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3,353,978

SELF-EXTINGUISHING PITCH FOAMS

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The present application relates to the foaming of coal tar pitch and aromatic pitch.

This application is a continuation-in-part of my application Ser. No. 281,335, filed May 17, 1963, entitled Maleic Foam, and now abandoned.

It has previously been proposed in Overstreet Patent 2,271,498 to foam rubber in the presence of sulfur, asphaltum and gilsonite at elevated temperature and pressure. The sulphur is converted in part to hydrogen sulfide. Asphalt and gilsonite when mixed with sulphur in the absence of rubber do not produce hydrogen sulfide at a significant rate when heated to 180° C. When gilsonite is foamed with sulfur the product is not self-extinguishing.

It is an object of the present invention to employ sulfur as a gas producing agent in the preparation of a foam.

Another object is to prepare a thermoplastic foam from coal tar pitch.

A further object is to prepare a thermoplastic foam from an aromatic pitch.

An additional object is to prepare foamed compositions which are self-extinguishing.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiment of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

It has now been found that these objects can be attained by heating coal tar pitch or other aromatic pitch, e.g., an aromatic pitch from petroleum to 150° C. or above, preferably 180°-190° C. High temperatures, e.g., 200° C., 220° C., or even 250° C. can be employed. The upper temperature limit is not critical and can be any temperature up to the stability limit of the pitch. There can be used 0.5 to 20% of sulfur based on the total of sulfur and pitch, although preferably at least 1% and better 2 to 4% of sulfur is employed. Each one percent of sulfur added up to 10% and reacted with the pitch increases the melting point of the pitch by about 20° C. Apparently the initial coal tar pitch or other aromatic pitch is soft and low melting because of the lower molecular weight alkyl substituted aromatic compounds that they contain. Heating with sulfur greatly increases the molecular weight and the aromaticity of these materials and with their solvating action gone the melting point of the pitch increases tremendously.

The coal tar pitch and the aromatic pitch of petroleum origin expand and foam up to about 4 to 6 times their previous volumes with as little as 2% of sulfur. The foaming is caused by the formation of hydrogen sulfide gas.

The resulting foams are thermoplastic and self-extinguishing when subjected to a flame. They are useful as building insulation, acoustic tiles, etc.

It is critical that coal tar pitch or other aromatic pitch, i.e. an aromatic pitch obtained from petroleum, be employed. Aliphatic materials such as asphalts and gilsonite show little, if any, reaction with sulfur at 180° C. to produce hydrogen sulfide. Also polycyclic naphthenic pitches are unsatisfactory. Aliphatic pitches contain a hydrogen to carbon ratio of almost 2:1 and do not give

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self-extinguishing foams. The coal tar pitch and aromatic pitch used in the present invention have hydrogen to carbon ratio of less than 1:1 and the foams are self-extinguishing. A typical aromatic pitch from coal tar that produced a self-extinguishing foam contained 88.57% carbon and 4.56% of hydrogen, this corresponding to an elemental ratio of about 0.62:1 hydrogen to carbon.

The coal tar pitch and aromatic pitch foams of the present invention have softening points, ring and ball method of at least 90° C.

While preferably the starting pitches have softening points of at least 90° C. or even 100° C. or higher, there can be used lower softening coal tar pitches and aromatic pitches. Thus there can be used a Wilton pitch having a ring and ball softening point of 50° C. since the addition of the sulfur raises the softening temperature. Similarly there can be used an aromatic pitch having an initial softening point of 70° C. by the ring and ball procedure.

The aromatic pitches generally contain a relatively large number of short aliphatic, e.g., alkyl, side chains.

The self-extinguishing rigid foam compositions are very inexpensive in contrast to rigid foams made from conventional plastics which require additives costing up to 20% of the cost of the plastic material just to make them self-extinguishing.

The rigid, self-extinguishing foams can be made tougher by incorporating solid fillers. A particularly desirable solid filler is magnesite which, in addition to being very inexpensive and toughening the foams includes flame resistance in two ways:

(1) The magnesite produces an ash covering that helps to insulate the foam from the flame.

(2) Magnesite decomposes above about 350° C. to produce carbon dioxide and hence aids in extinguishing any flame.

The magnesite or other filler is used in an amount of 1 to 60%, preferably 10-40% based on the weight of the pitch and fillers.

Modifying agents, e.g., butadiene-acrylonitrile copolymers (containing about 30-40% acrylonitrile) and polyvinyl chloride can also be incorporated in minor amounts, i.e., less than 10% by weight based on the total composition, to give improved toughness. Greater amounts of such modifying agents do not significantly improve the physical properties, and have the disadvantage of increasing the cost and, except for chlorinated resins, increase the hydrogen to carbon ratio to the point where the compositions are not self-extinguishing. The increased viscosity of the aromatic pitches at elevated temperatures produced by the fillers, especially the fibrous fillers, and the modifying polymers helps to increase the safety of these self-extinguishing foams by inhibiting their flow into burning areas and by helping the foams to hold their structural shape behind the protective ash.

In place of sulfur there can be employed maleic anhydride as the blowing agent. In such case the foam is formed at a temperature of 100° C. The maleic anhydride decomposition to form gases is triggered by the basic tertiary amines which occur in the coal tar pitch.

These aromatic pitch self-extinguishing foams can be blown by most of the well-known blowing agents used commercially or disclosed in the literature. Sodium bicarbonate with an acid such as citric acid, azo bis compounds such as azobisisobutyronitrile, or azobisformamide, and volatile organic materials such as pentane and Freons, e.g., dichlorodifluoromethane, dichlorotetrafluoroethane, can be used in extrusion blowing of these aromatic pitches.

The use of sulfur as a blowing agent is advantageous in several respects. During the blowing operation, in addition to raising the melting point of the aromatic pitch, it can thermoset any vulcanizable polymers that may have been

added. Since it increases the melting point of the aromatic pitch, in the event of a fire, higher temperatures will be required to cause the pitch to flow. If the foam has been produced with an excess of unreacted sulfur present, in the event of a fire and resulting tendency of the pitch to flow at elevated temperatures, the sulfur produces an additional foaming and helps to protect structural members from intense heat.

When using maleic anhydride the pitch should not be so fluid at the temperature at which the maleic anhydride decomposes (100° C.) that the bubbles break as they are formed. Thus, while a Wilton pitch having a ring and ball softening point of 50° C. can be used with sulfur as the foaming agent, it cannot be employed with maleic anhydride unless viscosity control agents are also employed to increase the melting point of the pitch.

The maleic anhydride has been used in an amount of from 0.1 to 20% and higher, e.g., up to 50% of the total formulation of aromatic pitch, e.g., coal tar pitch, and maleic anhydride but is generally employed in an amount between 1 and 10% and preferably between 2 and 4% of the total formulation.

With maleic anhydride the preferred foaming temperature range is 100°–180° C. Below 100° C. the reaction is slow and no additional advantages are obtained for the increased cost of heating above 180° C., although high temperatures can be employed, e.g., 200° C. and above.

Unless otherwise indicated, all parts and percentages are by weight.

In order to greatly increase the strength of foams from pitches, fibrous fillers such as asbestos, cellulosic fibers, e.g., cotton flock and rayon, nylon flock, glass fibers, polyethylene terephthalate fibers, etc. can be used in an amount of 1–60%, e.g., 10–40% of the total composition.

The pitch compositions are conveniently foamed as they emerge in the hot stage from the extruder.

Example 1

Coal tar pitch, specifically hotline pitch (ring and ball softening point of about 120° C.) was heated to 160°–170° C. and then 3% by weight of maleic anhydride was rapidly stirred in and the pitch permitted to foam up. The volume of foam was approximately five times the volume of the original pitch. The foam was a fairly uniform, rigid, thermoplastic foam which was self-extinguishing. Greater uniformity can be obtained by extrusion foaming.

Example 2

2 parts of hexamethylene tetramine (a tertiary amine employed to aid the foaming action of the maleic anhydride), 4 parts of maleic anhydride were added to 94 parts of coal tar pitch (ring and ball softening point about 100° C.) and the mix was foamed from an extruder at 165° C. to give a self-extinguishing rigid thermoplastic foam.

Example 3

The procedure of Example 2 was repeated replacing the hexamethylene tetramine by 2 parts of triethylene diamine to produce a similar foamed coal tar pitch.

Example 4

98 parts of hotline pitch (ring and ball softening point of about 120° C.) was heated to about 170–180° C. and then 2 parts of sulfur was rapidly stirred in and the pitch permitted to foam. It foamed up to about 6 times its previous volume.

Example 5

96 parts of a 100% aromatic petroleum pitch (ring and ball softening point of 90° C.) from Kendall Refining Company was heated to 150° C. with 4 parts of sulfur and produced a rigid thermoplastic self-extinguishing foam. Hydrogen sulfide was produced in the reaction.

Example 6

99 parts of coal tar pitch (ring and ball softening point of 100° C.) was heated with 1 part of sulfur to a temperature of 180° C. There was produced a rigid thermoplastic self-extinguishing foam which had a softening point of 120° C.

Example 7

The procedure of Example 6 was repeated using 10 parts of sulfur with 90 parts of the pitch to produce a rigid, thermoplastic, self-extinguishing foam.

Example 8

A mixture of 77 parts of coal tar pitch (ring and ball softening point of 120° C.), 3 parts of sulfur and 20 parts of magnesite were heated to 180° C. to produce a rigid, tough, thermoplastic, self-extinguishing foam.

Example 9

The procedure of Example 8 was repeated replacing the magnesite by 20 parts of chrysotile asbestos fibers to produce a foamed product having increased strength.

What is claimed is:

1. A process comprising heating an aromatic pitch having a hydrogen to carbon ratio of less than 1:1 to at least 150° C. in the presence of sufficient sulfur to foam the composition and permitting said composition to foam and cooling while retaining the voids therein to form a solid, thermoplastic, self-extinguishing foam.

2. A process according to claim 1 wherein the aromatic pitch is coal tar pitch.

3. A process according to claim 1 wherein the aromatic pitch is petroleum pitch.

4. A process of producing a solid, self-extinguishing, thermoplastic foam comprising heating coal tar pitch with 0.5 to 20% of sulfur and permitting said mixture of pitch and sulfur to foam and cooling while retaining the voids therein to form said solid, self-extinguishing, thermoplastic foam.

5. A process according to claim 4 wherein the sulfur is 1 to 10% of the composition.

6. A process according to claim 1 wherein there is 10 to 40% of magnesite in the composition.

7. A process according to claim 1 wherein there is included 10 to 40% of a fibrous filler in the composition.

8. A process according to claim 1 wherein the foaming is accomplished by extruding the hot composition to give the self-extinguishing rigid thermoplastic foam.

9. A process according to claim 1 wherein the composition includes 1 to 60% of a filler.

10. A process according to claim 9 wherein the filler is magnesite.

11. A process according to claim 9 wherein the filler is a fibrous filler.

12. A solid composition of matter produced by the process of claim 1.

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