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[54] **ABLATIVE COMPOSITES CONTAINING NOVOLAC FIBERS**

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[63] Continuation of Ser. No. 764,731, Oct. 3, 1968, abandoned.

[52] **U.S. Cl.** **260/38,** 260/DIG. 23

[51] **Int. Cl.** **C08k 1/80**

[58] **Field of Search** ..... 260/38, DIG. 23

[56] **References Cited**

UNITED STATES PATENTS

3,314,915	4/1967	Baughman et al.	260/38
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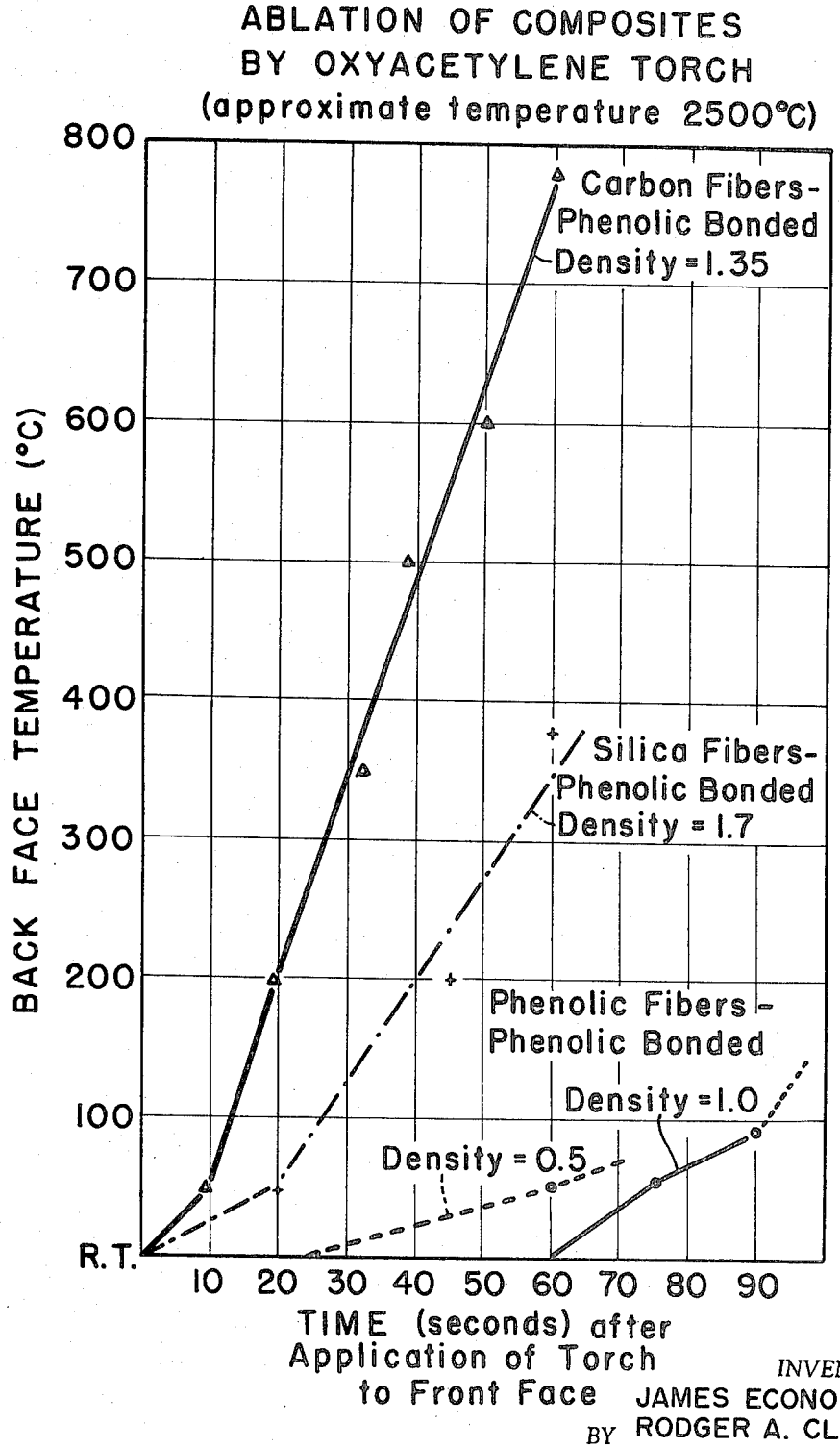
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[57] **ABSTRACT**

A composite comprising a charrable resin or plastic reinforced by fibers prepared from the resin condensation products of phenols and aldehydes which can be fiberized and cured.

7 Claims, 1 Drawing Figure



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ABLATIVE COMPOSITES CONTAINING NOVOLAC FIBERS

This is a continuation of application Ser. No. 764,731, filed October 3, 1968 and now abandoned.

THE BACKGROUND

Composites are two-phase materials in which fibers that have excellent tensile strength are bonded by a matrix phase. When the composite is deformed under loads the fibers are constrained to take up the same deformation as the matrix phase thus effectively reinforcing the matrix. In addition, the presence of fibers helps to retard the propagation of cracks and thus to produce a material which is tough as well as of high strength. Organic resins are occasionally strengthened with organic polymer fibers, some of which are very strong with good strength to weight ratios. These composites must be used at room temperature because organic polymer fibers lose strength rapidly at temperatures only slightly above room temperature. For this reason, most plastics have been reinforced by glass fibers, asbestos fibers or carbon fibers.

Composites have been used in various structural and friction applications. An exotic use of composites is as ablative structures. The ablative structures are used primarily to enable the reentry of rockets and satellites. Other applications include the protection of rocket nozzle structures from attrition by hot propellant gases and the insulation of rocket motor case structures from the heat from the burning propellant.

The materials that have been found most useful for ablating heat protection systems for reentry vehicles and rocket nozzles usually do not merely melt or sublime in response to heating but rather decompose to give large volumes of gas leaving a porous refractory residue. When such materials are exposed to a stream of hot gas the surface temperature rises to the decomposition temperature of the material which then begins to char or carbonize and evolve rather low molecular weight gases. Then the interface between the char layer and the virgin material moves into the material away from the hot face. During this period, gases generated in the course of the char forming process move through the char and absorb heat. These heated gases are then ejected. As the char layer thickens, the amount of heat reaching the moving interface is reduced by the insulating effect of the porous char combined with the cooling effect of the diffusing gases. As a result, the surface temperature of the char eventually rises until the char itself begins to ablate.

The usefulness of an ablating material does not depend altogether on the rate of ablation, but rather on the net ability to prevent heat from the environment from damaging the structure or payload on which it is applied. The effect of this in a given composite may depend on the temperature of the hot face. That is, composites of one composition may be superior at temperatures between 2,000° and 3,000° C but inferior to other composites at higher temperatures and vice versa.

According to this invention, there is provided an organic polymer fiber reinforced plastic or resin composite which does not rapidly lose strength on heating above room temperature and which has outstanding ablation properties.

THE INVENTION

Composites with superior ablating properties according to this invention comprise a charrable resin reinforced by fibers prepared from the resin condensation products of phenols and aldehydes which can be fiberized and cured. (Hereafter, these synthetic fibers will be referred to as phenolic fibers.) Preferably, the charrable resin is a phenolic resin. Alternatively, any other resin which produces a high char yield may be used, such as furane resins or polybenzimidazole resins. To a certain extent the fibers may include not only phenolic fibers but, in addition thereto, asbestos, glass, silica, boron nitride, or carbon fibers or other similar refractory fibers which do not degrade below about 500° C. It is also permissible to include limited quantities of some other fibers, such as polyamides, in the composite. This, of course, depends on the particular application.

The figure is a graph comparing the ablation properties of several composites described in detail hereinafter.

Phenolic resins are prepared by the condensation reaction between phenols and aldehydes. The most common reactants are phenol, itself, and formaldehyde. The various phenols and aldehydes that can be used to make phenolic resins are well-known. See, for example, Phenolic Resins by D. F. Gould, Reinhold Publishing Co., New York (1959). The condensation reaction proceeds very slowly in the absence of a catalyst.

When alkaline catalysts are used and the molar ratio of formaldehyde to phenol is greater than 1:1, the primary reaction products are phenol alcohols which are called resoles. When acid catalysts are used and the molar ratio of formaldehyde to phenol is somewhat less than 1:1, the primary reaction products are probably also phenol alcohols but they rearrange rapidly to yield diphenyl methane derivatives to which the name novolac has been given Resoles are thermal setting whereas novolacs are permanently fusible. However, novolacs can be cured by treatment with aldehydes or hexamethylene tetramine, among others, in the presence of an appropriate catalyst. The fundamental difference between resoles and novolacs is the presence of one or more free methylol groups on the former; it is through reactions of these methylol groups that the cross-linking occurs.

Phenolic fibers can be made from resoles and novolacs or combinations of each in varying proportions. Additives and modifiers, either reactive or nonreactive, can be used to alter the fiber characteristics either for attenuation or the end use properties. When resoles are used as a starting material, they should be dried prior to fiberization. The fibers may be drawn from a viscous mass or may be formed by forcing the viscous mass into a turbulent air stream. Heating will cause curing of the resoles. Novolacs may be fiberized in a similar manner. When a pure novolac is fiberized, curing is accomplished by treating the fibers with an aldehyde in the presence of an appropriate catalyst. Fibers can be made from novolacs according to the process described in U.S. patent application Ser. No. 710,292, filed Mar. 4, 1968 by Economy and Clark entitled "Fibers From Novolacs And Method For Their Production." That application and this application are assigned to a common assignee.

Composite phenolic fiber-resin structures can be fabricated by mixing the fibers with the uncured resins prior to casting or shaping. The ratio of fiber to resin matrix can be varied to obtain optimum results. Preferably, the fibers should constitute at least about 35 percent, by volume, of the composite. Practically, the maximum attainable fiber content is about 85 percent by volume.

Composites according to the teachings of this invention have outstanding properties even at elevated temperatures. The ultimate tensile strength of phenolic fibers is three to six times the strength of the bulk phenolic resins. The fibers have a modulus of elasticity at least as high as or greater than the bulk resin. Therefore, on deformation the fibers being constrained to take up the deformation of the matrix effectively reinforce the matrix. The strength and the modulus of elasticity of phenolic fibers is about the same at 250° C as at room temperature. At even higher temperatures, the phenolic fibers char or carbonize resulting in carbon fibers that have even higher tensile strengths. Other organic fibers rapidly lose their strength on heating above room temperature. The very best polyamide fibers retain their strengths only to temperatures of about 225° C and at about 325° C decompose into a friable char. Hence, composites according to the teachings of this invention, maintain good tensile strengths on heating. This is especially important where the composites are used as ablating materials as well as in many other applications.

The following experiments demonstrate that phenolic fiber composites having a phenolic resin matrix have excellent ablative properties. Specimens of the following composites were prepared:

Fibers	Matrix	Density
Carbon	Phenolic resin	1.35 gm/cc
Silica	Phenolic resin	1.70 gm/cc
Phenolic resin	Phenolic resin	0.5 gm/cc
Phenolic resin	Phenolic resin	1.0 gm/cc

The specimens had a ¾ inch diameter and were one-half inch thick. One face was submitted to the flame of an oxyacetylene torch, the blue cone of which was centered normal to the test specimens at a distance of about 1 mm. The temperature of the back face was measured and plotted against time after application of the torch to the front face. The results of this test are shown graphically in FIG. 1. The figure shows that phenolic fibers bonded with phenolic resins excelled in their capacity to maintain low back face temperatures over long times. The denser phenolic fiber-phenolic resin composite was superior to the less dense composite. The temperature of the oxyacetylene flame in this experiment is estimated between 2,200° and 2,700° C or about 2,500° C. It had been considered that organic fiber containing composites were inferior to silica or carbon fiber containing composites in this temperature range.

Phenolic fibers in phenolic resin matrices are superior to other organic fiber fillers as they do not generate gas prior to the time at which the matrices begin to degrade. Where the organic fiber starts to generate gas prior to the time the matrix begins to degrade and develop porosity, pressure build-ups are caused in the composites which can result in premature failure of the composite.

Having thus described our invention in detail and with the particularity required by the patent laws, what is desired to have covered by Letters Patent is as follows.

We claim:

1. A composite comprising a charrable resin reinforced by cured phenolic fibers prepared from novolac resin condensation products of phenols and aldehydes which can be fiberized and cured.

2. A composite according to claim 1 in which the charrable resin is a phenolic resin.

3. A composite according to claim 1 which comprises, in addition to phenolic fibers, refractory fibers that do not degrade below about 500° C.

4. A composite according to claim 1 which comprises in addition to the phenolic fibers, fibers selected from the group consisting of asbestos, glass, silica, boron nitride and carbon and mixtures thereof.

5. A composite according to claim 1 in which the fibers are present in an amount of from about 35 percent to about 85 percent by volume of the composite.

6. A composite according to claim 2 having a density in excess of 0.5 gm/cc.

7. An ablative heat shield comprising a composite according to claim 1.

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