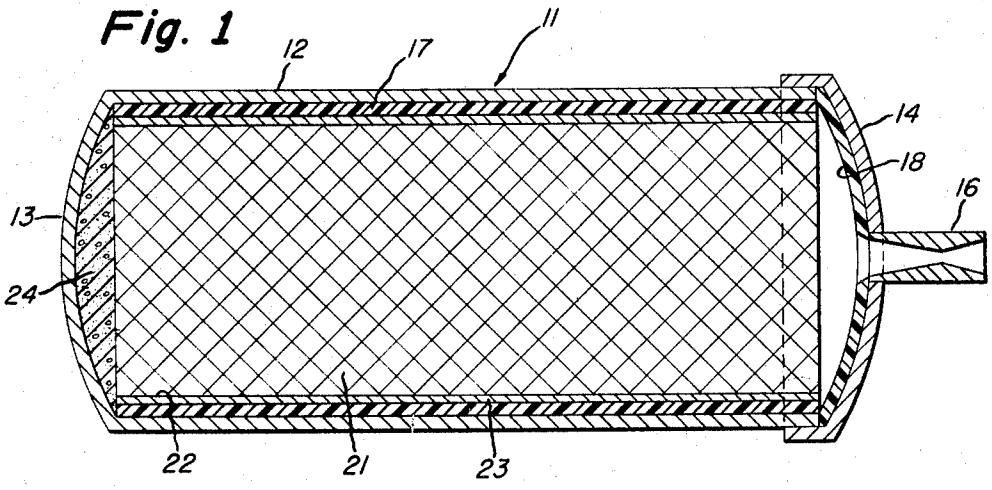
July 2, 1968 R. K. MAJOR 3,391,102

INSULATOR COAT FOR COMBUSTION CHAMBERS

Filed June 10, 1965

Fig. 1



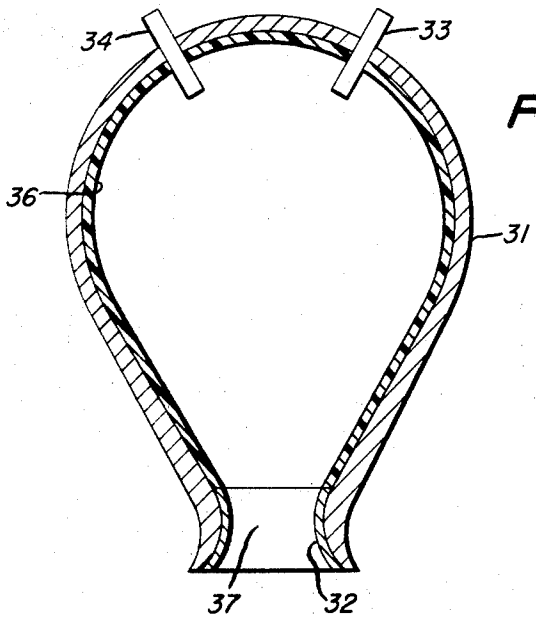


Fig. 2

INVENTOR.
Richard K. Major

BY Michael Dorfman
ATTORNEY

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INSULATOR COAT FOR COMBUSTION CHAMBERS

Richard K. Major, Seymour, Ind., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana

Continuation-in-part of application Ser. No. 176,876, Feb. 26, 1962. This application June 10, 1965, Ser. No. 462,881

6 Claims. (Cl. 260—38)

This is a continuation-in-part of application Ser. No. 176,876, filed Feb. 26, 1962, now abandoned.

This invention relates to combustion chambers wherein surfaces are held below a specified maximum temperature for a substantial period of combustion time by means of an insulator coat applied to that surface; primarily to methods of producing these coats or linings from uncured thermosetting resins which produce water during curing; and more particularly to such methods which essentially avoid problems with the removal of water during the curing operation. The invention also relates to the heat-curable insulator mixtures which produce the coatings or linings.

With the growth in rocketry and in the use of propellants for the generation of gases at high temperature and in elevated pressure, the problem of protecting the construction material of the combustion chambers from the high temperatures in the combustion chamber, without an excessive increase in weight due to insulation, has become of great importance. In the case of rockets, every unnecessary pound added to the weight of the rocket represents a loss in payload or in range. The duration of the rocket firing or gas generation periods has an important bearing on the materials of the construction and the amount of insulation needed in the case of extremely short firings. The fact that the metal wall of the chamber has reached a temperature at which it has no appreciable strength any longer is of no importance if the period of utility is also at an end. The serious problem comes when the surface is exposed to a high temperature for an appreciable period of time, where the loss of strength could occur before the firing period is at an end. For example, in the firing of large rockets, burning times of 60–120 seconds are common. Gas generators are now being called upon to deliver full power for periods of 10–20 minutes. On the other hand, certain operations are at such a high temperature that exposure for even a fraction of a second may result in the surface reaching a temperature wherein disastrous loss of strength occurs.

The problem of re-entry of missiles encounters a very serious temperature effect on the nose portion of the missile. Not only does air friction very rapidly heat up the nose cone to several thousand degrees Fahrenheit, but erosion by the air battering against the nose of the missile causes changes in configuration of the nose. The enormous velocity of the missile as it is entering the atmosphere means that the time over which the missile is exposed to these extremely high temperatures is also extremely short. Thus, protection for the nose and missile is needed for a very short period, and the problem of keeping the nose below specified maximum temperature is merely that of preventing heat transfer for this fractional second of time; a nose cone positioned at the nose of the missile needs to insulate and to protect against erosion during this short period of time, yet nose cones of simple construction and relatively light weight, and of reasonable price have not become available.

Don E. Kennedy and William G. Stanley discovered an insulator of outstanding utility for the above purpose. This insulator consists of expanded-vermiculite particles dispersed substantially uniformly throughout a

a thermosetting synthetic resin matrix. This insulator as applied to articles needing heat protection is the subject mater of a Kennedy-Stanley U.S. patent application identified as S.N. 176,855 filed Feb. 21, 1962, now abandoned.

The Kennedy-Stanley insulator is prepared from a plastic mixture of the exanded-vermiculite and raw resin capable of forming a thermoset cured resin. Water is produced in the curing operations of these resins or is introduced along with the cure accelerator or even with the raw resin. It is necessary to effectively remove this water during curing; otherwise, its presence can damage the gas generator. For example, water can act on the solid propellants and/or ignitors used in gas generators to prevent ignition and to adversely effect the burning characteristics of the propellant. Although it is important to remove the water, the usual procedures for this purpose have not been entirely successful. During the cure, it is difficult, if not impossible, to remove all the water from the hardened mixture. In addition, when higher cure temperatures and/or longer cure times are utilized to remove most of the water, the coats or linings tend to shrink away from the metal surface to which they have been applied.

Although the Kennedy-Stanley insulator is excellent in situations where coatings of ¼–1 inch are used, the problems inherent with entrained water in the coatings are not entirely absent. In thinner coatings, the above-discussed problems associated with water are more evident.

Among other objects, it is the principal object of this invention to provide an insulator coat which overcomes the disabilities of the Kennedy-Stanley insulator coat.

It has been discovered that insulator linings can be prepared from water-forming, uncured thermosetting resins by a technique which essentially avoids the need to remove water formed during curing and the problems associated therewith. The method for such preparation is carried out by forming a mixture consisting essentially of an uncured thermosetting resin which produces water during curing at a cure temperature, expanded-vermiculite particles, and inorganic salt particles; the salt being capable of forming a salt hydrate with water at temperatures not more than the cure temperature and capable of releasing water above the cure temperature and below the combustion temperature; followed by the curing of the mixture to produce the insulator linings. In the method, heat-curable insulator mixtures are produced which are very useful for protecting metal surfaces against combustion temperatures, commonly above 2000° F. The mixtures consist essentially of the uncured thermosetting resins which produce water during curing at a cure temperature, expanded-vermiculite particles, and inorganic salt particles. The vermiculite particles and salt particles are dispersed in the resin in a substantially uniform manner, with the vermiculties particles being present in about 20–80 parts by weight per 100 parts by weight of resin. Usually, the salt is present in an amount to combine with the water produced during the curing of the resin.

Having thus indicated the general nature of the invention, reference is made to the accompanying drawings, forming a part of the specification, wherein:

FIGURE 1 shows a solid propellant gas generator or rocket motor utilizing the construction of the instant invention.

FIGURE 2 shows a simplified embodiment of a liquid fuel rocket motor utilizing the insulator coat of the instant invention.

As disclosed above, the resultant insulator lining is very useful for protecting construction material of combustion chambers from high temperatures generated in

the chambers, without an excessive increase in weight due to insulation. It is to be understood that the time of exposure to the high temperature is at least about the time over which this surface would have reached the specified maximum temperature and usually is in excess of that time—that is, in the absence of the insulator coat. An appreciable period of time may, in the case of a nose cone positioned on a missile nose during re-entry into the atmosphere, be as little as 0.1–0.5 second; more usually, such as in gas generator operation, times of 10–60 seconds will be involved. Times which exceed about one minute are considered as a substantial period of operation and in the case of certain types of air-borne weapons, and gas generators, periods of time of operation of 10–20 minutes are necessary. By a combination of the composition of the insulator and the thickness of the insulator coat present, it is possible to hold the temperature of the surface to be protected below almost any specified maximum temperature.

The insulator mixture utilized in the invention consists essentially of a water-forming, uncured thermosetting resin having dispersed therein in a substantially uniform manner particles of expanded-vermiculite and inorganic salt particles, which salt is capable of forming a salt hydrate having hydrate stability at the cure temperature of said resin and hydrate instability or capable of releasing water above the cure temperature and below the temperature to which said insulator coat is to be exposed.

The preferred thermosetting resins are phenol-formaldehyde resins. Especially suitable are the two-stage phenol-formaldehyde condensates wherein a novolak, for example, is cured to the finished state by addition of a catalyst or curing agent such as a formaldehyde source, e.g., paraformaldehyde, hexamethylenetetramine or trioxane. For example, to a novolak made from 1 mol of phenol and 0.83 mol of formaldehyde there cen be added 15% by weight of the novolak of hexamethylenetetramine as a curing agent.

Other thermosetting phenolic resins can also be used, e.g., phenol-furfural, m-cresol formaldehyde, cresylic acid formaldehyde, xylenol formaldehyde, e.g., 3,5-dimethylxylenol formaldehyde, as well as mixed xylenol formaldehyde resins, resorcinol-formaldehyde, etc. Furthermore, other thermosetting resins can be employed such as urea-formaldehyde resin, aminotriazine-aldehyde resins, e.g., malamineformaldehyde, furfuryl alcohol resins, furfuryl alcohol formaldehyde resins, furfuryl alcohol furfuryl resins, etc.

The expanded-vermiculite particles are those available in commerce and used for insulation purposes, refractory concretes and light weight mortars. The size of the particles has some bearing on the degree of insulation obtained in the insulator therein. In general, the commercial grades contain a number of particle sizes. Particularly suitable are expanded-vermiculites wherein 65% are retained on a No. 30 sieve and about 90% retained on a No. 50 mesh sieve; another particularly suitable size distribution shows 80% retained on a No. 8 mesh sieve and about 90% retained on a No. 16 mesh sieve. Lower density insulators are obtained by having a wide particle size distribution; this also reduces the amount of resin needed for matrix purposes.

In general, the insulator has present about 20–80 parts by weight of expanded-vermiculate particles for each 100 parts by weight of the thermosetting synthetic resin. More usually, the insulator will have present about 25–50 parts of the expanded-vermiculite particles per 100 parts by weight of the resin. It is to be understood that the parts by weight of the raw mixture which is applied to the surface to be protected will differ somewhat from the proportions after the raw resin has been cured to form the insulator matrix. However, the proportions of the raw mix and the final cured insulator are essentially the same when the cure accelerator (hardener) is considered as part of the raw resin which produces the final cured resin. For a particular raw resin and hardener, it is a matter of a simple trial or two to determine the proportions of the raw mix needed to produce the cured insulator of the desired proportions.

The inorganic salt is introduced into the raw insulator mixture in a condition suitable for combining with water to fom a salt hydrate. Preferably, the salt is added in an anhydrous state, but may be added in a hydrate state less than the maximum hydrated condition. The added salt combines with the water present in the raw insulator mixture or produced during the cure, to form a salt hydrate and, thereby eliminates the need to evaporate this water out of the insulator coat to obtain an insulator of the proper state. This chemical removal of the water decreases cure times or cure temperatures or even both. (Salts can be selected which assist the hardeners, when used, to speed up the cure time or to decrease the amount of hardener needed.) Benefits are obtained by presence of even minor amounts of salt.

Usually sufficient salt is added to combine with the water present and/or produced. Preferably an excess of the salt is added because of the difficulty in this system to obtain the theoretical combination of salt and water.

Not only does the salt give the benefit of faster curing at a given temperature but also additional insulation effect is obtained by the chemical cooling of the decomposition of the hydrate when the insulator is exposed to temperatures higher than the decomposition temperature of the particular hydrate.

Illustrative anhydrous salts are: Al_2O_3, $Al_2(SO_4)_3$, $NH_4Al(SO_4)_2$, $(NH_4)Cr(SO_4)_2$, $NH_4Fe(SO_4)_2$, $Ba(OH)_2$, BeC_2O_4, CaO_2, $CaSO_4$, $Ce_2(SO_4)_3$, $CrCl_3$, $Cr(OH)_3$, $Cr_2(SO_4)_3$, $Co(SO_4)_3$, $CoCl_2$, $MgCl_2$, $Na_2B_4O_7$, Na_2CO_3, $Fe_4(F_2O_7)_3$.

The insulator mixture of uncured or raw resin, curing accelerator, if any, expanded-vermiculite and inorganic salt particles is applied to the surface to be protected or to a backing material having the configuration of the surface to be protected. The coat of insulator mixture is as thick as required for the particular task; the cured coat may be as little as a tenth of an inch to, in some instances, an inch or more. For most gas generator purposes where carbon steel is to be protected, ⅛–½" of cured insulator coat will afford protection against gases in the region of 2,000–4,000° F. for 10 minutes with the steel reaching temperatures only on the order of 300–600° F. In the case of high strength stainless steels, thinner coats may be used because these steels have a higher temperature strength relationship and normally will function at higher specified maximum temperatures. It is to be understood that the thickness of the coat will depend upon the composition of the insulator, the temperature of the gases striking the insulator coat, velocity of the gases striking the insulator coat, and the specified maximum temperature for the particular operation.

The coat of raw insulator is then heated to a temperature for a time suitable to cross-link the resin and to form the infusible cured resin. In the case of the phenol-formaldehyde raw resin, cures can be obtained in reasonable times at temperatures on the order of 212–302° F. (100–150° C.) by the use of a curing accelerator (hardener). These curing accelerators can be any of those known to the art for accelerating cures of a particular type of phenol-formaldehyde resin. It is preferred that the hardener be material which does not introduce water into the insulator mixture, as the presence of extraneous water increases the cure time. In general, coatings about ½" thick made from plastic phenol-formaldehyde raw resins when loaded with expanded-vermiculite in the amounts set forth hereinabove will cure in 4 hours at 257° F. (125° C.).

It is to be understood that the insulator may be positioned directly on the surface to be protected as inside a gas generator combustion chamber or a rocket motor. Or the insulator coat may be mounted on a back-

up plate such as would be suitable for use in a nose cone, and the combination then mounted on the surface to be protected. Or the insulator coat may be placed on a metal or plastic liner and the combination slid into place in a combustion chamber. Or an insulator of the proper size may be prepared by a casting technique and the cured insulator then put into position in contact with the surface to be protected.

It is to be understood that only the portion of the surface which needs protection against elevated temperatures need be covered with insulator coat. Also, that the thickness of the coat may be varied in a particular installation in accordance with the amount of protection needed by the particular surface.

The surface which is to be protected from heat or maintained at or below a particular temperature may be any material of construction which retains its rigidity at the particular temperature of operation. Thus, the insulator coat may be used to protect any metallic material of construction. The invention is particularly useful in that it permits the use of cheaper materials of construction by keeping the temperature below the point at which the strength of the material is completely lost. For example, ordinary carbon steel may be utilized, instead of expensive stainless steel by keeping the temperature of the metal on the order of 400–600° F. On the other hand thin stainless steel sheets may be utilized for the construction of gas generators instead of expensive titanium and hastelloy materials by keeping the temperature of the vessel wall below 1,000° F. Also it is possible to utilize plastics as materials of construction despite exposure to above atmospheric temperatures where normally the loss of strength would be prohibitive by the use of the insulator coat to protect the plastic surface from an otherwise normal temperature rise. Thus, the glass fiber re-enforced plastics may be used as extremely light weight materials of constructions in rockets and gas generators, by using the insulator coat alone or in combination with other insulating means to maintain the surface of the re-enforced plastic below its decomposition point.

The invention is further described in detail in connection with the annexed figures which form a part of this specification.

FIGURE 1 shows a simplified form of an insulated gas generator or rocket motor using a solid propellant as the source of combustion gases. In FIGURE 1 the gas generator comprises a metal vessel **11** which is formed of a substantially cylindrical central wall portion **12**, a domed end closure **13** and a domed forward end closure **14**. In this embodiment the vessel walls **12**, **13**, and **14** are made of stainless steel. It is to be understood that for clarity the vessel walls have been made disproportionately thick.

The cylindrical wall **12** and a part of closure **14** are protected from temperatures above the maximum permissible for the particular stainless steel by insulator coats **17** and **18**, respectively. In this embodiment a raw phenol-formaldehyde resin and expanded-vermiculite insulator having 40 parts by weight of said vermiculite per 100 parts of said raw resin and 15 parts by weight of anhydrous ferric pyrophosphate was applied to wall **12** to a thickness of about 3/16 inch. In the case of coat **18**, a thicker coating of 3/8 inch is placed in order to withstand the erosive effect of the gases striking against the coating **18** from the combustion of solid propellant **21**. It is apparent that as grain **21** burns the hot gases will flare out and impinge on coating **17** on wall **12**. The maximum temperature reached will be on or near closure **14**. The coats were cured for 3 hours at 125° C. (257° F.) to produce the thermoset matrix.

The combustion gases are produced by the burning of a solid propellant grain **21** positioned in the interior of the gas generator. In order to provide a long time burning solid propellant grain **21** is restricted on its cylindrical surface **22** with a restrictor **23**. Here a burning time of 10 minutes is obtained.

The solid propellant may be any one of the propellants known to the art such as, a perchlorate-asphalt mix, an ammonium nitrate-synthetic rubber mix, etc. The restrictor coating is any means applied to the surface of the grain which prevents that surface from burning. In this embodiment grain **21** burns in cigarette fashion from the surface closest to nozzle **16** toward closure **13**. The dead space **25** at the closure **13** end of the vessel is occupied by a lightweight filler.

FIGURE 2 sets out a simple form of an insulated liquid fuel rocket motor. The body of the motor is formed by the pear-shaped vessel **31**, which is provided with a gas exit conduit **32** and injectors **33** and **34** are to introduce the fuel and the oxidizer into interior vessel **31**. The fuel and oxidizer may be ignited by ignition means not shown or may be spontaneously ignited. A mono-fuel such as nitromethane may be used.

In this particular embodiment the wall of vessel **31** is of stainless steel and gas exit conduit **32** is an insert made of highly erosive resistant material such as titanium. An insulator coat **36** is positioned in direct contact with the inside surface of vessel **31**. It is normal in this type of operation to circulate liquid fuel through tubes encircling not only nozzle conduit **32** but the vessel **31** itself. The insulator coat system may be used alone or in combination to augment the cooling obtained by the conventional general circulation.

It can be seen from these embodiments that many other uses for the insulator coat protective system are possible, particularly when a one-time protection is all that is needed. For example, instruments that are to be protected against a destructive temperature may be positioned in a container to which an insulator coat has been applied on the side facing the source of heat; thereby the instruments operate in the safe temperature maintained within the compartment.

In the situation where the insulator is intended to protect the surfaces of a missile passing through the atmosphere, such as a missile nose cone, the insulator will be applied to a back-up plate of the proper shape for mounting on the nose of the missile and of a thickness to afford protection of the actual metal and the payload of the missile against the temperature rise above the specified maximum point during the time from re-entry into the atmosphere to impact on the earth. It may be desirable to protect other parts of the missile from re-entry temperatures by applying an insulator coat to these other parts of the missile.

TEST

Results obtainable with insulator coat system of the invention are illustrated by the following tests. In these tests a rocket motor of the general layout shown in FIGURE 1 was used for test purposes. In these tests the propellant grain was a rod having a diameter of 9 inches and a length of about 25 inches. The propellant comprised of ammonium nitrate, a plastic binder and a combustion catalyst. The grain was restricted with a synthetic plastic restrictor on the cylindrical surface causing the grain to burn cigarette fashion. In general the grain burned to deliver gas on the order of 800 p.s.i. for a time of about 8 minutes, the flame temperature of the gas was about 2400° F. The tests were carried out in concrete shelter with air temperatures of about 75° F. No artificial cooling means were directed toward the outside of the test motor and the test stand was protected from atmospheric wind. The temperature of various parts of the vessel and nozzle was determined by thermocouples using equipment which automatically recorded temperatures over the total time of gas generation.

In all cases, the insulation was applied by hand to the interior metal wall of the motor and cured at a temperature to give a rigid material adherent to the wall having a final thickness of 0.6".

One series of tests utilized an insulator coat where 30 parts by weight of expanded-vermiculite were admixed with 100 parts by weight of palstic phenol-formaldehyde and 10 parts by weight of hardener. The phenol-formaldehyde resin was purchased as Marblette 71. The hardener was a Marblette Hardener 175 which is an aqueous hydrochloric acid solution containing about 13% of HCl. The expanded-vermiculite was Zonolite BE–4 which has a particle size description: 5% retained by a No. 16 mesh sieve; 65% retained by a No. 30 mesh sieve; 98% retained by a No. 50 mesh sieve; and 100% retained by a No. 100 mesh sieve and also Zonolite BE–2 having a size description: 5% retained on a No. 4 mesh sieve; 80% retained on a No. 8 mesh sieve; 99% retained on a No. 16 mesh sieve and 100% retained on a No. 30 mesh sieve; these were used in a 50:50 weight ratio. (All the expanded-vermiculite had been acid treated.)

In all of the tests utilizing this insulator coat the insulator was cured for 6 hours at 125° C. (257° F.) In all of the tests with this insulator coat, the maximum wall temperature after eight (8) minutes of buring time was about 350° F.

In tests illustrating the invention here, the raw insulator mixture consisted of Marblette 71, 100 parts by weight; Marblette Hardener 75, 5 parts by weight; BE–2, 15 parts by weight; BE–4, 15 parts by weight, and anhydrous aluminum sulfate ($AL_2(SO_4)_3$). This coat cured in 4 hours at 125° C. (257° F). The maximum wall temperature after nine (9) minutes exposure to 2400° F. gases was about 350° F.

Visual examination of the insulator coat after all the firings described above showed that even around the nozzle opening, the insulator coat of the invention had successfully resisted erosion of the hot gases. At the hottest portions of the case, the coat had charred to some extent, but at no point had the charring gone more than ½ the thickness of the coat. The final low temperature shows that in spite of charring to this degree, excellent insulating qualities were retained for the firing period and would have permitted still longer operation with satisfactory wall temperatures.

I claim:

1. A heat-curable insulator mixture suitable for protecting metal surfaces against combustion temperatures of gas generators and suitable for being cured at lower temperatures or for shorter times, which mixture consists essentially of (1) an uncured thermosetting resin which produces water during curing at a cure temperature, said resin being a member of the group consisting of phenolic resins, urea-formaldehyde resins, aminotriazine-aldehyde resins, and furfuryl alcohol-aldehyde resins, (2) expanded-vermiculite particles, and (3) inorganic salt particles which are capable of forming a salt hydrate with water at temperatures not more than said cure temperature and capable of releasing water above said cure temperature and below said combustion temperature, said vermiculite particles and salt particles being dispersed in said resin in a substantially uniform manner, said vermiculite particles being present in about 20–80 parts by weight per 100 parts by weight of resin, and said salt particles being present in an amount which is sufficient to combine with the water produced during the curing of the resin.

2. The heat-curable insulator mixture of claim **1** wherein said resin is an uncured phenol-formaldehyde resin and said vermiculite is present in about 25–50 parts by weight per 100 parts by weight of resin.

3. The heat-curable insulator mixture of claim **2** wherein said salt is $Al_2(SO_4)_3$.

4. A method of producing insulator linings from an uncured thermosetting resin which produces water during curing, which method is being carried out at lower cure temperatures or shorter cure times and with the substantial elimination of the need to evaporate water out of the linings during the curing operation, said linings providing protection of gas-generator surfaces against temperatures above 2000° F., which method comprises forming a mixture consisting essentially of (1) an uncured thermosetting resin which produces water during curing at a cure temperature, said resin being a member of the group consisting of phenolic resins, urea-formaldehyde resins, aminotriazine-aldehyde resins, and furfuryl alcohol-aldehyde resins, (2) expanded-vermiculite particles, and (3) inorganic salt particles which are capable of forming a salt hydrate with water at temperatures not more than said cure temperature and capable of releasing water at temperatures above 2000° F., and curing said mixture to produce said insulator linings.

5. The method of claim **4** wherein said vermiculite particles are present in about 20–80 parts by weight per 100 parts by weight of resin, and said salt particles are present in an amount which is sufficient to combine with the water produced during the curing of the resin.

6. The method of claim **5** wherein said resin is an uncured phenol-formaldehyde resin and said curing takes place at about 212–302° F.

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MORRIS LIEBMAN, *Primary Examiner.*

L. T. JACOBS, *Assistant Examiner.*