

WADD TECHNICAL REPORT 60-899

PART I

## **SILICA MICROBUBBLES**

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## FOREWORD

This report was prepared by Emerson & Cuming, Inc. under USAF Contract No. AF 33(616)-5840. This contract was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task No. 73402, "Composite Materials." The work was administered under the direction of the Materials Central, Directorate of Advanced Systems Technology, Wright Air Development Division, with Dr. R. N. Evans acting as project engineer.

This report covers work conducted from July 1958 to November 1959.

Emerson & Cuming, Inc. manufactures glass microbubbles under license from Standard Oil Company (Ohio). Sohio has continued development work thereon. Their work consisted of process improvement, modification of composition and finally the design, construction, and test operation of a pilot plant high temperature (2700°F) unit for production of microbubbles of vitreous silica. The work was done by Mr. Harvey Alford under the direction of Dr. E. C. Hughes and Dr. F. Veatch, all of Sohio's Chemical and Physical Research Division. The information they obtained was transmitted to us and used extensively in our work. This information is designated in the text of this report.

It should be emphasized that the work done by Sohio is completely independent of the contract reported on herein. Sohio received no financial support from contract funds.

The help of Professor P. L. T. Brian of Massachusetts Institute of Technology in designing the high temperature furnace is gratefully acknowledged.

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ABSTRACT


Glass microbubbles 0.150 to 0.020 mm diameter, having a bulk density of 0.25 g/cc and a true density of 0.50 g/cc have been greatly improved by decreasing the alkali content and also by making them of vitreous silica. The improvements consist of marked decrease in moisture absorption, enhanced electrical properties, and great increase in maximum use temperature. An acid leaching technique applied to the commercially available 18% alkali "Eccospheres" of Emerson & Cuming, Inc. reduces the alkali content to 6% and increases the maximum use temperature from 500°C to 800°C. Formation from pure silica by a direct high temperature process to give a vitreous silica bubble retains the useful characteristics of the low-melting-alkali-glass bubble with the desirable properties of vitreous silica - low to negligible moisture absorption, outstanding dielectric properties even at high temperature, and a safe use temperature for most applications of 1300°C. The feasibility of the direct process has been briefly demonstrated on pilot plant scale at two pounds per hour rate.

Work on bonding the high temperature product into structural shapes is described.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

  
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Chief, Thermophysics Branch  
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## INTRODUCTION

Emerson & Cuming, Inc. produces a low density inorganic filler material consisting of tiny hollow glass spheres, called "Eccospheres". These spheres have thin uniform walls without holes. All are smaller than 0.5 mm, 40% are larger than 0.074 mm and 25% are smaller than 0.045 mm. The light hollow bubbles flow almost like water and have a bulk density of 0.25 to 0.40 g/cc. The low dielectric constant, 1.25 and dielectric loss tangent, 0.002, (at 9 kmc) make this material unique among inorganic products. It is physically stable to 550°C with sintering and some plastic flow in the 550°C - 600°C range. Fusion is rapid above 600°C. The material is somewhat hygroscopic and cakes badly in moisture because of its high specific surface. This hygroscopicity degrades its valuable electrical characteristics under moist conditions.

The valuable electrical properties of this product and its potential value in bonded form as a low density elevated-temperature-service thermal barrier and structural material made increase in service temperature and decrease in hygroscopicity of this product most desirable. This project was undertaken with these immediate objectives and the ultimate goal of an equivalent product of essentially pure silica, since these objectives would be most nearly attained with pure vitreous silica.

The present product is a sodium borosilicate glass. Increasing fusion point and moisture resistance of this product was undertaken by two routes. One was modification of the chemical composition of the glass. Much data is available on the physical properties of glasses as determined by their chemical composition. This data was utilized to arrive at compositions which could be fabricated in this bubble form and which should provide improved properties. Numerous compositions were prepared in small quantity for determining the effect of composition on physical and electrical properties. With minor exceptions, both categories improved as the fusion point increased and the pure silica composition was approached. This led to the design and pilot plant operation of equipment operative at 1700°C and capable of making microbubbles of pure silica.

The other route consisted of treating the standard production microbubble of the lower-melting sodium borosilicate glass by various chemical and physical means to enhance its properties. Criteria of value were density, fusion point, hygroscopicity and dielectric properties at the microwave frequencies.

The more desirable products were fabricated into consolidated blocks, usually by sintering techniques. Strength, porosity and density were determined on these blocks.

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I CHEMICAL MODIFICATION OF ECCOSPHERES

A. ACID LEACHING OF ECCOSPHERES

Standard Oil Company (Ohio) had made exploratory experiments on acid leaching of microspheres in the early part of 1958. A sample of this acid-leached material was transmitted to us. Preliminary tests showed that this material had a fusion point some 100°C to 150°C higher than the unleached material. This promising lead was explored here by extensive laboratory work and eventually pilot-plant operations.

While Sohio's analyses showed no appreciable reduction in sodium content resulted from this procedure, the disclosures of some of the Vycor glass patents<sup>(a)</sup> indicated that phase-separable sodium borosilicate glasses could be attacked by acid to remove most of the sodium-rich phase.

A table summarizing the more important leaching procedures, as well as the description of some unleached products, is shown below.

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(a) 2,106,744 1 Feb. 1938, H. P. Hood et al assignee Corning Glass Works  
2,215,039 17 Sept. 1940, H. P. Hood et al assignee Corning Glass Works

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TABLE I

DESCRIPTION OF PRODUCTS

<u>Designation</u>	<u>Description</u>
Std	Standard Product, bulk density 18 to 24 lb /cu. ft.
HCl	Std., leached 7 days in 36% hydrochloric acid. Stirred twice each day. g Feed/g Soln (R) = 0.1.
Lab I	Std., leached 7 days in 16% sulfuric acid, stirred three times each day, R = 0.12.
Lab IV	Std., leached 7 days in solution which had been used for three previous lots of feed R = 0.12, like Lab I. Stirred three times each day.
PP1	Std., leached 5 hours in 7% sulfuric acid, R = 0.15, continuous agitation.
PP2	Std., leached 20 hours in solution which had been used for PP1. R = 0.15, stirred 6 times.
PP3	Std., leached 30 hours in solution which had been used for PP2. R = 0.15, stirred 8 times.
PP4	Std., leached 30 minutes with 15 minutes of agitation in previously used solution, fortified to 8% H <sub>2</sub> SO <sub>4</sub> . R = 0.15.
KB	Sohio 1057-27B Potassium Borosilicate true density (T. D.) 0.44.
KNaB-1	Sohio 1057-27C Potassium-sodium Borosilicate T. D. 0.46.
KNaB-2	Sohio 1057-27D Potassium-sodium Borosilicate T. D. 0.50.
BS	Sohio 1057-41G Borosilicate T. D. 0.50.
S	Sohio "Pure Silica" 20 Nov. '58 T. D. 0.86.

The fusion point and hygroscopicity tests used for evaluation are time-consuming and results are frequently equivocal. Since the leaching techniques are thought to function primarily by removal of alkali, largely sodium, leaching experiments over a range of conditions were made. In these tests, the amount of alkalinity, calculated as grams of sodium extracted per gram of sample used was determined. The formula composition of the material used was 0.163g Na/g of material.

SODIUM EXTRACTED BY VARIOUS LEACHING PROCEDURES  
(g Na/g Sample)

Leach Conditions:	Cold Water	Boiling Water	0.75N HNO <sub>3</sub>	Boiling 0.75N HNO <sub>3</sub>
	2 hrs.	16 hrs.	2 hrs.	2 hrs.
Acid Leached, Lab I	0.00276	0.0104	0.00427	0.0206
Unleached, Std.	0.0278	0.1315	0.0720	0.108

These results show that extractable alkali is five to ten times greater in the unleached material and that these simple extractions differentiate the leached from the unleached material. The greater solution of alkali by hot water than by hot acid was surprising. This may be a better means of treatment than the present acid leaching if solution losses are not excessive. At present, it appears that the acid treatment renders the silica less soluble, as well as removing alkali, while water alone causes extensive rehydration of the silica.

B. TEMPERATURE STABILITY OF PRODUCTS

Resistance to elevated temperatures of the various products was evaluated by means of a modified pyrometric cone equivalent (PCE) test. Several cones of each composition were run. The results reported in Table 3 are typical of several tests run to 1090°C. Only one set of tests extending to 1475°C was made.

TABLE 3

FUSION POINT DATA ON VARIOUS PRODUCTS  
Heating Rate 70°C/hr. Above 500°C

<u>Product</u>	<u>Heat Treatment Results</u>
Std.	Tip bending 650°C, Melted 760°C
HCl	15° Bend at 1010°C, Remained the same at 1475°C
Lab I	No bending at 1475°C, Less than 10% shrinkage
Lab IV	No bending at 1475°C, Less than 10% shrinkage
PP 1	45° Bend at 1090°C, (Maximum of test)
PP 2	30° Bend at 1090°C, (Maximum of test)
PP 3	15° Bend at 980°C, Same at 1090°C (Maximum of test)
PP 4	15° Bend at 900°C, Same at 1090°C (Maximum of test)
Sohio KB	Bending at 650°C, Melted at 820°C
Sohio KNaB-1	Bending at 650°C, Melted at 820°C
Sohio KNaB-2	Bending at 820°C, 45° Bend at 870°C. Same at 1090°C (Maximum of test)
Sohio BS	10° Bend at 1090°C, Same at 1475°C
Sohio S	Shrinkage 5%, No bend at 1090°C (Maximum of test)

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The standard (Std. ) product melts at 760°C, while all acid leached products (the following seven) stood up at least 250°C higher.

These tests show that prolonged leaching in 16% H<sub>2</sub>SO<sub>4</sub> at room temperature (Lab I and Lab IV) are somewhat more effective in raising fusion point than leaching in 36% HCl under similar conditions (Sample HCl). Since use of sulfuric acid involves the lesser corrosion problem, it was used in subsequent work.

Modifications of the acid leaching procedure, both in laboratory and pilot plant work showed that cone stability at 980°C to 1090°C could be obtained by short-period leaching in 7% H<sub>2</sub>SO<sub>4</sub> (PP1 and PP 4) Treatment of fresh feed with previously used acid solution for longer periods of time gave a product with fusion point similar to that of fresh acid for shorter periods (PP 2 and PP 3). Fortification of previously used acid to 8% H<sub>2</sub>SO<sub>4</sub> and its use for a 30 minute leaching period gave a product of substantially the same fusion range (PP 4). This procedure has been used for most pilot plant production.

It was noted that these cones did not react to heat in the same way that pyrometric cones do. Pyrometric cones ordinarily bend slowly but regularly with increasing temperature until fusion is complete. With a few exceptions, cones from these products showed some softening at 810°C to 1040°C, but little change during subsequent 250°C to 350°C increase in temperature. One possible cause of this strange behavior may be volatilization of Na from the original low melting glass at a sufficient rate to leave a higher melting low alkali borosilicate. Heating for 16 hours at 500°C followed by 2 hours at 1000°C of Lab. 1, 3.0% Na, reduced the Na content to 0.65%, and the same treatment of PP 4, 8.4% Na, decreased its Na content to 2.5%, confirming the hypothesis of alkali volatilization.

Alkali analyses were made on some of these samples. Table 4 compares total alkali content of these products calculated as percent Na, and fusion point data.

These results show that complete removal of alkali is not required for greatly enhanced thermal stability. It appears that 5% to 8% alkali is the critical content for durability at 1090°C. This must be qualified, however, by the possibility that alkali volatilization from these small cones during heating is enhancing physical stability at the higher temperatures. This will be determined by analysis of material subjected to a heating schedule like that used in the tests.

TABLE 4

COMPARISON OF ALKALI CONTENT AND FUSION POINT

<u>Designation</u>	<u>Description</u>	<u>% Na</u>	<u>Fusion Data, °C</u>
Std.	Standard Production	13.4	Bend, 650, Melt 760
Lab I	7-day leach in 16% H <sub>2</sub> SO <sub>4</sub>	3.07	No bend at 1475, less than 10% shrinkage
PP 4	Pilot plant 30 min. in 8% H <sub>2</sub> SO <sub>4</sub>	8.44	Bend 900, No change at 1090 maximum
BS	Sohio Borosilicate, 1057-41-G	6.32	Bend 1090, No change at 1475 maximum

C. REDUCTION OF HYGROSCOPICITY

Inherent hygroscopicity of the standard Eccosphere product has been decreased by both acid leaching and surface treatment with Volan<sup>(a)</sup>.

Volan treatment has followed manufacturer recommendations for textiles; short (5 minutes) immersion in dilute aqueous solution of Volan (2% in most cases) followed by washing with water and drying.

The marked decrease in hygroscopicity resulting from small scale Volan treatment tests in the laboratory has not been obtained in pilot plant treatments. Possible causes of this are excessive dilution of the Volan solution by the occluded water in wet Eccospheres from the acid leach treatment and Eccosphere breakage during drying which, of course, exposes untreated surfaces.

Hygroscopicity is determined by exposure of the dried (two hours at 110°C) sample in a 0.3 to 0.8 cm layer in a static controlled relative humidity chamber at room temperature. The relative humidity control is obtained by a layer of saturated salt solution underneath the samples. Percentage increase in weight of the sample due to moisture absorption is obtained at intervals. A range of relative humidities was used at first to determine the value causing the greatest range of response to various treatments. These results are shown in Table 5.

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(a) Volan is a proprietary Werner type organic chromium compound marketed by duPont for waterproofing and surface modification of textiles and other hydroxyl-containing materials.



TABLE 5  
EFFECT OF SURFACE TREATMENT ON HYGROSCOPICITY

Relative Humidity, %:	Weight gain, Percent								
	75			60			95		
Room Temp. Hours Exposed:	48	144	216	48	144	216	48	144	216
<u>Material</u>									
Standard	2.3	3.9	4.3	3.0	4.5	5.4	14.7	32.0	43.0
Standard, Volan treated	0.9	0.7	--	--	--	--	--	--	--
Acid leached (Lab IV)	1.1	1.3	1.6	1.3	1.8	1.8	15.2	28.4	29.9
Acid leached (Lab IV) Volan treated	0.3	0.4	0.5	0.4	0.5	0.5	3.3	4.0	4.8

These tests show that both acid leaching and Volan treatment decrease hygroscopicity and that the separate effects tend to be additive. On the basis of these results, 75% relative humidity at room temperature was used for most subsequent work. Numerous sets of hygroscopicity tests have been made primarily for determining the value of different acid leaching techniques. Considerable variation among tests will be noted in percentage weight gain on a given material and in some cases ratios of weight gain between two materials vary with different tests in which the known variables are held at about the same level. We have no explanation for this. Possible factors are chamber-overload caused by too many samples in the static atmosphere chambers used, and variation in room temperature. The first tests were conducted in the early fall when daily temperature range was less and averaged somewhat lower than the more recent tests under winter heating conditions. These variations make comparisons between tests of limited value. For this reason, the test data is presented in sets which were run concurrently.

EFFECT OF VARIOUS ACID LEACHING PROCEDURES  
ON HYGROSCOPICITY

Relative Humidity, %: Exposure at Room Temp., Days:	Weight Gain, %					
	95		76		56	
	4	11	4	11	4	11
<u>Material</u>						
Eccospheres (Std) (a)	27.9	60	3.1	4.0	3.9	5.4
Eccospheres Leached 36% HCl (HCl)	11.8	20.2	0.7	3.6	0.9	0.9
Eccospheres Leached 16% H <sub>2</sub> SO <sub>4</sub> (Lab I)	4.3	5.4	1.7	2.0	1.8	2.0
Eccospheres Leached in spent H <sub>2</sub> SO <sub>4</sub> (Lab IV)	5.5	7.6	1.8	2.0	2.2	4.0

TABLE 7

EFFECT OF VARIOUS ACID LEACHING PROCEDURES  
ON HYGROSCOPICITY  
AT ROOM TEMPERATURE AND 76% RELATIVE HUMIDITY

Exposure, Days:	Weight Gain, %	
	3	7
<u>Material</u>		
Eccospheres (Std)	1.95	2.56
Eccospheres Leached in 16% H <sub>2</sub> SO <sub>4</sub> (Lab I)	0.58	0.71
Eccospheres Leached in 7% H <sub>2</sub> SO <sub>4</sub> 5 hrs. in pilot plant (PP1)	1.77	2.13
Eccospheres Leached 20 hrs. in pilot plant in acid used for PP1 (PP2)	1.22	1.29
Eccospheres Leached 30 hrs. in pilot plant in acid used for PP2 (PP3)	1.77	2.08

(a) Designation in parentheses refers to Table I where treatments are described.

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TABLE 8

EFFECT OF VARIOUS PROCEDURES ON HYGROSCOPICITY  
AT ROOM TEMPERATURE AND 76% RELATIVE HUMIDITY

Material	Exposure, Days:	Weight Gain, %	
		3	7
Eccospheres bulk density 0.32 (Std)		5.80	6.05
Eccospheres Water-floated bulk density 0.16		5.36	6.32
Eccospheres Leached in 16% H <sub>2</sub> SO <sub>4</sub> (Lab I)		0.52	0.55
Eccospheres Leached 30 min. in 8% H <sub>2</sub> SO <sub>4</sub> (PP4)		1.67	1.87
Eccospheres Leached in 36% HCl (HCl)		1.23	1.82
Eccospheres Water-floated, Dried and Volan treated, no acid leach		2.28	4.53

TABLE 9

EFFECT OF CHANGE IN CHEMICAL COMPOSITION OF ECCOSPHERES  
ON HYGROSCOPICITY  
AT ROOM TEMPERATURE AND 76% RELATIVE HUMIDITY

Material	Exposure, Days:	Weight Gain, %	
		3	7
Eccospheres (Std)		2.0	2.6
Eccospheres Leached in 16% H <sub>2</sub> SO <sub>4</sub> (Lab I)		0.6	0.7
Microspheres, Potassium borosilicate, Sohio 1057-27-B (KB)		1.4	3.9
Microspheres, Potassium sodium borosilicate Sohio 1057-27-C (KNaB-1)		0.13	0.68
Microspheres, Potassium sodium borosilicate Sohio 1057-27-D (KNaB-2)		0.15	0.32
Microspheres, Borosilicate Sohio 1057-41-G (BS)		0.84	0.89

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The data of Tables 6 to 9 is not concordant among sets. However, within any one set, even the shorter leaching periods in weaker acid as done in the pilot plant confer some decrease in hygroscopicity. Sulfuric acid is shown to be more effective than hydrochloric acid. Removal of the more dense fraction of Eccospheres by water floating does not change moisture pick-up appreciably. The Volan treatment without acid leaching decreases moisture pick-up, but not as much as the combination. The acid leaching is obviously effective in reducing hygroscopicity with the amount of reduction bearing a fairly regular relation to the strength of acid used and time of treatment. Initial results with Volan treatment alone and in combination with acid leaching were very good. Later tests indicate that the effect of Volan treatment varies from marked decrease of hygroscopicity to a negligible effect.

Three of the non-standard composition microspheres prepared by Standard Oil Company (Ohio) Research have shown reduced hygroscopicity in preliminary test equivalent to the best obtained by acid leaching. Unfortunately, these compositions fused near 815°C.

## D. PILOT PLANT TREATMENTS

### 1 Acid Leaching - General

On the basis of preliminary fusion point and hygroscopicity data from laboratory leaching tests, pilot plant operations were started as outlined in Table 1, PP 1 - PP 4.

Production Eccospheres were first floated in water to remove the higher density unfused feed stock and collapsed bubbles, both of which degrade the product and only consume acid. The weight loss in this step has been found to vary from 15% to 45%. The higher percentages were from Eccospheres produced during shake-down operation of the new plant. Closer sizing of feed stock for the expansion furnace has brought this figure into the 20% to 30% range.

The wet water-floated Eccospheres, as skimmed from the float tank, contain about 80% water. In the ratio of 16%  $H_2SO_4$  to wet Eccospheres used, this water dilutes the leach solution to 7% to 8%  $H_2SO_4$ . Several conditions of leaching time agitation and acid make-up were used. Fusion point and hygroscopicity data on the product showed little difference among the various pilot plant treatments, although they were considerably less effective than the laboratory procedures used. As a compromise between practicality and product characteristics, the procedure (PP4) was set up as standard.

## 2. Standard Pilot Plant Acid Leaching Procedure

The standard pilot plant acid leaching procedure consists of: (a) water floating, (b) transfer of skimmed wet Eccospheres to previously used acid fortified to 11% to 12%  $H_2SO_4$  to give a dry feed to leach solution ratio of 0.15 and leach solution concentration of 7% to 8%  $H_2SO_4$ , (c) agitation for 15 minutes followed by 15 minutes separation time, (d) transfer by skimming from acid solution to water wash, (e) agitate one minute, stand quiescent 5 minutes, drain 80% of free water volume from floating Eccospheres, add same volume of wash water from top, (f) repeat step (e) six more times, (g) transfer slurried Eccospheres to centrifuge with muslin filter cloth, (h) spin, (i) transfer damp Eccospheres to rotary dryer, an externally gas-heated cylinder on which the hot air bath is maintained at  $200^\circ C$  and having only convection circulation of air in the drying chamber itself, (j) drying to 2% moisture and (k) screening on 20 mesh screen to remove lumps formed in dryer.

This procedure gives a product that begins to sinter about  $900^\circ C$  but does not melt at  $1090^\circ C$ . Its hygroscopicity is also considerably less than that of unleached Eccospheres.

Losses, particularly mechanical ones, from the various washing and transfer operations, are substantial. Improved handling techniques can markedly decrease them.

Undesirable lumping occurs during drying. Drying at lower temperatures decreases this. Drying in a moving bed with temperatures held below  $95^\circ C$  causes some lumps, but most of them are friable enough to be broken down without much fracture of individual Eccospheres. It has been noted that acid leached Eccospheres have much less tendency to lump during drying than Eccospheres which have been only water-floated.

Overall yields on the acid leaching operation have been 25% to 50% to date. Most of this loss is in the initial floating operation where undesirable high density material is removed.

## 3. Pilot Plant Volan Treatment

Pilot plant Volan treatment consists of transferring wet skimmed acid leached Eccospheres after the third wash to a 2% Volan solution, using a dry feed-to-solution ratio of 0.15, agitation for five minutes, standing quiescent for ten minutes, skimming and transfer to water wash, three water washes, centrifuging and drying as in the acid leaching operations.

Several runs have been made, but the product was, in most

cases, almost as hygroscopic as the acid leached Eccospheres. Since hygroscopicity reduction was negligible compared to that obtained in laboratory tests, this operation has been stopped pending further laboratory work. We believe that dilution of the 2% Volan solution by the wet feed is too great for effective Volan deposition, although this is supposed to be a substantive process.

E. MICROSPHERES PREPARED FROM OTHER CHEMICAL COMPOSITIONS BY STANDARD OIL COMPANY (OHIO) RESEARCH

The process by which Eccospheres are made was developed before the initiation of this contract by Standard Oil Company (Ohio). Emerson & Cuming, Inc. had the process in operation under license from this organization in August 1957. Sohio has continued development work on the process without any use of funds from this contract. As a phase of this development work, microspheres of a number of different chemical compositions were made available to us for dielectric and physical evaluation. Two series of samples were tested. The properties are tabulated in Table 10, along with those of the "standard" Eccosphere sodium borosilicate composition and some of our acid leached products for comparison.

TABLE 10  
DIELECTRIC PROPERTIES OF VARIOUS MICROBUBBLE COMPOSITIONS

Ref. No.	Type	Abbreviation	Density g/cc(a)	Diel. Prop. at 8.6 kmc		Sintering Point °C
				Const.	Loss Tan. Pack. Dens. (b)	
1	Standard Eccospheres (c)	Std	0.45	1.31	0.0046	650
2	Acid Leached (d)	Lab I	0.26	1.19	0.0028	>1480
3	Acid Leached	PP1	0.29	1.11	0.0015	1055
4	Acid Leached	PP2	0.31	1.15	0.0019	1010
5	Acid Leached	PP3	0.33	1.16	0.0023	955
6	Silica Sohio 1193-80	---	0.32	1.15	0.0027	---
7	Borosilicate	---	---	---	---	---
8	Sohio 1243-1	---	0.43	1.20	0.0020	---
9	Low Na Borosilicate	---	---	---	---	---
9	Sohio 1193-88	---	0.42	1.15	0.0025	---
9	Zinc Borosilicate	---	---	---	---	---
10	Sohio 1193-82	---	0.59	1.27	0.0029	---
10	Potassium Borosilicate	---	---	---	---	---
11	Sohio 1057-27-B	KB	0.44	1.15	0.0032	625
11	Potassium Sodium Borosilicate	---	---	---	---	---
12	Sohio 1057-27-C	KNaB-1	0.46	1.36	0.0027	625
12	Potassium Sodium Borosilicate	---	---	---	---	---
13	Sohio 1057-27-D	KNaB-2	0.50	1.36	0.0030	775
13	Borosilicate	---	---	---	---	---
14	Sohio 1057-41-G	BS	0.50	1.28	0.0035	1070
14	Silica, 2350°F	---	---	---	---	---
15	Sohio 20 Nov. '58	S	0.86	1.35	0.0014	>1090
15	Silica, 2700°F	---	---	---	---	---
15	Sohio 9 Sept. '59	S2	0.66	1.30	0.0013	---

(a) Density by gas displacement  
 (b) Loose fill density for dielectric measurements  
 (c) Na<sub>2</sub>O 22%, SiO<sub>2</sub> 71%, B<sub>2</sub>O<sub>3</sub> 7%  
 (d) Na<sub>2</sub>O 4%, SiO<sub>2</sub> 88%, B<sub>2</sub>O<sub>3</sub> 8%

# Contrails

Of these, KB and KNaB-1 had fusion characteristics, Table 3, similar to the standard Eccosphere composition. KNaB-2 was similar in fusion characteristics to our production acid leached material. S showed no signs of sintering at 1090°C, the maximum to which it has been run. At this temperature, it appears the equivalent of our best acid leached material. The BS sample was better than our pilot plant acid leached material, but not quite equal to the laboratory product.

Preliminary hygroscopicity tests, Table 9, indicated that all except the KB material were equal to our best acid leached product. The S material has not been checked for hygroscopicity, but it is anticipated that it will be at least as good as the others.

Dielectric properties of these materials were determined at known packed densities. These properties were then normalized by means of the Lichtenecker formula<sup>(a)</sup>. This formula indicates that these dielectric properties are simply related to the volume percent of solids in the piece measured. The results are shown in Figure 1. In this figure, all materials lying on the same slope through the origin will have similar dielectric values at similar densities or volume percent solids. On this basis, it appears that only one potassium borosilicate composition, number 10, Sohio 1057-27-B, has a significantly lower dielectric constant than the rest of the compositions. For most of the compositions, those near the upper line on the loss tangent plot, including standard Eccospheres, the acid leached samples and two Sohio samples, Silica 1193-80 (number 6), and Low Sodium Borosilicate 1193-88 (number 8), the dielectric loss tangents are equivalent at comparable densities. Sohio compositions Borosilicate 1243-1 (number 7), Potassium Sodium Borosilicate 1057-27-C (number 11), Potassium Sodium Borosilicate 1057-27-D (number 12), and Zinc Borosilicate 1193-82 (number 9) appear to have equivalent and definitely lower loss tangents than the others. Numbers 11 and 12 have undesirably low fusion points, although 12 is better than the standard Eccosphere in this respect. Two of Sohio's "pure silica" samples, S made at 1300°C, received 20 November 1958, and S-2, made at 1485°C, were outstandingly desirable because of low dielectric loss, with the higher temperature preparation being somewhat the better of the two.

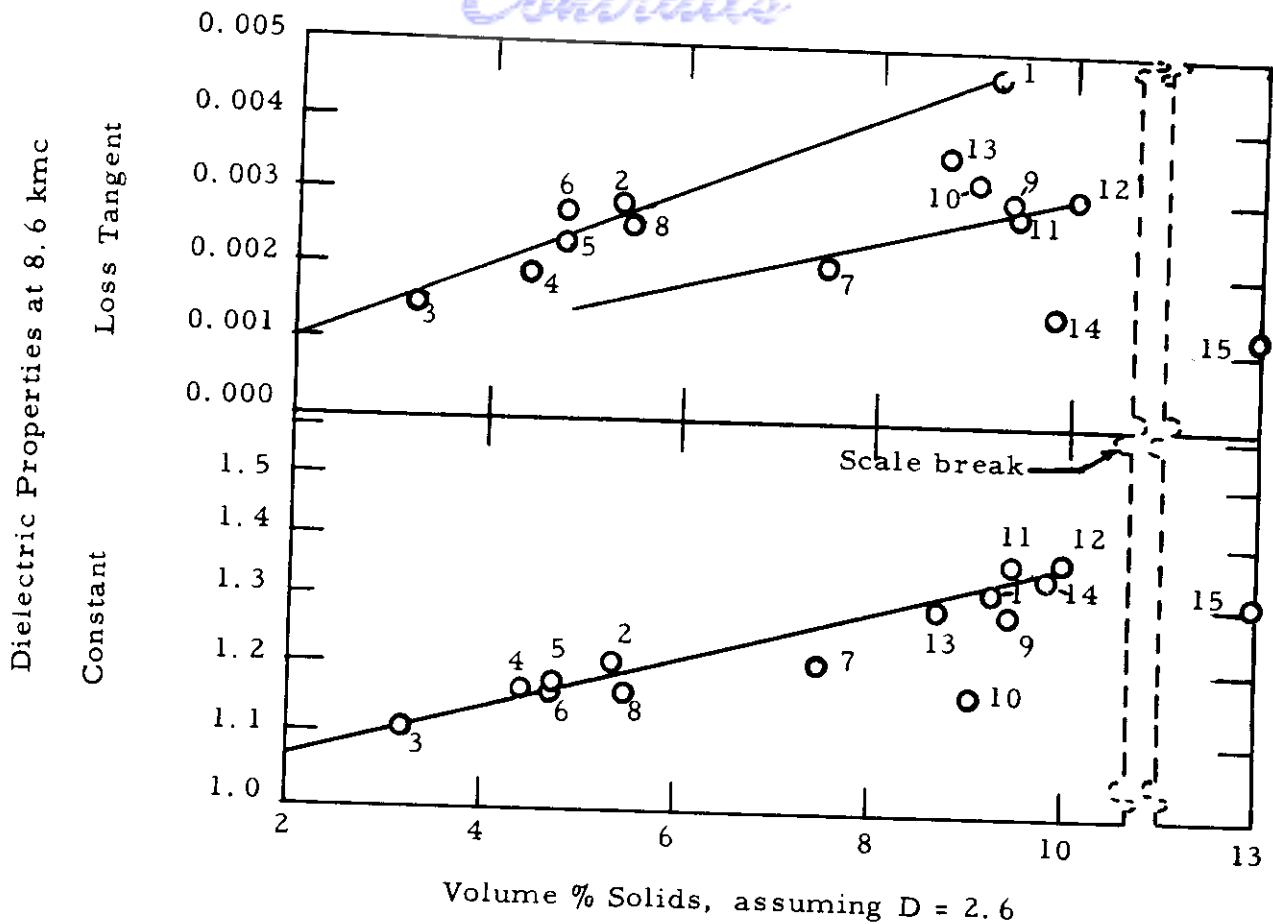
The previously described work was initiated before the preparation of microbubbles from pure silica feed stock. As the above data was obtained, it became increasingly apparent that the most desirable product would be pure silica, so major effort was diverted to calculations, design and construction of a pilot furnace capable of 1700°C operation.

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(a) Bjorksten, A. F. 30(602) 1481, p 33 See Appendix II



# Contrails



### Materials

- |  |   |
|--|---|
| <ol style="list-style-type: none"> <li>1. Standard Eccospheres</li> <li>2. Acid Leached (Lab I)</li> <li>3. Acid Leached (PP1)</li> <li>4. Acid Leached (PP2)</li> <li>5. Acid Leached (PP3)</li> <li>6. Silica, Sohio 1193-80</li> <li>7. Borosilicate, Sohio 1243-1</li> <li>8. Low Sodium Borosilicate, Sohio 1193-88</li> <li>9. Zinc Borosilicate, Sohio 1193-82</li> </ol> | <ol style="list-style-type: none"> <li>10. Potassium Borosilicate, Sohio 1057-27-B (KB)</li> <li>11. Potassium Sodium Borosilicate, Sohio 1057-27-C (KNaB-1)</li> <li>12. Potassium Sodium Borosilicate, Sohio 1057-27-D (KNaB-2)</li> <li>13. Borosilicate, Sohio 1057-41-G (BS)</li> <li>14. Silica, Sohio 20 Nov. '58 1290°C (S)</li> <li>15. Silica, Sohio 9 Sept. '59 1480°C (S2)</li> </ol> |
|--|---|

FIG. 1 COMPARISON OF DIELECTRIC PROPERTIES OF VARIOUS COMPOSITIONS ON EQUIVALENT DENSITY BASIS BY USE OF THE LICHTENECKER FORMULA

## II SILICA MICROBUBBLE PRODUCTION

### A. GENERAL

Experimental work on the silica microsphere is based on our knowledge of regular Eccosphere production. Glass particles are suspended in a gas stream which is passed through a hot zone to melt them. While molten, these particles are expanded by internally generated gas pressure to form bubbles. The formed bubble is cooled below its softening point before it is permitted to touch others in order to prevent agglomeration and deformation. Pure silica melts at 1710°C and has a very short viscous range as glasses go. The contained blowing agent must be able to function in the range of suitable viscosity. Most gas-forming agents decompose far below this range. Surface adsorption from the mass of molten glass is required to modify the surface tension of the bubble surface and provide the stable elastic film needed for bubble formation. The molten glass must be stabilized both while blowing the bubble and while it is solidifying in the stream. The formed liquid bubble must remain isolated from others and equipment walls until it is cooled below the softening point. All of this must take place in a hot zone within 200° of 1700°C. However, the process does work for production of the standard Eccosphere which has a fusion range of 550° to 700°C. In this operation, a furnace wall temperature of 900°C -- some 300° above the glass fusion point is required. Silica, with minimal residual water content from preliminary drying, melts between 1600°C and 1700°C. If we assume that a furnace temperature 300° above 1700°C is required to form microbubbles from pure silica, we are outside the temperature limits of any except the expensive, exotic refractories. Need for 2000°C operation and these refractories would likely prohibitively increase the cost of the product as well as greatly delay experimental work. Consequently, it was decided to proceed with experimental work aimed at operation below 1750°C. Feed stock preparation has followed standard Eccosphere feed preparation, except in the matter of composition. Two oxide compositions have been used in the present work. One is essentially pure silica; the other contains a small amount of boric oxide. See Table 11.

Feed is prepared by dissolving the blowing agent -- urea -- in a 30% silica sol and boric acid is also added for the composition in which it is used. The gelled feed stock is dried to remove all but 3% volatiles, ground and sieved to various particle-size fractions. This feed is suspended in a gas stream and injected into a hot zone where the bubbles are formed as described above.

The earlier laboratory scale work was on various furnace designs, heating arrangements, feed injection mechanisms and product recovery systems.

## B. LABORATORY SCALE TESTS

The first furnace used consisted of a vertical 3" diameter x 17" long insulated chamber, heated at the upper end by six downward projecting oxyacetylene jets with feed introduction axial to these jets. Gas and product flow was downward through the insulated chamber. Product was cooled by mixture with ambient air below the insulated chamber and caught in a settling chamber. This apparatus produced only a trace of tiny (less than 30 micron) hollow spheres with most of the material appearing as feed stock, having only slightly rounded edges. Obviously, heating was inadequate for the bulk of the feed since only the tiniest feed particles produced hollow spheres. The feed used in this case was minus 100 mesh feed stock. Three short runs followed in which minus 300 mesh feed stock was used. This material was found very difficult to feed at a uniform rate because of agglomeration in the feeding arrangement. This agglomeration may have been due to traces of moisture but we believe was largely caused by electrostatic phenomena. A trace of spheres was obtained in each case. These were all less than 30 microns in diameter and only occasional pieces of unfused feed stock were found. Recovery of microspheres was a negligible percentage of the feed stock but much airborne fume was observed. We believe many more microspheres were formed, but, because of their small size and negligible settling rate, were not recovered. These tests sufficed to show us that even the smallest practical size of feed stock would not be adequate to produce silica microspheres in quantity with this arrangement.

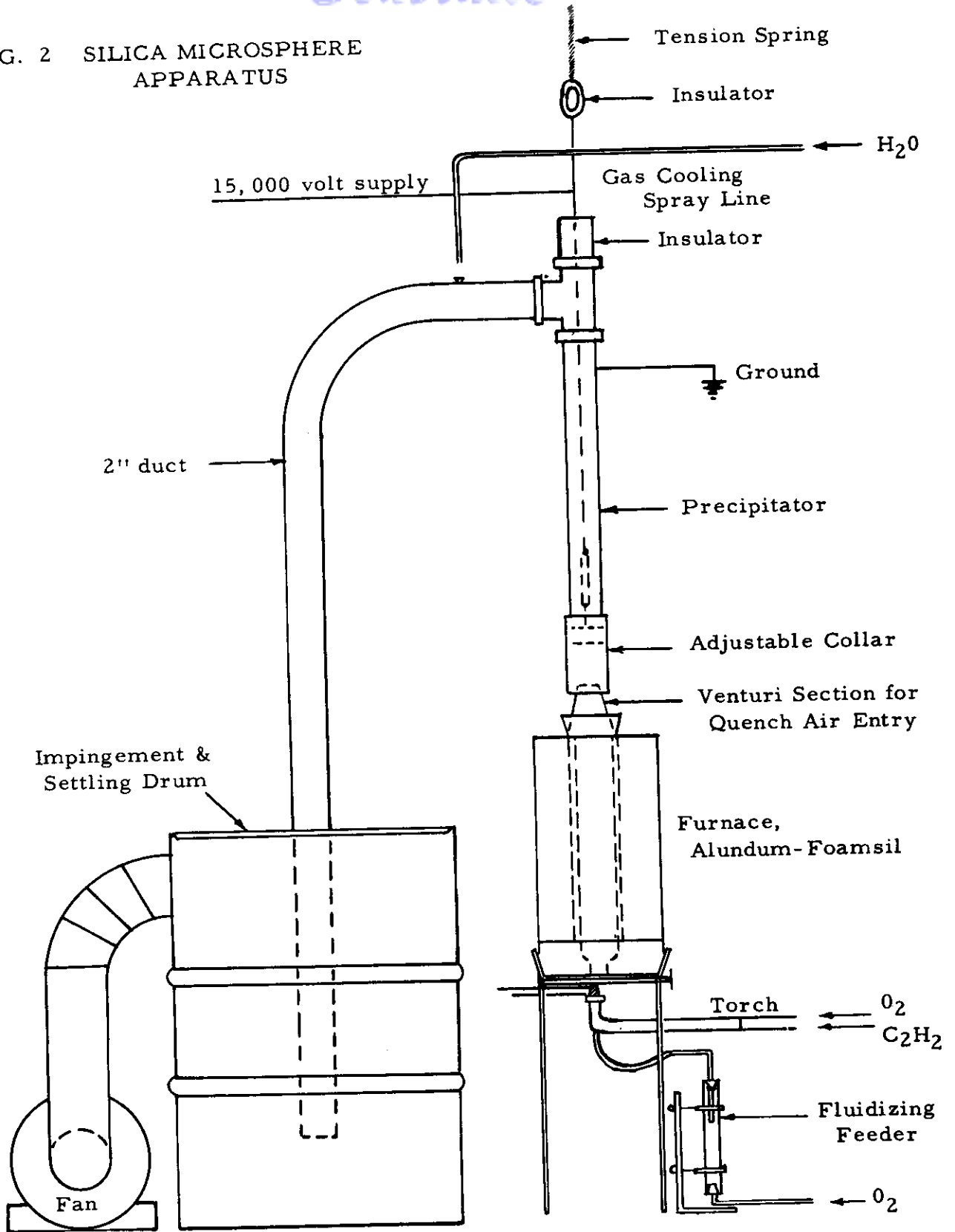
This apparatus produced beautiful Eccospheres in quantity when fed with standard Eccosphere feed stock, indicating that the arrangement was basically sound but lacked in temperature and sojourn time for the high fusion point feed stock used.

To increase sojourn time in the hot zone, the apparatus was converted to an upflow system, in which we hoped the larger particles would be retained in the hot zone longer, since, with this arrangement, gravity will be working for us. (Figure 2) A small electrostatic precipitator 2" in diameter and 4' high with a central discharge electrode the full length to be operated at 15,000 volts DC was built for product recovery.

Between the precipitator section and the hot zone, a Venturi section was placed to inspirate quench air for the hot gas stream. A small suction fan was attached to the exit end of the precipitator. The precipitator system was checked out on both raw feed stock and standard Eccospheres at room temperature and found to remove the solid particles almost quantitatively from the gas stream.

Because of the previously-mentioned difficulty in feeding

FIG. 2 SILICA MICROSPHERE APPARATUS



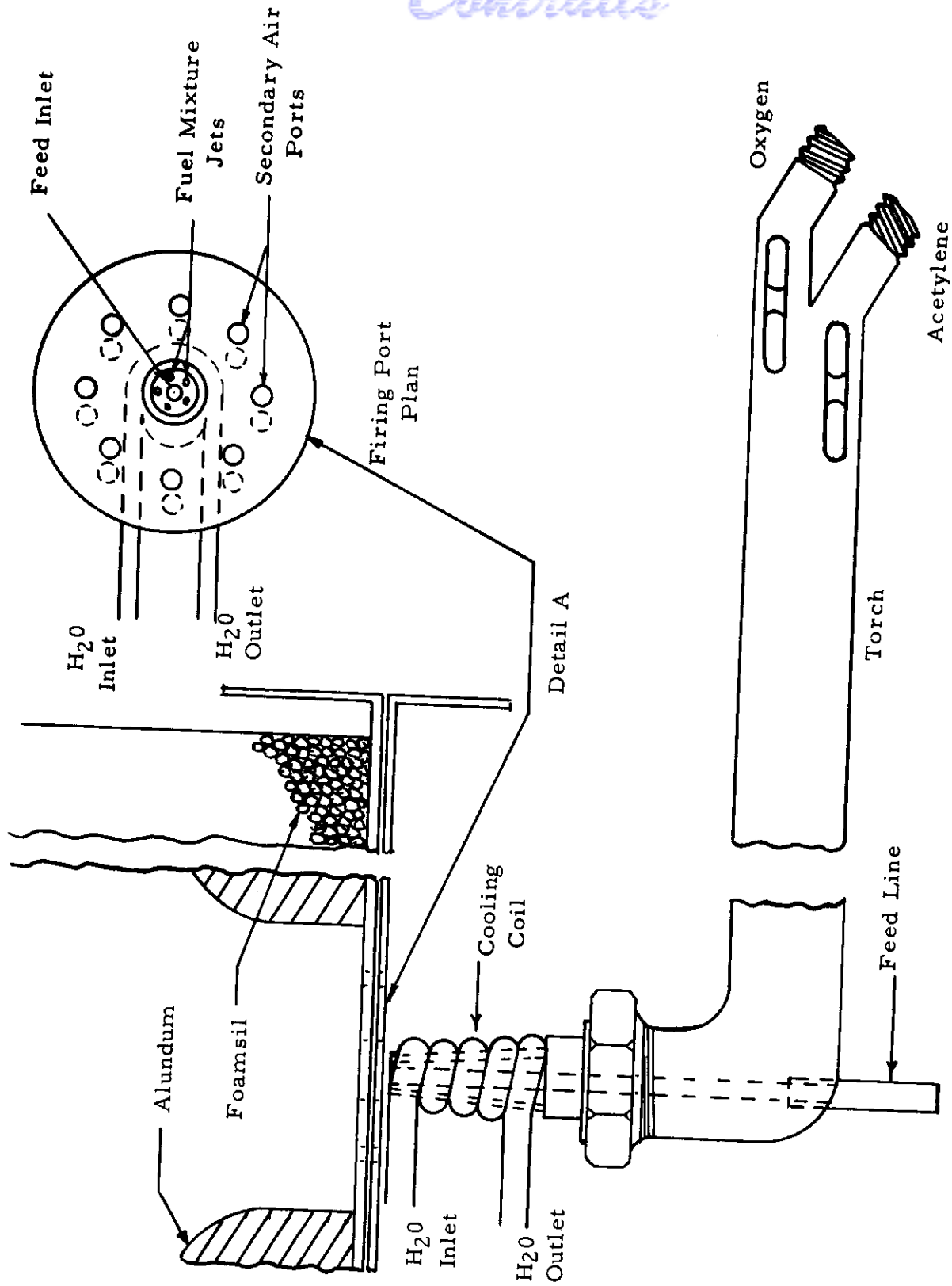
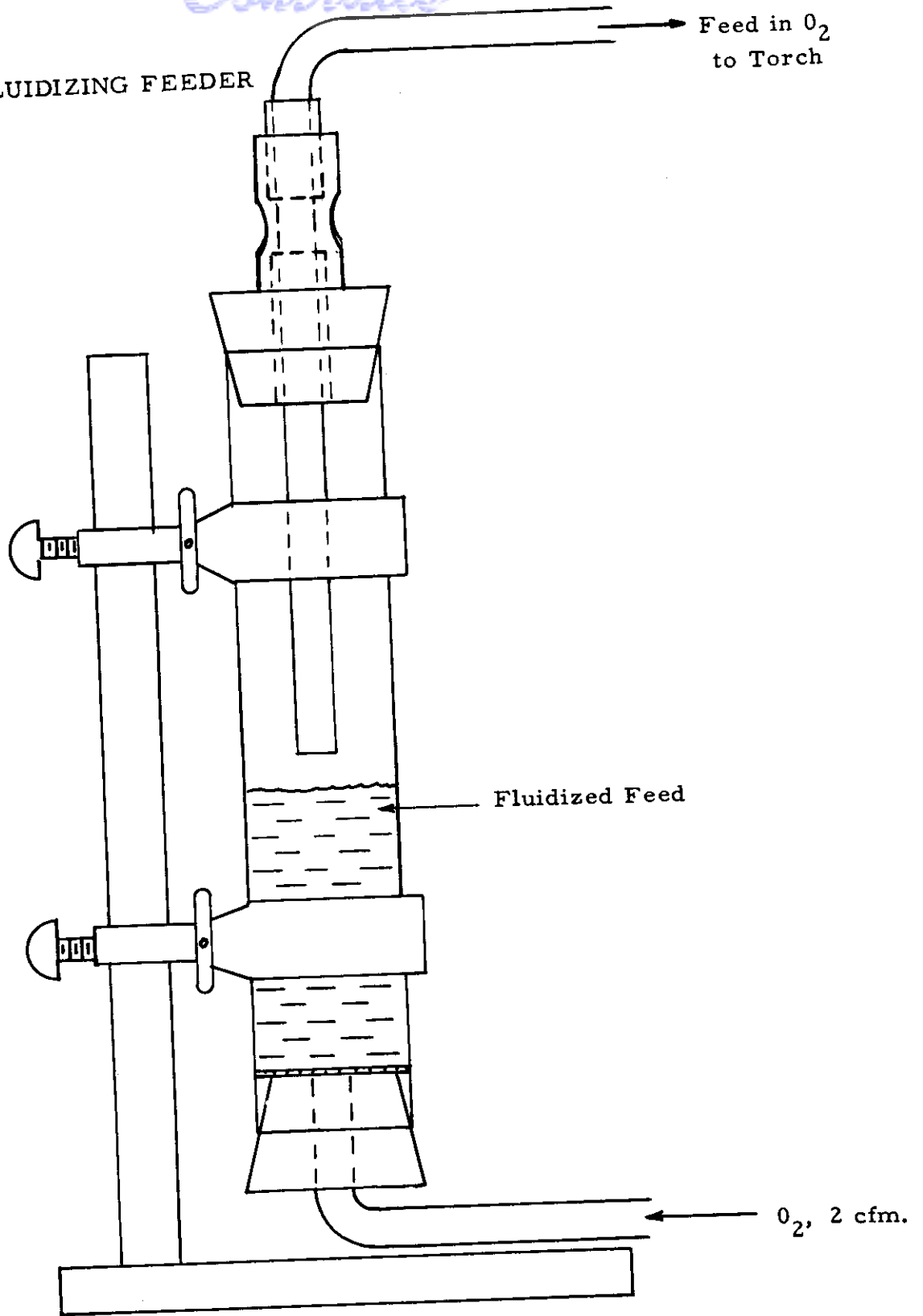


FIG. 3 TORCH DETAIL

FIGURE 4 FLUIDIZING FEEDER



# Contrails

minus 300 mesh material, this unit was fed with minus 100 plus 200 mesh feed stock. The torch was operated at its maximum capacity under slightly reducing conditions to minimize total gas flow. A considerably higher proportion of microspheres was obtained than in the previous runs. However, the only perfect microspheres were all less than 50 microns in diameter. Most of the balance of the product was larger frothy particles which contained many small bubbles and had rounded contours. This again appeared indicative of inadequate heat and perhaps sojourn time.

At this time, the feed system, which had consisted of an air-aspirating device for the powdered feed, was changed since it was recognized that the amount of air required was a substantial volume of the total gas stream and tended to decrease sojourn time in the hot zone. The feeding system was changed to a chamber in which the powdered feed was fluidized by an oxygen stream and the particles picked up by a small feed tube just above the fluidized bed surface and carried into the hot zone by the fluidizing oxygen. (Figure 4) This decreased the amount of gas input with the feed to about one-fifth what it had been and also provided a more uniform feed rate. Another run with this system was promising, but the torch and feed system was burned out in the process. It was thought we might obtain useful auxiliary heat by means of electrical resistance heating on a tube surrounding the hot zone. To this end, 85 feet of 12 gauge Kanthal wire was wound on a 3" I. D. x 18" long alundum tube. This was covered with a heavy layer of Lumnite cement for protection and heat transfer, and enclosed in silica insulating brick. The rebuilt torch was then used in conjunction with this, and the furnace wall was operated at 1100°C. A larger proportion of spheres, 2 - 5 volume percent of which were greater than 100 microns in diameter, were produced, indicating that extension of the hot zone by this means was an improvement. However, the bulk of the product was still frothy lumps indicative of inadequate heating.

The higher operating temperature used had burned the torch tip beyond the possibility of repair. An oxyacetylene cutting torch, a Tolman W 12, was modified so that a stream of feed stock particles suspended in oxygen could be injected through the central cutting oxygen orifice. This torch, fitted with a #7 tip, was wound with 1/8" diameter copper tubing to provide water cooling. The recovery system was changed from electrostatic precipitation to impingement because experience with fan overheating in previous runs showed that the gas stream had to be at a much lower temperature when it reached the fan. This required inspiration of a large amount of tempering or quench air. To handle this volume, an exhaust blower, 600 cu. ft./min. at 2-1/2" water column suction, was installed, and a simple impingement system was constructed since this blower provided velocity adequate for recovery by impingement.

The furnace was preheated to 1250°C measured on the outside wall of the electrically heated alumina tube and the oxyacetylene flame



# Contrails

started using 9 cu. ft. /hr. of acetylene and oxygen sufficient to give a neutral flame. Minus 60 plus 200 mesh feed stock was suspended in oxygen and injected into the flame at a rate of 2 g. per minute. The electric resistance winding burned out after 5 minutes' operation, although the furnace wall was still at 1250°C. Firing rate on the torch was increased to 16 cu. ft. /hr. acetylene. The wall temperature rose to 1400°C during a 5 minute period. A 10 cc. /min. spray of water was added to the hot gas downstream from the inspirated quench air because the fan was getting too hot at this high firing rate. Operation was continued for 10 minutes at this rate and with a wall temperature of about 1400°C when the run was stopped because of overheated ductwork. Six cc. of product was obtained from 30 cc. of feed. This product had about 50% of barely fused glass chips, many of which had sharp edges. The balance of the product was partially blown foam. Only very few spheres were found. Eight g. of slag was scraped from the furnace walls. This unusually large portion of unfused feed stock with sharp edges indicated even less effective heat transfer than the predominance of rounded-edge foam pieces from previous runs. This was not anticipated because for at least two-thirds of the run, the temperature was 300°C above that of the previous run (1400°C as compared with 1100°C exterior wall temperature). The gas flow was certainly much greater in this run because of the more powerful fan used, and the particle sojourn in the hot zone was consequently less because of the higher space velocity there due to air sucked in around the burner port and through various leaks.

It seems likely that the curtailed sojourn time prevented the necessary fusion and blowing in spite of the substantially higher temperature used. This pointed up the need for not only a high temperature but a substantial sojourn time in the hot zone.

For the next run, the firing (lower) end of the furnace was modified to provide some control of the secondary air drawn in by means of a shutter arrangement (Figure 3, Detail A) and by plugging leaks in the refractory as well as possible. After pre-heating the bottom half of the furnace to an outside wall temperature of 1350°C when using 16 cu. ft. /hr. of acetylene, feeding was started at a rate of about 1 g. /minute. During most of this run, the exterior wall temperature was held at 1475° to 1520°C. After 10 minutes' operation, the run had to be curtailed because the fan was getting too hot in spite of a 10 cc/min. flow of spray water in the hot gas line. One and one-half grams of fluffy microspheres was obtained from the walls of the impingement drum. Nothing was found in the area where impingement collection would ordinarily occur. It appeared that velocity was still not adequate for impingement collection or perhaps lack of trapping fluid in the impingement zone prevented collection. Three grams of slagged feed stock was collected in the quench air entry where turbulence presumably threw molten material against the wall. Of the fluffy product contained on the walls of the impingement drum, nearly all of it was -150 +20 micron perfect microspheres.



*Control*

This was the first run in which we obtained any quantity of perfect spheres larger than 100 microns. The +100 micron material was less than 10% by volume of the 1.5 g. obtained. All of the pieces smaller than 30 - 35 microns had a density such that they sank in water, although they certainly appeared to be hollow glass spheres. From this run, a number of necessary changes were apparent.

1. A 9" diameter cyclone separator was installed since it would give better collection efficiency with the gas flows in use.

2. More cooling for the hot gas stream by means of additional spray was installed.

3. The furnace chamber proper was extended from 18" to 36" high to provide more sojourn time.

Following the above changes, eight runs varying in length from 30 to 150 minutes in the 3" diameter by 34" long laboratory scale unit (Plates Ia and Ib) showed that hollow glass microspheres of essentially pure silica could be produced at 1700°C to 1750°C. Improved techniques and control made it possible to reduce the fuel rate from 7 to 2 lbs./hr. of acetylene. This increased theoretical sojourn time of feed particles in the furnace to about one second when the stoichiometric requirement of oxygen was supplied as oxygen rather than air. Small but critical additions of secondary air were necessary to control the sojourn time. Fairly uniform sizing of feed stock (-200 + 70 micron particle size range) was found desirable to minimize production of frothy agglomerates from excessively large pieces on one hand and small thick-walled bubbles from the undersize. Recovery of the small particle size, low density product had been partially accomplished on a small scale by electrostatic precipitation from the hot, 900°C, gas stream. Dilution and cooling of the hot gas stream to a temperature permitting use of standard inertial separation equipment required volume and draft capacities beyond anything readily available to us. Consequently, cooling by evaporation of water into the hot gas stream was resorted to. Evaporation of about one gallon of water per hour into the gas stream provided adequate cooling and permitted handling the resulting gas volume in a 9" diameter, high-velocity cyclone without pressure drop beyond the capability of an available blower. While some 30% of the feed was not accounted for, we believe we recovered 80% or more of the +60 micron product in the gas stream.

The stainless steel cyclone and fan recovery system had been borrowed and had to be returned after this series of eight runs. While we were procuring and fabricating replacements, design of a tenfold pilot unit was undertaken on the basis of the information we had from this series of runs.

## C. DESIGN OF TENFOLD SILICA MICROBUBBLE PILOT PLANT

While the laboratory work was in progress, Standard Oil Company (Ohio) Research and Development Department had designed and was building a 10" diameter propane and air fired unit in which they expected to attain temperatures of 1450°C for pilot production from pure silica feed stock. Their design and design calculations served as a basis for our work.

### 1. Temperature and Sojourn Time

Fusion is required for the production of microbubbles. Silica melts about 1700°C. Laboratory runs had indicated that this temperature was necessary for formation of microbubbles from silica feed stock. Best results were obtained in the laboratory unit when calculated sojourn time in the unit was about one second -- the maximum obtained. However, the sojourn in the 1700°C portion of the unit was less than one fourth of this. While electrical heating would have eliminated the hard-to-deal-with inter-relation of heating requirement and gas volume incurred in using the combustion of fuel in the operating chamber, it was considered an impractical approach in this situation. With combustion of fuel the only practical means of heating, it appeared necessary to minimize the combustion gas volume to decrease the gas velocity adequately in the hot zone. Use of pure oxygen would decrease the combustion gas volume to one fourth of that produced if air were used for the total oxygen requirement. If one half of the oxygen requirement were supplied as pure oxygen and the balance as air, the gas volume would be 60%; if one third of the oxygen requirement were supplied as pure oxygen, the gas volume would be 75% of that produced if air alone were used.

We were assured by manufacturers of high-velocity type burners that flame temperatures in excess of 1700°C were attainable with propane-air flames using this type of burner. Thermal Research Corporation, the source of the burner decided upon, said oxygen enrichment was feasible up to 33% but that higher temperature duty refractories than those supplied with their equipment would be required.

Minimum delivery time for the special refractory shapes needed was 80 to 90 days, so we decided to fabricate and fire our own out of commercially available ramming and casting mixes. Norton Company's Zirconia RZ 1601, usable to 2500°C, was chosen for the burner refractory and their Alundum 33I castable usable to 1810°C, for the hot face lining of the furnace proper.

For heating, we started with a design premise of 400,000 BTU per hour heat release, provided by burning three cubic feet per minute of propane with air and facilities for providing up to 40% of the oxygen requirement as pure oxygen. In a nine inch diameter furnace chamber 60 inches high, the combustion gases at 1800°C would have a velocity providing

*Contrails*

for 0.3 seconds sojourn. This chamber would be fired upward from the bottom with feed injection through the burner orifice. Combustion gases and product would go from the furnace to the quenching chamber through an orifice in the top of the furnace chamber.

Another way to decrease combustion gas volume and increase sojourn time is to minimize heat losses through walls and ends of the furnace chamber and thus decrease the firing required. To this end, we designed for minimum heat transfer through the walls subject only to the hot wall temperature limitations of the various refractories used. Several refractories were used in concentric cylindrical layers (Figure 5). The inner layer was one inch thick Alundum 33I castable. Surrounding this was a 0.75 inch layer of loose Alundum bubble to provide room for expansion of the lining rings. Both of these have 1800°C capability in this application. This was followed by a 4.5 inch course of insulating firebrick capable of 1540°C service. Outside of this was a 4.5 inch thick course of insulating brick capable of 1100°C hot face service. This was followed by a two inch layer of rock wool. This 13 inch thick furnace insulation may seem excessive, but calculation of a number of alternative constructions to get heat losses and temperature profiles through the insulation developed this as the best solution for readily available refractories. Calculated heat loss through the walls at 1800°C operating temperature was less than 20,000 BTU/hr.

## 2. Quenching Product and Cooling Hot Gas Stream

The microbubble once formed and blown to size in the molten condition must be cooled below the deformation temperature before it comes into contact with other bubbles or equipment walls. In the laboratory scale unit, both adding large quantities of cold air to, or spraying water into the hot product stream were used. When enough water was added to cool the gas to the 380°C maximum permissible in the recovery equipment, considerable quantities of liquid water appeared with the product. This might have been eliminated by better atomization equipment, but we were not successful in this although several types of spray devices were tried. Water itself in the product is not critical, but it seemed likely that hot bubbles striking water droplets would probably be broken due to thermal shock. Means for eliminating the need for water spray were therefore sought.

At the proposed firing rate with propane-air, we anticipated an 81 cfm STP product gas stream or 570 cfm at 1800°C. In any case, it was deemed advisable to dilute this at once with enough cold air to bring the stream below the softening point of the microbubbles in order to minimize deformation and sticking to equipment walls. This temperature was assumed to be 1400°C. This requires 28 cfm STP air. At least this much air will be drawn into the gas stream just beyond the orifice of the furnace

chamber to give a hot gas volume of 763 cfm at 1400°C.

Three possibilities for the necessary additional quenching were considered. The first was to cool this product stream to 210°C by adding air. It was assumed to be dry at 50°C. This would give a hot gas volume of 1800 cfm at 210°C. The second was to design gas handling equipment of stainless steel usable at 950°C and cool only to this temperature with room air. This would give a hot gas volume of 780 cfm at 950°C. The third was to cool the hot gas stream to 210°C by evaporation of water into it. This would give a hot gas volume of 330 cfm at 210°C.

Of these possibilities, the first was chosen with the provision for water cooling. A blower adequate for this was available on fairly good delivery, but it would develop only 3 inches water column of suction. This was not enough to take care of the pressure drop which would be incurred in handling 1800 cfm through inertial separation equipment adequate for complete product recovery. For complete product recovery, it would be necessary to reduce the hot gas volume by using water quenching.

### 3. Product Recovery

Electrostatic precipitation to recover the microbubbles from the hot gas stream proved partially effective in a crude device used on the laboratory unit. While this was a possibility for the pilot unit and offers some advantages, the equipment is highly specialized and delivery slow. Recovery was good in the laboratory unit using a specially designed high velocity cyclone separator. As indicated in the previous section, cyclones of this type would incur about 40 inches water column pressure drop to be effective on the gas volume involved. To provide the necessary draft at least a 4-stage turbo-blower -- an expensive long-delivery item -- would be required. We decided to use cyclones which would handle the gas volume within the draft limitations of the 1800 cfm blower. This developed to parallel 22" diameter cyclones between which the hot gas stream would be split. These units should handle the 1800 cfm with about two inches water column pressure drop and recover 80% of the +200 mesh product. We planned to make provisions for splitting off a side stream to the nine inch diameter high velocity cyclone and blower system used on the laboratory unit for characterizations of total particle size distribution in the product.

### 4. Heating

The 400,000 BTU per hour heat release would be obtained in a Thermal Research Corporation Model 212T burner. The regular burner block would be replaced with a block of our own design made from higher temperature service refractory. We anticipated that this block would spread the combustion gases better and cause a more uniform flow pattern in the furnace chamber. It would also permit the use of oxygen enrichment and thus decrease the total hot gas volume. We expected to burn 3 cfm of propane with air. Provision for use of up to one half of the oxygen

as pure oxygen was included. Instrumentation necessary for measurement of these gas flows and their manual control was included. Propane would be supplied from a 500 gallon liquid tank. Oxygen would come from a bank of standard 240 cubic foot cylinders and blast air would be provided by an AS47 Roots-Connerville blower.

#### 5. Injection and Control of Raw Feed into Flame

It was planned to suspend the sized, -60 +200 mesh, feed stock in the unignited combustion mixture in the burner throat. Pressure at this point would be 25 to 30 inches of water column. Metering feed from a hopper by means of a variable speed screw conveyor and inspirating this into the throat with part of the blast air would be attempted. This might cause us to lose effective control of too large a portion of the blast air. If this proved to be the case, we planned to fluidize the feed with a small air flow and transport it into the burner with the fluidized air. Control of rate would be by a variable diameter orifice on the suspension pick-up device.

#### 6. Construction

Construction followed design with minor exceptions. Fabrication of the inner refractory rings of Norton's 33I insulating castable alumina turned out very well. No failures in casting or firing occurred. Exploratory tests indicated that 11%, rather than the 18%, water recommended by the manufacturer gave a stronger block. The mix was placed in the mold, compacted by vibration and allowed to set 90 minutes. The mold was stripped and the piece allowed to cure in a saturated atmosphere for 48 hours before slow drying. This was followed by firing to 1450°C. Several failures with the zirconia RZ 1601 caused us to make the burner block of the alumina castable. In order to more effectively dissipate heat, the water pans were installed, rather than the refractory brick of original design. The rock wool coating was never applied to the outside of the furnace because its surface temperature never got above 65°C. The base plate of 1" thick steel under the burner block was drilled with 4-1/4" diameter transverse holes through which water was circulated to keep this area of maximum heat conduction cool. Because the inspirator had not been finished, operation was started with a double unit fluidized bed feeder. See Figures 5, 6, 7.

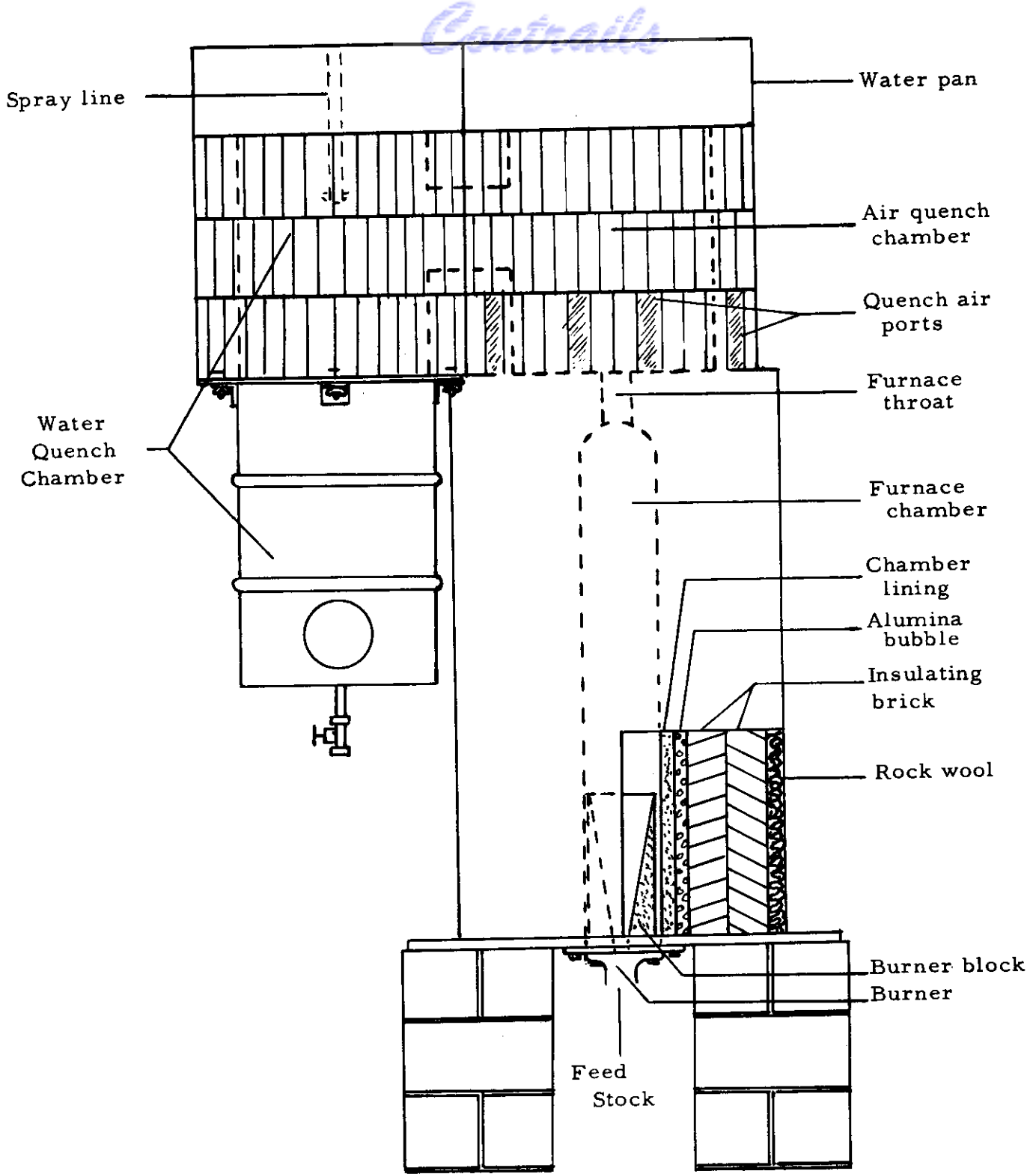


FIG. 5 PILOT UNIT SILICA MICROBUBBLE FURNACE - ELEVATION

- A. FURNACE.
- B. WATER SPRAY CHAMBER.
- C. FEEDER.
- D. COMBUSTION GAS & PRODUCT LINE.
- E. 9" CYCLONE.
- F. 9" 40 FAN.
- G. 24" 40 FAN.
- H. MAIN DRAFT FAN.
- I. CONTROL PANEL.
- J. BLAST BLOWER.
- K. AIR CONTROL.
- L. SURGE TANK.
- M. HIGH PRESSURE AIR SUPPLY FOR FEEDER.
- N. OXYGEN SUPPLY.

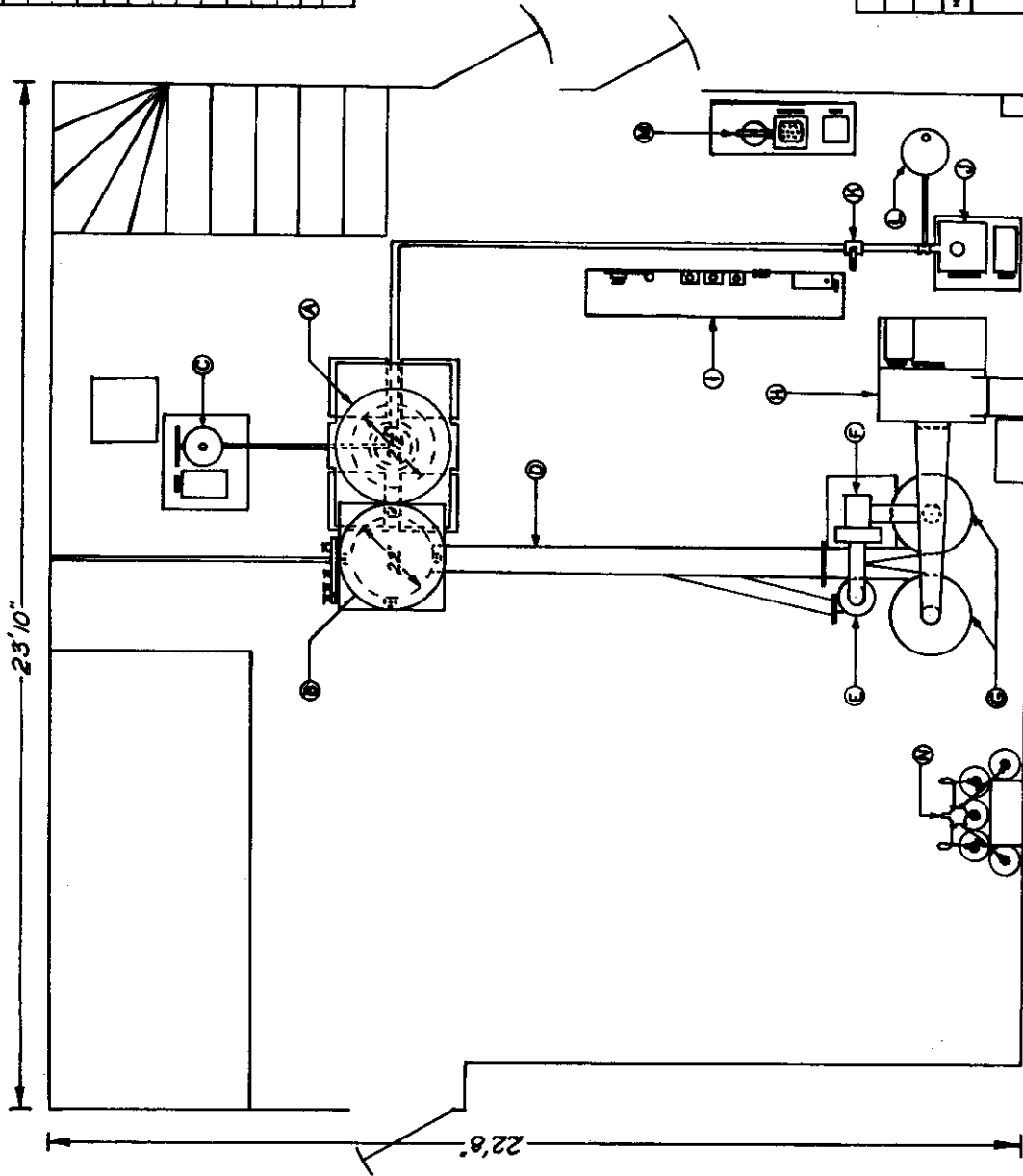


FIGURE SIX

NO.	REVISION	BY	APPR.	DATE
EMERSON & CUMING, INC. BOSTON, MASS.				
PILOT UNIT SILICA MICROBUBBLE - FURNACE LAYOUT - PLAN				
DESIGNED BY	DATE	CHECKED BY	DATE	SCALE
G. LOTHROP	2-23-40			
				C-34-1619



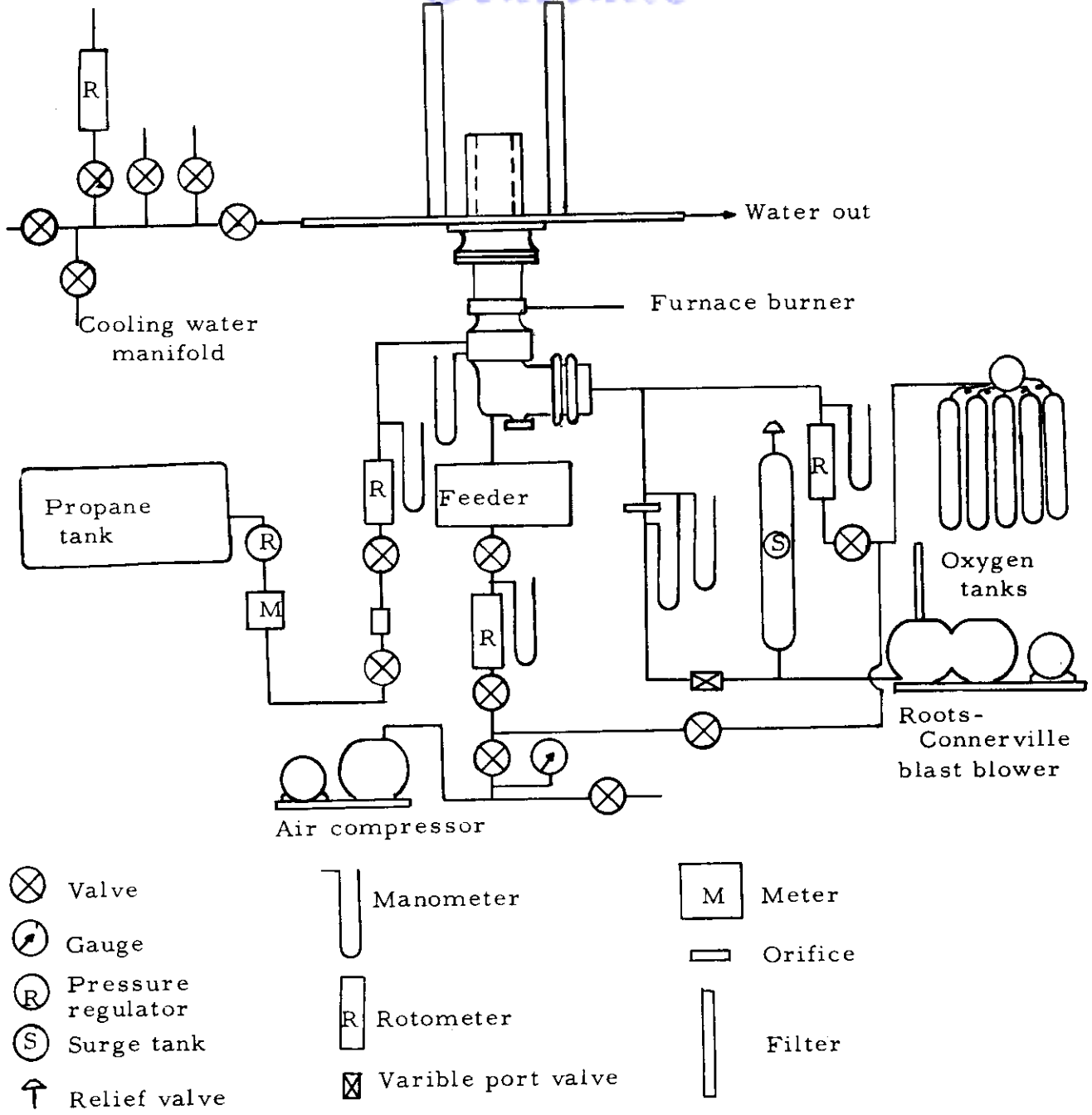


FIG. 7 PILOT SILICA MICROBUBBLE FURNACE - PIPING SCHEMATIC



*Carbide*  
7. Preparation of Feed Stock

The feed stock used is a dehydrated silica gel containing a blowing agent. The basic raw material is a 30% SiO<sub>2</sub> sol containing 0.01% Na.

During the course of the work here, Standard Oil of Ohio was working independently preparing and evaluating in a preliminary screening procedure various feed stock compositions. They gave us the results of their work. Our interest in this variety of compositions was minimum dielectric loss and lessened hygroscopicity which we evaluated. Sohio's prime interest was minimum density of product and maximum yield. In this connection, a number of blowing agents were tried in addition to the urea of the original formulation. Poly glycols were found to be more useful blowing agents than urea for the high temperature operation. Several "Carbowax" and "Polyox" (Union Carbide) materials were tried in preliminary tests. A considerable portion of the pilot plant work was done using hexane triol. Finally, the most common trihydric alcohol, plain old glycerine, was found in the screening test to be outstanding. Initial laboratory scale work was with the urea formulation. For latter part of the laboratory scale work and the initial part of the pilot plant campaign Polyox 35 was used. For most of the pilot plant campaign, hexane triol was the blowing agent. The final batch had glycerine as the blowing agent. Boric acid had been found to extend the viscous range of the lower melting compositions somewhat without degrading the final product, so it was included in the earlier formulations. The composition and dehydration treatment of the various formulations used is shown in Table 11.

TABLE 11

FEED STOCK FORMULATIONS

Designation	Composition			Dehydration		Used In	
	Silica Sol, %	H <sub>3</sub> B <sub>3</sub> O <sub>3</sub> , %	Blowing Agent, %	hrs.	at °C		
U	93	5	Urea	2	8	300	Lab. Unit
P35	94	5	Polyox 35	1	6	300	Lab. Unit & Pilot Plant to 23 Sept.
HT	99	0	Hexane-triol	1	5	270	Pilot Plant
Gly	99	0	Glycerine	1	4	270	Pilot Plant, last test only

## D. INITIAL PRODUCTION

After preliminary firing over a four-day period to dry out the refractory, the furnace temperature was raised to 1500°C and feeding started. Production operating data is summarized in Table 12. Feed was injected into the burner throat in an air suspension obtained by a 2 cfm air stream through a bed of sized feed stock which fluidized the bed and suspended the particles in the air stream. Although six operating shifts were spent attempting to get reasonably uniform feed rates with this system, we did not obtain it. The feed always entered the hot zone in slugs. Product from this feeding arrangement was characterized by the whole range of particle characteristics from unfused unblown feed stock which went through the hot zone too rapidly, foamy particles which got hot enough to blow but not hot enough to form single bubbles, good discrete vitreous bubbles, to small solid glassy balls which had gotten so hot that the previously formed bubble had shrunk to an almost solid sphere.

Design and testing of an inspirator feeding arrangement had been going on concurrently. This device was used to replace the fluidized bed unit. It required gas at 15 to 20 psig to inspire effectively against the back pressure in the burner throat. Since no high pressure air supply was available in the area, we attempted to run this unit on our supplemental oxygen supply which had an available operating pressure of over 50 psig. The inspirator functioned using this oxygen, but the amount of oxygen required to make it run was entirely too much for controllable combustion conditions. The hot zone in the furnace was very short, extending only about 12" above the burner block. In this zone, we got temperatures of 1790°C almost before we were aware of it and slagged up the furnace badly due to overheating while still blowing out unmelted feed particles. (Samples 1 - 4). We quit this just short of disaster, shut down, dug out the slag and installed a compressor to supply high pressure air for the feeder.

When operation was resumed the next day using 20 psig air on the inspirator feeder, feed input was steady and controllable. Combustion conditions could be controlled also. We knew that we had at most only a few days available for operation and demonstration of the process. Consequently, our test program used only the smallest possible, usually 500 g, lots fed during one to two hours operation, for each set of operating conditions. The operating conditions were set at what we deemed from laboratory scale work to be extremes so that we would be able to bracket optimum conditions as quickly as possible.

After four hours feeding, it was apparent that we were recovering as product only about 20% of the input. We suspected excessive loss through the cyclone recovery system of the finer particle sizes since the theoretical capability of the recovery system, limited by the suction

TABLE 12  
PILOT PLANT OPERATIONS SUMMARY

SAMPLE No.	Date	Time	FEED STOCK Size	B. A.	g.	FEEDER R.P.M.	C.H.R. cfm	AIR cfm	O <sub>2</sub> cfm	TEMP. °C	HOT ZONE ft./sec.	RECOVERY IN GRAMS		SACK WEIGHT %	FLOAT MID SINK		
												9"	22"				
1/2	22	1145/1600	-60 +200	P 35	1800	Fl. bed	2.0	48.6	--	1700	7.5	--	131	--	Fused solid		
3	22	1655/1725	-60 +200	P 35	1000	6	1.3	7.8	3.0 <sup>a</sup>	1750	1.8	--	26	--	Fused solid		
S	22	1145/1725	--	P 35	(2800) <sup>b</sup>	--	--	--	--	--	--	--	--	--	Fused solid		
5, 6, 7	23	1805/1920	-60 +200	HT	1000	1	2.0	47.4	--	1600	7.4 <sup>c</sup>	--	68	--	Fused solid		
8/9	24	1940/2230	-60 +200	HT	1000	1	2.2	46.2	--	1630	7.4 <sup>d</sup>	24	75	--	Fused solid		
10/11	24	0940/1230	-60 +200	HT	1000	1	1.75	47.4	--	1625	7.4 <sup>d</sup>	18	52	--	Fused solid		
12	24	1440/1545	-60 +200	HT	470	1	2.1	46.2	--	1625	7.4 <sup>d</sup>	26	27	--	Fused solid		
S	24/25	1545/1540	-60 +200	HT	(2470) <sup>e</sup>	1	--	--	--	1600/1650	--	--	--	--	Fused solid		
13/14	25	1120/1250	-60 +200	HT	500	1	2.1	53.4	--	1455	8.4	85	195	--	Fused solid		
15/16	29	1250/1415	-60 +200	HT	500	1	2.1/2.4	49.8	--	1460	8.0	95	118	--	Fused solid		
17/18	29	1415/1600	-60 +200	HT	500	1	2.5	54.6	--	1520	8.7	63	114	--	Fused solid		
19	29	1600/1725	-60 +200	HT	500	1	2.6	59.4	--	1540	9.7	46	88	--	Fused solid		
20/21	29	1733/1920	-60 +200 <sup>f</sup>	HT	500	1	2.6	59.4	--	1590	9.7	14	63	--	Fused solid		
22	29	2130/2330	-200 <sup>g</sup>	HT	500	1	1.5	31.8	--	1485	5.2	44	78	--	Fused solid		
23	30	1240/1330	-60 +200 <sup>h</sup>	HT	500	1	2.5	18.6	2.1	1530	3.8	9	9	--	Fused solid		
24	30	1400/1505	-60 +200 <sup>i</sup>	HT	500	2	2.5	16.8	1.5	1530/1590	3.4	4.5	16	--	Fused solid		
S	30	1240/1505	--	HT	(1000) <sup>j</sup>	--	--	--	--	--	--	--	--	--	Fused solid		
27	Oct.	1510/1650	-200	HT	500	2	2.4	55.2	--	1530	8.5	18	77	--	Fused solid		
28	1	1730/1840	-200	HT	500	2	2.44	55.2	--	1585	8.5	40	52	--	Fused solid		
29	1	1848/2010	-200	HT	500	2	2.44	55.2	--	1590	8.5	47	60	--	Fused solid		
30	1	2015/2145	-200	HT	500	2	2.44	55.2	--	1590	8.5	50	60	--	Fused solid		
31	1	2200/2330	-60 +200	HT	500	1	2.3	48.6	--	1580	7.8	40	39	--	Fused solid		
32	2	1100/1230	-60 +200	HT	500	1	1.1	22.2	1.0	1520	4.2	23	25	--	Fused solid		
33	2	1245/1355	-60 +200	HT	500	1	1.1/1.4	27/36.6	1.0	1430/1530	4/6	19	64	--	Fused solid		
34	2	1355/1505	-200	HT	500	2	1.7	36	1.0	1500/1600	6.3	27	78	--	Fused solid		
35	2	1505/1615	+60	HT	500	2	1.7	36.6	1.0	1640	7.1	30	36	--	Fused solid		
36	2	1630/1730	-200	HT	500	2	1.7	36.6	1.0	1625	7.1	18	65	--	Fused solid		
S	1/2	1510/1730	--	Gly	500	2	1.7	36.6	1.0	1625	7.1	18	65	4	47	4	49

(k) 2655g slag, friable, bubbly agglomerates. Product from spray chamber, 1515g, like cyclone product.

- (l) Feed irregular, but only a trace of slag
- (m) Walls not slagging noticeably even with fine feed.
- (n) Beginning to slag.
- (o) Slagging above burner block rapidly
- (p) 1108g slag from furnace 1240/1505 1000 g feed.
- (a) Used O<sub>2</sub> to run inspirator feeder. It took too much, slagged clear over 20" above burner block.
- (b) 1820g slag bulk of this during #3 run on O<sub>2</sub>. Cyclone product was largely unblown feed stock.
- (c) No slag forming
- (d) Trying to pull all this thru 9" cyclone, furnace pressure >0.5" H<sub>2</sub>O
- (e) 2071g slag - most of this between 1045/25 and 1540/25 when using only 9" cyclone and furnace pressure was positive.

BA - Blowing Agent - See Table VIII  
g - Grams  
FLOAT - % Floaters  
MID - % Middling  
SINK - % Sinkers  
p 35 - Polyoxy 35  
Fl. bed - Fluidized bed  
S - Slag  
( ) - Grams of feed, corresponding to slag collection period  
HT - Hexane Triol  
Gly - Glycerine

of the available fan and required gas flow was recovery of only those particles larger than 120 microns at the anticipated particle density of 0.4 g/cc. Feeding was stopped, the furnace was held on stand-by heat (1400°C) and the 9" diameter stainless steel cyclone and its high velocity fan from the laboratory unit were installed to take a cut from the main product stream. In this way, we expected to get at least a representative sample of our product. The test program was resumed. We found that this small high velocity cyclone did catch about 25% of the total cyclone product but that it was not substantially different in composition from that of the 22" cyclone pair.

We then attempted to put all the gas stream through the 9" cyclone for a test. The volumetric capacity of this cyclone and its high velocity fan is about 600 cfm while the combustion and quench air amounted to about 1100 cfm. A positive pressure was, of course, created in the hot zone which caused violent turbulence and severe slagging. Although the firing rate and quench air were minimized to hold 1500°C in the hot zone and quench air reduced by cooling with water evaporation in the hot gas stream, it was impossible to reduce the gas volume sufficiently for the small fan alone to handle it. After shutting down to clean out the 2000 g. of slag which had accumulated during this attempt, operation was resumed with the product gas stream split between the two recovery systems.

A series of runs at different hot zone temperatures followed. These covered the range 1450°C to 1590°C. It was apparent from these runs that somewhat higher temperatures or longer sojourn time was required, because most of the product was frothy underheated lumps of 60 to 200 $\mu$  size. The true bubbles obtained were generally smaller than 90 $\mu$ .

We elected to increase the sojourn time first by providing about one third of the oxygen required for combustion as pure oxygen. This reduced the space velocity (at hot zone conditions) from 9.7 to 3.6. The immediate result was rapid slag and cinder accumulation at and up to 12" above the burner block at a hot zone temperature of 1530°C. The temperature was climbing rapidly so another 500 g. was fed at a hot zone temperature of 1580°C. During the latter part of this test, slag and cinder accumulation was so rapid that almost the whole furnace cross section was bridged over at times. The 1530° product (#23) amounted to only 14 g. because of slagging. It was more than 50% frothy rounded agglomerates, mostly between 100 and 200 $\mu$  in size. There was a noticeable amount of small, 30 - 60 $\mu$  glass balls in this product, indicating excessive sojourn for some particles. The product (#24) from the 1575° test again amounted to only 16 g. because of slagging. It was almost entirely

100-150 $\mu$  frothy bubbles, actually much nearer good bubble formation than the previous product. No solid glass balls were evident. They probably all adhered to the accumulating slag.

From this, it was apparent that we could not tolerate such a low space velocity because of slag accumulation, regardless of how desirable it might be from the standpoint of increasing sojourn time.

In a short run previously -200 mesh, rather than -60 +200 mesh feed stock had given a relatively large proportion of good product, #22, at the relatively low temperature of 1485°. This indicated what seemed logical anyway, that effective bubble formation would occur at lower temperatures with smaller feed particles.

The next series of tests was therefore run using -200 mesh feed stock at temperatures of 1530, 1590, 1580, 1520 and 1475°C. Slightly the best results were obtained at 1590°C, there being the smallest proportion of frothy bubbles in that product, #29, of any seen. The heavy, density greater than 1.0 g/cc, portion of this product consisted largely of thick-walled, tiny, 10 - 40 $\mu$ , bubbles. These are difficult to distinguish from solid glass spheres, but they all had a density less than 2.0 g/cc. Since the glass itself has a density of over 2.2 g/cc, these are thick-walled bubbles.

Feeding with the standard coarser, -60 +200 mesh material was resumed. Somewhat better results, qualitatively, were obtained at 1580°C than at either 1520°C or 1475°C. This product contained about 25% having a density less than 1.0 g/cc, somewhat lower than that obtained with the -200 mesh feed stock. The material having a density over 1.0 g/cc was nearly all frothy agglomerates, somewhat smaller than those in the lighter portion. This heavier fraction had a smaller proportion, estimated at less than 20%, of the small thick-walled bubbles which were so evident in the product from -200 mesh feed.

One more lot of -200 mesh stock was run at 1500°C to 1600°C to confirm the comparison of the product with that of the coarser feed. A slightly higher proportion, 42%, of the product, #34, had a density less than 1.0 g/cc. This confirmed fairly well that temperatures of 1550°C to 1600°C were better even on -200 mesh feed stock than lower ones.

A lot of +60 mesh feed stock was then fed at an operating temperature of 1640 °C. In spite of the 50° to 75° increase in temperature, only 21% of the recovered product had a density less than 1.0 g/cc.

# Conclusions

No small thick-walled bubbles were found in this product. Most particles were somewhat rounded and contained bubbles, but the bubbles in an individual particle had not grown or coalesced sufficiently to form large ones. From these results, it appears that considerably higher -- possible two to three hundred degrees -- operating temperatures are necessary for bubble formation from larger particle-size feed stock.

One 500 g. batch of -200 mesh feed stock using a different blowing agent (see section on feed stock composition) was fed at an operating temperature of 1625°C. 47% of the recovered product had a density less than 1.0 g/cc. This fraction had the highest proportion of smooth, true bubbles of any produced. It had a true density of 0.7 and a bulk density of 0.33 g/cc. The higher density fraction was again characterized by a high proportion -- estimated greater than 70% by weight -- of tiny thick-walled bubbles.

During the feeding of the last 2000 g., a bag filter consisting of 50 square feet of 181 clove foot weave glass cloth was placed on the draft fan discharge. This glass cloth is so tight that only occasional 15/16 holes are visible when it is tightly stretched. Only four grams of product was found in this bag from the 2000 g. of feed stock! This showed that no significant portion of the product in the gas stream to the cyclones was getting by them.

In the course of the operation, the spray chamber was drained periodically. Since only insignificant amounts of solids were present in the drainings, it was assumed that little material was being caught in the spray chamber. At the end of the campaign, the spray chamber was dismantled. 1515 g. of product had collected as a cake in the flat bottom of the spray chamber.

A materials balance was made covering the campaign from 1805 on 23 September until its termination at 1730 on 2 October. This covered 36 hours of actual feeding during which 11,970 g. of feed stock was used. Cyclone product amounted to 2600 g., equivalent to 21.7%, slag in the furnace accounted for 48.8% and material caught in the spray chamber, to 12.6%. 16.9% of the input was unaccounted for.

This campaign showed that a furnace operating in the 1600°C - 1700°C range can produce vitreous microbubbles from pure silica feed stock, using the same basic operating principles governing the production of microbubbles from low melting feed stock at 900°C.

In spite of the fact that time available for experimental operation was very limited, a number of pertinent facts were



developed.

The unit is capable of operation at 1750°C. This is slightly above the safe limit of the refractory used, but we can operate here for brief tests at least.

Some bubble formation occurs at temperatures as low as 1500°C, but even for -200 mesh feed stock 1600°C - 1650°C seems to give the lowest density product with a minimum of small thick walled bubbles shrunken by overheating. For the coarser -50 +200 mesh feed stock, considerably higher temperatures appear desirable. The two brief tests at the start of the campaign at temperatures above 1700°C were made under unstable conditions and are not considered significant. During the latter part of the campaign, best product from -60 +200 mesh feed was obtained at the highest temperature (1600°C) used. Tests should be made on this material at 1700°C - 1750°C, because the wall-to-volume ratio of the bubble will decrease and so will density of the product if we can get enough heat and sojourn time to make bubbles out of this coarser feed stock.

Space velocity in the furnace was known to be important for its effect on sojourn time. We initially tried to get this as low as possible by providing combustion oxygen as such, rather than as air. It quickly became apparent that gas velocities at furnace temperature of less than 4.5 to 5 ft./sec. caused rapid slag formation. This is difficult to understand because the terminal velocity of the bubble in air is 1 to 2 ft./sec. Slagging is, of course, more severe with the 9" diameter hot zone than it would be with a larger one having a smaller surface-to-area ratio. Slag formation accounts for 20% to 30% loss even on the 42" diameter regular Eccosphere furnace. This high gas velocity requirement is unfortunate since it increases the fuel requirement due to the fact that much of the heat is taken out in the gas stream. (When using air alone for the oxygen, about two thirds of the heat generated is required to heat the combustion products alone to 1700°C.) This was shown experimentally when only 1.3 cfm C<sub>3</sub>H<sub>8</sub> was required to maintain 1750°C (at a gas velocity of 1.8 fps) when 45% of the oxygen requirement was supplied as pure O<sub>2</sub>, while 2.0 cfm C<sub>3</sub>H<sub>8</sub> was ordinarily required to maintain 1700°C when using air alone with a consequent gas velocity of 7.5 fps. In the latter part of the campaign, when the furnace dome had been removed and the layer of loose bubble insulation taken out, 2.3 to 2.6 cfm C<sub>3</sub>H<sub>8</sub> was required to maintain 1600°C to 1650°C when using air alone with a gas velocity of 8.0 to 9.5 fps.

During much of the campaign, a water spray of 1.6 gal./minute was evaporated into the hot gas stream just downstream of the quench air input. This served to cool the gas stream from about 330°C to 150°C, the safe upper limit of the fan. Use of more water resulted in wet

product. The possible thermal shock of water droplets on the hot product may be breaking up some bubbles, but we have no direct evidence of this effect.

Considerably the best product was obtained in the short test using feed stock made up with glycerine as a blowing agent, rather than hexane triol or polypropylene glycol. Since this was the last test run, part of this was undoubtedly due to skill we had gained in operating, but glycerine now appears to be the best blowing agent.

The direct process for making pure silica microbubble has been demonstrated to be feasible. The 36 hours actual operation to date has shown what needs to be done to improve the product and process. Specifically, pilot planting should be continued up to the maximum temperature limit (1750°C) of the refractory in the furnace using -60 +200 mesh feed stock with glycerine as the blowing agent and experimenting with gas velocities in the four to ten fps region to minimize slagging, increase recovery, and improve the quality of the product. Based on the information gained, it may prove desirable to change the design by inverting the operation. It is known now that a larger diameter unit would decrease slag losses, but the unit we have can be used effectively to get the necessary data.

### III CHARACTERISTICS OF MICROBUBBLES AT REDUCED PRESSURES

Both regular, 18% Na<sub>2</sub>O, and acid leached, 4% Na<sub>2</sub>O, microbubbles were subjected to several reduced pressure conditions to observe structural changes. Outgassing rates were measured on the materials from normal storage in sealed polyethylene bags and after heating in air to 150°C for 75 minutes. The rates are shown in Table 13 and Figures 8 and 9, the time versus pressure pump-down curves. A log-log plot of the slopes of these curves, Figure 10, follows. Since pumping rate is a function of system pressure, this curve facilitates comparison of rates of gas removal at various system pressures.

TABLE 13

#### OUTGASSING RATES OF SILICA MICROBUBBLES

Pressure	Outgassing Rate, liters/minute, at Indicated Pressure			
	18% Na <sub>2</sub> O		4% Na <sub>2</sub> O	
	Normal	After 75' @ 150°C	Normal	After 75' @ 150°C
mm Hg				
1 x 10 <sup>-4</sup>	8.7	7.5	15	9.3
5 x 10 <sup>-5</sup>	3.0	2.6	4.8	1.3
1 x 10 <sup>-5</sup>	0.07	0.02	--	0.3



# Contrails

The two empty system pump-down curves and the curve for preheated 18% Na<sub>2</sub>O grade are almost identical. This is also borne out by the substantial coincidence of the rate plots as a function of pressure. From this, it appears that for the preheated 18% Na<sub>2</sub>O grade, there is no substantial source of gas under these conditions. For the 18% grade that was not preheated, the absolute rate of pressure decrease with time is just about half that of the empty system as well as the preheated rate at 10<sup>-4</sup> mm Hg. and gradually approaches it as the pumping system's limit is approached near 10<sup>-5</sup> mm Hg. This indicates an additional source of gas which is being removed by the same mechanism as is operative on the system walls. The most likely source is, of course, surface moisture since moderate preheating eliminated it and this grade is markedly hygroscopic.

The preheated 4% Na<sub>2</sub>O grade shows rates as a function of pressure almost identical to that of the unpreheated 18% grade. This is surprising, since all of our work has shown this grade to be much less hygroscopic. The nominal surface areas of both types treated is comparable. If we accept the premise that this is not due to moisture, we must assume at least double the source of gas from the same mechanism. This could mean both inner and outer surfaces of the bubble are now in free communication so far as gas flow is concerned. It is also possible that the leaching operation applied to the 4% Na<sub>2</sub>O grade has greatly increased the microporosity of the bubble and also the surface capable of absorbing gas. By far the slowest pump-down rate observed was on the unpreheated 4% Na<sub>2</sub>O grade. This could, of course, be due to adsorbed moisture in the micropores. The greater than double amount of gas evolved makes it appear that this is from micropore surface rather than just from communicating interior bubble walls.

The true densities (by gas displacement) on the materials before and after the heating under vacuum, as well as bulk densities, are shown in Table 14. (See Figure 11 for pump-down curve).

TABLE 14

## EFFECT ON MICROBUBBLES OF HEATING UNDER VACUUM

Na <sub>2</sub> O Content %	Heating Temp., °C	Gas Release cc STP/g	Density			
			True		Bulk	
			Before	After	Before	After
18	485	0.13	0.49	0.90	0.32	0.30
4	705	2.0	0.30	0.66	0.19	0.19

# Conclusions

The much greater gas evolution from the low alkali material may be partly due to the higher temperature to which it was heated since silica holds to some of its hydrate water up into this range.

The calculated gas volumes evolved on heating the samples under vacuum was 4 cc STP from the 18% Na<sub>2</sub>O grade heated to 485°C and 35 cc from the 4% Na<sub>2</sub>O grade heated to 705°C. Bubble interior volume in both tests was 45 to 55 cc. At bubble formation temperature of 1000°C, the gas pressure inside the bubble may be presumed to be nearly atmospheric. Consequently, at room temperature, the STP interior gas volume would be about 18 cc. From this, it seems likely that the 4 cc evolved from the 18% Na<sub>2</sub>O grade came from the exterior surface while the 35 cc from the 4% grade came from a combination of both interior and exterior surfaces plus an undetermined amount, probably 10 to 20 cc, from the generated micropores. This speculation is assuming that there is no additional dehydration of the silica gel over the 485 to 705°C range.

It appears that individual bubbles of both grades retain their gross volume integrity as is indicated by lack of change in bulk density when heated under vacuum. The limited, 4 cc, of gas evolved upon heating to 485°C under vacuum of the 18% Na<sub>2</sub>O grade, as compared to the 18 cc STP of internal gas indicates that communication between interior and exterior is quite limited under these conditions with this grade. The much larger volume, 35 cc, obtained upon heating to 705°C under vacuum the 4% Na<sub>2</sub>O grade indicates not only free communication under these conditions but a substantial amount of adsorbed gas in micropores developed by the leaching. These pores may permit some gas flow at low pressures even at room temperature. Here again though, there is no substantial change in gross volume integrity since bulk density remains what it was before heat and vacuum treatment.

The report on this work, as submitted by the National Research Corporation, is given in its entirety in Appendix I

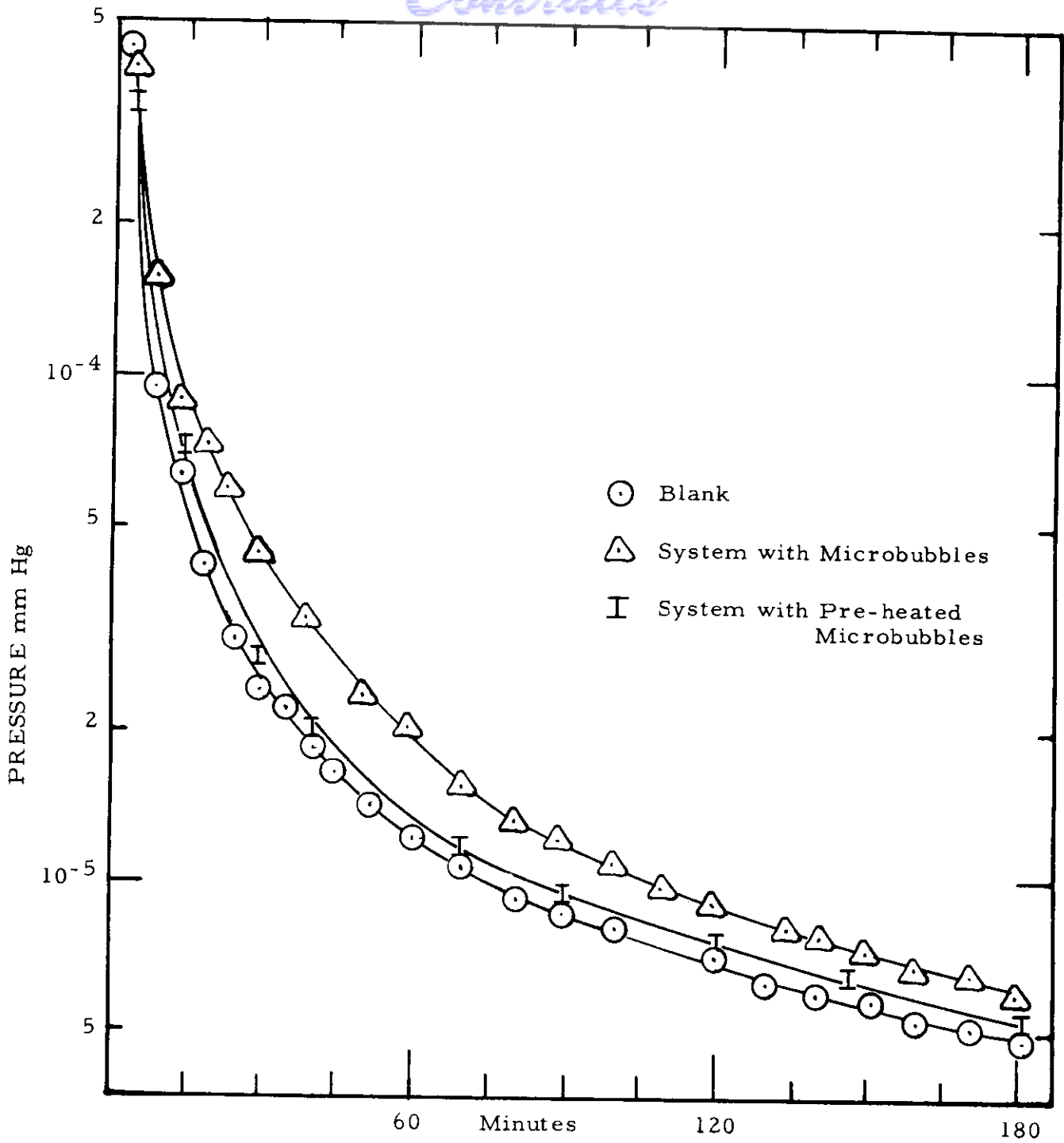


FIG. 8 EXPOSURE TO VACUUM OF 18% Na<sub>2</sub>O SILICA MICROBUBBLES

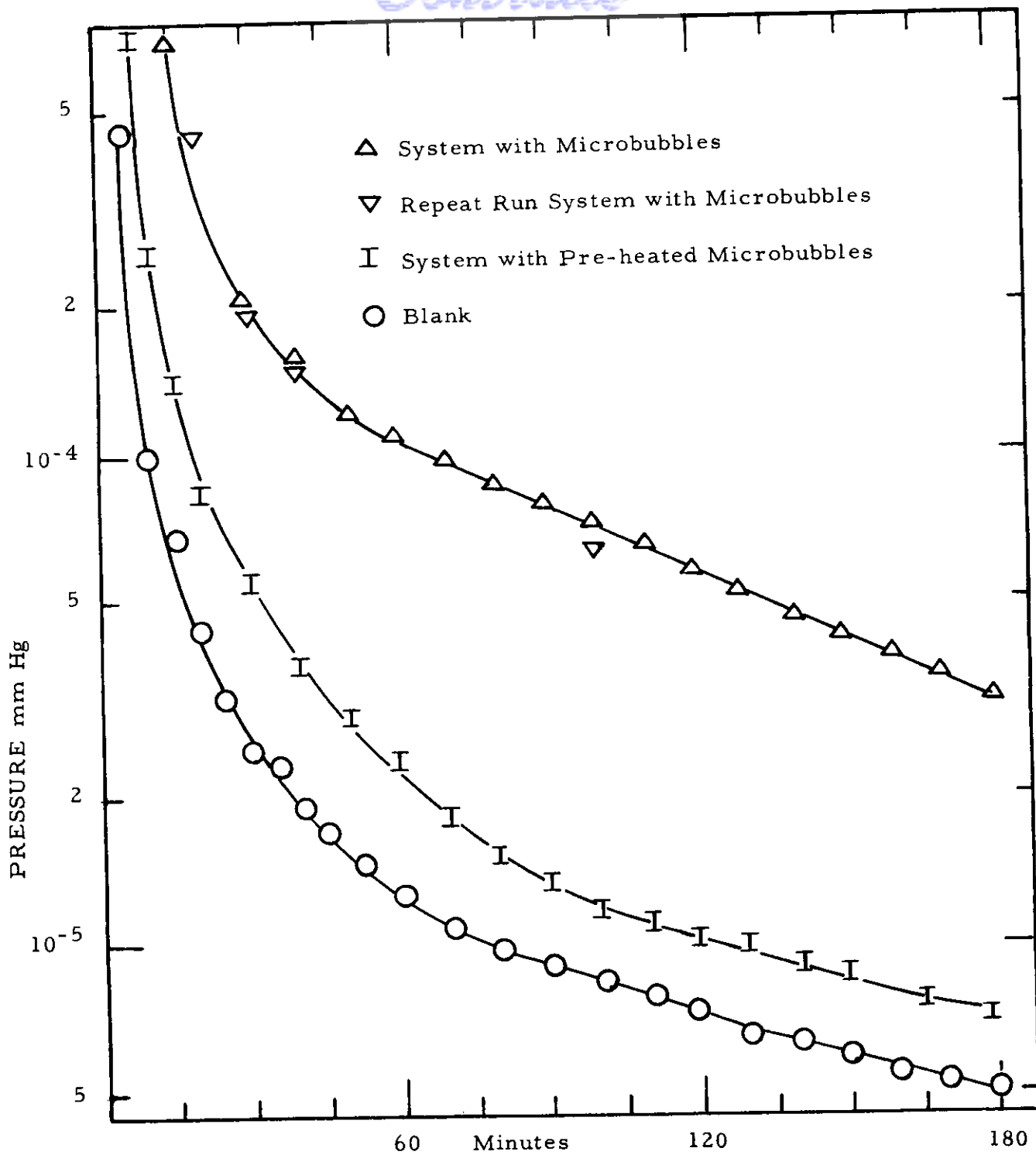


FIG. 9 EXPOSURE TO VACUUM OF 4% Na<sub>2</sub>O SILICA MICROBUBBLES

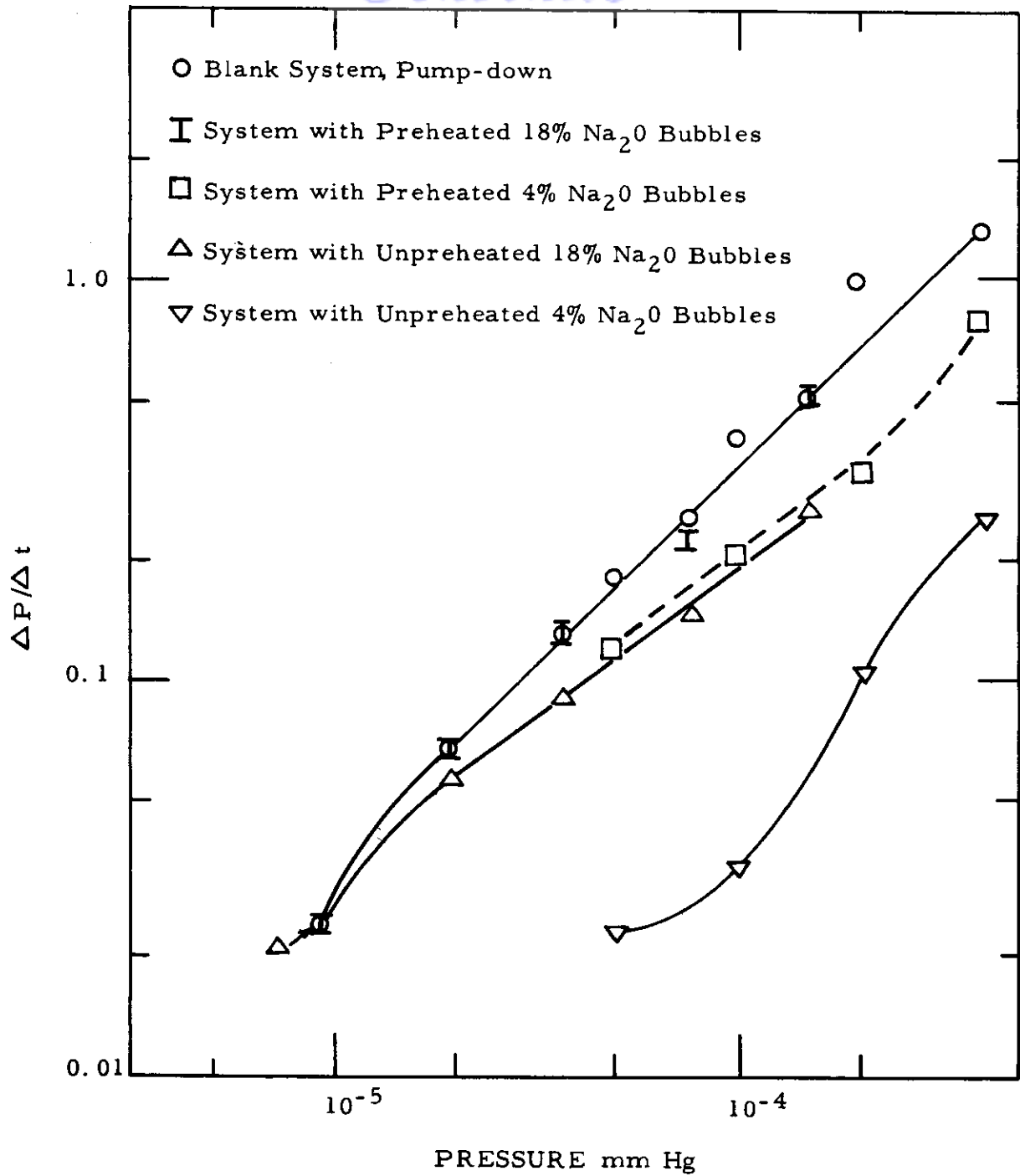


FIG. 10 PRESSURE DROP RATE ON MICROBUBBLES UNDER VARIOUS CONDITIONS

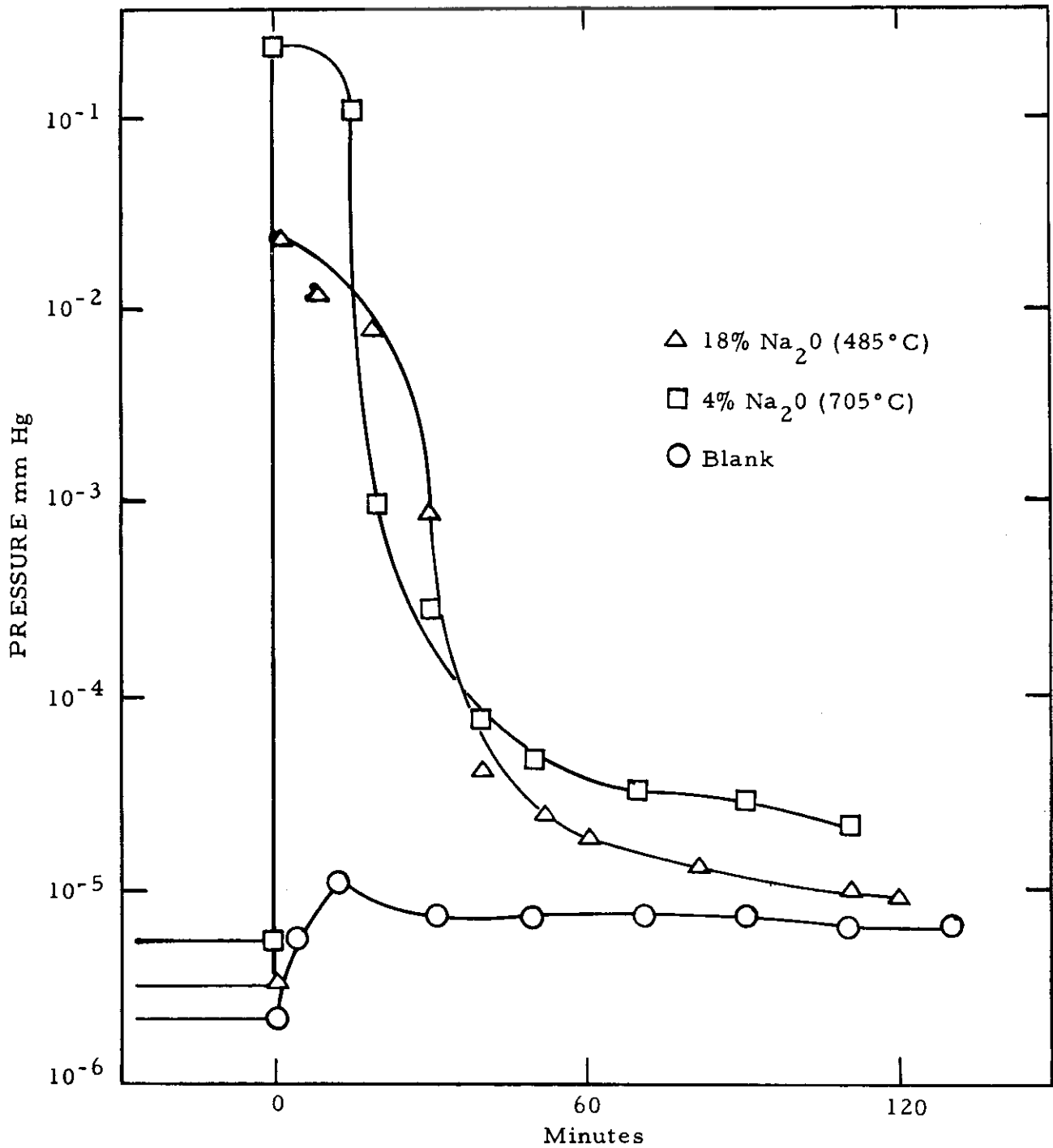


FIG. 11 EXPOSURE TO VACUUM AND HEAT OF SILICA MICROBUBBLES

## IV. FABRICATION OF MICROBUBBLES INTO STRUCTURAL SHAPES

### A. USE OF COLD SET BONDS

Because of the simplicity of the technique, exploratory experiments with cold set cementing techniques, using materials which would not degrade the desirable electrical and high temperature properties of the microbubbles were undertaken. Numerous commercial cold set cements were tried. In general, these had to be used in such quantity to get any sort of bond that density of the fabricated pieces was excessive. In all cases, the set obtained at room temperature failed on heating to much over 300°C. We suspect that this was due to chemical interaction of the bond with the tremendous surface of silica presented by the bubbles.

On this premise, bonding primarily by means of colloidal silica sol was undertaken. Only very weak bonds were obtained using either hydrolyzed ethyl silicate or 30% colloidal silica sol. Rate of gelation of the silica was never controlled adequately, although wide ranges of curing temperatures and humidity and several buffers to control gelation rate were tried. Typical results of these experiments are shown in Table 15.

### B. BONDING BY SOLUTION SINTERING

Bonding by sintering has the inherent advantage of retaining the chemical composition of the microbubbles themselves in the fabricated shape, and consequently the desirable electrical properties. This technique is in commercial use on regular Eccospheres to make a homogeneous, low density block, Eccofoam LM 43A. In this technique, a small amount, usually less than 5%, of water is mixed with the Eccospheres and the mixture subjected to heat (150°C) and pressure (20 to 40 lb./in.<sup>2</sup>) in a closed mold. This temperature is far below the softening point of the Eccospheres so presumably the water present causes some solution at the elevated temperature and consolidation of the bubbles.

It was found that the acid leached Eccospheres (4 to 6% Na<sub>2</sub>O) could be bonded similarly by using higher temperatures (210 - 240°C).

Typical properties of blocks made from 6% Na<sub>2</sub>O acid leached Eccospheres are: density 0.20 g/cc, breaking strength 122 psi, 51 volume percent porosity, retains 80% of room temperature load bearing capacities at 1100°C.

### C. BONDING BY FUSION SINTERING

Bonding by sintering at the softening point of the

TABLE 15  
FABRICATION OF MICROBUBBLES  
BY COLD SET CEMENT BONDS

No.	Composition			Cure				Lin. Shr. %	Density
	Micro-bubble Type <sup>(a)</sup>	Bond Type <sup>(a)</sup>	%	hrs. / °C					
1	R	16% HES	63	24/RT	16/110	2/150	1/1090	50	
2	AL	Same	72		Same				
3	WF	Same	80		Same			25	
4	R	30% SiO <sub>2</sub> "Synar" <sub>2</sub>	59		Same			<5	
5	AL	Same	68		Same			<5	
6	WF	Same	75		Same			<5	0.50
7	AL	Same	70		Same				
8	WF	Same	72		Same				0.43
22	AL	16% HES	75		RT only				
31	DAL	H <sub>2</sub> O	29		1/10 psi steam				
32	DAL	H <sub>2</sub> O	25		1/10 psi steam				
33	DAL	H <sub>2</sub> O	16		1/10 psi steam	1/1100		0	
34	DAL	H <sub>2</sub> O	16		2/10 psi steam	1/1100		0	
35	DAL	H <sub>2</sub> O	9		2/10 psi steam	1/1100		0	
36	DAL	H <sub>2</sub> O	0		2/10 psi steam	1/1100		25	
39	DAL	Bentonite	5		72/65	1/1100			0.32
47		Al. Phosphate	43		3 wks. RT	1/1100		6	0.33

R = regular production Eccospheres  
 HES = hydrolyzed Et SiO<sub>4</sub>  
 HES samples set more rapidly than Synar #1 - 6  
 1" h. 1.75" Ø  
 Acid Leached. Cracks throughout  
 Water Floated. Cracks throughout  
 Cracks after firing.  
 Best of 4, 5, 6. Cracks after firing.  
 Cracks after firing. Shattered in drying  
 7 x 7 x 1.6" block  
 Cracked in firing. 7 x 7 x 1.6" block  
 #9 - #20, similar data on Dri-film treated ES, omitted  
 Set very rapidly, warped and crumbled. Bond very poor.  
 #22 - #30 attempts to modify set of HES with H<sub>2</sub>O and buffers. Bonds of all too weak to be useful.  
 Double acid leached collapsed during steaming  
 Cracked up during drying. Very weak bond.  
 Weak bond. Cracked in firing.  
 Weak bond. Powdery texture.  
 Weak bond. Powdery texture. Firmer than 33 - 35  
 Held together surface cracks. (41 - 46 alkophos bonds 21 - 7% Al<sub>5</sub>H<sub>12</sub> (PO<sub>4</sub>)<sub>9</sub> Crumbled, very weak bond. Surface drying cracks.)  
 (48 - 63 various drying treatments, humidity, etc. Bond always weak and cracked)

(a) See notes at right.



# Contrails

microbubbles was investigated also. In this technique, no water was used. Heat and pressure are applied simultaneously. Typically, a 5" x 5" x 2" deep (inside dimensions) alloy steel mold was set up with follower plates allowing 1" vertical travel. This was filled with the material to be sintered, compacted lightly, about 20 lb./in.<sup>2</sup>, and heated up to pressing temperature over a five hour period. After holding at pressing temperature at least an hour, pressure was applied sufficient to get 50% compression to give a block 5" x 5" x 1". It was found that pressures much in excess of 150 lb./in.<sup>2</sup> simply crushed the microbubbles. Consequently, pressing temperatures high enough to permit compression with about 80 lb./in.<sup>2</sup> were aimed at. After pressing the mold and piece were allowed to cool in the furnace to minimize stresses.

To develop a suitable technique, most of this work was done with the regular Eccospheres (18% Na<sub>2</sub>O) that soften about 525°C. Below 590°C pressing temperature, the bond was very weak, and the surface soft and powdery. (Table 16 - - A, F, G). Texturally, the bubbles were barely tangent to each other. At 675°C, some bubble consolidation had occurred. Bubble surfaces had flowed together so that there were fillets of glass between the bubbles. Some bubble consolidation had taken place to make larger bubbles of 0.2 to 0.5 mm diameter, having continuous glass walls with the microbubbles trapped in the wall. This condition usually had the best combination of minimum shrinkage, minimum porosity and maximum strength. (Table 16 - - D and E). At a pressing temperature of 820°C, it appeared that too much fusion and bubble consolidation had occurred. Irregular voids as large as 5 to 8 mm were present and the resulting stress concentrations had caused numerous cracks and high porosity. (Table 16 - - B).

Two attempts were made to do this with acid leached 7% Na<sub>2</sub>O microbubbles. We attempted to heat and press at 900°C and 1350°C but got only a very poor bond typical of underheating. Incipient failure of the alloy steel mold prevented using the higher temperatures apparently necessary.

Experiments were made in which inorganic fibers - pyrex glass wool, fiberfrax (Carborundum Company's aluminum silicate staple fiber), asbestos, as well as glass fabric were laid between layers of bubbles. With the exception of the glass wool, Table 16 - - J, enhancement of strength was not obtained, partly because bonding to the fiber was poor and partly because some of the fibers, particularly the glass cloth and the asbestos became brittle.

If this tensile reinforcement of bonded microsphere blocks can be worked out, we have the possibility of a relatively strong

TABLE 16  
FABRICATION OF MICROBUBBLES  
BY SINTER BONDING

Micro-bubble Type	Firing			Shrink-age, linear, %	Appearance	Density g/cc	Apparent Porosity Vol. %	MR <sup>(c)</sup> psi
	Preheat hrs. / °C	Final hrs. / °C	Cooling hrs. to 100°C					
A R <sup>(a)</sup>	--	3/510	5	--	Bond weak. Surface powdery.	0.40	--	--
B R	--	2/820	6	35	Stuck to mold. Some 3-8 mm bubbles.	0.44	19	64
C R	--	2/675	5	<5	Brittle, little bubble consolidation.	0.55	38	720
D	--	1/675	5	17	Central cavity. Brittle. Numerous 0.2 - 0.5 mm bubbles, completely separated by intact micro-bubble walls.	0.59	3.2	940
E R	16/480	2/675	5	<5	No central cavity. Large shrinkage crack. Texture like (D).	0.64	4.6	840
F	--	2/590	5	<5	Soft powdery surface.	0.59	23.	520
G	--	4/590	5	<5	Surface harder than (F)	0.58	28.	560
H AL <sup>(b)</sup>	--	2/820	6	<5	Powdery surface	0.32	67.	310
I AL	6/540	4/900	7	--	Blew out of mold. Not pressed. Soft and powdery.	0.19	31.	117
J R - Glass wool	--	3/650	5	10	12 thin mats pyrex glass wool with ES between them. Rigid hard structure.	0.65	6.6	940
O R	--	1/650	5	<5	18 layers fine, 5 layers coarse. ES between them. Cracked along cloth layers.	0.61	55	150
P R	--	1/650	5	<5	6 layers fine, 1 layer coarse glass cloth. ES between. Cloth lost strength, became brittle as did (O)	0.58	54	229
T R	--	1/675	5	<5	Fiberflex (Carborundum Co.) Aluminum silicate staple 10% in 8 layers.	0.50	49	250
U R	--	1/675	5	<5	Acid washed asbestos staple 7% in 9 layers.	0.53	54	290

(a) Regular Eccospheres 18% Na<sub>2</sub>O  
 (b) Acid Leached Eccospheres 7% Na<sub>2</sub>O  
 (c) Modulus of Rupture 60% tension

resilient high temperature service structure with very desirable dielectric properties at microwave frequencies.

Resilience is a property conspicuously lacking in nearly all electrically non-conducting materials capable of service at high temperatures. This lack of resilience in ceramic structures creates major problems in minimizing stress concentrations. The microsphere itself is inherently resilient and properly bonded should confer a measure of this resilience to a structure in which it is used as a filler. To get some measure of this resilience, compressive strength and modulus was determined on specimens D, I and U of Table 16.

TABLE 17

PHYSICAL PROPERTIES OF BLOCKS FABRICATED FROM MICROSPHERES

No.	Type	Dens. g/cc	Ap. Por. Vol. %	Breaking Strength <sup>(a)</sup> psi	Compressive	
					Strength psi	Modulus psi
D	Reg. Eccospheres	0.60	3.2	900	2200, 2350	733000, 733000
I	Acid Leached Eccospheres	0.19	31.	100	Broke, 41	Broke, 232000
U	R. Eccospheres & Asbestos	0.56	54.	500	1580, 1530	766000, 598000

(a) 60% tension

These strength values are in the same range as those of other low density filler structures, such as polyester bonded glass cloth honeycomb and could be expected, if suitably reinforced tensile-wise, to be capable of fulfilling a similar function at much higher temperatures than are possible with any of the organic plastic bonded materials.

D. CHEMICAL IMPROVEMENT OF STRUCTURES MADE FROM REGULAR ECCOSPHERES

Acid leaching similar to that used on the Eccospheres themselves was applied to blocks fabricated from Eccospheres (18% Na<sub>2</sub>O) by the solution sintering method described in Section B. Leaching of pieces 3/4" thick in 16% H<sub>2</sub>SO<sub>4</sub> for 6 days with agitation twice daily was followed by thorough washing with water and slow, 45°C, drying. These blocks had a density of 0.24 g/cc, 48% volume percent apparent porosity, a breaking strength of 260 psi, and retained their load carrying capability to 900°C, compared to the 500°C of the unleached material.

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CONCLUSIONS

Acid leaching effectively decreases the alkali content of the standard 18% Na<sub>2</sub>O microbubble to 5% to 6% with concurrent increase in hot loading limit from 500°C to 900°C, marked decrease in hygroscopicity and substantial decrease in density. This is true for both the bulk microbubble and structures fabricated from it. This is probably the least expensive way to get substantial increase in temperature capabilities of the product, but of course this is far from the properties of pure silica.

The production of microbubbles from pure silica feed stock in a direct high temperature fusion and blowing process has been demonstrated in very little pilot plant operating time. This process and product can be greatly improved with adequate pilot plant development.



APPENDIX I

NATIONAL RESEARCH CORPORATION

Cambridge, Massachusetts

VACUUM EXPOSURE OF ECCOSPHERES

A. W. WINSTON

## VACUUM EXPOSURE OF ECCOSPHERES

### Introduction

At the request of Mr. J. Wm. Lefforge of Emerson & Cuming, Inc., Project 43-4-127 was initiated to test the behavior in vacuum of uncoated Eccospheres L (4% Na<sub>2</sub>O grade) and Eccospheres R (18% Na<sub>2</sub>O grade). Eccospheres are hollow glass microspheres with a particle size distribution ranging from about 30 to 300 microns. In order to remain within the funds available, not all the tests originally scheduled were performed; some time was lost in testing incorrect material supplied in error, and time was spent verifying a difference in the behavior of the two grades of Eccospheres. However, the tests performed provide an adequate indication of the behavior of the material upon exposure to vacuum.

### Tests Performed

The Eccospheres were exposed to vacuum in National Research Corporation's Materials Testing Chamber. Briefly, the Testing Chamber consists of a water-cooled steel chamber (104 liters in volume) mounted on a base plate. The chamber is connected through a slide valve to a diffusion pump - mechanical pump system. The pressure in the chamber is measured by a thermocouple gauge and by an ionization gauge. Electrical feedthroughs into the chamber provide means for heating materials placed in the chamber. The temperature of the material is monitored by three thermocouples. Sight ports permit visual observation inside of the chamber.

The following tests were performed on grades R and L Eccospheres:

- a. Exposure of Eccospheres at room temperature to vacuum with a measure of the pump-down curve (pressure versus pumping time) and a comparison of the pump-down curve with that of the empty system.
- b. Exposure of Eccospheres as in "a" above but preceded by heating in air at 300° F for 75 minutes.
- c. Exposure of Eccospheres at elevated temperature to vacuum in the range 10<sup>-5</sup> to 10<sup>-6</sup> mm Hg. For grade R material, the temperature was 900° F; for grade L material, the temperature was 1300° F. The materials were preheated as in "b".

Testing and storage of the Eccospheres was carried out in an air-conditioned laboratory. The materials were stored in the polyethylene bags

and metal cans in which they were shipped; the containers were opened only when necessary. For those tests in which the material was preheated, the material was transferred rapidly while hot to the vacuum system. For these tests made at high temperature, the materials were preheated and then exposed to an environmental vacuum of  $2-5 \times 10^{-6}$  mm Hg for a period of 12 hours before the heating in vacuum was commenced. Heating was continued for 2 hours.

110 cc samples of Eccospheres were used. For grade L, this corresponded to a sample weight of 17.78 grams and for grade R to a weight of 29.87 grams.

## Results

The pump-down curves obtained are shown in the attached figures. Figure 9 applies to grade L Eccospheres and Figure 8 to grade R Eccospheres upon their exposure to vacuum. Figure 11 shows the effect of heating both grade L and R Eccospheres in vacuum to high temperature (L - 1300°F, R - 900°F). Each figure includes a "system blank" plot, i. e. a pump-down curve for the empty chamber, to be used for comparison.

## Discussion of Results

Grade L Eccospheres exhibit more outgassing than do those of grade R as shown by the slower pump-down curve obtained for them. A repeat test, (also shown in Figure 9) has verified this fact. Based on data supplied by Wm. Lefforge, a calculation was made of the approximate surface area of the samples tested. The surface area is approximately 25,000 cm<sup>2</sup> for grade L and 26,000 cm<sup>2</sup> for grade R; to all intents and purposes to the degree of approximation used, the surface areas are equal. It appears that there is some surface film (water?) on the L material to a greater extent than on the R. The difference in the behavior of the two materials will depend on their histories prior to receipt and testing as well as on the surface areas involved. Spherical smooth surfaces were assumed in estimating areas; it may be that the surface contains small channels adding to the surface area estimated.

Preheating the samples definitely reduces the outgassing observed, presumably by removing the surface film. The reduction is greater in the case of the L material. After preheating, the two grades of materials do not differ too greatly in their outgassing characteristics from one another.

Estimates may be made of the outgassing rates as follows. The time it required for the pressure to fall from  $p_1$  to  $p_2$  in a system being

pumped is given approximately by

$$t = \frac{V}{S} \ln\left(\frac{P_1}{P_2}\right)$$

where  $V$  is the volume of the system and  $S$  is the effective pumping speed of the system.

The effective pumping speed of the system is determined by the speed ( $S_p$ ) of the pump (including baffles, apertures, etc.), the rate of outgassing ( $S_c$ ) of the walls of the chamber, and outgassing from whatever other material is present in the chamber ( $G_p$ ). Thus

$$\begin{aligned} S &= S_p - S_c - G_p \\ &= S_B - G_p \end{aligned}$$

Here  $S_B$  may be determined from the pump-down curve of the empty system.  $S$  may be determined from the pump-down curve with the Eccospheres present. Consequently  $G_p$  may be determined. Since the pumping speeds are functions of pressure, the same pressure interval must be considered. Thus

$$G_p = V \ln\left(\frac{P_1}{P_2}\right) \left( \frac{1}{t_B} - \frac{1}{t} \right)$$

where  $t_B$  is the time interval for the empty system and  $t$  is the time interval for the system containing powder.

The calculated outgassing rates are shown in Table I. The outgassing rates are actually low when considered on an area basis; however, the surface area is extremely large for a given volume of material.

The result of heating the Eccospheres in vacuum is shown in Figure 11. A relatively large amount of gas is initially produced. Following this, the pump-down is similar to that for the preheated Eccospheres that have not been exposed to high temperature. This leads to the conclusion that a large amount of gas is produced or liberated almost immediately upon application of the heat but that not much is subsequently produced. An estimate of the amount of gas produced may be made by assuming (quite fairly) that a given quantity of gas has been suddenly released into a previously well-evacuated system. The pressure consequently rises and the amount of gas is given by the volume of the system and the resultant pressure. For grade L, this leads to 26,000 micron liters of gas and for grade R to 3000 micron liters.



## *Contrails*

It is interesting to consider the volume that would be occupied by this gas at atmospheric pressure ( $760 \times 10^3$  micron liters is equivalent to 1 liter at standard conditions). For grade L, it is 35 cc and for grade R, it is 4 cc. These values are of the order of magnitude of the internal volume of the Eccospheres; together with the abrupt rise observed when the temperature is sharply elevated, this strongly suggests that the Eccospheres have been ruptured, permitting the escape of contained gas. A quick examination under a microscope failed to reveal rupturing. A sample of the material is being returned to Emerson & Cuming, Inc. to permit their further examination.

ESTIMATE OF OUTGASSING RATE OF ECCOSPHERES

Grade L    Volume of sample used = 110 cc  
              Weight of sample used = 17.78 gm<sup>2</sup>  
              Estimated surface area = 25,000 cm<sup>2</sup>

Pressure mm Hg	Outgassing Rate liters/min. at indicated pressure	
	Not Preheated	Preheated
$1 \times 10^{-4}$	15	9.3
$5 \times 10^{-5}$	4.8	1.3
$1 \times 10^{-5}$	-	0.3

Grade R    Volume of sample used = 110 cc  
              Weight of sample used = 29.87 gm<sup>2</sup>  
              Estimated surface area = 26,000 cm<sup>2</sup>

Pressure mm Hg	Outgassing Rate liters/min. at indicated pressure	
	Not Preheated	Preheated
$1 \times 10^{-4}$	8.7	7.5
$5 \times 10^{-5}$	3.0	2.6
$1 \times 10^{-5}$	0.07	0.02

SPECIAL METHODS

A. Density determination of microbubbles

1. Bulk density is determined by filling a standard 250 ml. laboratory graduate, 3.5 cm. inside diameter, 350 cm. high, and vibrating to a constant volume. The material is weighed and weight divided by the volume read gives bulk density in grams per cubic centimeter (g/cc). The vibration to constant volume is effected by holding the filled graduate upright on a Syntron shaking table operated at maximum amplitude for one minute. The volume is checked and is followed by vibration for another minute. This vibration and volume reading is repeated until the volume remains constant for two successive readings. Ordinarily this volume does not change after the first minute of vibration. This method serves as a routine control procedure.

2. True density by gas displacement

The actual displacement volume of the microbubbles is a better measure of their quality than is the bulk density. Uniform and reproducible packing is difficult to attain and spheres may have cracks or holes which would not affect the bulk density but would increase the true displacement volume of the product. Liquids of course may be used to measure the displacement, but a lower viscosity fluid - air - provides better assurance that even the tiniest flaws permitting communication to the interior of the bubble are detected.

The method used is an unpublished modification of a standard (1, 2) volumetric determination by gas displacement developed by R. W. Burhans and R. D. Croft of the Chemical and Physical Research Division of the Standard Oil Company (Ohio).

A dry powdered material is introduced into a flask and burette system which has been previously calibrated so that the total volume is known when empty. A barometer tube and mercury level bulb assembly is used to change the pressure and volume of the system to new values. Knowing the original volume of the system, the atmospheric pressure, and the change in pressure and volume as determined by the difference in levels of the mercury columns in the barometer tube and burette, the volume of the system containing the solid material can be

1. Reilly and Rae, Physico-Chemical Methods Vol. 1 pages 471-472
2. Francis and Oxnard, Ind. & Eng. Chem., Anal. 1 169 (1929)

calculated easily by Boyle's Law. This new volume calculation subtracted from the original volume calibration then gives directly the volume of the solid sample introduced into the system. From the weight of the sample, its density can be readily calculated.

## Apparatus

A detailed drawing of the apparatus is shown in Figure 12. The apparatus was mounted on a wooden board 49" x 6" x 3/4", with notches cut as shown to facilitate manipulation of the removable flask and stopcock. A calibrated 25 ml. pipet was introduced into the capillary tube to obtain a section in the system of known volume. The lower end of the pipet was attached to a bent all-glass T system containing a long straight barometer tube bent over and left open at its upper end. A meter stick was mounted vertically next to the barometer tube. A 29/15 male ball joint was attached directly to the stopcock and bent T system so that a 100 ml. flask containing a female 28/15 ground joint can be clamped securely in place. A piece of 1/4" vacuum tubing 4 feet long was attached to the lower end of the system and to a mercury level bulb. The entire apparatus was mounted vertically on a long ring stand by means of two clamps at the upper and lower ends of the board. The mercury level bulb was fitted to a leveling device traveling along the length of the rod of this ring stand behind the mounting board.

## Operation

The 100 ml. flask empty is clamped securely in place after thoroughly greasing the 28/15 ball and socket joint to prevent leaks. With the capillary stopcock left open to the atmosphere the mercury is leveled by means of the mercury level bulb to the bottom mark on the calibrated pipet. The capillary stopcock is now closed and the mercury level raised to the mark above the calibrated pipet. The new mercury levels are then recorded. The pressure increase is determined by subtracting the lower reading above the pipet from the upper reading of the barometer tube. With these measurements the volume can now be calculated. Similarly the volume can be calculated by manipulating the apparatus in exactly the same way when a known weight of material is introduced into the 100 ml. flask. The flask should be filled to the neck with sample for best accuracy.

After taking these measurements the mercury bulb should be returned to the original starting point and the mercury level in the pipet tube carefully set at the original starting level. The stopcock is then opened again. Any change noted in the level in the pipet tube at this point will then indicate a leak which will invalidate the measurements. For best accuracy three to five sets of measurements are taken on a given sample or calibration in calculating the final volume, but the method is sufficiently precise that one reading will give good approximations for rapid work.

## Calculations

The volume of the system is calculated from the following formula:

$$V = \frac{V_2(A + P_2)}{P_2}$$

- where,  $\underline{V}$  = volume of system from lowest pipet reading including the 100 flask and capillary tubing.
- $\underline{V_2}$  = volume change of system as known from calibration of pipet
- $\underline{A}$  = atmospheric pressure
- $\underline{P_2}$  = pressure change in system as indicated by mercury level difference between barometer tube and pipet tube.

At constant temperature, Boyle's Law states that the product of the pressure and volume of a closed system is constant. Therefore:

$$AV = (A + P_2)(V - V_2)$$

$$AV = AV - AV_2 + P_2V - P_2V_2$$

$$AV_2 + P_2V_2 = P_2V$$

$$\frac{V_2(A + P_2)}{P_2} = V$$

Figure 13 serves to illustrate the symbols used.

Comparison of several hundred bulk - and true - density values on microspheres as produced -250 to +10 micron diameter and screen partials of these showed that the true density was nearly always 1.6 times the bulk density. The voids volume in close packed uniform diameter spheres is 42%. This ratio of 1.0 to 1.6 corresponds to a voids volume of 38%, indicating that very few of the spheres have flaws permitting easy flow of gas through their walls.

B. Normalization of dielectric data by means of the Lichtenecker formula.

An empirical relationship between dielectric constant of structures at microwave frequencies and volume fraction of loading (higher dielectric constant material) has been established for air-polystyrene and polystyrene titania. In both cases it was found that the log of the dielectric constant was a simple linear

function of the volume fraction of the loading material, in the one case polystyrene, in the other case, titania. (3)

If (K) is the dielectric constant of the loaded matrix, (a) is a constant proportional to the logarithm of the dielectric constant of the low dielectric constant material; (b) is a similar constant for the loading material in massive form and (x) is the volume fraction of loading material in the matrix.

$$\log K = a + bx$$

For use with these microbubbles, the "matrix" is air, dielectric constant 1.0, and the loading material silica with a density of 2.6 g/cc. Volume fraction of silica is therefore measured density (D) divided by 2.6 or  $x = D/2.6$ . The equation thus becomes:

$$\log K = 1 + bD/2.6$$

When the dielectric constants were plotted in this manner using volume percent solids as determined by density as measured rather than volume fraction of solids, straight line plot resulted for similar compositions having different densities, with other compositions deviating from this line. We thus appeared to have a means for eliminating the effect of density and determining the effect on dielectric constant of changes in composition.

A similar plot of loss tangent data as a function volume percent solids gave much better correlation when the loss tangent rather than log of the loss tangent was used. In this case the effect of minimal impurities on loss tangent, in spite of increased density of the product, was quite striking.

### C. Method of dielectric measurements.

Dielectric measurements made at x-band (8.6 kmc) frequency are by means of a waveguide short-circuit-open-circuit method. Instrumentation is the Microwave Dielectrometer, manufactured by Central Research Laboratories, Inc., of Red Wing, Minnesota. Samples are ordinarily one inch diameter discs 0.750 inches thick. In the case of powders such as these microbubbles, a container cup of fixed volume is filled and compacted by vibration before measurement. The measured material is then transferred quantitatively and weighed to determine the density of the material as measured. The instrument functions with

3. Cody, W. M., Karelitz, M. B. & Turner, L. A. Radar Scanners and Radomes Radiation Laboratory Series, Volume 26, Section 13, pages 408-413 McGraw Hill Book Company, Inc. 1948

# *Contrails*

standing waves in a slotted wave guide as described by Roberts and Von Hippel. (4) Details of technique and calculations are those of the Laboratory for Insulation Research at the Massachusetts Institute of Technology. (5)

4. Roberts and Von Hippel Journ. App. Physics 17 610-616 July 1946
5. Westphal, W. B., Technical Report 36 July 1950

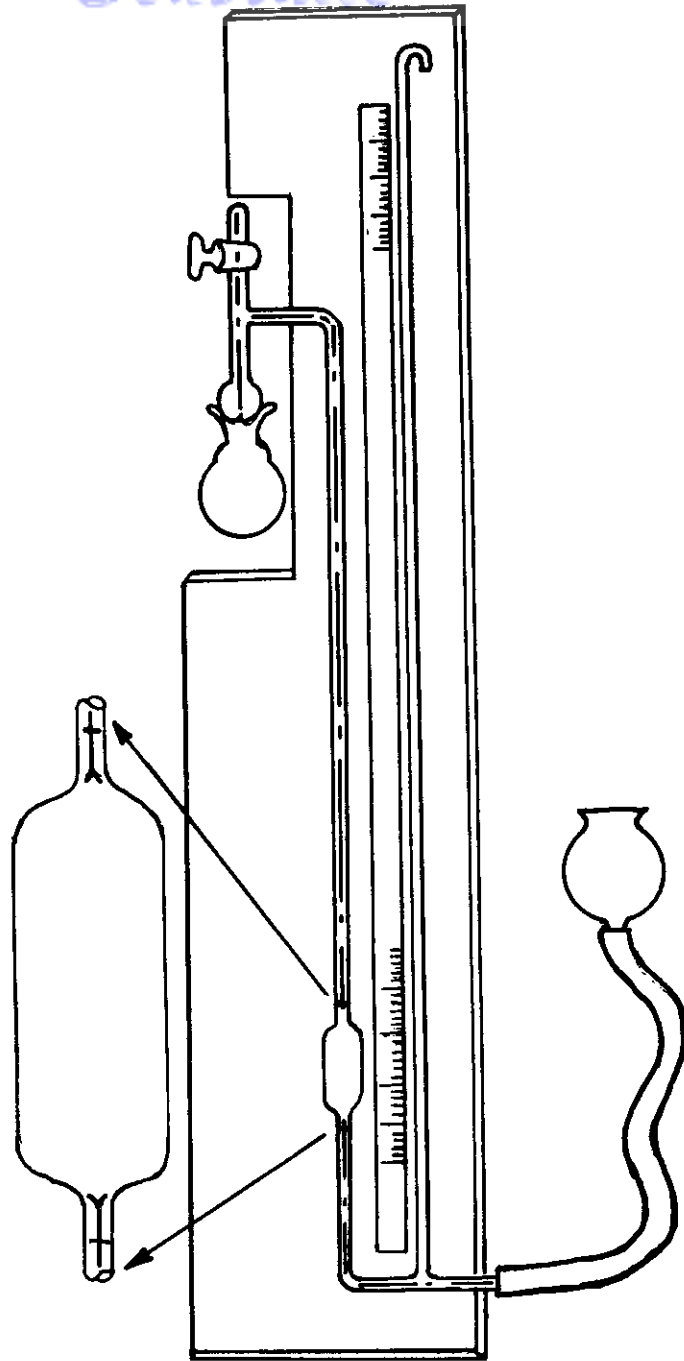


FIG. 12 TRUE DENSITY APPARATUS



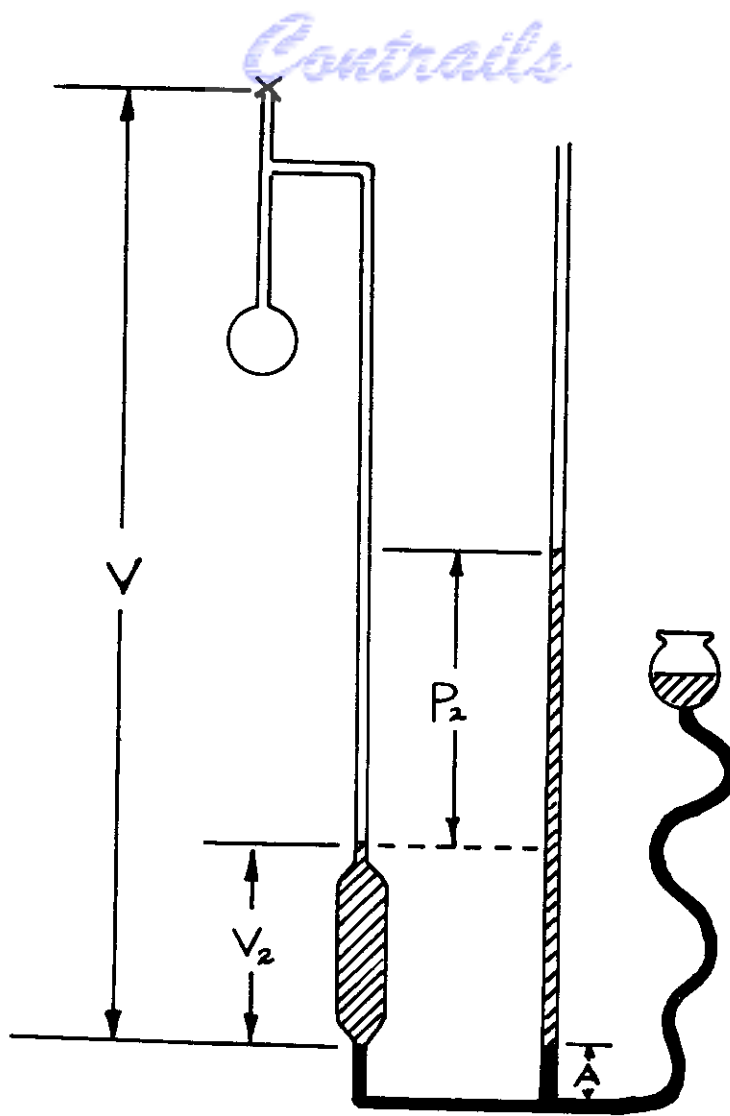


FIG. 13 TRUE DENSITY APPARATUS - SCHEMATIC

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