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[54] METHOD OF PRODUCING SILICEOUS FIBER CORROSION INHIBITING COMPOSITES

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[56] **References Cited**

UNITED STATES PATENTS

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[57] **ABSTRACT**

A method of producing siliceous fiber containing composites which inhibit chloride ion stress corrosion of stainless steel. The method comprises the production of a siliceous fiber batt, the fibers of which form the reinforcing structure of the insulation material, but which fibers will not of themselves inhibit the chloride ion stress corrosion. Alkali metal silicates having an alkali metal to silicate ratio of between 3.75 and 7.5 to 1, and which inhibit the corrosion, are bonded to the skeletal structure of the fibers with a porous binder to both rigidify the fibers and retain the corrosion inhibiting material. In the preferred method of producing the composite, the alkali metal silicate and binder are incorporated with the fibers during the forming process, and the binder is, thereafter hardened to simultaneously form the rigid composite and secure the alkaline metal silicate to the structural skeleton of the fibers. In a less preferred arrangement, the fibers are bonded together with an organic binder, which is then cured, and a slurry of inorganic cementitious material, incorporating the alkali metal silicate, is sucked into the bonded fiber skeleton and hardened to produce the composite.

7 Claims, No Drawings

METHOD OF PRODUCING SILICEOUS FIBER CORROSION INHIBITING COMPOSITES

BACKGROUND OF THE INVENTION

Austenitic stainless steel will withstand elevated temperature and corrosive conditions which destroy carbon steels. Stainless steels have been used extensively for petroleum, chemical, power plant, and atomic reactor equipment, because of their ability to withstand elevated and/or corrosive conditions. Stainless steels cannot be used, however, where chloride ion is present, as for example near sea water or salt water spray because of what is known as chloride ion stress concentration corrosion of stainless steel. The exact mechanism of chloride ion stress corrosion of stainless steel is not completely known, but the stainless steel at elevated temperatures when subjected to chloride ion undergoes cracking at the grain boundries which continue to grow until failure results. It is postulated that this type of failure caused the sinking of the submarine Thrasher. There has also been a long felt need in petroleum refineries and chemical plants for some means of inhibiting or stopping chloride ion stress corrosion of stainless steel.

SUMMARY OF THE INVENTION

According to one aspect of the invention, it has been discovered that potassium silicate and sodium silicate inhibit the chloride ion stress concentration corrosion of stainless steel. These silicates will form glasses which can be fiberized to produce a light weight material, but the fibers made from the silicates lose their strength when subjected to water. In addition the alkali metal silicates are dissolved by alkali at elevated temperatures so that these fibers do not have the necessary durability for use as an insulation material.

According to the invention, a light weight insulation material is made by forming a skeleton of siliceous fibers having less than 10 percent of an alkali metal silicate and which fibers therefore are durable and will withstand the leeching effect of water. The fibers are grouped together into a batt weighing from approximately 3.5 to 15 pounds per cubic foot and particles smaller than about 40 mesh of the sodium silicate and/or potassium silicate are bonded to the fibers forming the skeleton by means of a binder which is designed to withstand the temperature conditions. It has been found that particles of the sodium and/or potassium silicate when deposited from a slurry or dispersion of a binder that contains more water than is required for hardening of the binder, will when hardened and dried, produce sufficient porosity to perform its corrosion inhibiting function. The sodium and/or potassium silicate particles are bonded to the fibers by porous binder so that water running along the channels of the insulation between fibers enters pores and comes in contact with the sodium silicate and potassium silicate to a sufficient degree to counteract the chloride ion before it has penetrated the usual one inch minimum thickness of insulation material. Sodium silicate and potassium silicate having a silica to soda ratio of less than 3.25 to 1 will inhibit chloride ions stress corrosion of stainless steel but is quite soluble and deteriorates rapidly in water. According to the invention the sodium silicate and/or potassium silicate preferably has a silica to soda ratio of between 3.75 and 7.5 to 1 in order that the silicate does not leech out of the insulation material but will nevertheless inhibit the corrosion.

In the preferred method of making the composite, the siliceous fibers, binder and alkali metal silicate are injected into a high velocity gas stream and the solids caused to accumulate on a collection surface, following which the binder is cured into a hardened condition to form the composite. Under some conditions it will be helpful to first wet the fibers before introducing the binder and alkali metal silicate, and under some conditions it may be desirable to direct the binder onto the fibers either at the point of impingement or immediately after impingement of the fibers on the collection surface. Under still other conditions it may be desirable to apply the binder to the fibers in two stages with the particles of alkali metal silicate being bonded to the fibers by either one or both of the binders. Under some conditions the first binder may be an organic binder that is destroyed at elevated temperatures but which will provide rigidity prior to impregnation of the inorganic high temperature binder.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Example 1

A dimensionally stable glass fiber board having a density of 5.5 pounds per cubic foot, and which is 1 inch thick was prepared by spraying a water dispersion of a binder having 20 percent solids into a forming hood into which glass fibers are projected and carried by a high velocity gas stream onto a foraminous collection conveyor. The binder wetted glass fibers were compressed and passed through an oven, which held the fibers compressed, and in which the fibers were subjected to a temperature of 450° F for 5 minutes to cure the binder. The binder used had the following composition:

Components	Bonding Solids Ratio	Additives Percent by Weight Based on bonding Solids
Phenol-formaldehyde resin (water dispersed resite)	70	
Urea	30	
Ammonium sulfate		0.5
Silicone Oil		0.1
Emulsified Petroleum Oil		5.0

A high temperature insulation useful at temperatures above the softening point of the fibers is made by impregnating the skeletal structure produced above with a clay silica binder that includes a sodium silicate and/or potassium silicate corrosion inhibiting material. The binder may also include other materials which will act as fillers and/or materials which recrystallize at very high temperatures to provide structural integrity should the material encounter these very high temperatures. One such inorganic binder impregnant material has the following composition:

Ingredients	Parts by Weight
Sodium Silicate, -325 mesh (4.5 to 1 SiO_2 to Na_2O)	15.4
Feldspar	30
Ball Clay	45.4
Colloidal silica solids	2.6
Bentonite	3.2
Silicone Resin (Methyphenyl siloxane)	3.0
3,5-Dimethyl-1-hexyn-3-ol	0.3

The Feldspar has the following composition: SiO_2—67.53, Al_2O_3—19.40, CaO—1.36, Na_2O—6.83, K_2O—4.58, and traces of Fe_2O_3, TiO_2 and MgO.

The ball clay has the following composition: SiO_2—61.19, Al_2O_3—26.47, Fe_2O_3—0.89, TiO_2—1.72, CaO—0.31, MgO—0.23, Na_2O—0.33, K_2O—0.44, organic—9.42. The silica sol and bentonite form the binder and will generally comprise 2 to 25 percent of the mixture, and the remaining materials are fillers and will generally comprise from 74 to about 98 percent of the mixture. The colloidal silica and bentonite will usually be used in a ratio of from 1 to 19 to 19 to 1. The slurry is made by charging ⅔ of the total amount of water into a mixing vessel and dissolving therein 0.001 part of sodium hexametaphosphate, 0.01 part of boric acid, and the bentonite clay recited above. The silica sol is then added and mixed followed by the ball clay. Thereafter the feldspar and the sodium silicate is added with the remainder of the water to prepare a slurry having a solid content of 22.7 percent. A 75 percent aqueous solution using 0.005 parts of a sulfonated dicarboxylic acid ester is added as a wetting agent.

An aqueous dispersion of the organ o-silicone compound is made by stirring 10 parts with 1 part of the 3,5-dimethyl-1-hexyn-3-ol in a mixing tank and then adding ammonium hydroxide to produce an alkaline pH. Thereafter 2 parts of oleic acid are added. Following this 10 to 20 parts of water are added and the entire mixture is stirred until a creamy mix is obtained. This mix is then added to the large mixture containing the slurry and the material mixed for 15 minutes.

The slurry produced as above described is spread upon the basic skeletal board produced as above described and sucked down into the fibers to thoroughly saturate the fiberboard. The impregnated board was then heated for 4 to 10 hours at a temperature of about 450° F in an air circulating oven to produce an insulation material weighing 12.5 pounds per cubic foot. The insulation material prepared can be used at temperatures up to 1,200° F and when applied to stainless steel equipment, inhibits the chloride ion stress concentration corrosion of the stainless steel when the material is exposed to salt water spray.

In the preferred method of making the insulation material of the present invention the glass fibers and inorganic binder are brought together, and the finished composites made in one hardening step.

Example 2

The process of Example 1 is repeated excepting that an organic binder is not used and in its place the fibers are wetted at forming by spraying a 2 percent solution of a silica sol into the air stream and onto the fibers as they are being carried to the collection surface. Immediately after the injection of the silica sol solution to the air stream a dry mixture of the feldspar, sodium silicate, ball clay and bentonite given in Example 1, are blown by an air jet into the air stream carrying the wetted fibers so that the dry materials of Example 1 are codeposited with the fibers on the collection surface. After collection on the surface, a further light spray of a silica sol solution is applied to the top of the collected material. This second solution also includes the silicone resin emulsion of Example 1. A sufficient spray is used to thoroughly wet out the solids retained by the fibers using an excess thereof, and the excess is caught and recirculated. The board thereafter is dried in an oven at 450° F for 4 hours to produce an insulation material of substantially the same composition and characteristics as given in Example 1, excepting that it is devoid of the organic binder.

Example 3

Glass fibers were prepared by attenuating molten streams of glass by high pressure steam jets which carry the fibers to a forming hood. A 2 percent silica sol solution is sprayed onto the fibers immediately after forming and before entering the forming hood, and thereafter the flow of gases carries the fibers onto a foraminous conveyor where they are collected into a batt. The slurry prepared as in Example 1 is spread on top of the batt of fibers, and is caused to thoroughly impregnate the batt by means of a suction that is applied beneath the foraminous conveyor. After being thoroughly impregnated, the fibers are dried as in Example 1 to produce a product having substantially the same properties as given in Example 1.

Example 4

Continuous lengths of glass fibers are fed to the chopping apparatus shown in the Sonneborn et al. U.S. Pat. No. 2,790,741 and chopped into approximately 2 inch lengths. The chopped fibers are collected onto a moving conveyor which transfers the fibers beneath a hopper which applies the mixture of the dry solid ingredients given above in Example 1. This mixture is devoid of the silica sol and the silicone resin emulsion. Thereafter the layer of fibers and the layer of solid binder is broken up and allowed to fall onto another conveyor, and immediately thereafter an aqueous solution of the silica sol containing the silicone emulsion is applied to the composite to thoroughly wet out the solids and fibers. Thereafter the wetted material is transfered to an oven where it is cured for 4 hours at a temperature of 450° F. This procedure provides an insulation material having generally the same properties, including the corrosion inhibiting properties, of the material prepared above in Example 1.

Example 5

The process of Example 4 is repeated excepting that the fibers are Refrasil fibers. Refrasil fibers are acid leeched glass fibers of high silica purity. The product produced is extremely durable, can be used at temperatures of 2,000° F and prevents the chloride ion stress concentration corrosion of stainless steel when the insulation is exposed to salt spray, etc.

Example 6

The process of Example 4 was repeated excepting that the fibers which were used were bulk air blown "Fiberfrax," a trade name for ceramic fiber made from alumina and silica. The insulation material prepared had generally the same properties as that of Example 5 above. Alternately the ceramic alumina-silica fibers upon solidification after being blown can be processed in the same manner given above in any of the Examples 1 through 3 to produce an insulation material that is useful at very high temperatures and which will inhibit chloride ion stress corrosion of stainless steel.

Example 7

The process of Example 3 was repeated excepting that the fibers were prepared from molten streams of rock discharged from a cupola to prepare a mineral wool. The insulation material so prepared had generally the same properties as that given in Example 3 above.

Example 8

The process of Example 3 is repeated excepting that the inorganic binder used had the following composition: 100 parts of an aluminous cement purchased under the tradename Lumnite, 20 parts of 325 mesh (4.5 to 1 silica to soda ratio) sodium silicate, 80 parts of −325 silica flour and 200 parts of water. The material is sucked down into the batt and dried and provides a high temperature insulation material which inhibits chloride ion stress concentration corrosion of stainless steel.

Example 9

Steam blown glass fibers are prepared as given above in Example 3. The fibers are carried by the steam and secondary air to a collection conveyor. A slurry of the following composition is sprayed onto the fibers by means of compressed air using conventional equipment that is used to apply portland cement mud to buildings and other structures: 3 percent magnesium oxide, 15 percent magnesium sulfate, 7 percent sodium silicate, 4.5 to 1 silica to soda ratio and the balance water. All of the materials were −325 mesh. The material is thereafter dried as given in Example 1 to produce a material having a density between 20 and 25 pounds per cubic foot and which inhibits the chloride ion stress concentration corrosion of stainless steel.

Example 10

The process of Example 9 is repeated excepting that the slurry has the following composition: 10 parts of monoaluminum phosphate, 20 parts of potassium silicate having a K_2O to SiO_2 ratio of 4.5 to 1, 69 parts of silica and 22 parts of water. The potassium silicate has a particle size of approximately 40 mesh. The material produces a composite having good properties at elevated temperatures and which inhibits the chloride ion stress concentration corrosion of the stainless steel. Other silica phosphate binders which can be used are disclosed in U.S. Pat. No. 2,479,504.

Example 11

A chloride ion stress concentration corrosion inhibiting insulation material useful at lower temperatures can be prepared using portland cement and the sodium silicate and/or potassium silicate corrosion inhibiting material using any of the processes given above. By way of example, a slurry comprising 1 part high early strength portland cement, 1 part sand, 1 part sodium silicate (4.5 to 1 silica to soda ratio) and 6 parts water is prepared from solids all of which are less than 325 mesh. The slurry is blown by compressed air as a spray into the forming hood of fibers produced as described above in Example 3. The material thereafter is allowed to air dry for 2 days. The material has a density of approximately 20 to 25 pounds per cubic foot. The material has good green strength, inhibits corrosion of stainless steel, and is generally useful for insulation purposes at temperatures below approximately 400° F.

In general useful products are made from siliceous fiber batt of more than approximately 3.5 pounds per cubic foot, which for most purposes will have a density less than approximately 15 pounds per cubic foot. Usually fiber batt having a density of between 5 and approximately 10 pounds and most preferably between 5 and 7 pounds will be used. The corrosion inhibiting potassium silicate, and sodium silicate will have a silica to alkali metal oxide weight ratio of from approximately 3.75 to 7.5, and most preferably will have a ratio of approximately 4.5. The alkali metal silicate preferably has a particle size below 40 mesh, and is preferably used in amounts above 5 percent of the total product, and usually below 15 percent of the total product, so that in most instances it will comprise from approximately 0.25 pound to approximately 2 pounds per cubic foot of product. The inorganic binder is preferably used in approximately a 1 to 1 weight ratio with respect to the glass fibers, so that in most instances it will comprise from approximately 3.5 pounds per cubic foot to approximately 15 pounds per cubic foot of product. The inorganic binder is preferably deposited from a slurry containing more water than that required to produce the crystalline hydrate so that the resulting material is porous. In those instances where an organic binder is first used to knit the fibers together, it will usually comprise from approximately 4 to 12 percent by weight of the fibers, and preferably between 6 and 9 percent. When an organic binder is used, it can be used to adhere the particles of potassium silicate or sodium silicate to the glass fibers with the inorganic cementitious material deposited over the top thereof. Alternatively, the alkali metal silicate can be incorporated into the inorganic cementitious material itself. In at least some of the formulations given above, a siloxane dispersed by a fugitive material is used to provide water repellancy for the product. This is particularly desirable for those binders which would be deteriorated by water or which would become water logged. It will be understood that various other types of additivies can be incorporated into the slurries, such as antifoaming agents, wetting agents, coloring matter, other fillers, etc.

Example 12

The process of Example 1 is repeated except that no organic binder was used to produce the batt. In place thereof, the glass fibers were collected dry and fused together at a temperature of 1,200° F. The impregnated product has all of the properties of the product of Example 1.

Example 13

Alumina silicate fibers purchased under the tradename "-Fiberfrax" were put through a textile picker and sprayed with the organic binder given in Example 1. The coated fibers were pressed and curved to form a batt as in Example 1, and thereafter were impregnated with inorganic saturant and hardened as in Example 1. This product is useful at temperatures of 2,000° F. Alternatively Refrasil fibers can be used to produce an insulation product useful at 2,000° F.

While the invention has been described in considerable detail, I do not wish to be limited to the particular embodiments described, and it is my intention to cover hereby all novel adaptations, modifications and arrangements thereof which come within the practice of those skilled in the art.

What is claimed is:

1. The method of producing an insulation material which inhibits chloride ion stress corrosion of stainless steel including the steps of: forming a porous batt of siliceous fibers having a soda content of less than 10 percent by weight and a batt density of from 3.5 to 15 pounds per cubic foot; dispersing particles of an alkali metal silicate from the group consisting of sodium silicate and potassium silicate having a silica to alkali metal oxide molar ratio of between 3.75 and 7.5 and a particle size smaller than approximately 40 mesh, and an aqueous dispersion of an inorganic hardenable binder forming material throughout the batt; hardening the binder forming material in situ to bond the fibers into a bonded skeletal structure and to bond the alkali metal silicate particles to the skeletal structure; and removing the excess water therefrom to create pores in contact with the particles of alkali metal silicate.

2. In the method of claim 1 wherein molten streams of siliceous material are injected into a stream of high velocity gases to attenuate the molten streams into fibers, and wherein the stream of fibers and gases is passed through a collection surface which retains the fibers on the collection surface in the form of a batt; the dispersing step wherein the particles of alkali metal silicate and binder forming material are injected into the gases from which the fibers are retained by the collection surface.

3. In the method of claim 1 wherein molten streams of siliceous material are injected into a stream of high velocity gases to attenuate the molten streams into fibers, and wherein the stream of fibers and gases is passed through a collection surface which retains the fibers on the collection surface in the form of a batt; the dispersing step comprising wetting the fibers by injecting aqueous material into the high velocity stream of gases and fibers, and thereafter introducing the particles of alkali metal silicate into the stream on its way to the collection surface.

4. The method of claim 1 wherein the binder and alkali metal silicate are introduced dry to the gases on their way to the collection surface, followed by the step of applying water to the collected material.

5. The method of claim 3 wherein the fibers are wetted with an aqueous dispersion of an organic binder, followed by the step of hardening the organic binder to bond the particles of alkali metal silicate to the fibers.

6. The method of claim 5 followed by the step of impregnating the bonded fibers with a slurry of an inorganic binder material, and hardening the inorganic binder to produce a high temperature insulation material.

7. The method of claim 1 wherein the dispersing step includes forming a slurry comprising the particles of alkali metal silicate and an inorganic binder, and sucking the slurry into the batt of fibers.

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