.	Coating	1 wk	2 wks	3 wks
01	Control, no $SrCrO_4$, all other pigments present	■ (5d)		
02	Control, no $SrCrO_4$, all other pigments present	■ (5d)		
03	Control, no $SrCrO_4$, all other pigments present	■ (5d)		
04	10% pilot DNBM, no $SrCrO_4$, all other pigments present	✓	■ (10d)	
05	10% pilot DNBM, no $SrCrO_4$, all other pigments present	✓	■ (10d)	
06	10% pilot DNBM, no $SrCrO_4$, all other pigments present	✓	■ (10d)	
09	10% laboratory DNBM, no $SrCrO_4$, all other pigments present	✓	■ (10d)	
10	10% laboratory DNBM, no $SrCrO_4$, all other pigments present	✓	■ (10d)	
12	10% laboratory DNBM, no $SrCrO_4$, all other pigments present	✓	■ (10d)	
16	Silanized microcapsules, not leached in clear epoxy-polyamide	✓	✓	■ (17d)
17	Silanized microcapsules, not leached in clear epoxy-polyamide	✓	✓	■ (17d)
18	Silanized microcapsules, not leached in clear epoxy-polyamide	✓	✓	■ (17d)
22	Leached silanized microcapsules in clear epoxy-polyamide	✓	✓	✓ (24d)
23	Leached silanized microcapsules in clear epoxy-polyamide	✓	✓	✓ (24d)
24	Leached silanized microcapsules in clear epoxy-polyamide	✓	✓	✓ (24d)
14	Control, no $SrCrO_4$ or other pigments present	■ (5d)		
20	Control, no $SrCrO_4$ or other pigments present	■ (5d)		

■ Panels removed because of corrosion failures, principally lifting.
✓ · No evidence of lifting or blistering; rust in scribe lines.

exposure to 24d (576 h), whereas the nonextracted capsules in epoxy failed at 17d (408 h). Both 10% DNBM additions to the epoxy failed at 10d (240 h). The control coatings failed in 5d (120 h). An extended term of exposure ending at 1700 h (following the year-end facility closing, salt-fog test continuation) showed moderate undercutting and lifting at the scribe lines for the extracted-capsule epoxy. The reason for the microencapsulation/surface treatment concept is now made obvious, and the superior inhibition shown by the extracted silanized microcapsules is apparent. The reduced quantity of molybdate quaternary resulting in a concomitantly lowered sulfate content probably contributed to this improvement.

Section 6

RECOMMENDATIONS FOR FUTURE WORK

The principal tasks that should be performed to qualify the DNBM microcapsules for application in room-temperature cure primers, paints, and other coatings for Navy use are as follows:

(1) Improve the overall microencapsulation technique with regard to yield and uniform particle size. It is important that the DNBM core be prevented from depositing on and within the shell material. Improved emulsion technology is suggested. If improved emulsification is not practical, it may be possible to minimize the DNBM deposition on the shell exterior by decreasing the overall payload. In addition, a test simpler than ESCA for inspecting the capsule surfaces during production is needed to detect the undesirable deposits.

(2) Alternative source(s) of quaternary ammonium salts need to be developed, since Sherex Chemical Co. no longer (as of this report date) is developing these materials on an R&D basis. Akzo Chemical, the developer of the B salt, is one of a few sources that may be brought into the program.

Section 7

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Appendix A

TRADE-NAME IDENTIFICATION

	Trade Name or Designation	Source
Adogen 464	Methyltrialkyl (C_8-C_{10}) ammonium chloride	Sherex Chemical
Akzo RD5444A	Methyltrialkyl (C_{12}) ammonium borate, isopropyl alcohol diluent	Akzo Chemical
Akzo RD5444AT	Same as RD5444A, except toluene diluent	Akzo Chemical
Cabosil M-5	Fumed silica, hydrophilic	Cabot
Cabosil TS-530	Hexamethyldisilazane-treated fumed silica, hydrophobic	Cabot
Cabosil TS-720	Dimethylsilicone-treated fumed silica, hydrophobic	Cabot
Degussa R805	Trimethyloctylsilane-treated fumed silica, hydrophobic	Degussa
Culminal 255	Methylcellulose, low viscosity	Henkel
Methocel A15-LV	Methylcellulose, premium, very low viscosity	Dow
Epon 828	Polyamide resin, low viscosity	Shell Chemical
Genamid 151	Amidoamine resin, low viscosity	Henkel
Genamid 2000	Amidoamine resin, fast cure	Henkel
Versamid 150	Polyamide resin, low viscosity	Henkel
Versamine EH30	Tertiary amine accelerator for epoxies	Henkel

Appendix B

PRELIMINARY LABORATORY TRIALS

The descriptions are for samples made by the Sherex R&D Laboratory, Columbus, Ohio, preliminary to pilot-plant scale-up. Analyses were performed at LMSC.

B.1 QUATERNARY AMMONIUM DICHROMATE AND CHROMATE

During the initial period, Sherex supplied LMSC with laboratory samples from revised proprietary procedures. The procedures would, if successful, result in a significant diminution in Cr (VI) waste stream materials relative to the amounts produced in the original double-displacement process. As a result, manufacture of the salts could be brought closer to commercial reality. Results of testing by LMSC indicated that the dichromate (D) salt was not satisfactory. The principal cause was incompleteness of reaction to the extent that the inorganic anions were found to leach into pure water [10-MΩ deionized (DI) H_2O] when mixed and allowed to stand for several hours. The result of the presence of this leachate would be instability of the oil-in-water emulsions that are required to remain stable for several days as feed stocks for the spray-dry process to prepare the DNBM-containing microcapsules. The initial process DNBM salts (double exchange) produced no leachate in deionized water, and the resultant emulsions were stable for several weeks. Sherex returned to the original process for D pilot production following unsuccessful tests of materials ending with sample number 98B as a result of the instability.

Sherex No. 303-85

This material was prepared to determine whether the chromate salt would be less sensitive to light in the presence of oxidizable solvents than the dichromate quaternary. However, the sample was green in color, indicating that a significant portion of Cr (VI) had been reduced to Cr (III). The Cr contents were as follows:

Total Cr, AAS:	4.7 ± 0.1%
Cr (VI), polarography:	3.8 ± 0.5%
Cr (III), by difference:	Avg. 0.9%
Cr (III), in total Cr:	19.1%

Isopropyl alcohol had been used as solvent which resulted in the rapid reduction of the Cr (VI) values; as such, toluene was used for the next sample.

Sherex No. 307-87, Chromate

This sample had the expected dark brown color of Cr (VI) organic quaternary ammonium salts.

Total Cr, AAS: 4.0 ± 0.1%
Cr (VI): 4.3 ± 0.5%

Based on a value of 5.7% Cr in 100% chromate quaternary salt of gram formula weight 919 for $[CH_3(C_8 - C_{10})_3N]_2 \cdot CrO_4$, the Cr conversion was $(4.3/5.7) \times 100 = 75.4\%$.

Exposure of equal weights of dichromate and chromate quaternaries in toluene to laboratory fluorescent light indicated no difference in catalytic reactivity regarding light response. In addition, the lower quantity of Cr (VI) in the chromate versus the dichromate quaternary was a secondary reason for remaining with the original selection of dichromate as the D salt.

Sherex No. 303-88, Dichromate

Total Cr, AAS: 9.2 ± 0.1%

Percent Cr in the salt was $(9.2/10.2) \times 100 = 90.2\%$ of theoretical, based on 10.2% Cr in a 100% dichromate salt of molecular weight 1019. This sample showed a *rapid rate of leaching* in DI water in 1 h.

Sherex No. 303-96, Low Viscosity, Light Color

Total Cr, AAS: 8.62%

Total Cr conversion was $(8.62/10.2) \times 100 = 84.5\%$. However, reaction with seawater was unexpectedly slow (1-2 h). A recheck of Sherex 98A (the original double exchange reaction) to seawater was normal at 15 min, and there was no leaching/hydrolysis in DI water overnight.

Sherex No. 303-98B, Revised Process for Maximum Cr

Total Cr, AAS: 8.42%

Percent conversion was 86%. Rapid leaching of this sample in DI water also occurred in 1 h, similar to No. 303-88.

B.2 QUATERNARY AMMONIUM NITRITE

Initial samples made by the Sherex proprietary process contained excessively high levels of chloride ion, 0.78 to 1.5% Cl^-. With a different nitrite source, the chloride content dropped to an acceptable level, and therefore the process was adopted for the pilot-plant run of the nitrite salt.

Sherex No. 303-101

NO_2^-:	9.08%
Cl^-:	82 ppm
SO_4^{2-}:	< 100 ppm

B.3 QUATERNARY AMMONIUM MOLYBDATE

Sherex No. 103-85

This sample was a free-flowing, buff-colored liquid with a green tint, in contrast to the green, taffy-like molybdate salt prepared by the original process.

Total Mo, AAS:	10.44% (average 4 samples, $\epsilon = 0.3$)

Sherex No. 303-104, Reworked

Total Mo, AAS:	26.79% (average 3 samples)

The 100% conversion figure is 26.52, close to that developed previously in the laboratory (Reference 3, p. 5).

Appendix C

DNBM SULFATE IMPURITIES AND RELATED CALCULATIONS

Analysis at LMSC of 1-kg samples from the final vacuum-stripped lot (evacuated to remove toluene solvent) indicated the presence of a high level of a sulfur-bearing compound. Analysis was by Parr oxygen-bomb oxidation of the sample followed by sulfate determination via ion chromatography. The result was 1.6% or 16,000 ppm SO_4^{2-}.

Samples were then submitted to Galbraith Laboratories, Knoxville, Tennessee, to obtain independent verification. A sample was also sent to NAWCADWAR. Data are given in Table C-1.

Table C-1 SAMPLE DATA

DNBM	Identification	Galbraith Laboratory (%S)	SO_4^{2-} Average (ppm)
11056-80A	Grab sample from Sherex pilot plant, first evacuation	0.52 0.51	15,500
SC294-160	Pilot-plant DNBM components mixed and evacuated in Sherex Laboratory	0.50 0.50	15,000

Corroborative data from NAWCADWAR was 0.5%S, or 15,000-ppm SO_4^{2-}, thereby indicating the correctness of the original value of 16,000-ppm SO_4^{2-} for the pilot-plant grab sample reported.

To determine which of the components contributed to the high impurity level, the four individual DNBM components were analyzed. The values are given in Table C-2.

Table C-2 DNBM COMPONENTS

Component	%S	ppm SO_4^{2-}
D (Galbraith analysis)	0.31	9,300
N (Galbraith analysis)	0.039	1,170
B (LMSC analysis)	(direct to SO_4)	6,000
M (Galbraith analysis)	1.71	51,300

Contributions to the overall SO_4^{2-} content are calculated by multiplying the sulfate by the weight percent fraction of each component in the DNBM (calculated from data on p. 4).

		ppm SO_4^{2-} contribution
D 9300 × 0.265	=	2,460
N 1170 × 0.21	=	245
B 6000 × 0.31	=	1,860
M 51,300 × 0.216	=	11,060
	Total:	15,625

The 15,600-ppm SO_4^{2-} figure converted to %S is 5.2%, which is close to the figure reported by both Galbraith and NAWCADWAR, as well as LMSC in the 16,000-ppm SO_4^{2-} analysis.

Infrared analysis of the molybdate quaternary showed many features that identified the impurity as the quaternary ammonium methylsulfate salt, thereby indicating that the molybdate salt was not the diquaternary salt as originally assumed but the monoquaternary salt identified during the original R&D program. A large proportion of the methylsulfate starting material would therefore be present as an impurity. The following calculation gives the methylsulfate impurity.

$$1.7\%S \times \frac{CH_3(C_8-C_{10})_3\ N\cdot CH_3SO_4}{S} = 17\% \times \frac{512.6}{32} = 27.2\% \text{ quaternary methylsulfate}$$

or a yield of 72.8% monoquaternary ammonium molybdate. Calculated percent Mo in the monosubstituted product is 26.5% Mo. The %Mo in a disubstituted product is 17.3%, which is reasonably close to the 19.07% Mo analyzed in the pilot-plant product. However, it was apparently an incorrect assumption that the diquaternary salt that had been formed. Percent unconverted methylsulfate quaternary was back calculated from these figures.

$$19.07\% \times 100/26.52 = 71.91\%$$

$$100 - 71.91 = 28.09\% \text{ quaternary ammonium methyl sulfate}$$

The three remaining components (D, N, B) also contributed to the sulfate content. For the dichromate salt, its yield was 8.4% Cr × 100/10.2% = 82.4%, or 17.6% starting material. Regarding the borate sulfate content, Akzo indicated the presence of an oxidizable sulfur-containing compound in the commodity, which was apparently oxidized during the DNBM mixing process. This may have been the reason for the 20 to 30% loss of Cr (VI) in the final DNBM mixture analyzed by polarography. However, the original analytical data for sulfate were significantly lower, in the 1000-ppm range. This is attributed to poor detection on the ion chromatograph column used for some of the analyses.

The calculation of sulfate impurities contained in the 1988 LMSC laboratory-prepared DNBM (11048-26, Reference 3, p. 10) is given below. The value (maximum sulfate) was 3.3% SO_4^{2-}.

D (Dichromate) Sherex lot 150-195, %Cr 8.8%. Percent Cr in the salt was (8.8/10.2) × 100 = 86.27% of theoretical. Therefore, 13.73% is assumed the sulfate quaternary ammonium salt impurity, or [13.73/512.6 (FW salt)] = X/96 (FW SO_4^{2-}). X = 2.57% SO_4^{2-}.

N (Nitrite) Sherex lots 213-10/213-12 blended. %NO_2^- = 4.2%. Percent NO_2^- in the salt was (4.2/10.28) × 100 = 40.86% of theoretical. Therefore, 59.14% is assumed the sulfate salt, or 59.14/512.6 = X/96. X = 11.08% SO_4^{2-}. Note: Yields were low but were the maximum attainable at the time.

B (Borate) Akzo RD 5444 A. Assumed same as RD 5444 AT, 1800-ppm SO_4^{2-}.

M (Molybdate) Sherex lot 150-151, 0.64% SO_4^{2-}, previously analyzed (Reference 3, p. 5).

In lot 11048-26, the following quantities were mixed at LMSC:

D	301 g
N	238 g
B	394 × 90% solids = 355 g
M	277 × 81.5% solids = 226 g

Percent of 1120 g total weight is:

D	26.9%
N	21.2%
B	31.7%
M	20.2%
	100.0%

The amount of sulfate using the above weighted percentages yields:

D	0.269	×	2.57%	=	0.69
N	0.212	×	11.08%	=	2.35
B	0.317	×	1800 ppm	=	0.057
M	0.202	×	0.64	=	0.129
			Total SO_4^{2-}		3.23%

This is the maximum quantity calculated for the lot. The percent available in a 3.5% aqueous NaCl solution was determined at Naval Air Warfare Center, Aircraft Division, Warminster, Pennsylvania. Ultrasonic energy was used to disperse/dissolve/hydrolyze the DNBM in 3.5% aqueous NaCl as a simulant for seawater. The result attained was 1.7% SO_4^{2-} after several hours of sonic treatment. It was surmised that the two DNBM lots would yield similar results, therefore, as corrosion inhibitors in a similar 5% salt-fog environment.

Appendix D

PROCEDURAL NOTES FOR TWIN-SHELL BLENDER SILANIZATION PROCESS

1. Before starting MTMS (methyltrimethoxysilane) passage through the system, make sure that all leaks are plugged. Use Ar gas at approximately 10-ft^3/h air (use 0- to 20-ft^3/h air flow meter). Feed effluent Ar into a 1-L beaker filled with water to the top; use Tygon of same diameter as feed tubing. If there are no leaks, a bubble in the effluent beaker will form at the same rate as in the MTMS. A liquid nitrogen cold trap may also be used to condense the excess MTMS.

2. Place fumed-silica microcapsules in twin-shell blender up to the bottom level of the intensifier bar. **Keep Ar flowing at all times!** Note safety precautions in No. 4.

3. For MTMS, use Buchner flask (heavy wall side-arm, approximately 1 L). Fill approximately 75% with MTMS. Record pre- and post-silanization levels. Use crimped-end copper tube to obtain small bubbles.

4. Turn on bar and shell. Change gas settings to introduce Ar plus MTMS vapors into tumbling powders. Every 1/2 to 3/4 h, stop tumbling (keep gas flowing to avoid clogging the holes in the intensifier bar). Keep Ar flowing when changing to Ar plus silane, or vice versa. Open shell and, if necessary, brush sides using a disposable paint brush. Use gloves and a mask to avoid breathing the powders.

5. Rate of rotation of shell is preset. The bar feeder is 400 rpm, maximum. There is a rheostat on the frame which may be used to decrease the bar rpm, but its use is not necessary.

6. Time of exposure to silane is 2 to 2 1/2 h for 200 to 250 g of mixed fumed-silica microcapsules in the 3-quart shell. For the first 3/4 h, most of the silane vapors are absorbed by the capsules, and not much MTMS is readily detected in the exhaust. Experience in detecting breakthrough quantities of silane at the exit can be gained by lifting the exit tubing out of the water and briefly using the aroma to detect the level of gas in the Ar stream.

7. It is important to avoid the introduction of liquid silane into the rotating powder zone, since this will cause the formation of clumps and boluses of wetted microcapsules. If any are

formed, they must be removed from the product. If condensed MTMS occurs within the shell, a darker yellow color will be observed at the shell surface; this a sign that the reaction may be out of control.

8. Turn off the Ar plus silane by changing the gas input settings, but, at the same time, maintain the Ar flow for several minutes. The treated microcapsules are removed by gravity through the central port pointing downwards into a Pyrex baking dish or similar container.

9. Place the dish in a high-humidity chamber overnight to set the silane on the capsule surfaces. Excess humidity is not needed, but at least 80% RH at room temperature is required. Excessive humidity may cause clumping.

10. Check that the holes in the intensifier-bar exit feed are not blocked after a run.

11. Check O-ring on internal rod of intensifier bar for breakage or wear. Apply silicone grease.

12. Change cheesecloth filter at exit port. A 325 to 400 mesh screen may also be used to prevent powder from blowing out of the shell.

13. Note that metal end support will most likely not be required for the 10-quart shell.

14. CAUTION. Install shell clamps with proper direction to avoid hitting the frame.

15. The entire system should be adjacent to or inside a fume hood to avoid excess silane and/or microcapsule dispersal to air.

16. Excess MTMS that may collect or condense in the feed lines should be removed by opening briefly the subvalve under the wood pallet that supports the system.

17. Use fluorocarbon rubbers as gasket materials on twin-shell openings to avoid gasket deterioration.

Appendix E

FUMED-SILICA TREATMENT OF MICROCAPSULES

THe 20% Cabot TS-530 and 80% microcapsules, as received, are weighed into a gallon paint can and placed on a Red Devil Mixer for 15 min. At the end of the time, the mixture is homogeneous and free flowing. For the 3-quart shell (laboratory runs), 50 g of TS-530 are mixed with 200 g of microcapsules. It may be desirable to use a larger container to speed up the preparations. There should be no lumps observed in the mixture when the can is removed from the mixer and opened.

Appendix F

EPOXY-POLYAMIDE FORMULATION CALCULATIONS AND DETAILS

Calculations are given below for the addition of 100% DNBM to Mil-P-23377 epoxy-polyamide minus $SrCrO_4$. The Deft Coatings Co. designation Mil-P-23377 minus $SrCrO_4$ is 02W030.

For each 40 cm^3 part A and B to be mixed 1:1 by volume (the calculations are based on data supplied by Deft: sp. gr. and % solids):

40 cm^3 A × 1.05 g/cm^3, sp. gr. = 42.0 g
49.8% solids in A × 42.0 g = 20.92 g solids

40 cm^3 B × 0.839 g/cm^3, sp. gr. = 33.56 g
22.2% solids in B × 33.56 g = 7.45 g solids

In 40 cm^3 A + 40 cm^3 B, there are 20.92 g A plus 7.45 g B, a total of 28.37 g.

To prepare, for example, a 7% DNBM formulation, based on total solids,
solve for X:
$X/(X + 28.37) = 0.07$
$X = 2.14$ g. DNBM added to parts A + B

For formulation of 40 and 50% (wt) DNBM added directly to epoxy-amidoamine coatings, the mixing proportions were as follows:

Component A: Epon 828 epoxy resin (epoxy equivalent wt 185-192)
B: Henkel Genamid 2000 amidoamine catalyst

Mixing proportions: 40% DNBM
Epon 828 10.0 g
Genamid 2000 3.6
Thinner, Mil-T-81772B (Type II) ~20 cm^3
Mix. Let stand ~1/2 h.
Add 9.1 g DNBM. Mix thoroughly.

Mixing proportions: 50% DNBM
Epon 828 10.0 g
Genamid 2000 3.6 g
Thinner 20-25 cm^3
Mix. Let stand ~1/2 h.
Add 13.6 g DNBM. Mix thoroughly.

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