# FUSED SILICA SLIP REQUIREMENTS FOR SLIP CASTING RADOMES

Technical Report No. 1

June 1972



By

J. N. Harris
E. A. Welsh

Prepared Under Contract N00017-70-C-4438

For

Naval Ordnance Systems Command
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By

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# I. PURPOSE

The purpose of Contract No. N00017-70-C-4438 is to perform research and development directed towards the development of techniques to fully exploit the potential of readily available ceramic systems for use as structural components in hypersonic missile applications.

## II. INTRODUCTION

Prior to the production of slip-cast fused silica radomes a broad comprehensive specification for the fused silica slip raw material must be developed.

Slip casting is normally accomplished by placing a suspension of solid material in a liquid medium (slip), into a porous mold. The liquid is drawn outward through the porous mold leaving a moist cake of solids on the wall of the porous mold. Fused silica casting slips differ from most other ceramic slips in that mill additions other than water and the fused silica raw material are not required. The term fused silica raw material as used in this report refers to an amorphous form of silica prepared either by the fusion of quartz or to "synthetic silica" prepared by the pyrolization of silicon tetrachloride to give an amorphous form of silica.

The starting material is charged into a ball mill with water and the proper grinding media and ground until the desired particle size distribution is reached. This type of grinding gives a log-normal particle size distribution and produces a well suspended casting slip that requires no other additives.

There are a number of parameters that may vary in the production of a fused silica slip. Among these are: purity of raw material, liquid vehicle, per cent solids, particle size distribution, mean particle size, pH, and viscosity. These parameters and their interaction determine the characteristics of the final fused silica slip.

In the past when fused silica slip has been needed for the fabrication of radome hardware the slip has been procured on an acceptance test basis 1/.

A limited number of tests were performed by the purchaser on a sample from the slip lot. These included tests for slip stability (settling rate, viscosity, and pH), devitrification rate, and flexural strength of sintered test specimens. Acceptable ranges of property values were based on past experience in producing satisfactory radome hardware.

The acceptance test procedure is satisfactory for laboratory operations or for the manufacture of a few prototypes, especially if the source of slip is located close to the using agency. However, it is readily apparent that this qualification technique would not be acceptable for production operations where many batches of slip raw material would be required, the manufacturer did not have the testing facilities and/or the slip supplier was located at a considerable distance from the manufacturer.

What is needed by the manufacturer is a rigid specification for the raw material which will assure, with proper processing techniques, satisfactory production of acceptable radome hardware. At the same time such a specification should place the minimum number of testing requirements on the supplier to assure that each lot of slip will perform satisfactorily in processing.

The writing of a broad comprehensive specification is complicated by the end use requirements. That is, certain qualities of fused silica slip would provide satisfactory hardware for radomes operating up to Mach  or 4 at low levels, however, for operation at Mach 5 and higher more stringent requirements would have to be placed on the slip. The competency of the manufacturer and his equipment also influence the selection of criteria for a fused silica slip raw material specification. A manufacturer who can exercise very close temperature control in processing the slip-cast fused silica can make satisfactory radome hardware with lower grades of fused silica slip than can a manufacturer who cannot exercise close control of his kilns and other processing steps. Therefore, the specification presented here will only qualify the best (highest purity) grades of fused silica available at the current time.

The following section presents the rationale for specifying the criteria necessary to qualify a fused silica slip for radome hardware.

## III. SLIP QUALIFICATION REQUIREMENTS

### A. Particle Size and Distribution

Fused silica slips prepared by wet ball milling will have a log-normal particle size distribution. However, the slope of the distribution curve will be influenced by the milling conditions, (i.e., the mill feed distribution, the ball charge volume and distribution, the volume of water and the mill speed). Therefore, it becomes necessary to specify that the slip producer provide a particle size distribution curve with each lot of slip. In addition the producer must measure the residue retained on a 325 mesh screen. No more than 5 weight per cent of the slip should be coarser than 44 micrometers (μm) to prevent rapid settling of the solids from the suspension.

Murphy 1/ found that slips with mean particle sizes of 5 to 11 μm could be used to make satisfactory radome hardware in the laboratory under carefully controlled conditions. This range is too broad for normal production fabrication, however. Slips with mean particle size ranges near 5 μm form dense castings that work well for thin wall structures but become increasingly difficult to dry without cracking as thickness approaches 0.75-inch. For thicknesses greater than 0.75-inch it is almost impossible to dry fine ground slips without cracking of the cast piece. Slips with a mean particle size near 11 μm can be used to cast very thick sections with little or no drying problems, however, the cast piece has a high porosity and requires considerably longer sintering times to achieve the same final density as a slip with a mean particle size near 5 μm. Also the larger particle size slips settle more rapidly. This results in problems of wall thickness gradients and problems of stoppages in hoses and pipes containing slip. For walls of 1/4 to 1/2-inch in thickness the aforementioned casting problems should be minimized with a slip having a mean particle size of 6-1/2 to 8 μm.

B. Chemical Compositions

Analyses of two technical grade and six high purity fused silica slips are shown in Table I. Analyses were made by emission spectroscopy, with the exception of the alkalies, which were determined from flame photometry. From these results it can be seen that the term "high purity" when used to describe fused silica type is somewhat of a misnomer. The designation "low alkaline earth" would be more descriptive. Based on total alkali content, there is no clear cut line between high purity and technical grade materials. With respect to alkaline earth oxide content, the lesser of the technical grade values is 0.44 per cent, while the maximum for high purity is 0.033 per cent which suggests a limit in the vicinity of 0.035 per cent alkaline earth oxide content for high purity fused silica slips. Perhaps the best difference is the sum of alkalis, alkaline earths and iron oxides. In this case, the difference between maximum high purity and minimum technical grade contents is 0.021 with the high purity materials having less than 0.060 per cent impurity, excluding aluminum and titanium oxides, which in small amounts seem to have less effect on devitrification behavior. The fact that devitrification rates for the two materials vary so greatly indicate that the slight changes in impurities have major effects on devitrification rates, or that the difference is more subtle; for instance remnant crystalline nuclei in the technical grade material.

Therefore a fused silica slip with chemical analysis indicating 99.5 per cent $SiO_2$ with not more than 50 parts per million (ppm) total alkali metals

TABLE I

SPECTROGRAPHIC ANALYSIS OF FUSED SILICA CASTING SLIPS

| | Technical Grade | | High Purity | | | | | |
|---|---|---|---|---|---|---|---|---|
| | T1 | T2 | HP1 | HP2 | HP3 | HP4 | HP5 | HP6*** |
| $SiO_2$** | 99.570 | 99.510 | 99.610 | 99.600 | 99.580 | 99.540 | 99.660 | 99.730 |
| $Al_2O_3$ | 0.340 | 0.340 | 0.310 | 0.340 | 0.370 | 0.420 | 0.300 | 0.248 |
| $Na_2O$ | 0.008 | 0.002 | 0.008 | 0.008 | 0.008 | 0.001 | 0.001 | 0.004 |
| $K_2O$ | 0.001* | 0.010 | 0.001* | 0.001* | 0.001* | 0.001* | 0.001* | 0.003 |
| $Li_2O$ | 0.001* | 0.001* | 0.001* | 0.001* | 0.001* | 0.001* | 0.001* | * |
| MgO | 0.014 | 0.011 | 0.011 | 0.008 | 0.009 | 0.006 | 0.011 | 0.014 |
| CaO | 0.030 | 0.050 | 0.022 | 0.010 | 0.004 | 0.015 | 0.015 | 0.003 |
| $Fe_2O_3$ | 0.027 | 0.050 | 0.017 | 0.027 | 0.021 | 0.008 | 0.010 | 0.001 |
| $TiO_2$ | 0.013 | 0.020 | 0.001 | 0.003 | 0.003 | 0.002 | 0.005 | 0.001 |

*Not detected (number indicates limit of detection).
**$SiO_2$ by difference.
***HP6 is laboratory batch - all others commercial slips.

and not more than 300 ppm total alkaline earth oxide should be satisfactory for production of radome hardware.

## C. Crystalline Phases

X-ray analysis should be used to determine if crystalline phases of silica are present in the slip. The presence of minute quantities of quartz, cristobalite or tridymite may serve as a nucleation point for the growth of cristobalite, thus causing a high rate of devitrification.

## D. Water Content

The reasons for specifying a water content of not more than 18 per cent by weight are as follows. Too much water creates an economic problem from the standpoint of weight and shipping. Satisfactory casting slips can be handled with as little as 17 per cent water, however, most slips are of the order of 17.5 weight per cent water. Slight variations in water content change the rate of casting and the porosity of the cast piece. A dilute slip is more difficult to handle because there is more liquid to get rid of in the casting and drying process.

## E. Appearance

The requirement for freedom from particles of dark colored material is brought about by the problem of bulk impurities when care is not exercised in processing the raw material into slip. Such dark colored impurities are usually iron from the size reduction process which was not removed by careful magnetic screening prior to ball milling.

## F. Viscosity and pH

The requirements for pH and viscosity have purposely been left out of the specifications. Both of these properties are dependent on the three requirements specified, namely, particle size, chemical composition, and water content. If these three items are controlled pH and viscosity will be in the range required for a satisfactory casting slip.

## G. Cristobalite Content

With high purity slips cristobalite growth rate is not a problem. Processing time and temperature can vary widely without excessive cristobalite formation. There is no need for specifying cristobalite content as a requirement for raw material procurement. However, cristobalite content of the processed hardware should be specified as part of the acceptance test criteria.

APPENDIX I

MATERIAL SPECIFICATION

CASTING SLIP, FUSED SILICA

1. SCOPE This specification covers the requirements for fused silica casting slip for applications involving cast wall thickness in the range 0.25 - 1.50 inches.

2. APPLICABLE DOCUMENTS

2.1 The following documents of the issue in effect on date of initiation for bids or request for proposal, form a part of this specification to the extent specified herein:

SPECIFICATIONS

<u>MILITARY</u>

MIL-M-15176 Mica (Extender Pigment)

STANDARDS

<u>MILITARY</u>

MIL-STD-129 Marking for Shipment and Storage

2.2 <u>Other Publications</u>. The following documents form a part of this specification to the extent specified herein. Unless otherwise indicated, the issue in effect on the date of invitation for bids or request for proposal shall apply:

American Society for Testing and Materials

| | |
|---|---|
| C92 | Test for Sieve Analysis and Water Content of Refractory Materials |
| D422 | Particle Size Analysis of Soils |
| E137 | Evaluation of Mass Spectrometer for Use in Chemical Analysis |
| E311 | Practice for Sampling and Sample Preparation Techniques in Spectrochemical Analysis |

(Application for copies should be addressed to the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.)

Official Classification Committee

Uniform Freight Carrier Classification Rules

(Application for copies should be addressed to the Official Classification Committee, 1 Park Avenue at 33rd Street, New York 16, N.Y.)

3. REQUIREMENTS

3.1 Qualification. The material furnished under this specification shall be a product which has been tested and has passed the qualification tests specified herein. Any changes in composition or methods of manufacture of a qualified product shall require requalification as a new product.

3.1.1 Manufacturing Process Procedure. When required by the procuring activity, a titled, numbered and dated manufacturing inspection document containing the detailed, in-sequence operations used in manufacturing and for control of manufacturing variables shall be submitted by the contractor to the Government and its procuring activity for approval before production parts are delivered. After approval, the manufacturing document shall form a part of this specification and copies shall be made available by the contractor for use by authorized personnel from the Government and its procuring activity in the contractor's plant. The manufacturing document shall not be changed without the approval of the Government and its procuring activity.

3.2 Material

3.2.1 General. The material shall be supplied in the form of a viscous suspension of fused silica in water.

3.2.2 Particle Size

3.2.2.1 Particle Size Distribution. Particle size distribution shall be determined as specified in 4.5.1.1. The mean particle diameter, when measured on a weight basis, shall be in the range 6.5-8.0 microns.

3.2.2.2 Coarse Particles. Residue retained on a Standard No. 325 (44 micron) sieve shall not exceed five per cent when the material is tested as specified in 4.5.1.2.

3.2.3 Chemical Composition. The chemical composition of the material shall be as follows: the material shall contain a minimum of 99.5 weight per cent silica, a maximum 50 parts per million total alkali metals (sodium, lithium, potassium), and a maximum 300 parts per million total alkaline earth oxides (calcium and magnesium); all percentages to be calculated on a moisture free basis.

3.2.4 Residual Crystalline Phases. All silica material should be amorphous. There should be no detectable crystalline forms of silica present in the slip.

3.2.5 Water Content. The water content of the material shall not exceed 18.0 per cent by weight.

3.2.6 Appearance. Both the material, and hardware subsequently fabricated therefrom, shall be a uniform off-white color, and shall be free from particles of dark colored material.

4. QUALITY ASSURANCE PROVISIONS

4.1 Responsibility for Inspection. Unless otherwise specified in the contract or purchase order, the supplier is responsible for the performance of all inspection and test requirements as specified herein. Except as otherwise specified, the supplier may utilize his own facilities or any commercial laboratory acceptable to the Purchaser. The Purchaser reserves the right to perform any of the inspections set forth in the specification where such inspections are deemed necessary to assure supplies and services conform to prescribed requirements.

4.2 Qualification Testing. The qualification of a supplier's product shall consist of meeting all the requirements specified in Section 3 using tests outlined in Section 4.

4.2.1 Qualification Samples. Unless otherwise specified, for purposes of qualification, at least one pound test sample shall be provided from each of three different manufactured lots as specified in 4.3.3.

4.2.2 Qualification Test Report. The formulator of the material components shall provide a test report showing actual test data covering all tests required in Section 3.

4.3 Acceptance Tests. The acceptance tests required for each lot of material shall be all tests as outlined in Section 3.

4.3.1 Acceptance Test Report. For each lot the supplier shall furnish a report of the test results for those tests performed to verify conformance with the acceptance requirements of this specification.

4.3.2 Representative Sample. Material for acceptance testing shall be adequate -- both in quantity and location -- for characterizing the material tested and to verify that material tested is typical of the material submitted for acceptance.

4.3.3 Lot. A lot shall consist of that material manufactured from one batch of raw material under identical processing conditions and submitted for acceptance at one time.

4.4 Visual Inspection. The fused silica material shall be visually examined with normal or corrected normal vision to verify that the materials, marking, packaging and workmanship shall be as specified.

4.5 Test Methods. The test specimens shall be conditioned and tested in accordance with the following methods.

4.5.1 Particle Size.

4.5.1.1 Particle Size Distribution. Particle size distribution will be determined in accordance with ASTM D422 except that prior to sampling the material container shall be roll agitated for 15 hours to insure thorough dispersion of solid particles. Results will be in the form of a plot of weight per cent less than indicated diameter versus log particle diameter for particle sizes greater than 1 micron. Mean particle diameter shall be determined graphically as the diameter corresponding to the 50 per cent level.

4.5.1.2 Residue retained on Standard 3... a ... eve shall be determined in accordance with MIL-M-15176, except that pri to testing the test sample shall be roll agitated for 15 hours to disperse .id particles and a 100 gm sample shall be used in a 100 ml beaker.

4.5.2 Chemical Composition. Chemical composition shall be determined by comparative mass spectrometer methods after establishment of comparative standards in accordance with ASTM E137, or by spectrochemical analysis techniques in accordance with ASTM E311.

4.5.3 Water Content. The water content of the material shall be measured in accordance with ASTM C92.

5. PREPARATION FOR DELIVERY

5.1 Packaging. Unless otherwise specified by the procuring activity, the fused silica slurry shall be packaged in a manner that will ensure the chemical purity is maintained throughout all handling, transportation and storage activities. Containers shall meet Uniform Freight Classification Rules or the regulations of other common carriers as applicable to the mode of transportation.

5.2 Marking. In addition to any special marking required in the contract or order, marking for shipment shall be in accordance with MIL-STD-129.

Markings shall include, but shall not be limited to, the following information:

a. Manufacturer's name, and his product designation.

b. Type of material.

c. Lot or batch number of material.

d. Purchase order number.

e. Quantity.

f. Precautionary Label-Do Not Freeze

## REFERENCE

1. C. A. Murphy, Characterization of Fused Silica Slips, Special Technical Report No. 2, Contract N00017-67-C-0053, Georgia Institute of Technology, Engineering Experiment Station, April 1968.