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AEC RESEARCH AND DEVELOPMENT REPORT

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PREPARATION AND PROPERTIES OF CARBON FOAM

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R. Paluzelle

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

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

**UNION
CARBIDE**

OAK RIDGE Y-12 PLANT
P. O. Box Y
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Date Issued: March 23, 1970

Document   Y-1706

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Oak Ridge, Tennessee

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ABSTRACT

The preparation and properties of carbon foam have been studied under production conditions at the Oak Ridge Y-12 Plant. The material has been prepared with densities ranging from 0.02 to 1.0 gm/cc; carbonization has been carried out at temperatures between 1,000 and 2,500° C. Powder additives have also been employed in the formulation.

Compared with rigid organic foams, carbon foam is better for high-temperature applications, possesses higher compressive strengths at most densities, and maintains its dimensional stability even when immersed in water.

4

CONTENTS

SUMMARY

Carbon foam has been prepared, at the Oak Ridge Y-12 Plant,[a] with densities ranging from 0.02 to 1.0 gm/cc. In brief, the processing steps consist of mixing a polymerized furfuryl alcohol resin (Varcum 8267)[b] with a rigid urethane foam system, pouring the mix into a mold to form a green casting, curing the casting at room temperature for several days, then carbonizing the cured casting at a temperature of 1,000° C. The material can be cast in a variety of shapes and is readily machinable by using standard machine tools.

Carbon foam can replace rigid organic foams in many applications, especially for use at high temperatures where organic foams would decompose. In the absence of air, carbon foam is stable up to temperatures of at least 2,500° C. Unlike organic foams, the dimensional stability of carbon foam is not affected by humidity; indeed, even immersion in water does not affect this property. The compressive strength of carbon foam is higher than that of rigid organic foams at many densities.

(a) Operated by Union Carbide Corporation's Nuclear Division for the US Atomic Energy Commission.
(b) A product of Reichold Chemicals, Inc; Varcum Chemical Division.

INTRODUCTION

Rigid organic foams have found wide use in industry for structural and insulation purposes and have been investigated for aerospace use. While possessing such valuable properties as a high strength-to-density ratio and low thermal conductivity, there are at least two characteristics of rigid organic foams that may limit or preclude their use for some purposes: (1) they lack close dimensional stability when subjected to wide variations in humidity; (2) they cannot be used at very high temperatures.

Most urethanes, for example, undergo thermal decomposition at temperatures between 300 and 400° C; and, even before the decomposition temperature is reached, increasing the temperature results in deterioration of the physical properties of the material. The products of thermal decomposition are extremely irritating and no doubt toxic. Carbon foam, on the other hand, is unaffected by moisture; no dimensional change can be determined even after immersion in water; and, in the absence of air, the material can be heated to 2,500° C without damage.

Several years ago, small quantities of a cellular carbon material had been made at Y-12 by the rapid polymerization of Varcum 8251[c] with the aid of heat and maleic acid as a catalyst. The material was then carbonized by heating first to 450° C and later to 2,500° C in an inert atmosphere. However, the finished material contained cells of varying size which were unoriented, and there appeared to be no good way to control the density of the product.

In order to make a carbon foam of finer and more uniform cell structure, with controllable density and with other desirable properties, a process was developed whereby a mixture of urethane and Varcum 8251 was foamed, cast in a mold, and the resulting casting carbonized to yield a carbon foam billet that could be machined to any desired shape. In the meantime, changes have occurred in the Varcum and urethane raw materials as well as in the processing steps. This report is concerned with describing the present method of preparing carbon foam and in listing some of its properties.

(c) Varcum 8251 is a partially polymerized furfuryl alcohol, less highly polymerized than Varcum 8267.

CARBON FOAM

PREPARATION

Formulation

Carbon foam is prepared from a two-component rigid urethane system to which Varcum 8267 is added. There are many proprietary rigid urethane systems on the market, several of which have been tried. The one found to be the best for preparing a wide range of densities is known as Thermalthane 4002-45.[d] As has been mentioned earlier, the Varcum 8267 is a partially polymerized thermosetting furfuryl alcohol resin.

The formulation used depends on the density. Density can be controlled both by the amount of water added and the ratio of Varcum to urethane. The usual practice for a given density is to keep the ratio of Varcum to urethane constant and vary the water content. Variations in the chemicals and especially the Varcum which contains 0.3 - 0.5 percent water may make it necessary to vary the amount of water with different lots of chemicals. Figure 1 is a plot showing the relationship between the amount of water added (expressed as a percentage of the urethane "R" component) and the density. Although the plot is based on some old data, it serves to illustrate how density varies with the amount of water added and also how density varies between low-temperature-cured material and foam carbonized at 1,000° C.

The 120 and 230° C cures (in air) shown in the graph are no longer used. Also, the cited ratio of Varcum to urethane (1.1:1.0) is not generally used. Currently, for lower density material, a Varcum-to-urethane ratio of 0.55:1.0 is used; for densities above 0.1 gm/cc, a Varcum-to-urethane ratio of 1.0:1.0 is employed. Illustrative of the two ratios are the formulations given in Table 1 for 0.05 and 0.22 gm/cc foam.

Depending on the volume of the casting to be poured, the batch sizes given in Table 1 can be proportionately increased or decreased. Also, due to changes in the chemicals, the water added may be decreased or increased (increasing the amount of water lowers the density and vice versa).

Mixing

Batches of the sizes indicated may be mixed in three-gallon (for the 0.05 gm/cc) or five-gallon (for the 0.22 gm/cc) containers (lard cans). Buckets (paint pails)

(d) Developed by the Bendix Company, Kansas City, Missouri.
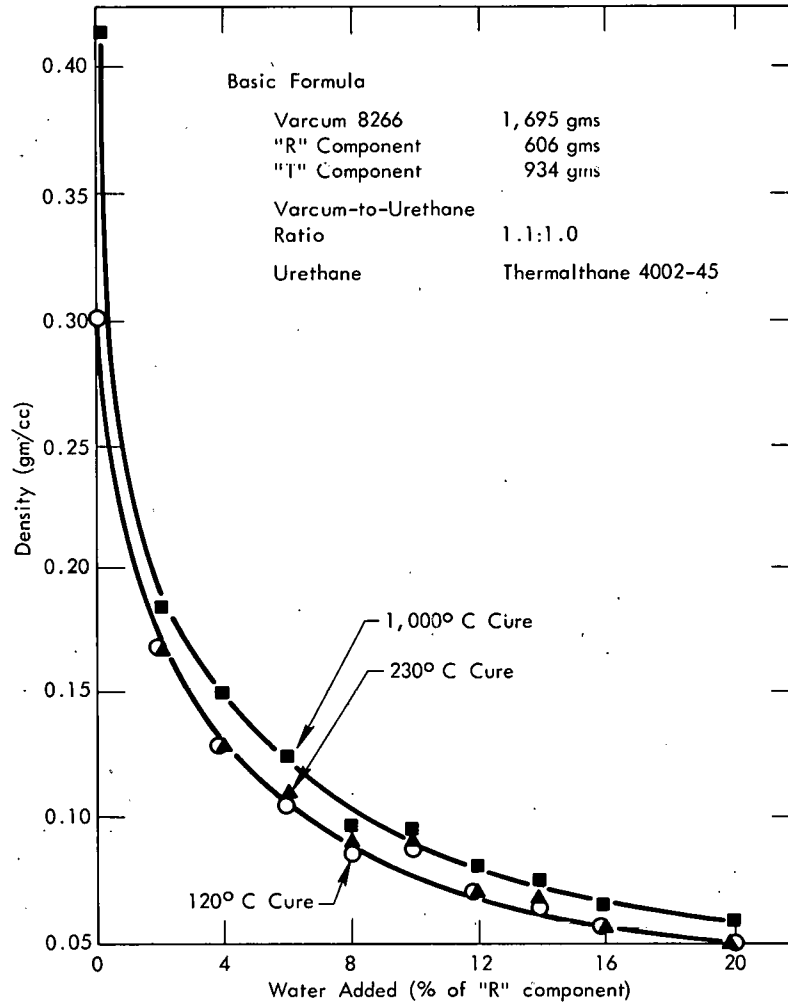
Figure 1. RELATIONSHIP BETWEEN THE AMOUNT OF WATER ADDED TO A CARBON FOAM FORMULATION AND THE RESULTING DENSITY.

Table 1

FORMULATIONS FOR CARBON FOAM OF TWO DENSITIES

Constituent	Formulation Weight (gms)	
	0.05 gm/cc Density Foam	0.22 gm/cc Density Foam
Varcum 8267	2,263	5,576
Urethane R	1,536	2,076
DC 193 Cell Regulator	76	103
N-Methyl Morpholine Catalyst	9	12
Deionized Water	120	46
Total Premix	4,004	7,813
Urethane T	2,492	3,385
Total Formulation Weight	6,496	11,198
Varcum-to-Urethane Ratio	0.55	1.00

with plastic throw-away liners[e] are also convenient and economical. Reuse of containers without plastic liners is not economical because of the labor and solvent cost required to clean them.

There are two approaches to mixing. In one case, the premix ingredients are weighed into the mix container, the material mixed for five to six minutes, mixing stopped, and the "T" component added with mixing resumed for 45 - 105 seconds (depending on the desired density). The other method is to make a large batch of premix (enough for 30 - 60 castings); and, with the premix continually mixing, draw off the required amount directly into the mix container which is tared on a scale. The second method is preferred.

The master-batch premixer is shown in Figure 2 and has a working capacity of 100 gallons. The mixer-propeller assembly is driven by a three-horsepower Lightnin mixer (gear-drive type) and is provided with a variable speed. The mix is pumped from the bottom of the tank through a three-horsepower Moyno pump, then through a heat exchanger equipped with an automatic temperature control, thence to the inlet manifold where the return flow can be admitted at any of several levels. A scraper rotating at about one revolution per minute clears any material which might adhere to the tank wall. A draw-off valve between the heat exchanger and inlet manifold is provided for admitting the premix for a casting. Indicating dial-type thermometers are provided at the pump inlet, pump outlet, and heat-exchanger outlet.

All components of the premix are weighed on a platform scale; the weights taken are the weights listed under "Formulation Weight" (Table 1) multiplied by the desired number of castings to be made. After all of the ingredients are added to the tank, the tank lid is seated and the propeller-mixer device started. The pump is not started until the Varcum and "R" component are fairly well mixed so that the viscosity will not be too high, a situation which might overload the pump.

When the pump is started, the return to the tank should enter at the top valve on the tank inlet manifold. This path will give a maximum turnover of the master batch. As the tank level becomes lower with the removal of several batches, the return point should be progressively lowered to avoid excessive splashing which might result in an undesirable amount of air-bubble entrainment.

(e) "Payliners", which fit three-gallon paint pails, are supplied by the Hedwin Company.
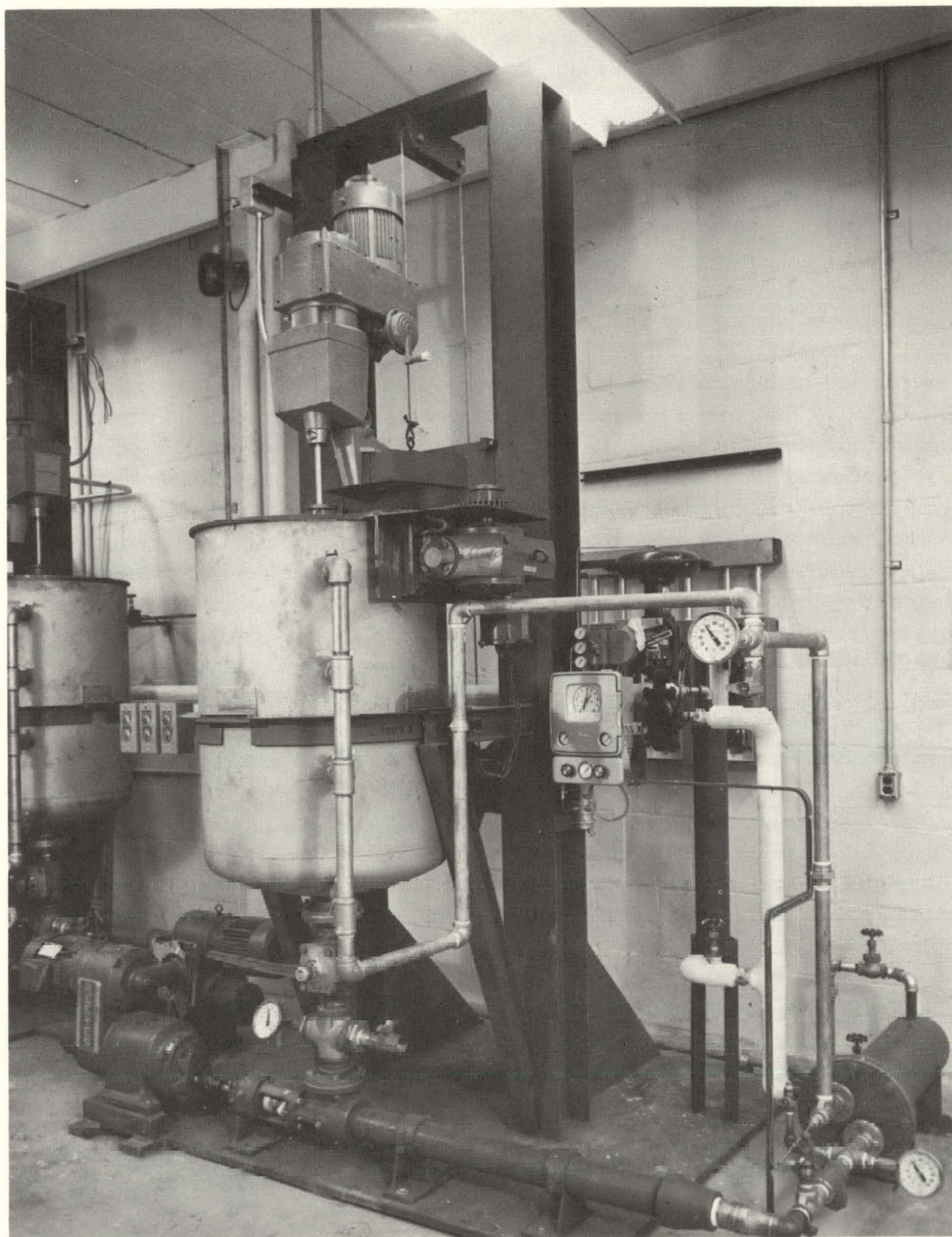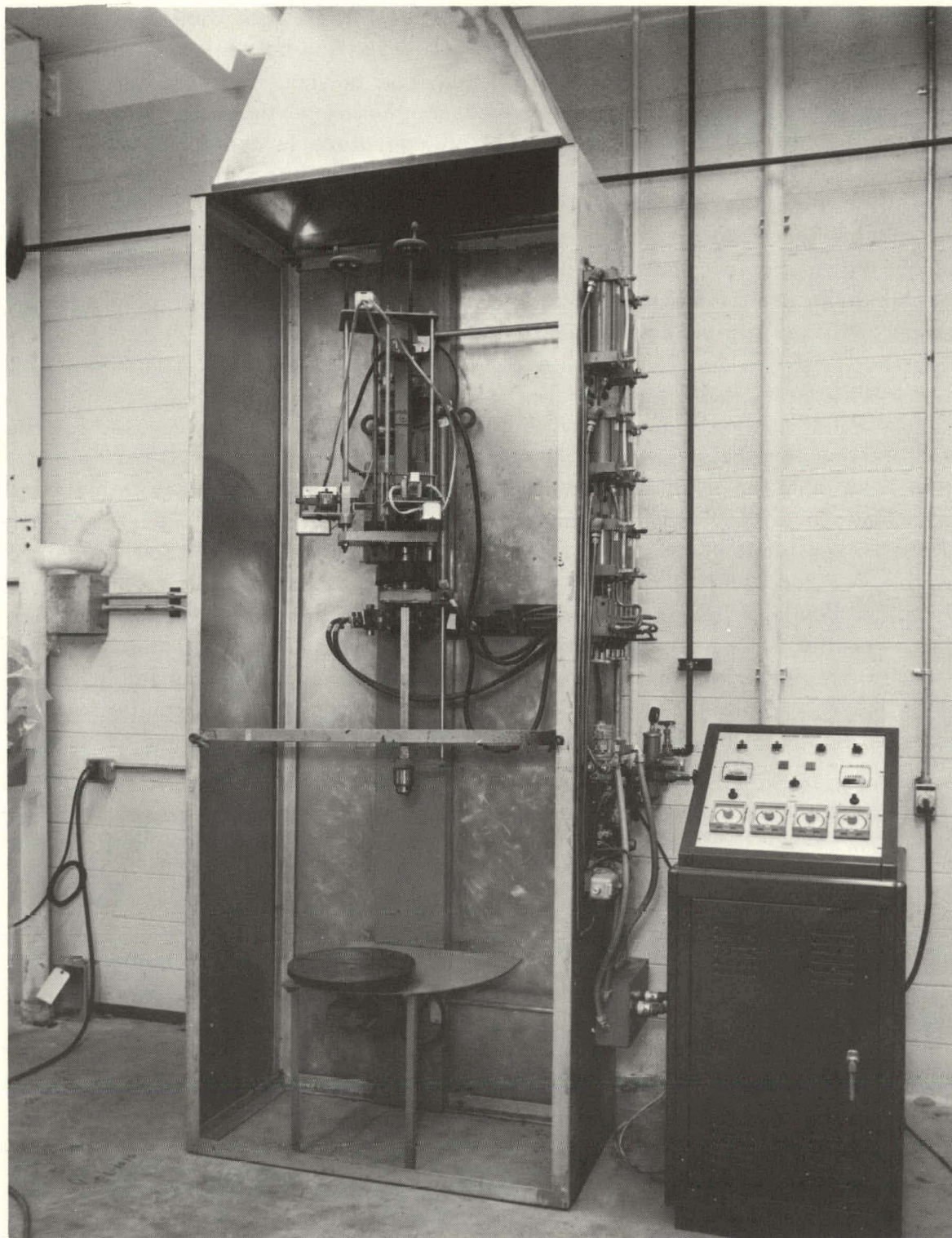
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Figure 2. MASTER-BATCH MIXER FOR THE PREPARATION OF THE PREMIX.

Although warming the contents of the tank facilitates good mixing (especially of the water), too high a temperature of the casting batch during withdrawal may result in cross fracture. (The phenomenon of cross fracture is discussed on Page 30 and following.) For this reason, the temperature of the withdrawn mixture should not exceed 35° C. This temperature is controlled by the heat exchanger; but, because of the limited capacity of the heat exchanger, consideration must be given to the amount of mechanical energy (heat) added to the mix by the agitator and pump. The speed of these should be limited to that necessary to achieve good mixing. Modification of the carbon-foam process involving the use of the master batch for premix is covered in an patent application by the US Atomic Energy Commission.

Figure 3 is a photograph of an automated mixer which may be used for the final mixing of the urethane "T" component with the premix. It may also be used for mixing the premix if the master batch is not used. The mixer is installed in an enclosure provided with an exhaust system to remove fumes. The depth of the mixer blade (preferably a 6" Conn blade) can be adjusted to the desired depth. For batches to have a density of 0.05 gm/cc and of the size previously listed, a depth of 1/2 inch from the bottom is preferred; for the larger batch listed for the 0.22 gm/cc density material, a somewhat greater distance from the bottom is preferred—in the range of 3/4 to 1 3/4 inches. The turntable, which holds the mix container, rotates counterclockwise and its speed can be set by a control dial on the console. A speed of 10 rpm has been found to be best.

The speed of the mixer (which rotates clockwise) can be set by another control dial on the console. Speeds of 500 rpm for the lower-density batch and 400 for the higher-density mix have been found to give the best results for most lots of chemicals. Length of the mix time (45 seconds for 0.05 gm/cc batches and 100 - 110 seconds for 0.22 gm/cc batches) can be set by still another dial on the console.

The "T" component is conveniently measured volumetrically by taking into consideration the required weight and its specific gravity. Immediately upon completion of the "T" addition, the mixer is started by pushing the "start" button. The inside wall of the mix container should be scraped with a spatula for most of the mix period. At the end of the period, the mix blade is raised, swung to the right, lowered into a can of solvent, automatically started spinning for a time set by another control dial, then raised out of the solvent and spun for a preset period to dry the blade. In the meanwhile, the mix container is removed from the turntable and the batch poured into a mold.

132518

Figure 3. AUTOMATED MIXER.

Pouring

The mix time is established so that pouring into the mold can be accomplished before foaming begins. This timing is important since pouring foam upon foam will result in excessive voids and oversize cells. Hence, no time should be lost between termination of the mixing and pouring the mixture into the mold. The material is poured into an aluminum mold in a circular path as close as possible to the edge. With experience, the rate of pouring can be gauged so that the pour is completed in one rotation without overlapping the first material poured. (Pouring in one spot has been found to be undesirable.) Prior to use, the mold bottoms should be warmed to a temperature of about 50° C to prevent bad bottoms on the castings. Figure 4 shows 0.22 gm/cc density castings with good and bad bottoms.

The batches described in this section of the report have been used for making castings that were 20 inches in diameter. The lower-density batch produces a green casting about 25 inches high; the higher-density batch produces a casting about 13 inches high when a 10-inch-diameter mold core is used. To avoid
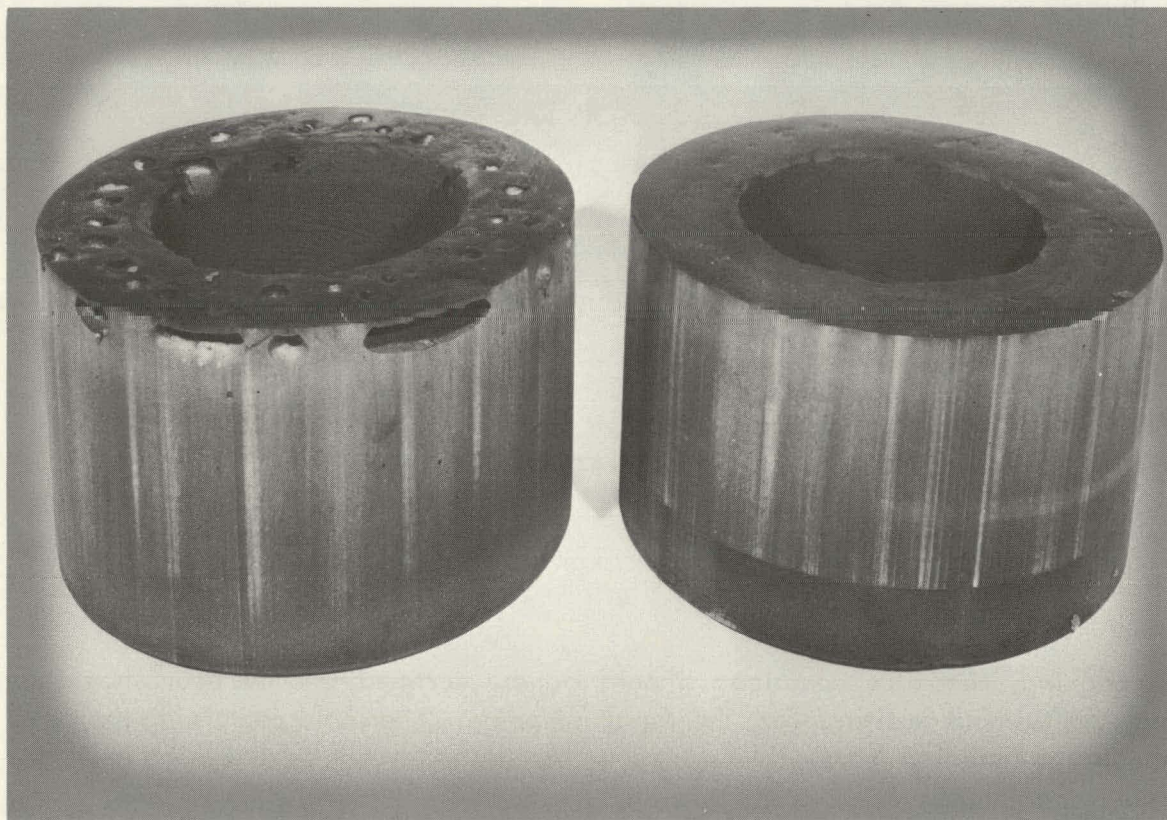
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Figure 4. CASTINGS WITH GOOD AND BAD BOTTOMS. (0.22 gm/cc Density Material)

pouring from a height of 25 inches, which tends to entrap air bubbles, a two-piece mold was designed (Figure 5). The bottom portion is five inches deep and the top part is 20 inches deep. An additional advantage of the two-piece mold is that the bottoms can be easily warmed in an oven without treating the entire mold. After the pour is complete, the two parts are connected together at the flanges by means of Camloc[f] fasteners. Another type of closure which has been used successfully is the Knu-Vise fastener.[g] Other types and sizes of molds have been used. For the cylindrical castings, a variety of diameters and heights have been tried. For example, for making the castings already mentioned, the use of 22-inch-diameter molds of the same height as the 20-inch-diameter molds is under study. Present indications are that the allowance for more trim off on the radius, which is permitted by the 22-inch mold, is advantageous.
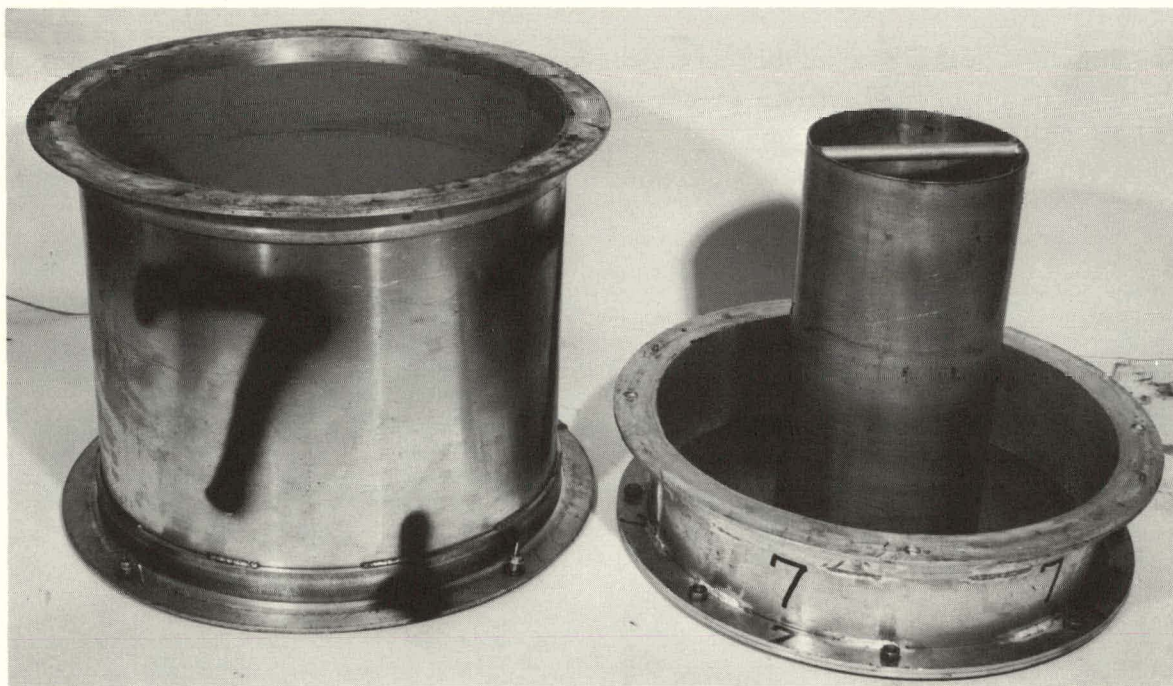
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Figure 5. TWENTY-TWO-INCH-DIAMETER DIVIDED MOLD. (With Removable Core)

In pouring, the mix container should not be scraped, and the pour should be cut off without waiting for the final dripping. The mold containing the pour should be handled carefully in order that material not be disturbed until the rise is complete.

(f) Supplied by the Camloc Fastener Corporation.
(g) Supplied by the Lapeer Manufacturing Company.

A variety of mold-release compounds have been used to prevent the casting from sticking to the mold, namely: paste floor wax, paste automobile wax, a variety of proprietary liquid and spray-on mold releases, and Dow-Corning silicone grease. This latter material has proved to be the most successful. At this time, the use of the liquid DC 193 silicone oil used as a cell regulator is being studied for use as a possible mold-release compound. Results, so far, show promise. A liquid is much easier to apply and it is also easier to control the quantity used to the minimum needed. Notwithstanding the use of mold releases, occasional trouble with sticking has been experienced. Roughness on the mold interior due to sanding during mold fabrication can contribute to this difficulty.

Sticking can initiate a vicious cycle. When the casting sticks to the mold, some of the casting skin remains firmly adhered to the mold; then, removal of this skin by scraping with wide-blade spatulas may result in further scratching. A great contribution to the elimination of sticking difficulties has been the lining of molds with a composite aluminum foil/Teflon material known as "Trifoil".[h] Earlier attempts to coat molds with a spray-on Teflon were not too successful. Perhaps a more skillful application of Teflon, such as is used on cookware, might give better results.

Removal from the Mold, Trimming, and Curing

Rise of the casting in the mold is probably complete within ten minutes, but the casting should not be removed from the mold for at least an hour—longer, if feasible. Delay in removal permits the casting to become more firm, thus reducing the danger of tearing or deformation.

For the cylindrical castings made in the molds described and illustrated in this section, removal from the mold is not difficult. As gelation continues and the casting cools, shrinkage from the mold wall occurs; and, when the two-part mold is separated, the casting will generally fall from the upper part of the mold or can be shaken from it.

Castings made in other shaped molds such as cubes, slabs, and large-diameter cylinders may be more difficult to remove. In many cases, running a spatula or a long, specially made thin blade between the casting and the mold may help. Another useful technique is to provide a small-diameter hole in the mold bottom, then seal the hole with plastic tape or a screw before pouring. The casting can then be removed from the mold by opening the hole and blowing the casting

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(h) Supplied by Tri-Point Industries, Incorporated.

from the mold by placing a compressed air hose over the hole. In some cases, inverting the mold and dropping it to the floor may loosen the casting.

After removal from the mold, the casting should be permitted to age 16 - 24 hours before scoring and trimming. The scoring and/or trimming is performed in order to permit the casting to "breathe", to accelerate air curing, and especially to permit gaseous pyrolysis products to escape from the casting during carbonization. While scoring alone has been found to permit carbonization without cracking, less blistering occurs when the high-density skin is removed.

The skin of the casting of 0.05 gm/cc material is readily removed by a band saw; scoring is accomplished with the same tool. In removing the skin, some degree of "hourglassing" may require removal of a greater thickness in the larger diameter portions in order to completely remove the skin from the hourglassed sections. If the skin is not completely removed, blistering may occur. After skinning, the casting may be scored to a depth of about 3/8 - 1/2 inch with the slots approximately 3/4 inch apart. While the advantage accrued from scoring is dubious if the skin is removed, there is some evidence that scoring reduces canting or slumping. Perhaps the scored surface gives rigidity in a manner similar to that effected by the corrugation of sheet metal.

Castings should be permitted to cure at room temperature for at least ten days; fifteen days may be preferable. Cross linkage of the urethane is known to continue (at room temperature) for several days. There may also be some interaction between the diisocyanate and Varcum. As this curing continues, the castings become harder. (It is believed that this action reduces the softening during the carbonization, with consequent reduction of slumping or canting.) Photographs of such deformed billets are given in Figure 6. Oven curing can expedite the cross linking. (Formerly this step was carried out at 70° C and later at 120° C.) However, this practice was discontinued because the castings would catch on fire. While oven curing in a nitrogen atmosphere would preclude oxidation or combustion, there is some indication that air (oxygen) is necessary for effective curing. In early work, a "first bake" in air at 250° C (later 230° C) was carried out; and, with the Varcum 8251 then used, few fires occurred. (Varcum 8251 has a higher content of furfuryl alcohol and a lower content of the higher polymers.) Later, with the use of a more completely polymerized Varcum having a lower furfuryl alcohol content, it was found that it was impossible to avoid oxidation.

Carbonization

Conversion of the Varcum-urethane foam castings to carbon foam is carried out in furnaces having an inert (nitrogen) atmosphere and heated to 1,000° C using a

132589

Figure 6. CANTED AND SLUMPED BILLETS.

time-temperature program which is maintained by a cam-operated controller. A very great amount of experimentation has established the importance of the selection of a proper program. The rate of temperature rise must be restrained during the softening and decomposing range of the urethane. After a temperature of 340° C has been reached, the rate of temperature rise can be increased somewhat; and, after 400° C, further acceleration of temperature rise may be permitted. As the density of the foam increases above 0.2 gm/cc, lengthening of the cycle is required.

Table 2 outlines a program used in carbonizing carbon foam in the density range from 0.02 to about 0.2 gm/cc. This program was developed by comparing the furnace temperature with the temperature at the center of a casting for different heating rates. After several "cut and try" runs, a program was established which kept the temperature gradient between the furnace and casting center limited to a maximum of about 30° C. For higher-density material, where the program must be extended, the same cam can be used by either changing the gears which drive the cam or by the use of a pulse timer which interrupts the motion of the cam by whatever amount is desired. For example, by interrupting the current to the cam drive motor on a 30-seconds-on, 30-seconds-off basis, the 60-hour cycle of Table 2 may be extended to 120 hours. In this manner, the carbonization period can be extended to as long as 240 hours. The castings are placed in the

Table 2

CARBONIZATION HEAT CYCLE

Elapsed Time (hrs)	Temperature (°C)
0	170
2 1/2	170
5	170
7 1/2	195
10	213
12 1/2	229
15	245
17 1/2	261
20	278
22 1/2	294
25	310
27 1/2	326
30	343
32 1/2	371
35	446
37 1/2	521
40	596
42 1/2	671
45	746
47 1/2	821
50	896
52 1/2	971
55	1,031
57 1/2	1,031
60	1,031

furnace on shelves made of graphite boards. The boards should be arranged edge to edge so that no gap exists between the boards. If a casting spans a space between boards, it may be caught in such a manner as to interfere with normal shrinkage, resulting in deformation or cracking. The pyrolysis gases evolved during carbonization are noxious and undoubtedly toxic. For this reason, to prevent atmospheric pollution, the furnace off-gas line is conducted to a checker-brick chamber where the oils and gases are burned before discharge to the atmosphere.

Figures 7 through 10 give views of a cylindrical carbonization furnace. Figure 7 shows the front of the furnace with the door closed. The nitrogen distribution pipe which admits the inert gas at several points around the door can be seen. Figure 8 shows the power panel. The saturable core reactors (variable transformers) can be seen at the side of the furnace. Figure 9 gives a view of the
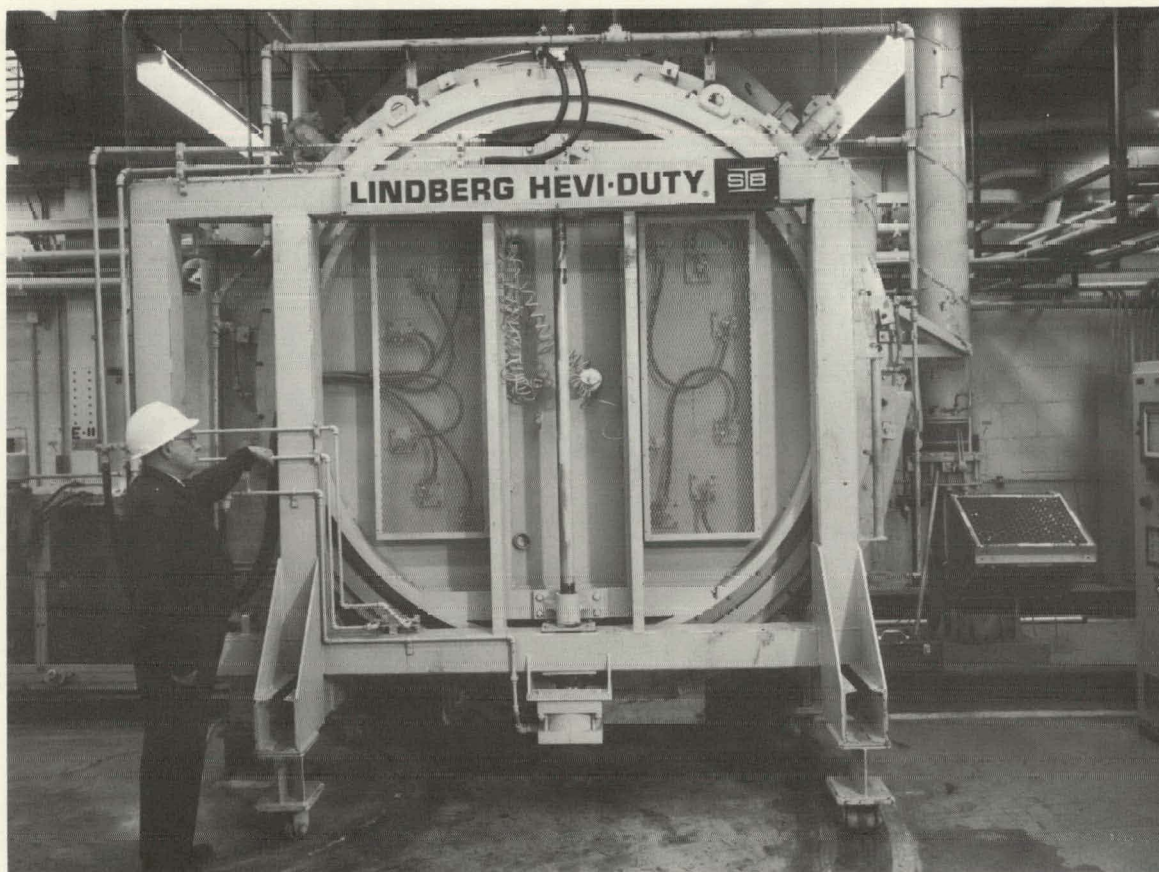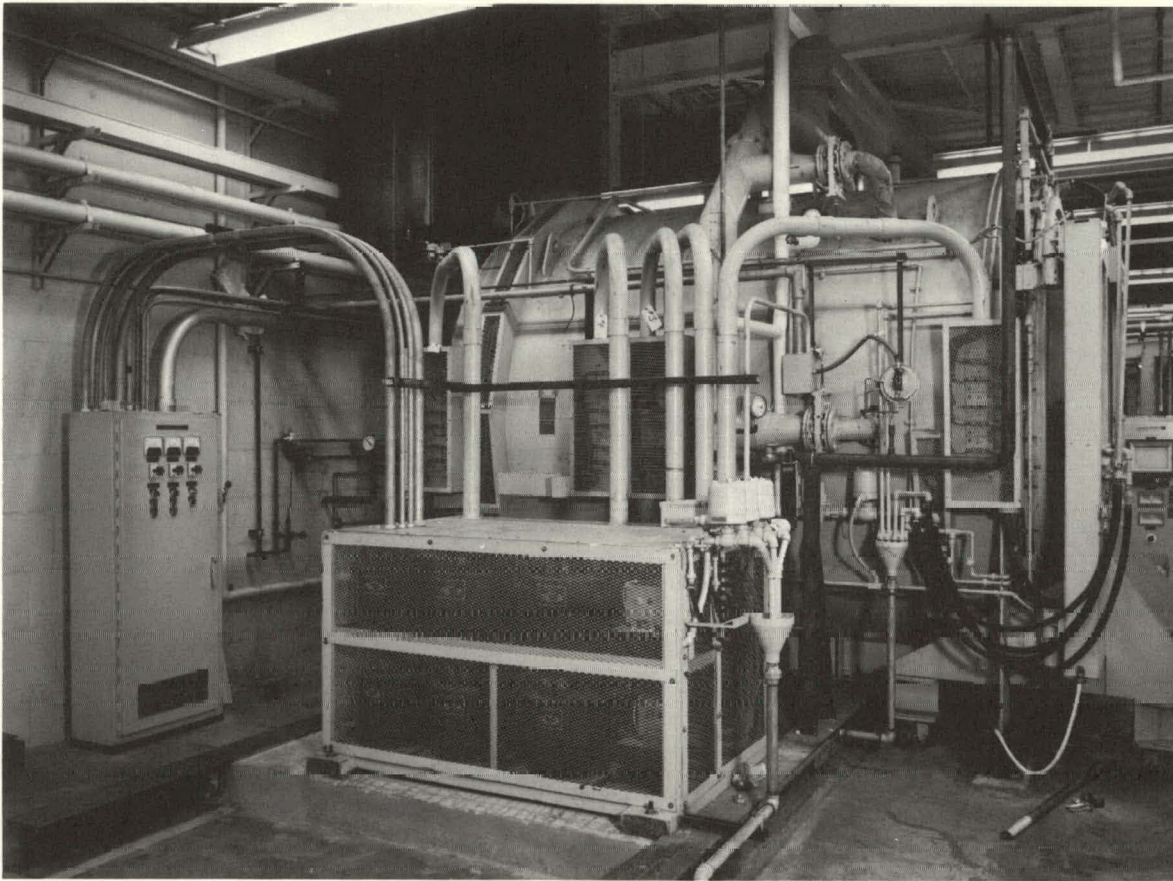
Figure 7. CARBONIZATION FURNACE WITH DOOR CLOSED.

control panel with the temperature recorders for the three furnace zones (back end, sides, and door). Figure 10 shows the furnace door open. The carbonized billets can be seen on the graphite shelves.

After considerable experience with rectangularly shaped muffles, which gave trouble with cracking and warping, furnaces with cylindrical muffles were purchased. It was believed that less tendency to crack would be experienced with this design. At this time there has been insufficient operation to evaluate this design, but the first runs look promising.

After the carbonization cycle has been completed, natural cooling of the furnace is permitted to take place. When the temperature has reached 500° C, cooling of the muffle may be accelerated by blowing cooling air between the furnace elements and muffle. While castings have been removed when the muffle temperature has been as much as 200° C, it is perhaps somewhat more conservative to wait until the muffle temperature has reached 100° C. In a large furnace, those castings further from the muffle walls may be considerably hotter than the muffle itself. Furthermore, the center of the castings will be hotter than the exterior surface by perhaps as much as 70° C.
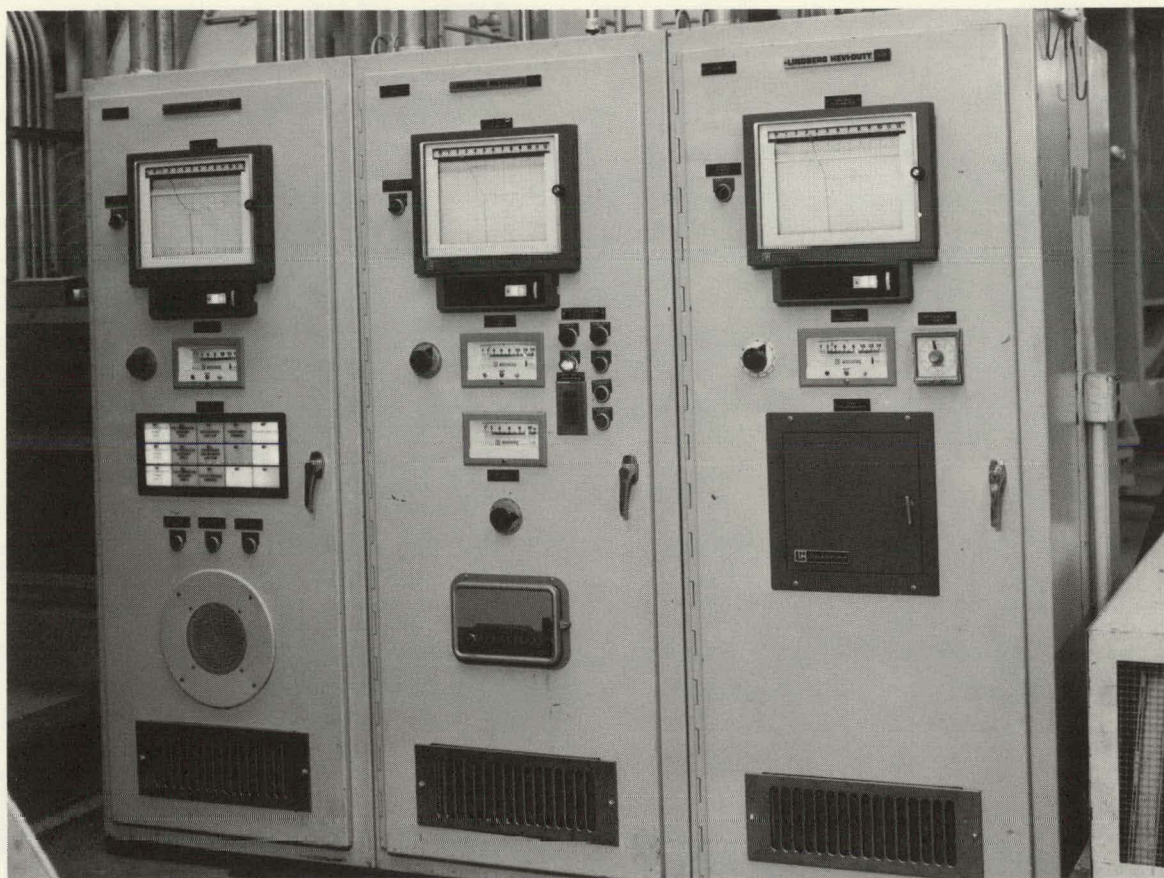
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Figure 8. CARBONIZATION FURNACE WITH POWER PANEL AND SATURABLE CORE REACTORS.

After removal from the furnace, the billets must again be trimmed to produce true cylinders. Since there is a density gradient from the outside of the billets to the center (higher on the outside) and from the top to the bottom (generally higher at the bottom), trimming a liberal amount from the sides, top, and bottom will produce a more uniformly dense material. This step may be accomplished by the use of a band saw. For trimming castings to produce hollow cylinders, a hole saw has been used. This machine successfully trims the outside and inner hole (if the casting is hollow); or, if the casting is solid, can produce a cylindrical hole in the center of the billet. A hole saw with only one cutter may be used for trimming the outside of billets only, without removing the center. A similar saw can also be used for the trimming operation on green castings.

Safety Considerations

Tolylene diisocyanate, which is a constituent of the "T" component of the urethane, is a toxic substance and may cause severe asthmatic symptoms when inhaled by susceptible individuals. Exposure to the fumes may be irritating to the eyes. The best protection for exposed individuals is an all-purpose gas mask equipped with an organic vapor cartridge. In early work with carbon foam,
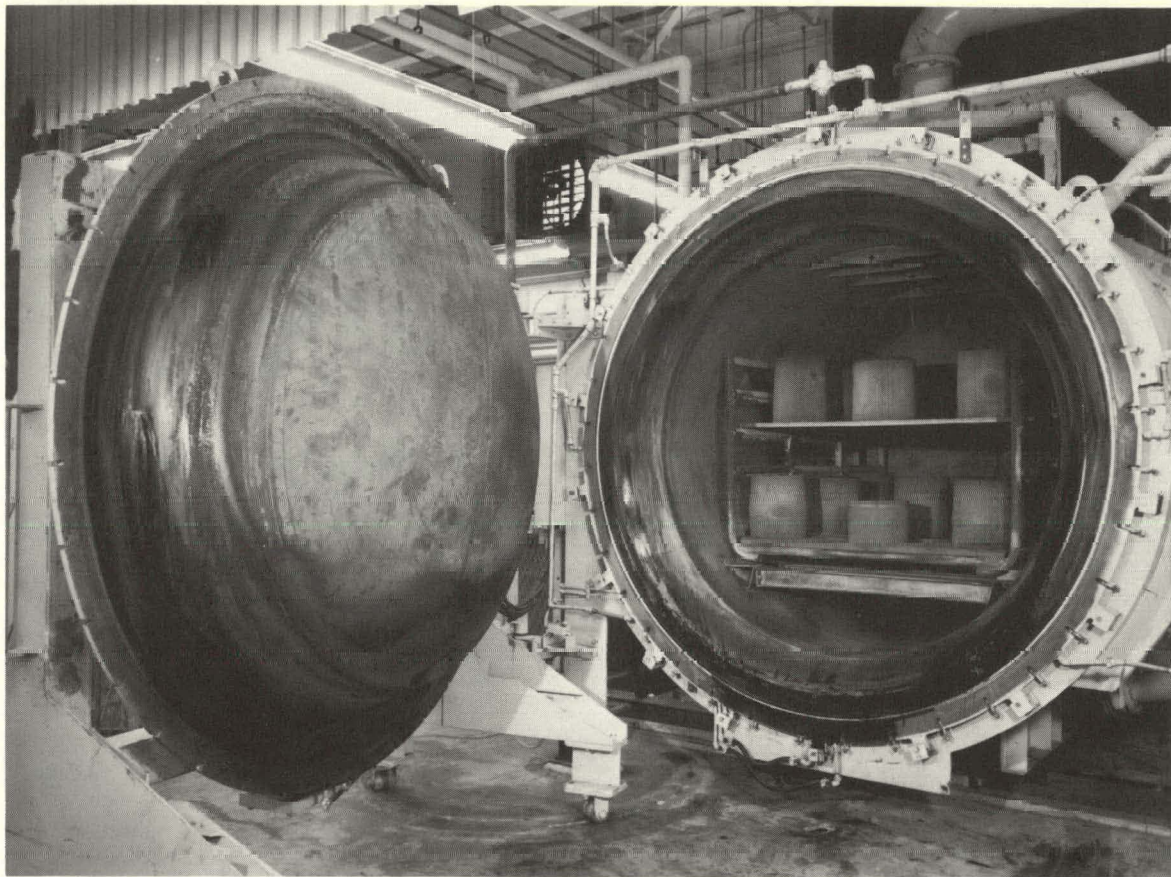
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Figure 9. CONTROL PANEL FOR THE CARBONIZATION FURNACE.

a different urethane system was used which employed 100 percent TDI ("C" component) instead of the "T" component used in the Thermalthane 4002 system. The "T" component presently used is a quasi-prepolymer type; and, because most of the diisocyanate has been reacted with some of the "R" component, the vapor pressure of the diisocyanate from the mixture is at a much lower level. With this product it is possible to work without gas masks or respirators in well-ventilated areas. It is noteworthy, however, that the maximum permissible limit of tolylene diisocyanate in air is below the detectable odor level. In the event of a mishap which would cause pyrolysis gases to escape into the room, gas masks should be worn until the situation is corrected. Such gases are extremely irritating and toxic.

Green castings when ruptured before cooling to room temperature are capable of spontaneous combustion. Air getting into the material (hot from the exothermic reaction which produces the foam) has often caused the castings to catch fire. Unbroken and uncracked castings have not been known to catch fire except in some cases where oven curing at 120° C was attempted. Cracked or broken green castings should be removed from the operating area to a safe location.

132516

Figure 10.   CARBONIZATION FURNACE CONTAINING CARBONIZED BILLETS.

Dust from the cutting operations on green and carbonized castings is irritating to the bronchia and lungs. Unless ventilation is sufficient to remove this breathing hazard, respirators should be worn during the cutting operations.

CHARACTERISTICS

Density

Most of the characteristics of carbon foams depend on their density. For this reason, in citing properties it is necessary to specify the associated density. However, foams of the same density may have different characteristics if prepared from different formulations or processed by different procedures. Thus, even at the same density, the compressive strength of carbon foam will be lower if graphite flour is used in the formulation or if it is baked at 2,000° C instead of 1,000° C. Addition of organic powders, it will be shown, gives higher compressive-strength values. For carbon foams made from similar formulations and processed in identical manners, however, there is generally a direct relationship between their properties and densities.

Typical Properties for Two Densities

Tables 3 and 4 list the characteristics of carbon foams having two different densities. The materials were prepared using the formulations and procedures already described. Table 3 lists the miscellaneous properties of the two foams, while Table 4 gives the mechanical properties. Table 5 gives typical chemical analyses of the foams.

Table 3

MISCELLANEOUS PROPERTIES OF CARBON FOAM SAMPLES

Property	Condition	Density (gm/cc)	
		0.05	0.22
Coefficient of Thermal Expansion (in/in/°C x 10^{-6})	500° C	2.30	2.45
	1,000° C	2.80	3.00
Coefficient of Thermal Conductivity (Btu-in/ft^2-°R-hr)	500° F[1]	0.57	1.70
	1,000° F[1]	0.76	1.90
(watt-cm/cm^2-°K)	1,500° K - vacuum[2]	–	0.007
	2,000° K - vacuum[2]	–	0.010
	2,500° K - vacuum[2]	–	0.022
Static Coefficient of Friction	Uncoated	0.59	0.48
	Coated	0.45	0.36
Hygroscopicity (wt % gain)	12% RH	0.12	0.20
	50% RH	5.5	8.5
	100% RH	9.8	13.0
Mean Cell Diameter (mm)	Parallel	0.433	0.250
	Perpendicular	0.220	0.160
Porosity, Micropore (% less than 10 microns)	Hg Porisimetry	1.0	16.0
Surface Area (m^2/gm)	BET	0.60	0.20
Electrical Resistivity (ohm-cm x 10^{-3})	25° C	–	95.0
	1,000° C	–	65.0
	2,000° C	–	38.0
Open Cells (%)	Immersion	89.0	85.0
Specific Heat (gm-cal/gm/°C)	400° C	0.37	0.37

(1) Specimen mean temperature.
(2) Specimen maximum temperature.

Most of these data require little explanation. In Table 3, the entry for the coefficient of friction lists values for "uncoated" and "coated" foam. The uncoated specimens are as-carbonized foam; coated specimens are similar material that have been given a smooth coating. The coating was prepared by the application of a thin slurry of fine graphite flour in a benzene-coal tar pitch solution, followed by carbonization at 1,000° C. Such a coating reduces friction and protects the surface against abrasion. Abrasion can be particularly troublesome with low-density foam. The uncoated and coated entries in Table 3 refer to the same type specimens. It may be noted in Table 4 that coating the foam increases the compressive strength as well as protecting the surface. In Table 4 the term "bonded" refers to the technique of preparing compressive-

Table 4

MECHANICAL PROPERTIES OF CARBON FOAM

Property	Samples	Orientation	Density (gm/cc)	
			0.05	0.22
Compressive Strength (psi)	Uncoated[1]	Parallel	60.0	1,300.0
		Perpendicular	40.0	950.0
	Coated[2]	Parallel	105.0	1,495.0
		Perpendicular	63.0	1,150.0
	Bonded[3]	Parallel	120.0	–
		Perpendicular	80.0	–
Compressive Modulus (psi x 10^3)	Uncoated[1]	Parallel	13.0	50.0
		Perpendicular	7.0	40.0
	Coated[2]	Parallel	14.5	65.6
		Perpendicular	7.8	47.0
	Bonded[3]	Parallel	28.0	–
		Perpendicular	12.0	–
Tensile Strength (psi)	Bonded[4]	Parallel	50.0	–
		Perpendicular	27.0	–
Tensile Modulus (psi x 10^3)	Bonded[4]	Parallel	29.0	–
		Perpendicular	12.0	–

(1) Failure by surface abrasion; strength reported as maximum within 20 percent deflection
(2) Failure by subcoating fracture; strength reported as maximum at point of fracture.
(3) Failure by internal fracture; strength reported as maximum at point of fracture.
(4) Failure by internal fracture; strength reported as maximum at fracture, based on initial sample cross section.

test specimens by bonding (gluing) a thin aluminum disc to each end of the small cylindrical specimen. This technique tends to give higher compressive-strength values and perhaps more consistent results.

There is one characteristic of carbon foam that may be surprising to those familiar with rigid urethane foams, namely: the high percentage of open cells

Table 5

CHEMICAL ANALYSIS OF CARBON FOAM

Component	Density (gm/cc)	
	0.05 (%)	0.22 (%)
Ash	0.15	0.23
Carbon	94.57	96.39
Chlorine	0.002	0.003
Hydrogen	0.62	0.44
Nitrogen	2.72	2.22
Oxygen	2.02	0.70

listed in Table 3. Rigid urethanes typically have 90 - 95 percent <u>closed</u> cells. The difference might be explained by postulating that the closed cells formed during foaming the Varcum with urethane were ruptured during carbonization. However, another investigator[i] has found that the as-cast green carbon foam has 90 - 95 percent of open cells. It is evident that the presence of the Varcum results in the open-cell configuration. This fact probably explains why carbonization of urethane (at least, Thermalthane as used in the Y-12 carbon foam work) does not produce an orientated cell structure but rather a weak, feathery mass. Rupture of urethane cells (in the absence of Varcum) during carbonization destroys the cellular structure.

Compressive Strength

A few general observations may be made about the compressive strength of carbon foam. It has already been indicated that the strength increases with density. Data presented in Table 4 also show higher strength for coated than uncoated samples, and that the strength is greater parallel to the direction of rise than perpendicular. This latter characteristic is shown in greater detail by the data of Table 6. In addition, this table shows lower compressive strengths at an elevated temperature and gives additional data on the effect of coating.

Table 7 presents data which show the effect of the carbonization temperature on the compressive strength in the parallel and perpendicular-to-rise directions. In examining data such as these, some consideration must be given to the effect of density changes. One factor which has been found to have an important effect on compressive strength is the ratio of Varcum to urethane used in the formulation. Table 8 points out that a Varcum-to-urethane ratio value of 0.55 gives considerably greater strength than a Varcum-to-urethane ratio value of 1.0. Prior to investigating the effect of changing the ratio it had been expected that the higher Varcum proportions would give higher strength. This belief was based on observations of carbonized urethane (no strength) and carbonized Varcum which resulted in a strong, glassy carbon. It is quite evident that the characteristics of carbon foam are quite different from what might be expected from the nature of rigid urethane and Varcum by themselves.

Figure 11 offers a graphic comparison of the compressive strength versus density in the low-density range (< 0.1 gm/cc) for carbon foam and a proprietary rigid urethane foam. Figure 12 presents a similar comparison of carbon foam and rigid urethane in the higher density range (0.1 gm/cc and above). The data for these graphs were taken from some of the earlier work when a greater variety of densities was being studied.

(i) Thoeni, A. Kent; <u>Private Communication</u>; The Bendix Corporation, Kansas City, Missouri (1969).

Table 6

COMPRESSION TESTING OF CARBON FOAM AT VARIOUS TEMPERATURES

Specimen Number	Test Temperature (°C)	Surface Condition	Orientation to Direction of Rise	Raw Density (gm/cc)	Coated Density (gm/cc)	Ultimate Strength (psi)	Young's Modulus (psi x 10³)
5	72	Coated	Parallel	0.233	0.235	1,620	64.1
9	72	Coated	Parallel	0.217	0.221	1,478	69.9
24	72	Coated	Parallel	0.216	0.219	1,379	62.9
3	72	Uncoated	Parallel	0.222	–	1,401	38.1
15	72	Uncoated	Parallel	0.222	–	1,352	48.4
18	72	Uncoated	Parallel	0.221	–	1,341	48.4
30	72	Coated	Perpendicular	0.218	0.220	849	44.9
42	72	Coated	Perpendicular	0.222	0.224	849	46.6
44	72	Coated	Perpendicular	0.218	0.219	866	46.6
29	72	Uncoated	Perpendicular	0.213	–	850	43.4
35	72	Uncoated	Perpendicular	0.215	–	861	41.9
37	72	Uncoated	Perpendicular	0.220	–	890	44.0
6	1,000	Uncoated	Parallel	0.222	–	1,280	34.0
7	1,000	Uncoated	Parallel	0.220	–	998	30.7
14	1,000	Uncoated	Parallel	0.225	–	943	31.4
26	1,000	Uncoated	Perpendicular	0.221	–	783	18.0
32	1,000	Uncoated	Perpendicular	0.219	–	749	15.4
43	1,000	Uncoated	Perpendicular	0.215	–	807	19.6
5A	72	Coated	Parallel	0.050	0.059	89	4.6
9A	72	Coated	Parallel	0.052	0.064	124	7.2
24A	72	Coated	Parallel	0.049	0.064	117	7.7
3A	72	Uncoated	Parallel	0.049	–	59	3.8
15A	72	Uncoated	Parallel	0.051	–	65	5.6
18A	72	Uncoated	Parallel	0.051	–	65	4.7
30A	72	Coated	Perpendicular	0.055	0.066	35	2.2
42A	72	Coated	Perpendicular	0.059	0.065	32	2.1
44A	72	Coated	Perpendicular	0.061	0.062	36	2.1
29A	72	Uncoated	Perpendicular	0.054	–	27	2.2
35A	72	Uncoated	Perpendicular	0.055	–	27	1.4
37A	72	Uncoated	Perpendicular	0.059	–	33	1.8
6A	1,000	Uncoated	Parallel	0.050	–	56	5.5
7A	1,000	Uncoated	Parallel	0.051	–	72	4.5
14A	1,000	Uncoated	Parallel	0.050	–	64	5.0
26A	1,000	Uncoated	Perpendicular	0.057	–	25	1.3
32A	1,000	Uncoated	Perpendicular	0.061	–	24	1.0
43A	1,000	Uncoated	Perpendicular	0.055	–	24	1.4

Table 7

COMPRESSIVE STRENGTH AND MODULUS VARIATION
WITH CARBONIZATION TEMPERATURE

Carbonization Temperature (°C)	Orientation to Foam Rise Axis	Density (gm/cc)	Strength (psi)	Modular (psi x 10^3)
		0.05 gm/cc Foam		
650	Parallel	0.049	46	10.1
650	Perpendicular	0.049	14	1.8
800	Parallel	0.058	63	12.3
800	Perpendicular	0.060	17	1.8
1,000	Parallel	0.058	79	13.2
1,000	Perpendicular	0.060	34	3.6
		0.22 gm/cc Foam		
650	Parallel	0.220	890	46.5
650	Perpendicular	0.213	514	32.8
800	Parallel	0.240	1,196	53.3
800	Perpendicular	0.235	683	41.7
1,000	Parallel	0.228	1,500	61.0
1,000	Perpendicular	0.216	906	45.6

It will be noted that in the higher-density range, the strength of carbon foam is superior to that of rigid urethane. On the other hand, the lower-density rigid urethane foam is shown to have higher strength than corresponding densities of carbon foam. However, because of improved techniques now used for the preparation of carbon foam, present samples probably have superior strength

Table 8

VARIATION OF THE VARCUM-TO-URETHANE RATIO
EFFECT ON 0.10 GM/CC CARBON FOAM

Number of Samples	Varcum-to-Urethane Ratio	Average Compressive Strength (psi)	Range of Values	Average Modulus Value (psi x 10^3)	Range of Values
		Samples Parallel to the Direction of Rise			
17	0.55	288	250 - 321	20.0	10.9 - 33.5
12	1.0	225	200 - 236	6.2	3.8 - 7.4
		Samples Perpendicular to the Direction of Rise			
18	0.55	214	185 - 247	13.3	12.0 - 18.0
15	1.0	136	128 - 141	5.8	3.8 - 7.4
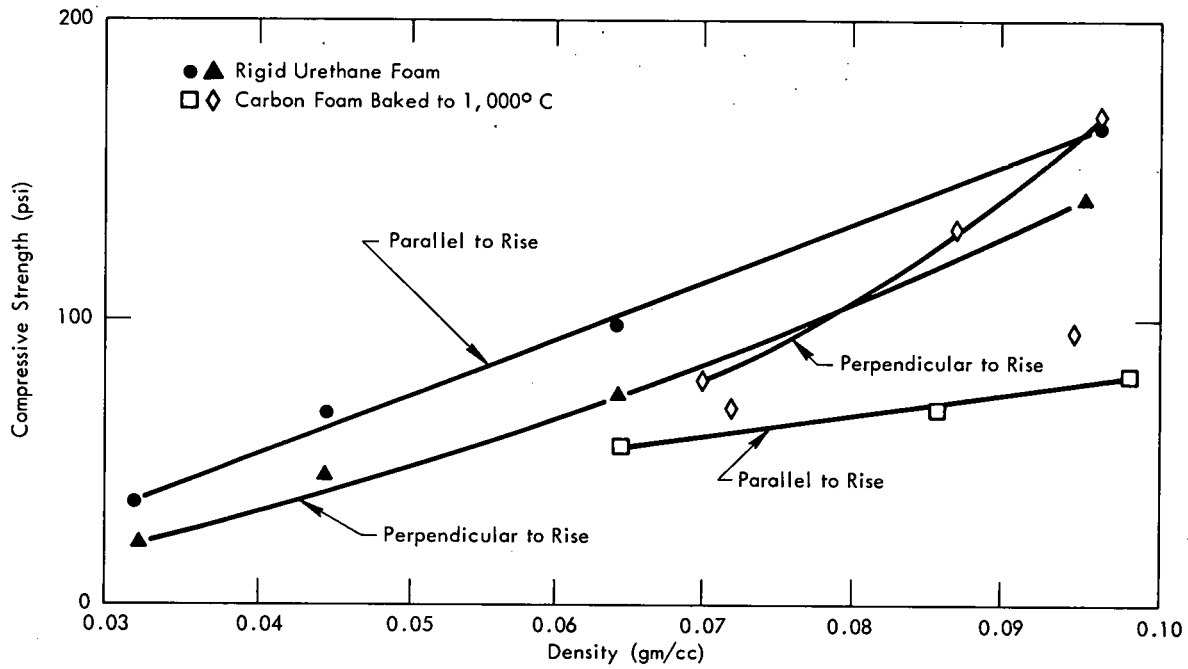
Figure 11. COMPRESSIVE STRENGTH OF TWO FOAM TYPES AS A FUNCTION OF THE DENSITY. (Low-Density Range)
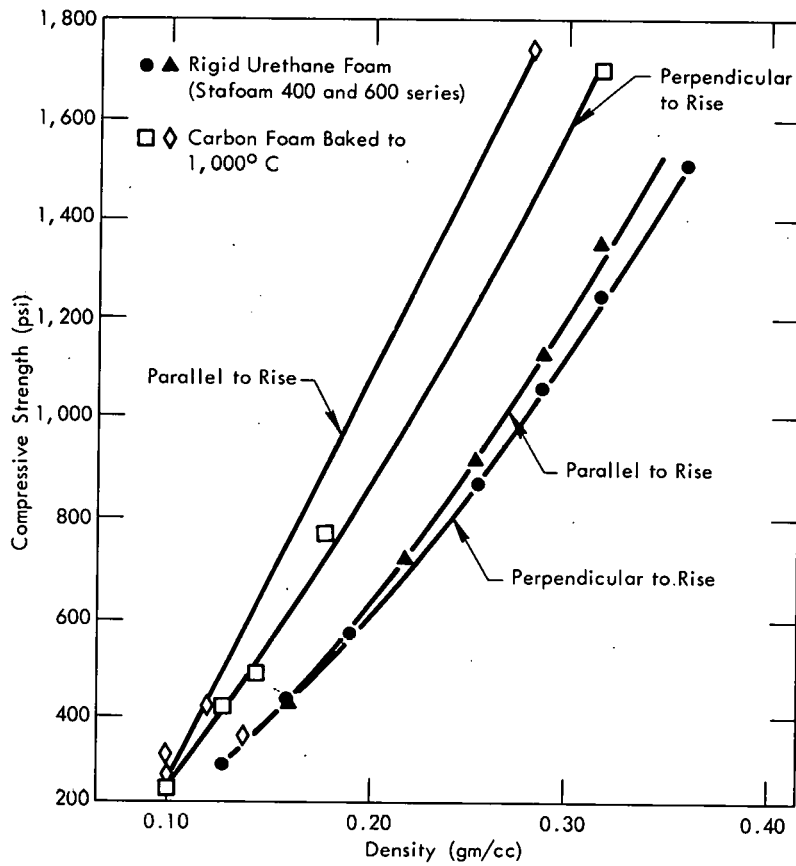
Figure 12. COMPRESSIVE STRENGTH OF TWO FOAM TYPES AS A FUNCTION OF THE DENSITY. (High-Density Range)

over both density ranges. This improvement can be shown by comparing the older data of Figure 12 with the data of Table 9.

Some inconsistencies in the data of Table 9 can, no doubt, be discerned. An exception is noted to the "fundamental law of carbon foam", namely: the compressive strength is always less in the perpendicular-to-rise direction at the same density. This law is upset in the case of Batch 1327 where the perpendicular-to-rise strength is almost twice that of the parallel-to-rise strength. The slightly higher density of the former is not sufficient to explain this anomaly.

Table 9

COMPRESSIVE STRENGTHS OF RIGID URETHANE FOAM

Batch Number	Density (gm/cc)	Compressive Strength (psi)	Varcum/Urethane Ratio	Orientation to Direction of Rise
1,327	0.26	1,118	1.1	Parallel
1,327	0.28	2,106	1.1	Perpendicular
1,329	0.30	2,092	1.5	Parallel
1,331	0.42	3,243	1.7	Perpendicular
1,331	0.43	3,297	1.7	Parallel
1,248	0.42	2,972	1.1	Perpendicular
1,316	0.42	3,213	1.1	Perpendicular
1,316	0.46	3,586	1.1	Parallel
988	0.68	9,538	1.1	Parallel

All batches listed in Table 9 employed Varcum 8266 except Batch 988 which was prepared using "cooked" Varcum 8251. Varcum 8266 is essentially the same as Varcum 8267. The "8267" designation was used simply to provide a means of describing Varcum 8266 that had been modified to conform to the Y-12 Plant specifications. "Cooked" Varcum is similar in nature to Varcum 8266 or 8267, but was prepared by heating Varcum 8251 at 120° C for 48 hours.

Any investigator in the field of carbon foam technology soon becomes aware that results obtained are by no means always consistent. Many inexplicable results are obtained, not only with respect to the final product characteristics; but, more especially, with respect to the casting operations. This phenomenon will be further explored under DISCUSSION.

Table 10 presents data for a single casting which, after trimming the carbonized billet, had a diameter of approximately 12 inches and was approximately 18 inches high. Compressive specimens were taken around the casting and from top to bottom. While the variation in density is well within ± 10 percent of the intended 0.10 gm/cc value, the variation in compressive strength is much wider than might be desired. This casting was prepared with a formulation containing graphite flour. The elimination of graphite flour, as currently practiced, would give higher compressive strengths on the average and very likely might give more uniform compressive strengths throughout the billet.

DISCUSSION

Raw Materials

Most of the difficulties associated with the preparation of green castings have been due to trouble with raw materials. The problem has been aggravated because, at least with the urethane chemicals, analytical methods do not reveal the difference between lots of the chemicals which give good results and lots which do not. The Varcum can be well defined, but considerable difficulty has been experienced in getting material from the manufacturer to meet specifications.

Thermalthane 4002-45 - The urethane system is purchased on a specification which emphasizes close adherence to its manufacturing procedure, including raw materials used, their proportions, temperatures for reaction, and especially the cool-down procedure in the case of the "R" component.

In the manufacture of the resin ("R" component), pentaerythritol and E-caprolactone are reacted at an elevated temperature. An excess of pentaerythritol is always used; and, in order to maintain the excess in a fine crystalline state, rapid cooling with high shear agitation is important. Even with this precaution, the crystals tend to agglomerate and build up on the walls of the drum in storage. When this situation occurs, the material should be scraped from the walls and the resin thoroughly agitated either with a propeller agitator or by the use of a drum tumbler in order to stir in the separated crystals. The urethane "T" component can be agitated by rolling on a drum roller or by the use of a drum tumbler. While this component is supposedly a true solution, in some cases improvement in casting results has been observed after rolling the "T" drums. This discrepency would indicate some degree of segregation within the "T" component.

Differences between lots of urethane (even between drums of the same lot) have been observed with respect to casting results. Cross fracture and splitting of green castings have sometimes been eliminated by changing to a different drum of "R" or "T".

Table 10

COMPRESSIVE STRENGTH, DENSITY, AND MODULUS OF ELASTICITY OF CARBON FOAM

(From Batch 1084; Baked at 1,000° C; Batch Density, 0.10 gm/cc; Axes of Samples Perpendicular to Rise)

Specimen Number	Compressive Strength (psi)	Density (gm/cc)	Modulus of Elasticity (psi x 10^3)
2880-59-0237-1	265	0.095	17.7
-2	175	0.098	14.8
-3	157	0.103	12.5[1]
-4	286	0.102	15.1
-5	293	0.095	19.2
-6	115	0.105	10.4[2]
-7	280	0.096	17.1
-8	291	0.096	17.9
-9	208	0.092	16.2
-10	225	0.096	14.4
-11	304	0.097	17.7
-12	214	0.100	12.6
-13	288	0.094	18.3
-14	199	0.099	12.6
-15	228	0.097	14.4
-16	251	0.097	16.8
-17	215	0.097	14.7
-18	187	0.104	12.5
-19	178	0.100	13.0
-20	271	0.097	18.0
-21	260	0.097	18.0
-22	300	0.096	18.6
-23	282	0.094	20.5
-24	208	0.099	13.9
-25	251	0.101	14.2
-26	281	0.100	14.9
-27	275	0.096	17.9
-28	305	0.095	18.5
-29	170	0.099	11.9
-30	231	0.095	14.2
-31	191	0.100	12.8
-32	252	0.095	15.3

If Specimen 2880-59-0237-3, which was chipped when received at the testing laboratory, and Specimen 2880-59-0237-6, which failed at the glued joint between the aluminum disc and carbon foam specimen, are omitted, the following values would apply:

Maximum Compressive Strength (psi)	305	Maximum Modulus of Elasticity (psi x 10^3)	20.5
Minimum Compressive Strength (psi)	170	Minimum Modulus of Elasticity (psi x 10^3)	11.9
Average Compressive Strength (psi)	245.5	Average Modulus of Elasticity (psi x 10^3)	15.8

(1) Specimen was chipped on the edge when received.
(2) Specimen failed at the glued joint.

As has been stated, the difference in performance cannot be correlated with analyses of the urethane. Actually, the analytical specifications are rather simple. They follow:

	"R"		"T"
Hydroxyl Number	605 ± 10	Viscosity	450 ± 150 centipoise
H_2O	0.20% (max)	Amine Equivalent	135 ± 5
Acid Number	3.0 (max)		

Many drums and lots of poor-performing urethane have been analyzed for these criteria and found to be within the specified values. More sophisticated analytical methods, including infrared and gel-permeation chromatography have also failed to reveal differences between "good" and "bad" urethanes.

Cell Regulators - A number of different surfactants have been investigated for use as cell regulators. Originally, Dow-Corning's DC 113 was used, but when this material was withdrawn from the market it was necessary to investigate other surfactants.

Some of the materials did not work well at all, giving ragged cells and large voids. Some of the surfactants gave reasonably good results at times, but in some trials gave numerous, moderately large, cigar-shaped voids. (Some of this erratic performance might have been compounded by nonoptimum mix conditions since this work was carried out before the automated mixer was available and before systematic mixing studies were completed.)

The cell regulator which was found to perform successfully without making compensatory changes in formulation was Dow-Corning's DC 193, and this is the cell regulator in use at the present time. Since it has been found that this cell regulator may spoil with age, it is desirable not to stock too large a supply.

Catalysts - The urethane catalyst which was originally contained in the "R" component was N-methyl morpholine. For several years both the cell regulator and catalyst were received in separate containers so that the amount of each could be varied, if desired, or other materials substituted. Actually, although substitution of other catalysts and variation of the amount has been investigated experimentally, the original amount of catalyst and type has been retained in the present carbon foam formulations. In special instances, triethylamine has been used and for some very large (or tall) castings appeared to have some

advantage. According to the urethane literature,[i] triethylamine catalyzes the foaming reaction relatively more than it does the gelation. Its use, therefore, might be expected to aid in completion of the foam rise before gelation takes place, thus averting fractures due to gas pressure rupturing the gelled casting.

Stannous octoate has also been used. Although a very powerful catalyst, it appears to have no advantage for carbon foam work under the circumstances in which it was used.

Varcum 8267 - After early work in which Varcum 8251 was used, the desirability of a more highly polymerized material was conceived. Accordingly, Varcum 8251 was heated at 120° C for an extended period (48 - 72 hours). Later, consultation with the Varcum manufacturer revealed that, actually, Varcum 8251 was prepared by "cutting" a more highly polymerized product with furfuryl alcohol. By obtaining the product before it was diluted, a more viscous and more highly polymerized material would result. This product was denoted as Varcum 8266. Later, it became evident that still further polymerization was required to be equivalent to the material prepared by "cooking" Varcum 8251.

After a considerable period of trial and error, collaboration between the manu- facturer and Y-12 produced a more suitable Varcum. Later, a specification was prepared for the Y-12 Plant's requirements. While perhaps further minor modification may be desirable, Table 11 gives the specification values in current use. Modification of the carbon foam process involving utilization of the more highly polymerized furfuryl alcohol is covered in an application for a US Patent filed by the Atomic Energy Commission.

Table 11
SPECIFICATIONS FOR VARCUM 8267

Hydroxyl Number	135 (max)
Average Molecular Weight	360 (min)
pH	4.5 - 5.5
Water Content	0.50% (max)
Resin Solids Content	73 - 79%
Sheared Viscosity	8,000 - 14,000 cps

(i) Saunders, J. H. and Fresch, K. C.; Polyurethanes, Chemistry and Technology, Part II; Interscience Publishers, New York (1964).

Hydroxyl number is determined by the method used in urethane analysis. It decreases with higher polymerization and increases with higher concentrations of the monomer and lower polymers. For example, Varcum 8251 has a typical hydroxyl number around 257.

Average molecular weight is determined by vapor pressure osmometry. Obviously this is a measure of the degree of polymerization. Resin solids content is another polymerization index. It is determined by weighing the residue from a sample heated in an oven for three hours at 135° C. The percent residue is the value for resin solids content; higher values indicate more extensive polymerization. A Brookfield viscosimeter is used to determine viscosity. Because of the thixotropic nature of Varcum, the sample must be thoroughly agitated—perhaps for as long as 20 minutes—to get consistent results. This shearing has been known to reduce an observed viscosity from 15,000 to 8,000 centipoises. Water is determined by the Karl Fischer method.

It appears that the viscosity of Varcum is a property of the greatest importance. While viscosity can be so high as to make mixing difficult or impossible, too low a viscosity can result in a high failure rate for green castings due to cross fracture or cracking. Figures 13 and 14 present photographs of cross-fractured castings. For some time, differences in performance of identical raw materials in the master batch premix compared with individual premix batches was noted. The difference in behavior was finally traced to a lowered viscosity of the master batch due to the shear effect caused by the agitator and probably the Moyno pump. Both the Varcum and urethane "R" component are thixotropic. Mechanical energy input from the agitator and pump also warms the mixture. The effect of all this is a lower viscosity. The detrimental effect of lowered viscosity can be overcome by lowering the temperature and reducing the amount of shear. By starting with a more highly polymerized Varcum, a higher viscosity of the premix can be maintained even with higher temperatures and higher shearing.

A premix from the master-batch mixer which produced cross fractures was withdrawn as several batches and allowed to stand over 72 hours. Castings produced from these batches did not crack or cross fracture. It is evident that by standing for 72 hours, the sheared viscosity increased. Also, the temperature of the premix withdrawals dropped. Prior to this, there had been some hypotheses advanced (not concurred in by those connected with this study) that the difference between some single premix batches which were successful and some master batches which produced cross-fractured castings was due to a deterioration of the master-batch chemicals. But, master batches have been used in this program that were several days old without trouble. For this reason, it was difficult to believe that the chemicals deteriorated within an eight-hour day.
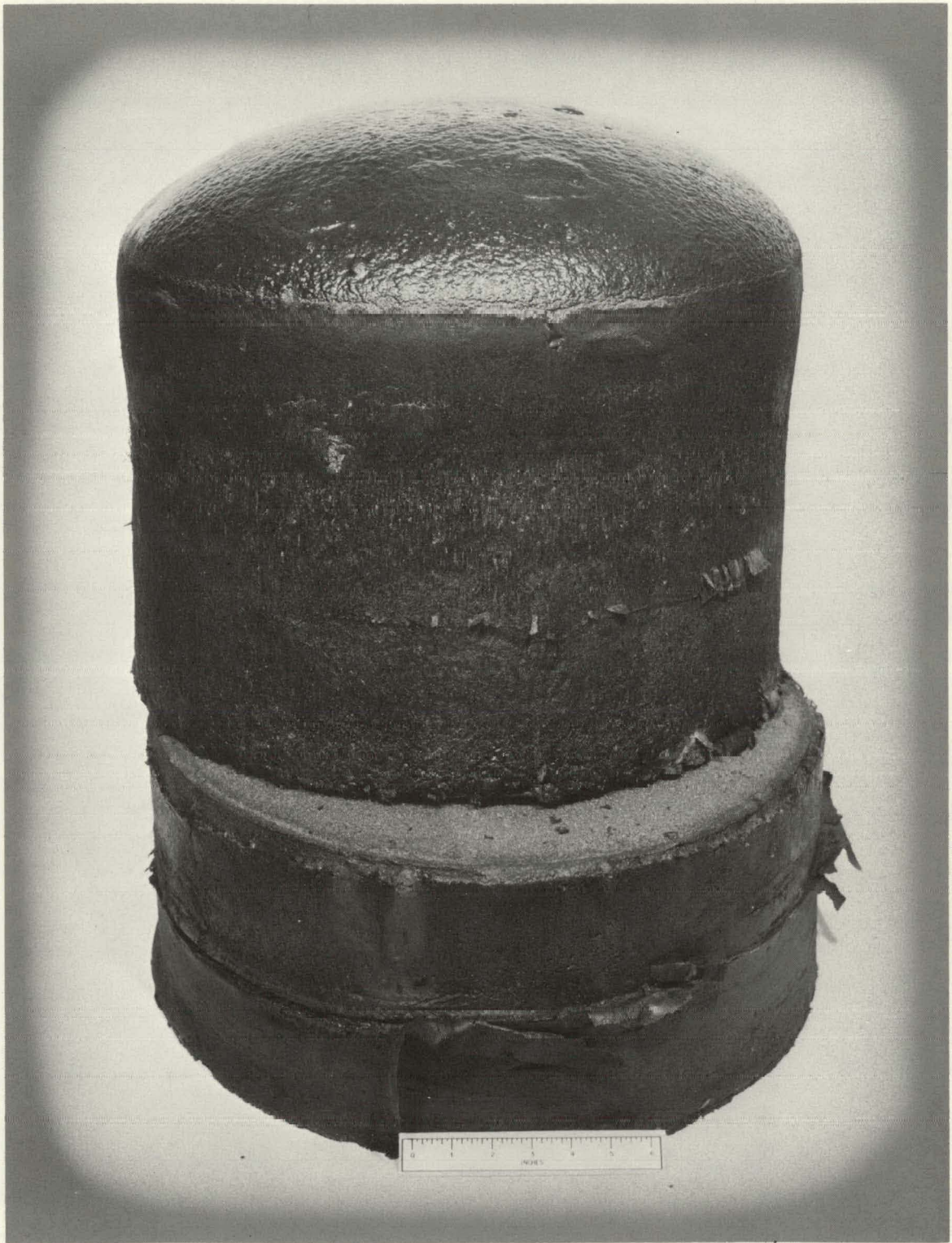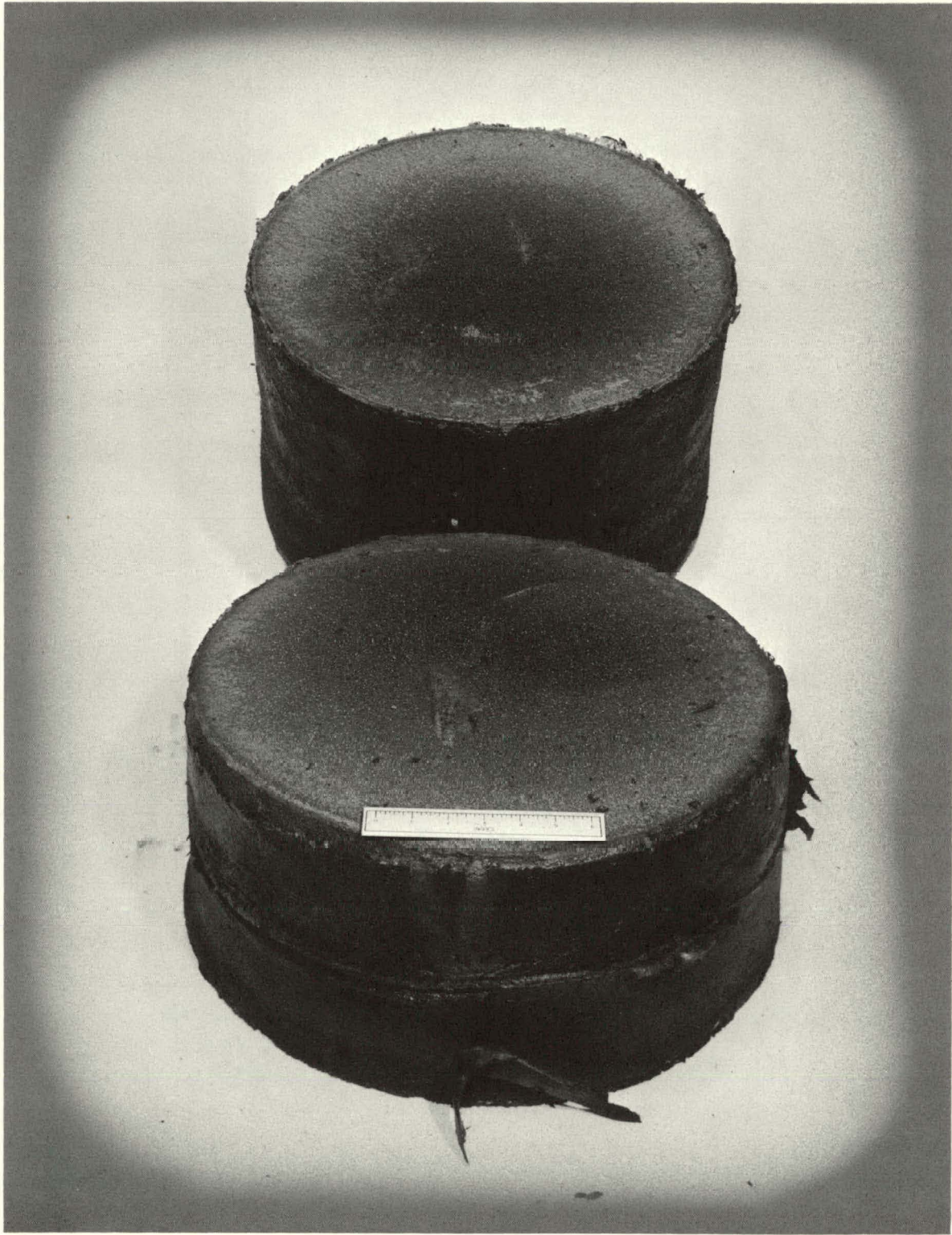
Figure 13. CROSS-FRACTURED GREEN CASTING. (Elevation View)

130664

130670

Figure 14. CROSS-FRACTURED GREEN CASTING. (Showing Mating Surfaces of Fracture)

An extremely viscous Varcum may give mixing difficulties; and, if a poor mix results, cross fracturing may occur. Also, highly viscous Varcum (giving a high viscosity premix) may result in a greater number of moderate-to-small cigar-shaped voids. This problem is believed to be due to entrapment of air (or perhaps carbon dioxide from the foaming reaction) so that instead of leaving the casting, it is caught as a bubble and stretched to form the cigar shape, retaining this shape as the material gels.

The data of Table 12 correlates the casting performance with the analytical data for ten lots of Varcum 8267. Where performance is indicated as "too thick", the viscosity of the Varcum was so great that mixing was either impossible or was very poor. Marginal performance indicates that a number of cross-fractured or cracked castings were produced in some master batches, with some master batches giving few such castings. This situation might be a case where performance varied due to temperature changes or changes in the degree of shear achieved in mixing. "Good" and "bad" performance indicated very few and many bad castings, respectively.

One lot (Run 37) gave a different performance from drum to drum. On a more recent lot, the first drums used gave poor results (requiring further cooking to make them usable), but later drums from the same lot performed well without further heat treatment. The reason for this is not established, but is believed to be due to an increase in viscosity on standing. Heating and agitating the material at the factory prior to loading the drums would lower the viscosity, and the return to a higher viscosity might take several weeks. This problem may have been the case with Run 37, or the variable performance may have been due to a variable temperature and shear. The importance of shear and temperature were not appreciated at the time Run 37 was used, but now these factors are carefully controlled. There does appear to be considerable difference in analysis between some drums of Run 37. Table 13 reports these analytical results. While several drums appear to be close together in character, a spread in hydroxyl number of from 133 to 159 is noted. On resampling Drum 84870, a high value of 154 was reduced to 134, so there may be involvement of an analytical error or nonuniformity within drums. The fact remains, however, that performance did vary from drum to drum. Even with a well-performing Varcum, some differences in analysis from one drum to another within a lot are reported. Run 40 reported in Table 12 to have an average molecular weight of 380 gave different values for different drums, as shown in Table 14. This table also shows appreciably different values for viscosity. It is believed that the difference in viscosity results could be attributed to insufficient shearing in the laboratory prior to running the viscosity. The laboratory at that time was agitating samples for four minutes. Later work in the laboratroy indicates that a 20-minute agitation period may be required to reach minimum

Table 12

AVERAGES OF VARCUM 8267 ANALYTICAL DATA

Specified Property	Run Number									
	26	30	31	32	33	37	40	11	12	13
Hydroxyl Number	117	142	116	122	127	144	133	131	142	138
Average Molecular Weight	434		408	408	411	344	380	380	320	349
Weight Percent Water	0.22	0.67	0.35	0.58	0.42	0.49	0.43	0.52	0.62	0.49
pH							4.7	4.5	5.0	5.4
Resin Solids						76.4	73.7	75.0	77.4	71.2	70.7
Viscosity (cps)	43,900	14,000	44,500	29,200	13,200	7,400	9,700	10,086	4,900	6,500
Performance	Too Thick	Marginal	Too Thick	Too Thick	Good	Varied between Drums	Good	Good	Bad	Marginal

values. (Minimum values are desired in order to put all samples on the same basis.) However, extended agitation presents difficulties for the analysts since this treatment also warms the material. The standard temperature for the determination is 25° C.

On the whole, except for viscosity, the results shown in Table 13 are in good agreement.

Other Formulations

Use of Inorganic Powders – The two formulations described earlier in this report were given as typical of low and high-density foams. Other formulations have been used. Some of the higher Varcum-to-urethane ratios have been indicated in Table 9. Higher Varcum-to-urethane ratios are of doubtful merit although they may be necessary when making the highest densities (0.8 to 1.0 gm/cc). Addition of graphite may be necessary for those densities also. Besides graphite flour, other particulate materials may be added to the formulation, if desired. For example, a silicon carbide foam was prepared by adding silicon powder or silica to a normal formulation, carbonizing it at 1,000° C, then high firing it in an induction furnace to 2,000° C. Excess carbon was later burned out in air. The end product was a silicon carbide foam, but the strength of the material was rather low.

Table 13

VARCUM ANALYSIS FOR RUN 37

Drum Number	Laboratory Sample Number	Viscosity (cps)	Hydroxyl Number	Acid Number	H$_2$O (%)
83242	236247	7,600	133	2.2	0.43
84867	466734	7,800	137	1.8	0.48
84868	466733	8,000	136	1.8	0.49
84869	466728	6,800	144	1.8	0.50
84870	466727	6,400	155	1.8	0.51
84871	466739	7,800	147	1.7	0.50
84872	466737	8,000	147	1.8	0.48
84873	466738	7,700	152	1.7	0.51
84874	466735	7,400	140	1.8	0.48
84875	466730	7,000	140	1.7	0.47
84876	466732	7,100	138	1.7	0.50
84877	466731	7,700	139	1.7	0.51
84878	466736	7,900	142	1.8	0.48
84879	466729	6,700	159	1.8	0.51
84880	466226	6,900	153	1.7	0.47
84870	466743	8,400	134	2.0	0.44 (resample)

Table 14

ANALYTICAL DATA ON VARCUM 8267, RUN 40

Drum Number	Hydroxyl Number	Acid Number	pH	H₂O Content (%)	Viscosity[1] (psi)	Average Molecular Weight
810879	133	1.7	4.5	0.43	9,700	
810880	134	1.8	4.6	0.48	11,000	
810881	134	2.3	4.5	0.43	8,600	367
810883	133	1.7	5.0	0.52	12,000	
810885	135	1.9	4.5	0.44	10,000	363
810886	132	1.9	4.6	0.42	9,800	352

Elemental Analyses

	Requisition 810881	Requisition 810886	Requisition 810885
Carbon	67.9%	67.6%	67.4%
Hydrogen	5.7%	5.6%	5.4%
Oxygen	26.51%	26.36%	26.53%

(1) At 25° C.

Boron and tungsten powders have also been used experimentally. In general, the addition of powders aids nucleation, giving a fine cell structure; but, in most cases, the compressive strength is lower than carbon foam of the same density without the powder additives. For the preparation of the highest-density foams (0.8 - 1.0 gm/cc), a Varcum-to-urethane ratio of at least 1.0, together with graphite flour, must be used. Furthermore, usually no water can be added. As a matter of fact, the amount of water content of the Varcum may be too high to achieve the desired density. In this situation, the water content of the Varcum may be reduced by warming the Varcum and then by placing it in a vacuum chamber to remove some of the water by vacuum distillation. Another technique useful in making high-density material is to make a premix of Varcum and "T"; and, after about a six-minute agitation, adding the required amount of "R". The reaction of water and "T" during the premix agitation evolves some of the carbon dioxide which might otherwise serve to lower the density.

Use of Organic Powders - An exception to the lowering of strength by powder additions is the increase of strength achieved by the addition of fine (-200 mesh) organic powders. Table 15 gives compressive-strength values for carbon foam prepared with varying amounts of corn starch added to the formulation. Three of the batches were prepared with the percent of additive based on the weight of urethane resin ("R" component) in the formulation. The one with six percent of the total mix was taken on that basis to compare with foam formerly prepared with six percent graphite flour based on the total mix.

Table 15

PROPERTIES OF CARBON FOAM CONTAINING CORN STARCH
(Castings have a Density of 0.05 gm/cc ± 2%)

Corn Starch Content	Average Modulus of Elasticity (psi x 10^3)	Average Maximum Compressive Strength within 0.2 Inch Deflection (psi)
None	5.0	53
5 wt % of Resin	5.9	71
10 wt % of Resin	8.4	90
15 wt % of Resin	8.6	86
6 wt % of Total Mix	6.1	64

Figure 15 compares two levels of starch addition at different densities versus the compressive strength. A value for a control sample containing no additive is shown for comparison.

Other batches of carbon foam were made in which reagent-grade soluble starch, wheat flour, and powdered sugar were added. Soluble starch had about the same effect as corn starch. Wheat flour and powdered sugar gave erratic results— some specimens taken from the same casting gave higher compressive strength versus density and some showed no improvement. For example, from a casting to which powdered sugar amounting to five percent of the urethane "R" was added, one specimen having a density of 0.052 gm/cc gave a compressive strength of 82 psi while another specimen having a higher density of 0.056 gm/cc gave a compressive strength of 56 psi. This discrepency may indicate poor mixing or perhaps a nonuniform solution of part of the sugar.

A patent covering the use of fine organic particulate materials in carbon foam formulations for the purpose of increasing compressive strength has been filed by the Atomic Energy Commission with the US Patent Office. It is believed that the reason organic powders give increased strength whereas graphite flour or carbon black give reduced strength is due to the fact that graphite remains unchanged during carbonization whereas the organic powders decompose along with the remainder of its formulation. Thus, the matrix of the carbon foam is shrinking around the graphite nuclei while the decomposing organic powders become part of the matrix. While both graphite and organic powders may serve as nucleating agents, the different behavior during carbonization gives different resulting characteristics to the carbon foam.

Problems

Cross Fracture and Cracking - Cross fracturing and cracking of green castings has already been mentioned. This problem has been attributed to a low-viscosity
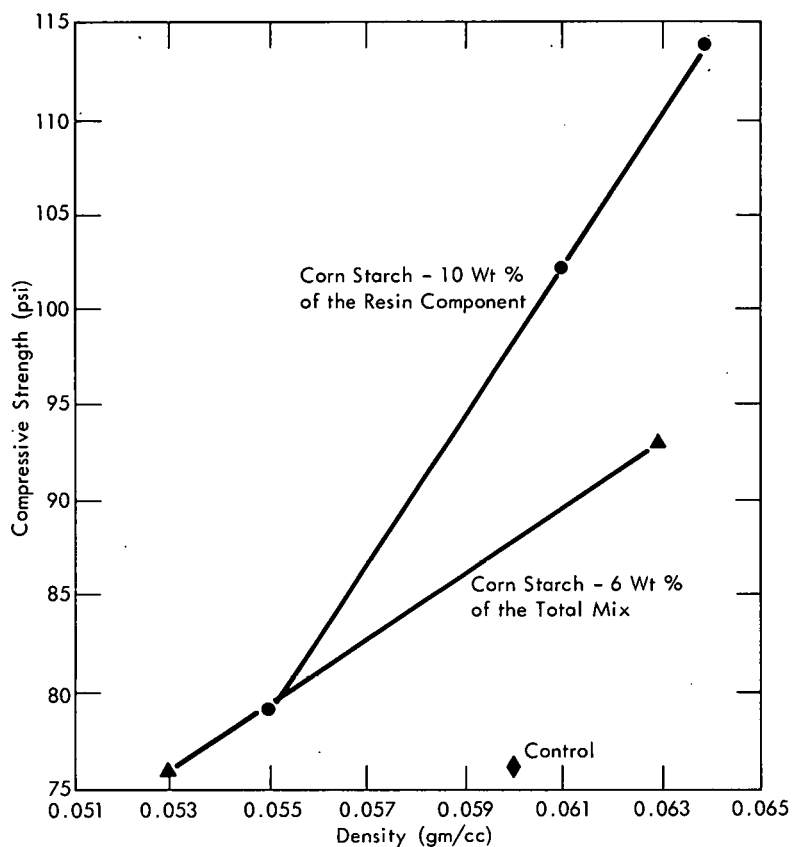
Figure 15. COMPRESSIVE STRENGTH AS A FUNCTION OF THE DENSITY FOR CARBON FOAM CONTAINING CORN STARCH.

Varcum in the premix. For a long time, cross fracturing was attributed to an excessive content of unpolymerized furfuryl alcohol together with the lower polymers. Further polymerization by cooking at 120° C corrected the difficulty. Whether the difficulty was corrected by the concomitant increase in viscosity or by the reduction in concentration of the monomer and lower polymers cannot be stated definitely. It is believed that probably both low viscosity and excessive monomer content contribute to cross fracturing. However, it has been established that with the same premix, cross fracturing may be promoted by excessive shearing and temperature; by restraining the degree of shear and temperature rise, cross fracturing may be dramatically eliminated. Regardless of the mechanism of the improvement, there is no question but that the chemical nature (degree of polymerization) and viscosity are both changed by cooking. Table 16 shows a decrease in hydroxyl number, increases in molecular weight and resin solids, and a marked increase in viscosity.

Sometimes a vertical crack occurs near or on the top of the casting. This situation may or may not cause rejection of the casting, depending on how deep the crack extends. Ocassionally, a blister rises on the top of the green

Table 16

EFFECTS OF COOKING VARCUM 8267

| Property	Run 12		Run 13		Run 0741	
	Before	After	Before	After	Before	After
Hydroxyl Number	142	132	138	133	129	122
Average Molecular Weight	320	375	349	394	365	404
Water (wt %)	0.62	0.42	0.49	0.50	0.30	0.40
pH	5.0	5.4	5.4	5.5	5.5	5.5
Resin Solids (%)	71.2	76.5	70.7	77.6	72.5	77.2
Viscosity (cps)	4,900	12,500	6,500	17,000	12,000	17,400

casting. Invariably if the blister is removed, a large gas bubble will be found underneath. Cracking and blistering have been attributed to the occurrence of gelation before gas evolution is complete. Two views of such a formation can be seen in Figures 16 and 17.

It is believed that lower-viscosity (less polymerized) Varcum is the prime cause of green casting failures. However, on several occasions, with a given drum of Varcum, good and poor casting yields have been realized that appear to depend solely on the particular drum or lot of urethanes used. Without changing the Varcum used, changing the urethane (or perhaps only one of its components) has resulted in a change from good to bad casting yields (or vice versa). There may very well be a synergistic effect whereby a moderate deficiency in either urethane or Varcum can be tolerated; but, with a moderate deficiency in both, very poor casting yields will result.

Carbonization - One of the most common troubles with carbonization has been a slumping or canting of billets. Some degree of prevention has been achieved by long-term room-temperature curing (for a period of 10 - 20 days). Because canting toward the center of the furnace appears to be more common with the castings nearest the hot muffle wall, lining the muffle with about three to four inches of carbon foam was tried, but this modification did not improve the situation. The canting phenomenon appears to differ with different furnaces even though the same carbonization cycle is used. There is a possibility that changes in the chemical raw materials may play a part in causing this trouble, but there is no conclusive evidence. The first run made in the furnace shown in Figures 7 - 10 gave practically no evidence of canting or slumping.
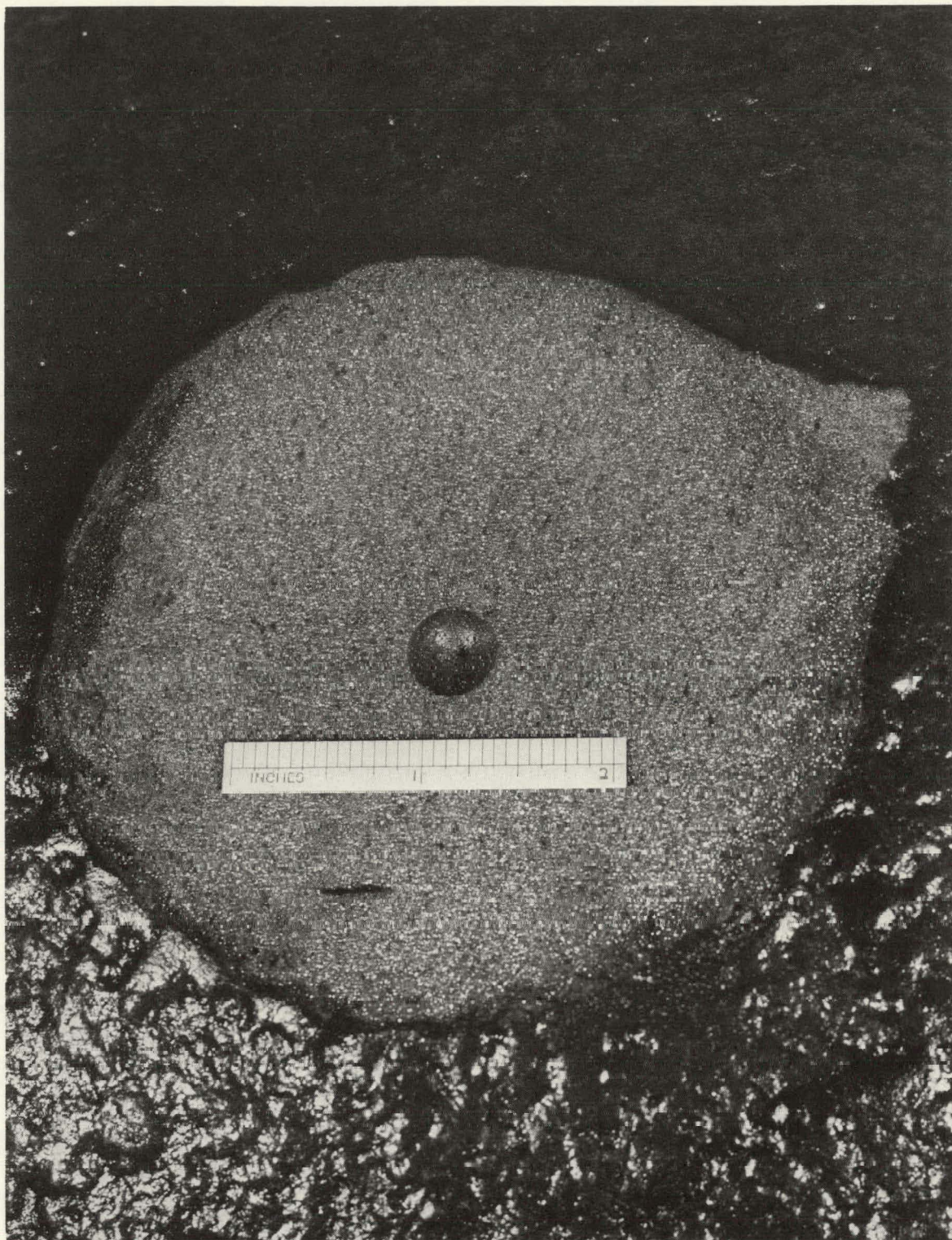
Blistering during carbonization may occur. This problem arises because there is not a sufficient depth of the denser material removed near the surface prior to
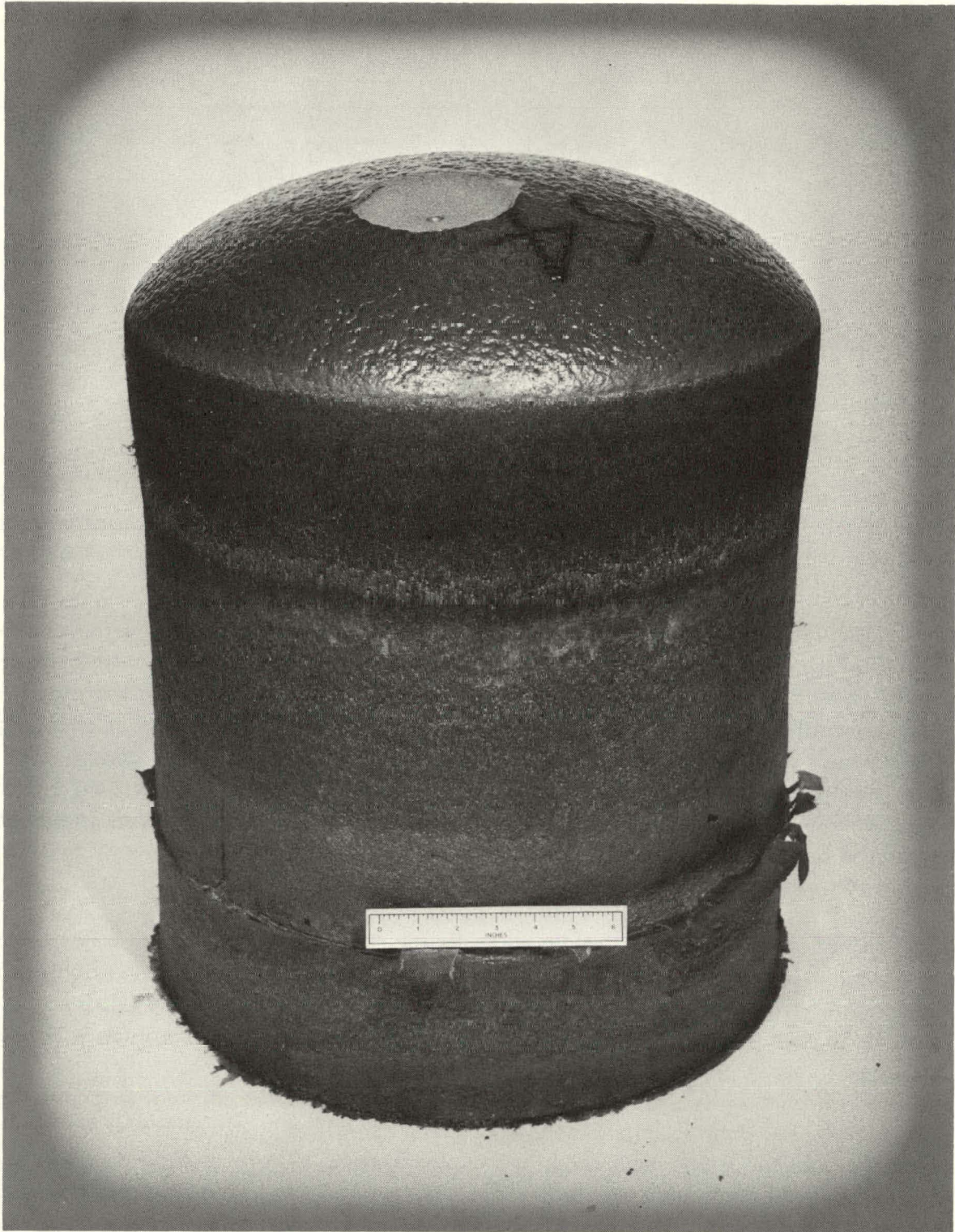
Figure 16. GREEN CASTING WITH BLISTER REMOVED, SHOWING BUBBLE.

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Figure 17.   TOP VIEW OF GREEN CASTING WITH BLISTER REMOVED, SHOWING BUBBLE.

carbonization. Because there is approximately 1/3 reduction in the dimensions of a carbonized casting from the green casting dimensions, there may be a tendency to remove too little material in order to avoid undersized billets. If this is the case, going to a larger mold size is the solution. For carbon foam having a density of 0.05 gm/cc, if a 10-inch-diameter blank is desired, a 22-inch-diameter mold should be used. This size will permit removal of 1 1/2 - 2 inches from the radius, will allow for about 1/3 shrinkage, and will permit trimming off about one inch from the carbonized billet. Removal of a liberal amount from the green casting facilitates outgassing (reducing blistering) and may contribute to crack elimination. The allowance for trimming after carbonization will ensure an ability to obtain a straight cylinder if the billet should cant or slump.

Cracking of castings appears to be related to erratic control of furnace temperature. If furnace power is lost and the temperature should drop 100° C, a high probability of cracking is assured. Cycling of temperature—overshooting followed by dropping below the control temperature on a repetitive basis—commonly results in billet cracking. Cracking has been more prevalent in the higher-density billets. For billets having a carbonized density of 0.8 gm/cc, the mortality due to cracking is very high, even when a 120-hour cycle is used; with the 60-hour cycle, cracking is more likely to occur with the 0.2 gm/cc material than with the 0.05 gm/cc foam. However, there have been occasions when a mixed load of castings resulted in cracks in the 0.05 gm/cc billets but not in the 0.22 gm/cc billets. Curing time and temperature, types of chemicals, and variance in furnace performance may be variables individually or in combination which cause cracking.

Figure 18 shows a green casting before and after trimming together with a carbonized billet as removed from the furnace and after preparation of a blank. This material has a green density of about 0.042 gm/cc and a carbonized density of about 0.05 gm/cc in the blank. Figure 19 presents a view of the same combination of items but having a density of 0.22 gm/cc in the blank.

The relationship of the size of a trimmed green casting and of a billet as removed from the furnace is striking. With such a large change in volume, it is not surprising that the development of carbonization time-temperature programs has been a problem.

Density Control - In work with rigid urethane, the specification tolerance for product density is frequently ± 10 percent, and this tolerance has been carried over into the work with carbon foam. Continuing with the two densities used for illustration purposes, this means that for the nominal 0.05 gm/cc material, a range of 0.045 to 0.055 gm/cc would meet specifications; for the nominal 0.22
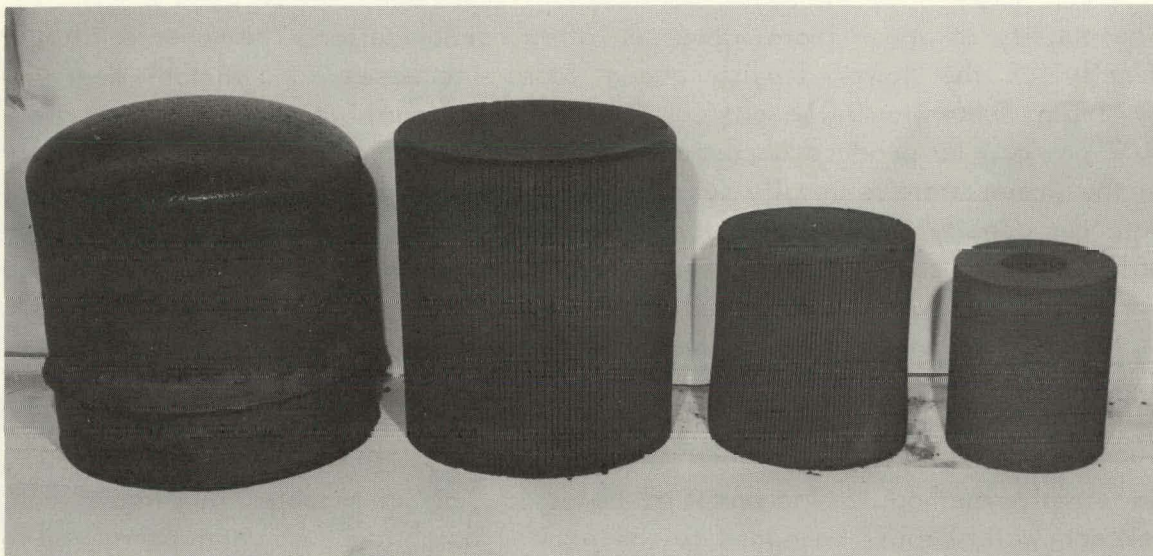
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Figure 18. FROM LEFT TO RIGHT—GREEN CASTING, GREEN CASTING AFTER TRIMMING, CARBONIZED BILLET, BLANK CUT FROM BILLET BY HOLE SAW. (0.05 gm/cc Density)

gm/cc foam, the range would be 0.20 to 0.24 gm/cc. In actual practice, there is little difficulty in controlling the density of the heavier material; there is sometimes trouble with the lower density foam.
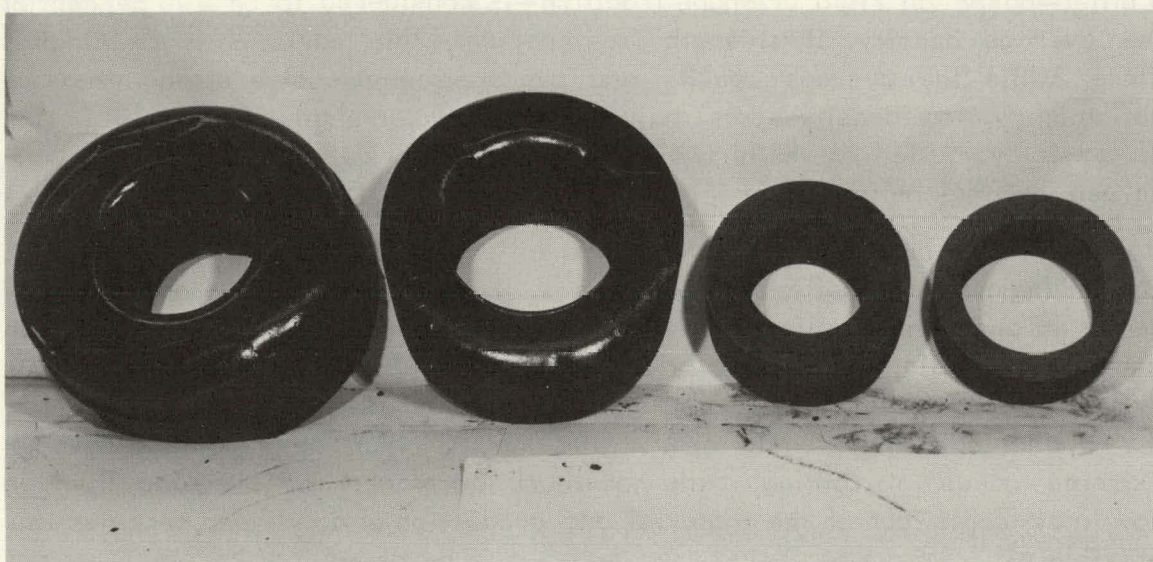
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Figure 19. FROM LEFT TO RIGHT—GREEN CASTING, GREEN CASTING AFTER TRIMMING, CARBONIZED BILLET, BLANK CUT FROM BILLET BY HOLE SAW. (0.22 gm/cc Density)

The density of green foam increases after carbonization. The superficial bulk density of the lower-density green foam increases to a variable degree—by from 0.007 to 0.012 gm/cc. The heavier foam increases approximately 0.02 gm/cc. To produce a carbonized density of 0.05 gm/cc, the target density in the green state is usually set at 0.040 to 0.043 gm/cc. For the heavier foam, a target density in the green state is set at 0.18 to 0.19 gm/cc. On a production basis, density control is effected by filling the mold (of known volume) with the corresponding weight of pour for the density in question. The weight of pour is taken (from experience) to be the total batch weight (premix plus "T") less the experienced value for holdup in the mix pail. If the mold is not filled, the density is too high and water must be added to the premix. Care is taken to avoid too low a green density. Water can be added to lower the density, but there is no simple method to increase it. If too low, either more premix ingredients (except water) must be added to the master batch tank, or water permitted to evaporate therefrom.

With a new master batch, the first one or two castings are checked for density by observing the height reached at the end of the rise. Occasionally, it is necessary to add water to the master batch to lower the density. If the green density is borderline on the low-density side, the casting may not be rejected because there is an increase in density during carbonization, and this increase has sufficient variability (0.007 - 0.012 gm/cc for 0.05 gm/cc nominal density) so that the final density cannot be exactly predicted.

Density Variation Within a Billet - The permissible variation of density within a billet—based on rigid urethane tradition—is considered to be ± 10 percent of the average density. If strength is important, this variation is meaningful; since, while the average density and average compressive strength may be satisfactory, low-density spots may result in low-strength areas. A limitation of density variation on the high side is not important as far as strength is concerned, but may be important if a uniform material is desired.

Normally, the outside and bottom of a billet are the higher-density regions. By making castings sufficiently oversized, these higher-density volumes may be cut off and a more uniform density throughout the blank result. This provision for oversize billets is especially important if billets are canted. It is obvious that, in such cases, cutting out a true cylinder will result in some parts of the cylindrical blank being nearer the surface than other parts. Indeed, in extreme cases of canting, with not much allowance for trimming, the hole saw may come out of the material and production of a cylinder becomes impossible.

Density variation is determined radiographically by the DXT (density times thickness) measurement. Incidently, the average density of blanks is also determined radiographically by comparison with a standard density block.

Radiographic Failures - Obviously, a carbon foam part should not contain gross cavities. In early work with a 0.50 gm/cc density foam, cavities as big as a fist were observed. Such cavities are not normally observed in current work. Cigar-shaped voids, most of them having an area in any plane less than 0.15 square inch, are observed. It is believed that a high incidence of such voids is associated with the higher viscosity of the mix. Other causes of excessive voids of this nature may be: (1) a greatly excessive speed of agitation during the final mix, and (2) a too shallow immersion of the mix blade. Both actions tend to whip in air bubbles. Additional causes of these voids may be: (1) entrapment of air by careless pouring (too rapid), (2) pouring from too great a height (made unnecessary by present mold design), or (3) pouring foam upon foam by delaying pouring until after foaming has begun. There appears to be more difficulty with void formation from single premix batches than with batches employing the master batch for the premix. This problem may be due to a higher-viscosity mix (less shearing and a lower temperature) in the case of the small premix batches.

High-density inclusions, though very small in size, have been observed by X-ray study. These problem areas are believed to be high-density particles of carbon, probably resulting from the incorporation into the mix of flecks of skin which forms on the surface of Varcum drums after standing. This skin is probably caused by a reaction with oxygen from the air. To prevent the skin from being mixed into the formulation, the drums of Varcum are skimmed prior to use. However, this procedure is not completely efficient and some particles of the higher-density skin do get into the batches.

Other Source of Information Regarding Carbon Foam

While not used as source material, other information with respect to carbon foam can be found in the report: Carbon Composite Materials Report, Second Issue, compiled by L. M. McLaughlin, Y-DA-2654, Pages 81 - 296; September 18, 1969. This reference includes work covered by this report (Pages 81 - 134) and work on carbon foam chemistry (Pages 135-184 and Pages 200-296).

ACKNOWLEDGEMENTS