The present invention relates to the manufacture of cellular products adapted for use for sound absorbing and heat insulation purposes.

In the United States patent to Walter M. Scott, 2,065,757, granted December 29, 1936, and the co-pending application of Gustavus J. Esselen, filed January 18, 1934, Serial No. 707,714, there is described the manufacture of such a cellular material by beating a mixture of a soluble silicate solution, a granular finely divided solid, such as limestone, and a fibrous solid, such as rock wool, to form a cellular foamy mass of predetermined increased volume which could be molded and dried to form tiles.

In cellular products for heat insulation and, more particularly, four sound absorbing purposes the form of the cell structure is an important factor. Thus, in a sound absorbing material the type of sound waves which are most efficiently absorbed depends in large measure upon the size of the cells and the degree of intercommunication between the cells. While a given sound absorbing material may be particularly suitable for a certain installation, a material having a cell structure of a different character may be most suitable for a different installation, or a material which possesses, to a certain degree, a combination of these cellular characteristics may be most suitable for a particular installation. On the other hand, the degree to which the material depends in large measure upon the size of the cells, the number of cells per unit volume, and the degree of intercommunication between the cells.

The present invention makes possible the production of a cellular product by a method involving foaming a mixture of a finely divided solid and a soluble silicate solution and drying the foamed material, which method involves such a control over various factors affecting the character of the finished product that it is possible to obtain a finished product having practically any desired cellular characteristics. In addition, the resulting product not only is fireproof but it is also highly resistant to water.

I have now discovered that there are various factors which affect the cellular character of the final product, that is, the size of the cells and the degree of intercommunication between the cells. Thus, I have discovered that the presence of a fibrous material tends to increase the size of the cells and to render them elongated in character. The alkalinity of the soluble silicate used also affects the size of the cells, that is, the use of a soluble silicate having a high alkalinity tends toward small cells, and vice versa. An excess of water in the mixture tends to increase the size of the cells in the finished product. The size of the cells as well as the degree of intercommunication between the cells is affected by the character of the drying operation. Thus, if the molded foamed material is placed in an oven in which the initial temperature is above a predetermined maximum temperature, the size of the cells will be increased, whereas, if the initial temperature of the oven is below a predetermined minimum the material will slump and the degree of intercommunication between the cells is reduced. Furthermore, the degree of intercommunication between the cells is effected by the relative proportion of solids to liquids present in the mix. As the proportion of solids is increased, the degree of intercommunication is decreased.

In the manufacture of cellular products of this general character prior to the present invention, the finished product often was found to contain a few relatively large cells intermingled with the remaining cells. There are two principal causes for this, namely, inclusion of air either due to improper wetting out of the solid material during the mixing of the solids and liquids prior to beating, or the inclusion of air as the foamed material is being handled between the beater and the molds. This difficulty may be overcome, as described and claimed in other co-pending applications, on the one hand by mixing the material at certain temperatures and by adding them in a certain order and on the other hand by pouring the foamed material into molds in such a way as to prevent the inclusion of air.

While it is preferred to increase the alkalinity of the mix by the use of a more alkaline silicate, it is within the contemplation of the invention to increase the alkalinity of the mix by an added alkali, such as sodium hydroxide. If an alkali, such as sodium hydroxide, is added to the formula used should be adjusted to compensate for the water added with the alkali.

The more alkaline the silicate, the more easily is it re-dissolved after drying. Consequently the product becomes progressively less water resistant as its alkalinity is increased. The invention further contemplates a method for treating the cellular product after it has been set by heat, to impart increased resistance to water in a product produced from a mix having either high or low alkalinity.
In the preferred practice of the invention, the following formula is employed:

Limestone .................................. pounds..... 36
Sodium silicate .................................. do....... 35
Powdered glass ................................. do......... 2
Frothing agent ................................. grams.... 138
Water .............................................. cc.... 1800

The sodium silicate used has a specific gravity of 52° Bé, and contains 13.8% sodium oxide, 33.7% silicon oxide and 52.5% water. The ratio of silicate to alkali is 2.44 to 1. The limestone contains at least 95% calcium carbonate and not over 2% magnesium carbonate and should be pulverized to such a degree of fineness that at least 95% will pass through a 100 mesh screen. If the particle size of the limestone is too small, difficulty may be encountered in wetting out. The frothing agent may be, for example, a material of the type of the sodium salts of sulfates of fatty acids or the sodium sulfonates of fatty acids. The powdered glass employed is ordinary milk bottle glass having a ratio of soda to silica of about 1 to 6.

The above ingredients are thoroughly mixed in an apparatus suitable for mixing and efficiently beating them from the beater to the frother. The mixer is then started at low speed and the powdered glass at room temperature added slowly. The limestone at room temperature is then added slowly during the mixing. When the materials are thoroughly mixed and wetted out, the speed of the mixer is increased and the volume of the mixture is gradually increased until a volume of about 72 quarts is obtained which represents an increase in volume of about six times the original volume.

Preferably, the foamed material is handled to prevent it from the beater to the molds by placing the foamed material in a hopper having a portion with straight vertical walls. Molds are then placed under the hopper and successively filled. Care must be taken to maintain the level of the foamed material in the hopper between the vertical side walls thereof in order to avoid the inclusion of air.

The molds containing the foamed material are then placed in an oven, the initial temperature of which is about 45° C., and allowed to remain at that temperature for about four hours. Then, the temperature of the oven is raised at the rate of about 5° Ca per hour until the temperature of the oven is about 55° C. The oven is then maintained at that temperature about 13 hours or until the foamed material is sensibly dry, that is, has the appearance and feel of a substantially dry material. At the end of this time the cell structure of the material is thoroughly set and will not be changed by subsequent heating. In the further drying of the material care must be taken not to increase the temperature of the oven too rapidly in order to avoid warping and cracking of the material.

Preferably, the temperature of the oven is raised at the rate of about 10° per hour until a temperature of about 105° C., is reached and the material is held at the latter temperature for about one hour. The heating may be continued at gradually increasing temperatures up to about 300° C. If desired, the material may be removed from the molds after a temperature of about 105° C., has been reached and subjected to further treatment to increase its reaction to water. When preparing the material for sound absorbing purposes, and in some cases for heat insulation, the initial temperature of the drying oven should not be less than between 30 to 60° C., depending upon the formula of the foamed material being dried. Otherwise, the foamed material tends to slump and become more dense and the degree of intercommunication between the cells in the final product will be reduced. On the other hand, the initial temperature of the drying oven should not be greater than between 45° to 65° C., depending upon the formula from which the foamed material was produced. If this temperature is exceeded, the foamed material tends to puff up increasing the size of the cells during the first few hours of drying. With the specific formula given hereinbefore, we have found that on an initial temperature of the drying oven of 45° C., is between the upper and lower limits mentioned for this particular formula.

Where maximum strength of the finished product is desired, puffing up should be avoided because it tends to weaken the structure.

If the foamed material produced from the specific formula given hereinbefore is dried as above described, it will have a uniform cellular structure containing a multiplicity of intercommunicating small cells. If, however, the temperature of the oven is gradually raised from 45° C., to about 70° C., during the first four hours, and then maintained at a temperature of about 70° for eight or ten hours, the resulting product will have a surface layer containing small intercommunicating cells and the remainder of the product will have larger intercommunicating cells.

It appears that the surface layer sets more rapidly and, consequently, when the latter heating procedure is followed the cell structure of the surface layer is set substantially its original form containing small cells while the remaining portion of the material has been caused to puff up more or less depending upon the cycle employed.

Other characteristics of product may be produced by varying the drying cycle. For example, if the mix is allowed to slump slightly as by drying for the first hour at room temperature, which is below the slumping temperature of the formula in a current of air, then raising the temperature gradually for several hours until the desired drying is effected, the resulting tile will have very dense, hard and strong surfaces with a very soft core of much larger pores in the center. Such a tile would be useful as an insulating floor for a drier. Many other variations in the characteristics could be produced as desired by suitable changes in the cycle, and these variations lie within the scope of this invention.

In order to increase the resistance of the final cellular product to the passage of sound, one of several procedures would be effective, such as (1) treatment of the cellular product, either before or after having been set by heating, with an acidic material, such as a weak acid, acid gases or acid salts, (2) the incorporation in the mix before heating of materials, such as sulfur, cer-
tain metallic oxides, metallic salts or neutral glasses, which will coalesce or unite with the binder at some time during the manufacture of the product, for example, while the product is being heated at high temperatures, and (3) by coating the surface with water repellants, such as liquid silicone, mica soaps, drying oils or waxes.

My present preferred practice, however, is to treat the tile, after it has been dried at a temperature up to about 300°C, by dipping the tile in a solution of a salt formed by a weak alkali and a strong acid, such as a solution of calcium chloride in the proportion, preferably, of one part calcium chloride to 7 parts of water by weight. The tile is allowed to stand in the solution until the solution has wet the cell walls and the tile then is removed from the solution and allowed to stand for an extended period. The tile is then placed in an oven and dried in an atmosphere containing carbon dioxide, for example, the products of combustion of the fuel for heating the oven, and at temperatures controlled so as to prevent cracking and warping of the tile. The treatment in a heated atmosphere containing carbon dioxide accelerates the desired action but is not essential inasmuch as substantially the same result is obtained by allowing the tiles to stand in air for an extended period. The tile thus treated possesses great resistance to water.

There is evidence, however, indicating that the tile thus treated contains some free sodium chloride, which can be removed by leaching in clear water. Also, a tile completed by the foregoing process reacts with phenolphthalein unless it is leached, when it becomes substantially neutral. The leaching operation is not an essential for producing a satisfactorily water resistant tile but if employed the tile should be subsequently dried. There is evidence strongly indicating that the cell walls of the finished cellular product comprise a finely divided solid, such as limestone, held together by a binder of calcium silicate and calcium carbonate. Probably, the binder contains some residual sodium silicate but the sodium content is so low as to render it highly water insoluble.

I have also obtained tiles having good resistance to water by treating the tiles, after the cellular structure has been formed, with other agents adapted to react with the sodium or potassium of the soluble silicate to form salts therewith. Such salts are less reactive toward the residual ingredients of the product in the presence of water than is sodium hydroxide, which tends to be formed in the dried untreated product in the presence of water. Thus, I have obtained good results by dipping the set tiles in a substantially saturated solution of the sulphates or chlorides of aluminum or zinc. The procedure when using these materials is similar to that when using calcium chloride as above described. After dipping the tiles in such solutions the tiles are dried, but it is not necessary to heat them in an atmosphere containing carbon dioxide, such as one containing products of combustion. I have also obtained good results by adding a quantity of finely divided sulphur to the original mixture in an amount up to about 400 grams in the specific formula given herebefore. The sulphur is inert at the mixing temperature but will chemically combine with the sodium of the silicate at an elevated temperature, namely, at a temperature between the melting and boiling point of the sulphur. When sulphur is employed, the remaining steps in the manufacture of the finished product are the same as previously described.

Another method which I have found to be particularly satisfactory involves the treatment of the tiles after they have been dried at temperatures up to 300°C, with fumes of zinc chloride. While it is preferred to employ sodium silicate in the practice of the invention, it will be understood that other soluble silicates may be used and it is intended that the term sodium could include any of the other alkaline metals of any of the well known soluble silicates.

In the preferred practice of the invention as described it will be noted that 6 lbs. of powdered glass is used. The purpose of this glass is to increase water resistance. The glass is chemically similar to the silicate employed except that the ratio of alkali to silica in the powdered glass is much lower. It has been proven that this glass dissolves in the silicate in the drying after the cell structure is substantially set so the result is a less alkaline binder in the finished product and as has been pointed out the less alkaline the binder the more water resistant the tile. Where waterproofing treatment is used, the glass may be omitted.

I claim:

1. The method of making a cellular product which comprises mixing granular filler with a soluble silicate solution, beating the mixture to aerate the same to form a cellular foamy mass of predetermined increased volume, immediately heating the foamed liquid material at a temperature within the range above its slumping temperature and below that which would cause the material to puff up, continuing said heating for a period to set the cell structure, and thereafter more completely drying the material at higher temperatures.

2. The method of making a cellular product which comprises mixing granular filler with a soluble silicate solution, beating the mixture to aerate the same to form a cellular foamy mass of predetermined increased volume, immediately heating the foamed liquid material at a temperature within the range above its slumping temperature and below that which would cause the material to puff up, continuing said heating until the cell structure of the surface of the material is set, thereafter heating slightly above said puffing up temperature until the entire cell structure of the material is set, and thereafter more completely drying the material at higher temperatures.

3. The method of making a cellular product which comprises mixing granular filler with a soluble silicate solution, beating the mixture to aerate the same to form a cellular foamy mass of predetermined increased volume, immediately drying the foamed liquid material at a temperature below its slumping temperature for a short period of time, and thereafter drying at a gradually increasing temperature until the desired moisture content is reached.

4. The method of making a cellular product which comprises mixing granular filler with a soluble silicate solution, beating the mixture to aerate the same to form a cellular foamy mass of predetermined increased volume, drying the foamed material until set, setting the set foamed material with a solution of calcium chloride, subjecting the treated material to the action of a heated atmosphere containing carbon dioxide.

5. The method of producing a cellular product which comprises mixing a soluble silicate solution with an agent which is inert at the mixing
temperature and is adapted to chemically combine with the sodium of the silicate only at an elevated temperature to form a salt, beating the mixture to aerate the same to form a cellular foamy mass of predetermined increased volume, and drying the foamed material sufficiently to set the same to a substantially solid condition and continuing the drying at a temperature sufficiently elevated to cause said agent to chemically combine with the sodium of the silicate only to form a salt whereby the cellular product is rendered water-resistant.

The method of producing a cellular product which comprises mixing a soluble silicate solution with finely divided sulphur, beating the mixture to aerate the same to form a cellular foamy mass of predetermined increased volume, and drying the foamed material sufficiently to set the same to a substantially solid condition, then drying at a temperature sufficiently elevated to cause said sulphur to chemically combine with the sodium of the silicate only to form a salt whereby the cellular product is rendered water-resistant.

The method of making a cellular product which comprises beating a mixture containing a suitable frothing agent to aerate the same to form a cellular foamy mass of predetermined increased volume, and immediately drying the liquid product, said mixture comprising the following ingredients in substantially the proportions:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Pounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>36</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>36</td>
</tr>
<tr>
<td>Powdered glass</td>
<td>1</td>
</tr>
<tr>
<td>Water</td>
<td>1800</td>
</tr>
</tbody>
</table>

The method of making a cellular product of predetermined cell size comprising preparing a mixture of an aqueous solution of a soluble alkaline silicate and a granular filler, adding an alkali hydroxide to control the alkalinity of the solution in the ratio of not more than three parts of SiO₂ to one part of the alkali oxide in order to regulate the cell size, heating the mixture in the presence of a foaming agent for a time period sufficient to form an aerated liquid, and immediately drying the aerated liquid under conditions to solidify the same and form a porous body of required cell size.

The method of making a cellular product which comprises mixing a granular filler with an aqueous solution of an alkali silicate, beating the mixture to aerate the same and form a cellular foamy liquid of predetermined increased volume, immediately heating the aerated foamed liquid at a relatively low temperature to dry the same until it has set to a substantially solid cellular structure, and thereafter continuing the drying at elevated temperature.

The method of making a cellular product which comprises mixing a granular filler with a soluble silicate solution, beating the mixture to aerate the same to form a cellular foamy liquid of predetermined increased volume, immediately drying the aerated foamed liquid at a temperature above its puffing temperature for a short period of time, and thereafter drying at a gradually increasing temperature until the desired moisture content is reached.

The method of producing a cellular product which comprises mixing an aqueous silicate solution and a granular filler, aerating the same to form a cellular foamy mass of predetermined increased volume, drying the foamed liquid material until set, completing the drying at elevated temperature until the desired moisture content is reached, then subjecting the material to an acidic gas and chemically combining the same with the sodium of the silicate to form a salt, whereby the cellular product is rendered water-resistant.

RICHARD C. THOMPSON.