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RIGIDIFIED FIBROUS SILICA
THERMAL INSULATION

Z. L. Ardary
D. H. Sturgis

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NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

operated for the ATOMIC ENERGY COMMISSION under U. S. GOVERNMENT Contract W-7405 eng 26

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Oak Ridge Y-12 Plant

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ABSTRACT

Low-density, low-thermal-conductivity thermal insulation materials have been developed that have sufficient mechanical integrity to permit fabrication by routine machining techniques.

Specific interest was in a silica-bonded silica fiber material having a density near 10 pcf and which exhibited coefficient of thermal conductivity values of less than 0.4 Btu-in/hr-°F-ft² at approximately 1,000° F.

CONTENTS

SUMMARY	5
INTRODUCTION	6
SILICA THERMAL INSULATION	7
Insulator Preparation	7
Pulp-Molded, Silica-Bonded Insulators	7
Compression-Molded Insulators	9
Future Plans	10
REFERENCES	12

SUMMARY

Two general types of insulators have been studied. One group consisted of pulp-molded, fused silica fibers (Micro-Quartz), either self bonded or bonded with silica derived from ethyl silicate or various forms of colloidal silica. The other type of insulation contained a compression-molded, ultrafine, fused silica powder reinforced with a small fiber content. Densities ranged from 8 to 15 pcf for the pulp-molded insulators and from 30 to 40 pcf for the compression-molded compositions.

Thermal-conductivity values for several of these insulators in argon have been determined. Pulp-molded insulators were found to have thermal conductivities similar to Palarite and carbon fiber insulation (ie, 0.3 to 0.4 Btu-in/hr-° F-ft² at 1,000° F); compression-molded parts showed somewhat higher values—0.6 to 1.1 Btu-in/hr-° F-ft² at 1,000° F.

INTRODUCTION

High-temperature thermal insulators have been developed at the Oak Ridge Y-12 Plant^(a) which are fibrous materials that have been rigidified by the effective utilization of bonding agents. These materials essentially retain the low density and low thermal conductivity of refractory fibrous insulation while providing the convenience, fabricability, and structural properties of porous solid insulations.⁽¹⁾ The first material of this type was comprised of relatively pure 0.5-micron silica fibers bonded with carbon derived from gelatinized starch and has been referred to as "Palarite". Typically, this material had a density of 9 pcf and a coefficient of thermal conductivity of 0.4 Btu-in/hr-°F-ft² at 1,000° F. A rather wide range of mechanical properties were derived by making minor tradeoffs in density and thermal conductivity.

While Palarite and a more recently developed analogous material substituting carbon fibers for silica have proved to be excellent thermal insulators in inert gas and vacuum environments, a serious limitation has been that in oxidizing environments the carbon begins to be attacked above 500° F.

The value of an insulation comprised of materials compatible with an oxidizing environment is apparent. Not only are there broader applications for the material, but processing would be simplified in that furnacing can be accomplished without the necessity for maintaining an inert or reducing atmosphere.

Three approaches were used in considering the fabrication of an insulator which could be processed and utilized in air:

1. A sintered, pulp-molded body consisting of fused silica fibers (Micro-Quartz), self-bonded with the aid of minor fluxing ingredients.
2. Pulp-molded, fused silica fiber insulators bonded with an ethyl silicate or colloidal silica gel which, on firing, would decompose into a strong resilient bond.
3. A compression-molded body with a higher bulk density than pulp-molded insulation, but with particulates sized to minimize heat transfer by gas conduction.

(a) Operated for the US Atomic Energy Commission by the Union Carbide Corporation—Nuclear Division.

SILICA THERMAL INSULATION

INSULATOR PREPARATION

Pulp-Molded, Silica-Bonded Insulators

Pulp-molded Micro-Quartz fiber bodies were used as the basis for the self-bonded, sintered insulation work and also for the silica-bonded structures. Minor additions of opacifiers were considered necessary to replace the excellent infrared absorption characteristics of the carbon webs and fillets in starch-bonded Micro-Quartz, or carbon-fiber insulation. Titania was selected because of its excellent opacifying characteristics and because it also improved the sintering characteristics, as did minor additions of magnesium oxide. The addition would, of course, tend to reduce the deformation temperature of the insulator.

Ethyl silicate-bonded bodies were of similar composition, but relied largely on the excellent bonding properties of the gelled silica rather than sintering. Successful use of ethyl silicate requires that there be a proper preparation of the material. This work entails hydrolysis to produce silicic acid and ethyl alcohol in the following reaction: (2)

The silicic acid then dehydrates to an adhesive form of amorphous silica. This silicate is not miscible with water at room temperature, but requires the addition of an alcohol as a coupling agent. Hydrolyzed sols are readily converted to a rigid gel by the action of basic salts, oxides, or such basic gases as ammonia. Gelation of the binding solution is necessary to prevent migration of the binder to the surface of molded parts during their drying cycle.

Other colloidal silica binders have been evaluated, particularly those supplied by the Nalco Chemical Company. These colloidal silica sols (Nalcoag colloidal silica) are produced by the removal of sodium ions from sodium silicate using a patented ion-exchange technique, are sensitive to various salts and gases, and gel quite readily. Acid sols are available which readily gel in the presence of ammonia gas, thus making these sols suitable for use with the forming process shown in Figure 1.

A self-bonded and sintered pulp-molded Micro-Quartz fiber insulator containing five percent titania and one-half percent magnesium oxide as a sintering aid was successfully formed using conventional pulp-molding techniques. Firing shrinkage after one hour at 1,000° C was approximately seven percent linear, and the strength and machinability were acceptable for most applications. Dimensional stability of the insulator above 1,000° C is questionable due to the fluxing action of titania. Thermal conductivity was quite low, as seen in Figure 2 for ES-5 which has a K value of 0.475 Btu-in/hr-° F-ft² at 1,000° F. Scaleup of this composition to surfaces of resolution one foot in diameter (cones and cylinders) proved difficult, with poor sintering being experienced in this larger part.

Ethyl silicate-bonded Micro-Quartz fiber bodies were pulp molded without a starch binder, impregnated, and exposed to anhydrous ammonia gelation, as indicated on the schematic flow sheet given in Figure 1. This technique was thought to be the optimum, as a minimum of binder was added to the fibers and internal gelation effectively prevented possible binder

Figure 1. PROCESSING STEPS IN THE PRODUCTION OF ETHYL SILICATE-BONDED, PULP-MOLDED INSULATION.

migration problems. This technique could also be readily adapted to producing parts of any size.

Green strengths before and after curing were very good. The thermal conductivity, K , of one such insulator was determined, and is shown for ES-7 as a function of temperature in Figure 2. It is evident that the thermal conductivity of this material is comparable to that of Palarite and Y-12 carbon fiber insulation.

Fired bulk densities of these insulators range from 12 to 25 pcf, depending on the binder content, but could conceivably be made lower.

Nalcoag colloidal silica-bonded insulators were also studied. The main development effort was concerned with attempts to

Figure 2. THERMAL CONDUCTIVITY OF PULP-MOLDED MICRO-QUARTZ INSULATION WITH A SILICA BOND. (Argon Atmosphere)

optimize the gelation technique. One 12-inch base-diameter, frustum-shaped insulator was successfully formed using anhydrous ammonia gelation of an acidic sol. Firing temperatures in the 1,000° C range were utilized, and rapid firing cycles (<5 hrs) are feasible. After firing, machining was accomplished with single-point tooling with no difficulty.

Compression-Molded Insulators

Compression-molded insulators were formed using thermosetting silicone resin with a high silica yield as a binder. Polymers of chief concern in this investigation were those derived from the trichlorosilanes. Such polymers may be blended and crosslinked to produce three-dimensional resin structures through thermosetting. Condensation reactions are as shown in the following reaction: (3)

Only four molecules are represented in Reaction 2; whereas, in actual synthesis of such resins, a very large three-dimensional network is developed.

It should be noted that a catalyst is indicated in Reaction 2. Such catalysts are not always necessary; but, in general, they are used to speed the condensation reactions, thus making the process more economically feasible.

Catalysts used for hydroxyl condensation cures are usually selected from neutralized quaternary amines, primary amines, secondary amines, tertiary amines (triethanolamine, used in this investigation), metallic octoates of amphoteric metals (especially zinc, iron, cobalt, and manganese), and weak acid salts of such amphoteric metals as zinc.

Heating the resins, as was done in this investigation, caused decomposition of the silicone to a high-purity, amorphous silica by removing the methyl and hydroxide radicals, and water, as noted in Reaction 2.

Klerer⁽⁴⁾ reported that the gases evolved on heating an ethyl triethoxysilane polymer were water, hydrogen, ethanol, and propane. Gases evolved will depend on the resin that is pyrolyzed. Pyrolysis of General Electric's SR-350 silicone resin resulted in an amorphous silica residue, with a yield of 81 weight percent silica.

Filler materials were chiefly Cab-O-Sil, a very fine amorphous silica having a surface area of 175 to 200 m²/gm, eight to ten weight percent Micro-Quartz fibers for strength, and five to 15 weight percent titania to give infrared opacity to the insulator. The pressed insulation

was processed according to the cycle indicated on the flow sheet shown in Figure 3. Although this technique for putting together such a body is perhaps not the best, it was chosen for its convenience and adaptability to existing processing equipment. One of the biggest problems encountered was the uniform dispersion of the fibrous fused silica addition. Some clumping of fibers was observed in all samples. Techniques for overcoming this problem were investigated. Premixing of the fibers by rolling them in a polyethylene jar with methyl ethyl ketone and a few steel balls seemed to aid considerably in fiber dispersion.

Figure 3. SILICONE-RESIN-BONDED, COMPRESSION-MOLDING PROCESS.

Thermal conductivity of two of the compression-molded insulators was determined, and is indicated in Figure 4. It is evident that the conductivity was very sensitive to density. None of the insulators formed thus far were in the target range of 0.2 to 0.3 Btu-in/hr-°F-ft², but optimization of the density should effect significantly lower K values.

Quantitative strength characteristics and machinability of the compression-molded compositions were not obtained, but a qualitative assessment of these parameters appears to surpass commercial low-K particulate-based insulators.

FUTURE PLANS

Optimization of the binder system remains the main objective of the investigation of pulp-molded fibrous insulators. The wide variety of binder systems and processing techniques available makes the study of these variables a sizable task. Thermal stability studies, machinability evaluations, and more thermal conductivity testing are also necessary before a reproducible, stable product can be realized.

Figure 4. THERMAL CONDUCTIVITY OF COMPRESSION-MOLDED, SILICONE-BONDED INSULATION. (Argon Atmosphere)

The attainment of low thermal conductivities with compression-molded insulators depends, to a large extent, on achieving a lower-density body with a minimum of binder. Development efforts are proceeding in this direction. Further characterization of these insulators with respect to mechanical and thermal properties is also needed.

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