Aerotherm Project 6596

INTERIM REPORT

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MXSA PACKAGING

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OBJECTIVE

Investigate the applicability of compounding MXSA ingredients into a two or three part system which would require a minimum of handling by the user. The major portion of the solvent shall be excluded from the premixed kit and only used to produce homogeneity or a dust-free kit.

SUMMARY

Preweighed two part MSA (MXSA)* kits have been developed which require that the user supply only the solvent. The kits consist of all of the powdery materials in Part A, and the epoxy resin (AA397) in Part B. Recent aging data on the kits indicate that they are useable for at least 6 months.

DISCUSSION

Acurex has developed a two-part drum-size kit based on the MSA formulation supplied by MSFC. The powdery materials, including microballoons, fiberglass, thixotropic agent and curing agent have been combined into Part A, while Part B consists of the AA397 binder. The solvents for the formulation are supplied by the user, thereby reducing shipping weight. The kits as supplied by Acurex are easily handlable as Part A weighs less than 80 lbs including the fiber drum, while Part B is supplied in a 5-gallon steel pail. The formulation of the kits is shown in Table 1. The only formulation change between the kit and the material developed by NASA is that the liquid eutectic curing agent (Shell Z) has been replaced by its two solid amine components (71 percent methylene dianiline and 29 percent meta-phenylene diamine). This change was necessary because the liquid Shell Z does not disperse well in the powdery components of the formulation. This change causes no mixing problems as the amines are soluble in the solvent system.

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*The acronym MXSA (Marshall experimental sprayable ablator) has recently been replaced with MSA (Marshall sprayable ablator).

TABLE 1. MSA FORMULATION

	Ingredients for 8 gal of MSA	Ingredient in Acurex MSA Drum Size Kit		
		Metric Units	English Units	
Phenolic Microballoons BJO-0930	2700 grams	16.1 kg	35.47 lbs	Part A 27.0 Kg (59.5 lbs)
Eccospheres IG 101	900 grams	5.37 kg	11.8 lbs	
1/4-inch Chopped glass K847	90 grams	0.537 kg	1.18 lbs	
1/16-inch milled glass fibers 731CA	225 grams	1.34 kg	2.96 lbs	
Bentone 27	246 grams	1.47 kg	3.23 lbs	
Shell Z { 71% methylene dianiline	368 grams	1.56 kg	3.44 lbs	
Shell Z { 29% m-phenylenediamine		0.635 kg	1.39 lbs	
AA 397 resin	2625 grams	15.66 kg	34.49 lbs	Part B
Denatured ethyl alcohol	124 grams	0.739 kg	1.63 lbs	Solvents
Methylene chloride	9 quarts	50.8 liters	13.42 gal	
Perchloroethylene	9 quarts	50.8 liters	13.42 gal	

Requirements for developing a kit from the formulation supplied by MSFC include the following.

1. The components must form a homogeneous blend
2. The components must not react with each other
3. No significant changes in formulation are permitted
4. The density of cured MSA foam must be in the 16- to 18-lb/ft^3 range
5. The flatwise tensile strength must be in excess of 150 psi
6. The kits must be stable for 6 or preferably 12 months
7. The kit must be easy to use

These requirements were used to evaluate the seven schemes shown in Figure 1; of these seven schemes, Kit No. 2 was eventually selected. Kits Nos. 1, 3, 5, and 6 were eliminated on the basis that the addition of the liquid AA397 or Shell Z to the fillers resulted in lumps which are not dispersible unless the mixture is heated, or solvent is added. The addition of 25 percent of the solvent does give a uniform mixture with a consistency of damp sand, however, the long-term stability of this mixture is questionable due to potential solvent evaporation.

Formulations No. 7 (also Nos. 3 and 5) were eliminated because it was found that Bentone 27 Thixotropic agent reacts with epoxy resins as reported by Celanese (Tech. Bull. No. 0168; Long-term Stability of Thixotropic Epoxy Resins and Curing Agents), and confirmed at Acurex.

Formulation No. 2 was then selected over formulation No. 4 on the basis of the good results obtained and the fact that formulation No. 4 is three-part kit while Formulation No. 2 is a two-part kit, thereby cutting down the number of operations required by the user.

Typical flatwise tension strengths obtained are shown in Table 2. The values of 230 and 200 psi for Samples 1 and 2 are considered to be equivalent because of the small number of samples and the greater density of Sample 1. The lower value obtained with Sample 3 compared to Sample 2 is due in part to the greater thickness and in part to insufficient drying times

KIT #1

Part A	Part B
All Fillers + Shell Z	AA397

KIT #2

Part A	Part B
All Fillers + Dry Shell Z Components	AA397

KIT #3

Part A	Part B
All Fillers + AA397	Shell Z

KIT #4

Part A	Part B	Part C
All Fillers	AA397	Shell Z

KIT #5

Part A	Part B
All Fillers (Except Bentone 27) + Shell Z	AA397 Bentone 27

KIT #6

Part A	Part B
All Fillers (Except Bentone 27) + AA397	Shell Z Bentone 27

KIT #7

Part A	Part B
All Fillers (Except Bentone 27)+ Dry Shell Z Components	AA397 Bentone 27

Figure 1. MSA kits.

TABLE 2. FLATWISE TENSILE STRENGTH OF MSA FOAM[a]

Amine Curing Agent	Kit Storage Time	Sample Density	Sample Thickness	Flatwise Tensile Strength[b] (psi)	No. of Specimens
1. Shell Z	—	16.4	1/4 inch	230	4
2. MDA/mPDA	initial	16.2	1/4 inch	200	4
3. MDA/mPDA	6 months	16.3	3/8 inch	151	5

[a]Using Type K832, 1/4-inch glass fibers

[b]Tested after 2 weeks room temperature cure

between applying layers of MSA in the sample billet preparation. The excess solvent carried epoxy resin to the surface of the sample during evaporation, giving a sample with a nonuniform cross section. This was evidenced by the failure mode of the samples which was generally near the low resin surface of the billet. This work will be repeated with 1/4-inch thick samples and uniform resin content samples, and the data will be presented in the next report.

The 1/4-inch chopped glass fibers used in these kits has proven to be unsatisfactory for spray applications, as it does not break up properly in the solvent, thereby causing spray nozzle plugging problems and nonuniform distribution of the glass in the foam composite. Acurex and MSFC are currently processing a contract modification to remake the MSA kits, using 1/4-inch Owens Corning Type K847 chopped fiberglass, which is known to disperse properly in the solvent and the foam composite.

A proposed Materials and Formulation Specification for MSA is included in this report as Appendix A. This specification details formulation procedures for the MSA kits along with quality control requirements for the raw materials. It also gives mixing instructions for the use of the kit.

EXPERIMENTAL

Accelerated aging studies were conducted by mixing the filler materials with (1) AA397 resin, (2) Shell Z curing agent and (3) a dry blend of Shell Z components (71 percent MDA and 29 percent m-PDA). The mixtures were sealed in cans and heated to 165°F (74°C) for 1 week. This aging cycle is equivalent to approximately 30 weeks of natural aging at 70°F based on the approximation that reaction rates double for each 18°F (10°C) of temperature rise.

An examination of the samples showed no significant change in the Shell Z or dry-blend of Shell Z components, with the fillers. However, the blend of fillers and AA397 resin contained hard lumps in the mixture which undoubtedly are due to polymerization of AA397, possibly catalyzed by Bentone 27.

The resistance of blended MSA dry components to stratification by vibrations was tested. This was done to simulate the settling or separation of components during shipment.

A gallon can half-full of the dry blend was shaken 16 hours on a sieve shaker. Then the top and bottom halves of the mixture were sieved to determine particle size distribution and component distribution. The results are shown in Table 3. The sieve analyses are nearly identical for both halves of the mixture with no migration of the glass fibers. Thus it appears that the MSA dry blend is quite stable to vibration and shippable without self-sieving.

TABLE 3. 16-HOUR VIBRATION TESTING OF MSA COMPONENTS

Sieve Size	Top Half	Bottom Half
+60 (primarily 1/4-in. glass fibers)	3.2%	2.5%
-60 + 100	5.5%	6.3%
-100	91.3%	91.2%

Lap shear tensile testing was done as a quality control test for the AA397 (Lot 10-4) adhesive in Part B of the MSA kit. AA397 was cured with Shell Z at 121°C (250°F) on dichromate etched aluminum substrate. An average of six bonds tested at room temperature gave a lap shear tensile strength of 5120 psi which passes our 5000-psi minimum specification for the Shell Z cured AA397.

APPENDIX A

MATERIAL AND FORMULATION SPECIFICATION
FOR
MARSHALL SPRAYABLE ABLATOR (MSA)

A.1 SCOPE

This specification details formulation requirements and vendor specifications for the materials necessary to produce MSA foam kits. Incoming receiving inspection requirements for the materials have not been established.

A.2 DESCRIPTION

The MSA kits produced by this specification consist of Part A, a dry blend of microballoons, fillers and curing agent; and Part B, the epoxy resin.

A.3 PROCESS DESCRIPTION

A.3.1 Raw Material Requirements

A record of lot numbers and incoming inspection results shall be kept on each lot of raw material.

A.3.1.1 Bakelite BJO-0930 Phenolic Microballoons (Union Carbide Chemical Company.)

The BJO-0930 phenolic microballoons shall be in accordance with the following specifications:

a. Apparent density (untamped): 64 to 104 kg/m^3 (4 to 6.5 lb/ft^3) (Method: Union Carbide WC-2-J)

b. True density (liquid displacement in 1 percent Dupanol OS in Toluene): 210 to 250 kg/m^3 (13.1 to 16.7 lb/ft^3)

c. Floatation in 1 percent Dupanol OS in Toluene solution — not less than 90 percent shall float. (Method: Union Carbide WC-245-A-2)

d. Particle size, percent on 40 mesh (Method: Union Carbide WC-7-D-4) — 0.2 maximum

e. Moisture content, percent (Method: Union Carbide WC-6-G-1) — 4.0 maximum

A.3.1.2 Eccospheres Glass Microballoons 1G-101 (Emerson & Cumming)

The 1G-101 microballoons shall be in accordance with the following specifications:

a. True density (liquid displacement) 300 to 350 kg/m^3 (18.8 to 21.8 lb/ft^3)

b. Bulk density (tamped) 160 to 240 kg/m^2 (10 to 15 lb/ft^3)

c. Particle size, percent on 40 mesh — 0.2 maximum

A.3.1.3 1/4-Inch Chopped Glass Fibers (Owens Corning Type K 847)

A.3.1.4 1/16-Inch Milled Glass Fibers (Owens Corning Type 731 CA)

A.3.1.5 Bentone 27 (National Lead Industries)

A.3.1.6 Methylene Dianiline

The methylene dianiline shall be in accordance with the following specification.

a. Melting point: 90°C minimum

b. Grindability — must be capable of being ground in a hammer-mill to pass through a 35 mesh sieve at 0°C

A.3.1.7 Meta-phenylenediamine (Shell CL)

a. Melting point: 63°C minimum

b. Grindability — must be capable to be ground in a hammer-mill to pass through a 35 mesh sieve at 0°C

A.3.1.8 AA397 Epoxy Resin

a. Infrared spectrum — the Spectrum shall not have an isocyanate band at 2300 cm-1

b. Lap shear strength — the lap shear strength at room temperature shall be 3.44×10^7 N/m^2 (5000 psi) or greater when cured with Shell Z (14 phr) at 250°F for 1 hour on etched* 2024-T3 clad aluminum adherents.

A.3.2 MSA Formulation Procedures

A.3.2.1 Equipment

The equipment for MSA formulation include a 0.25 m^3 (9 ft^3) paddle-type mixer, a hammer-mill and screens of 50, 40, 35, 30 and 8 mesh.

A.3.2.2 Formulation (drum size kit)

a. Add 16.1 kg (35.47 lb) BJO-0930 phenolic microballoons to mixer.

b. While stirring, screen 5.37 kg (11.8 lb) Eccospheres IG-101 through 50 mesh into the mixer.

c. Screen the 1/4-inch chopped glass fibers through an 8 mesh sieve two times to remove long fibers then screen 0.537 kg (1.18 lb) 1/4-inch chopped glass fibers through an 8 mesh sieve into the rotating mixer.

d. While stirring screen 1.34 kg (2.96 lb) 1/16-inch milled glass fibers through 8 mesh into the mixer.

e. While stirring, screen 1.47 kg (3.23 lb) Benton 27 through 30 mesh into the mixer.

f. While stirring, screen 1.56 kg (3.44 lb) methylene dianiline (MDA) through 30 mesh into the mixer.

NOTE: MDA and Shell Z should be ground (separately) in a hammer-mill to to pass through a 35 mesh sieve.

g. While stirring, screen 0.635 kg (1.39 lb) Shell CL into the mixer.

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*$H_2SO_4/Na_2Cr_2O_7/H_2O$ (25/3/72 PBW) at 160 ±10°F for 10 to 15 minutes.

h. Continue stirring for a minimum of 2 minutes after the mixture appears uniform.

i. Pour into a lined 55-gallon fiber drum and record the weight, lot and batch numbers. This comprises Part A.

j. Weigh 15.66 kg (34.49 lb) AA397 into an unlined 5-gallon steel pail and record the lot and batch numbers.

	Part By Weight	Drum Size Kit
Part A	1.725	1 drum (27.01 Kg)
Part B	1.000	1 drum (15.66 Kg)
Denatured Ethyl Alcohol	0.047	739 grams (0.92 liters)
Methylene Chloride, Industrial	4.304	67.4 Kg (50.8 liters)
Perchloroethylene, Industrial	5.265	82.45 Kg (50.8 liters)

For best results, Part B is added to a stirred mixture of the alcohol and solvents. All of Part B must be added and the material on the sides of the can should be removed by dissolving in a little solvent. Stirring is continued until all Part B is dissolved. Part A is then added to the stirring solvent and mixing continued for at least 10 minutes prior to spraying.

An alternate mixing procedure is to add Part A to approximately three-fourths of the solvent using the other one-fourth of the solvent to dissolve Part B.