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MOLDING COMPOSITION FOR MAKING THERMAL BARRIERS AND METHOD OF MAKING SAME

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This invention relates to a molding composition useful for making thermal barriers and a method of making the same.

In order to develop aerospace vehicles with a high degree of reliability and capable of carrying pay loads or equipment and/or personnel into sub-orbital and orbital flight, it has been necessary to develop materials which are capable of serving as thermal barriers under extreme conditions of temperature with accompanying high velocity gas flow. For example, the temperature encountered in a rocket motor will be in the 4000–7000° K. range. At these temperatures, all materials are destroyed. However, the destruction rates and thermal conductivity of materials vary broadly. The ideal material for such applications will be only partially consumed during the interval of time when the extreme conditions exist. It will have a low rate of heat transfer and it will be light in weight. There are many well known metals such as steel alloys and titanium alloys which retain good structural properties at temperatures under 1000° F. and thin shells of these metals can be used as support members for layers of the insulating material previously described, if the insulating material is not completely destroyed and if it does not transfer too much heat to the support shell. The use of filament wound structures which are fiberglass-resin combinations for support shells is also becoming a standard practice where proper insulation layers are present.

In efforts to obtain materials of the proper characteristic, structures consisting of alternate layers of asbestos cloth and nylon cloth laminated with phenolformaldehyde resins have been found to perform well, as long as the flow of hot gases is perpendicular to the plane of lamination. However, when flow is parallel, large chunks of the laminate peel off and sub-marginal performance results.

In accordance with this invention, there is provided a molding composition which can be used to form a thermal barrier which is of light weight, a good thermal insulator and which erodes slowly (ablates) even when subjected to a flow of hot gases parallel to its exposed surface.

In accordance with the method of this invention, a mat of advantageously from 0.010 to 0.030 inch in thickness is formed of asbestos fibers and nylon fibers randomly dispersed. The mat may be formed by any one of a number of well known techniques. Thus, for example, it can be formed by using the water laying process used in the paper industry employing paper making equipment conventionally employed to form a web from long fibered stocks. Similarly the mat can be formed by conventional textile type operations such as carding.

The length of the asbestos fibers in the mat advantageously will be in the range of from 0.010 to 0.50 inch. The weight of asbestos fibers in the mat will be from about 45% to about 55%, advantageously from about 51% to about 53% by weight of the total fiber weight. Any asbestos fibers may be employed such as, for example, fibers of the Crocidolite, Chrysotile, Amphibole or Amosite types. The asbestos fibers desirably are of relatively high purity.

The weight of nylon in the mat will be from about 45% to about 55%, advantageously from about 47% to about 49% by weight of the total fiber weight. The nylon may be, for example, in the form of a cut staple of from 0.125 to 2.50 inches in length and advantageously 0.125 to 0.50 inch in length. Any of the well known nylons may be employed such as, for example, nylon-6/6, nylon-6, nylon-6/10, nylon-8 and nylon-11. Nylons of these common designations are well known to the art and hence need not be further described here. Reference may be had, if desired, to the 1962 issue of Modern Plastics Encyclopedia, September 1961, vol. 39, No. 1A, published by Breskin Publications, Inc., Bristol, Conn.

The thus formed mat in a dry state is then impregnated with a straight or branch chain natural or synthetic polymeric solid thermoplastic compound having a minimum hydrogen atom to carbon atom ratio of 1.3:1.0. The polymeric compound advantageously will be from about 10% to about 14% by weight of the thus impregnated mat. In general the impregnation is carried out by forming a solution of the polymer in a suitable solvent, impregnating and then evaporating the solvent. The polymers can also be applied by first heating to form a melt and applying the melt to the mat.

Alternatively, when the polymeric compound is a natural or synthetic rubber, a rubber emulsion can be added to the fiber slurry and the rubber precipitated with, for example, alum adjusting the pH of the slurry to a range of from about 6.5 to about 4.0.

Irrespective of the polymeric material employed, it acts as a binder for the fibers of the mat. However, its most important function is to act as a heat sink in the ablative condition. In the latter connection, the impregnating polymeric material will produce a large volume of gas when exposed to high temperatures and absorb energy by virtue of the fact that the molecular species is not thermodynamically stable and atomic hydrogen is formed with a resulting cooling effect at the interface of the hot gas and thermal barrier. Exemplary of such polymeric compounds are natural rubber, Buna N rubber, Buna S rubber, synthetic polyisoprene, and polyolefins such as polypropylene and polyethylene and ethylene-propylene copolymers. Suitable solvents are benzene, carbontetrachloride, methylenechloride, acetic acid and ethyl acetate.

The thus impregnated mat is further impregnated with a phenol-formaldehyde resin which preferably will be present in an amount of from about 47% to about 52% by weight of the completed mat. The resin employed may be a two-stage phenolformaldehyde condensate wherein a novolak, for example, is cured to the finished state by the addition of a catalytic curing agent such as a formaldehyde source, e.g., paraformaldehyde, hexamethylenetetramine or trioxane. The impregnating step may be carried out, for example, by passing the mat through a bath of a one-step resin dissolved in alcohol to form a varnish, removing excess resin with squeeze rolls, and placing the mat in an oven to remove volatile matter and partially polymerize the resin. These resins and their formation are extremely well known and reference may be had, if desired, to Modern Plastic Encyclopedia, 1962 issue (September 1961, vol. 39, No. 1A).

The commercially available Monsanto SC–1008 and Cincinnati Testing Laboratories 91LD are typical of satisfactory resins.

Other thermosetting phenolic resins can be substituted for phenol-formaldehyde. Exemplary are resorcinol-formaldehyde, phenol-furfural, xylenol-formaldehyde, m-cresol formaldehyde.

The thus formed mat is then cut into squares using conventional cutting equipment, the squares preferably having a volume and a range of from 0.0025 to 0.0075

cubic inch. The thus formed squares are thoroughly mixed to provide a random dispersion and are then ready for a molding operation. In this condition the thus formed molding composition can be stored for a long period of time.

In order to form a thermal barrier of any usual design, the above formed molding composition is placed in a mold and subjected to a temperature in the range of 300° F.–375° F. and a pressure in the range of 100–2000 p.s.i. for generally 10 to 90 minutes depending on the size and the shape of the molded structure and the conditions used. When the resin is cured the thermal barrier is removed from the mold.

Alternatively, the mat can be cut into lengths and plied together to form laminated shapes of the desired thickness and then cured by heat and pressure in the ranges given above.

The invention will be further clarified by reference to the following example.

EXAMPLE

A typical paper pulp refining beater is charged with 6000 gallons of water and crocidolite asbestos fiber of a length of 1" to 1.5" to form a suspension of about 2% solids by weight. The minimum amount of pressure is applied to the beater roll with a clearance of 0.002 to 0.005 inch between the roll and bedplate in order to separate the coarser asbestos fiber bundles without shortening their length appreciably. The asbestos fiber slurry is agitated in the beater until the degree-of-refining of the fibers registers a 300 to 320 ML value using a standard Schopper-Riegler Freeness Tester. The asbestos fibers at this stage are in the range of 0.01" to 0.15" in length. Then a sufficient quantity of 3 denier, ½" nylon staple fiber is added, to bring the total fiber content to 3.9% by weight of the slurry.

Mixing is continued in the beater until the asbestos and nylon fibers form a homogeneous suspension. Buna N rubber in latex form is added in the amount of 12% by weight of the total weight of the asbestos, nylon and rubber in the slurry and mixing continued until the rubber latex is dispersed uniformly. The mixture is finally adjusted to 4.0 pH with a 10% alum solution in order to precipitate the rubber as discrete particles on the fibers. The rubber particles effect a fiber-to-fiber bond upon application of heat during the sheet drying process. The completed mixture of constituents is processed into an 0.020 inch thick web on a conventional Fourdrinier paper machine and dried. A roll of web is fed through a resin pan between metering rolls, and carried horizontally through an exhausting oven and rewound on a roll. The impregnating resin in the pan is phenol-formaldehyde reduced to 55% solids content with denatured alcohol. The temperature of the resin bath is maintained at 85–90° F. and specific gravity at approximately 1.060. The metering rolls are adjusted to a nip opening of 0.017".

The resin-wet web is carried on a conveyor through two zones of heat, 200° F. for the first zone and 240° F. for the second zone, dwell in each zone being approximately 6–7 minutes. The resin is 50% by weight of the mat.

A portion of the thus coated web is cut into 16" squares. 3.25 pounds of these squares are stacked and cured under pressure of 1000 p.s.i. and temperature of 300° F. for 30 minutes to form a ¼" thick sheet having a specific gravity of 1.4. A portion of the remaining web was cut into ½" squares and 3.25 pounds molded in matched metal dies under a temperature of 300° F. and a pressure of 1000 p.s.i. for 30 minutes to produce a sheet having a specific gravity of 1.4. Both products are excellent thermal barriers.

What is claimed is:

1. A thermal barrier structure comprising a mixture of asbestos fibers from about 0.010 to about 0.50 inch of length and nylon staple from about 0.125 to about 2.50 inches in length, the weight of asbestos fibers being from about 45% to about 55% by weight of the total weight of the asbestos and nylon, said mixture of fibers being impregnated with a thermoplastic polymeric compound having a minimum hydrogen atom to carbon atom ratio of 1.3 to 1, the polymeric compound being from about 10% to about 14% by weight of the total of the weight of the nylon, asbestos and polymeric compound and with a phenolic aldehyde resin in an amount of from about 47% to about 52% by weight of the composition, said thermoplastic polymeric compound being rubber.

2. A thermal barrier structure in accordance with claim 1 in which the phenolic resin is a phenol-formaldehyde resin.

3. A thermal barrier structure in accordance with claim 1 in which the phenolic resin is a phenol-furfural resin.

4. A thermal barrier structure in accordance with claim 1 in which the phenolic resin is a resorcinol-formaldehyde resin.

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