

1

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**PROCESS OF BONDING ASBESTOS FIBERS WITH A TITANIUM POLYMER AND ARTICLE PRODUCED THEREBY**

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This invention relates to fabricated asbestos fibers of improved wet strength and to a process for treating fabricated fibers.

Asbestos fibers in the form of paper, rope, batts, etc. are used as insulation in numerous applications but have the disadvantage that they become seriously weakened when soaked with water. As a result the wet materials disintegrate under slight stress and the insulating value is lost.

One object of this invention is to provide asbestos fibers having a relatively high wet strength.

A further object is to provide a process for improving the wet strength of fabricated asbestos fibers.

Still another object is to provide asbestos paper having improved wet strength.

A still further object is to provide asbestos fibers bonded with a water-insensitive polymeric product derived from a straight-chain polymer of a tetraorgano derivative of orthotitanic acid.

These and other objects are attained by impregnating fabricated asbestos fibers with an anhydrous organic solvent solution of a straight-chain polymer of a tetraorgano derivative of orthotitanic acid, removing the solvent and reacting the straight-chain polymer with water to thereby form a polymeric water-insensitive reaction product.

The following examples are given in illustration and are not intended to limit the scope of this invention. Where parts are mentioned they are parts by weight.

*Example 1*

A strip of asbestos paper about 0.017" thick was passed slowly through a 5% solution in anhydrous xylene of a condensation of polymer of tetrabutyl ortho titanate having an average degree polymerization of about 2.2. A resin pickup of about 0.75% by weight based on the weight of the paper was obtained. The impregnated paper was air dried in a humid atmosphere for several days. The dried paper was then tested for tensile breaking strength by ASTM method D829-48 with the following results:

	Untreated Paper	Treated Paper
Dry:		
With.....	17.88	17.4
Across.....	6.78	6.46
Wet:		
With.....	0.78	5.34
Across.....	0.14	1.80

The figures given above are in pounds per inch of width of the test sample and represent averages of five samples for each test. "With" indicates that when the sample was tested, the stress was applied in the machine direction of the paper and "across" indicates that the stress was applied at right angles to said direction. In the test, the sample was wet with water and the test was run at 23° C. with the rate of travel of the lower clamp in the testing machine set at two inches per minute.

2

The results show that the dry strength of the asbestos paper is substantially unaffected by the impregnant but that the wet strength of the treated paper is six times greater than that of the untreated paper in one direction and twelve times greater in the other direction.

The impregnated paper was also tested for tear strength with the Elmendorf tear tester according to ASTM D689-44. The following results reported in gram-centimeters indicate the work necessary to tear single sheets of the paper. The results are an average of three samples in each test.

	Untreated Paper	Treated Paper
Dry:		
With.....	117	203
Across.....	125	186
Wet:		
With.....	51	64
Across.....	35	99

These results indicate that the treated paper has increased resistance to tearing in both the dry and wet conditions.

The method of this invention comprises impregnating asbestos fibers in paper, rope, batt, etc. form with a condensation polymer of an organo titanium compound, followed by drying of the impregnated fibers in a humid atmosphere. Since the polymers are either viscous liquids or solids, it is necessary to use a dilute solution of the polymer in an anhydrous solvent such as benzene, toluene, xylene, alcohols, etc. for the impregnation step. The amount of polymer picked up by the paper may be varied from about 0.5 to about 3% by weight based on the weight of the paper.

It is essential that the titanium polymer be in an anhydrous medium when applied to the paper and that the impregnated paper be dried in an atmosphere containing at least 30% relative humidity. It is possible although unnecessary to dip the impregnated paper in water and then dry it in a substantially dry atmosphere.

The condensation polymers of this invention are described and claimed in copending application S. N. 122,844 filed October 21, 1949, now abandoned.

The polymers there described are prepared by reacting 0.5 to 1.5 mols of water with 1 mol of a tetraorgano derivative of orthotitanic acid at room temperature in an otherwise anhydrous inert organic solvent such as an aromatic or aliphatic hydrocarbon or a halogenated hydrocarbon. Thus, for example, as is shown in Example I of S. N. 122,844, when tetra-n-butyl orthotitanate is dissolved in anhydrous butanol and about 0.9 mol of water per mol of orthotitanate is added thereto and the resultant solution is maintained at about 30° C. for 24 hours, there is obtained on vacuum distillation of the solvent a residual transparent liquid polymeric product having a viscosity of about 5-25 poises.

The polymers prepared by the process described in the aforesaid application S. N. 122,844 range from liquids to hard solids depending on the starting derivative of orthotitanic acid and the amount of water used. In general, if 0.5 mol of water is used, the product is essentially a dimer. As more water is used, longer straight-chain polymers are formed until the amount of water becomes greater than 1 mol per mol of orthotitanic derivative. At this point a substantial amount of cross-linking takes place, the viscosity of the polymers rises abruptly and the majority of the resulting polymers are solids. The polymers to be used as starting materials in accordance with the present invention are the straight-chain polymers of tetraorgano derivatives of orthotitanic acid prepared by reacting each mol of the tetraorgano derivative with 0.5-1 mol of water. The

straight-chain polymers are cross-linked by further reaction with water.

Among the titanium organic compounds which may be polymerized to form the polymers of this invention are esters of ortho titanic acid including the methyl, ethyl, propyl, isopropyl, butyl, isobutyl, secondary butyl, tertiary butyl, pentyl, octyl, isooctyl, 2-ethyl hexyl, decyl, lauryl, stearyl, eicosanyl, etc. saturated esters, the allyl, ethallyl, methallyl, crotonyl, oleyl, vinyl, etc. ethylenically unsaturated aliphatic esters, the phenyl cresyl, resorciny, naphthyl, etc. aromatic esters. The organic groups may contain inorganic substituents such as halogen, nitro, amino, sulfone groups, etc.

A second class of titanium organic derivatives which may be used are the mixed anhydrides of ortho titanic acid and organic acids. These compounds are sometimes called esters of the organic acid with the ortho titanic acid since the latter is amphoteric in character and may react as an alcohol. Among the mixed anhydrides which may be used are the tetra-acetate, tetrapropionate, tetrabutyrate, tetra-isobutyrate, tetralaurate, tetrastearate, tetra-oleate, tetrabenzoate, tetranaphthoate, tetracinnamate, etc. Substituents such as halogen, nitro groups, amino groups, etc. may be present.

A third class of titanium compounds which may be used comprises the amides of ortho titanic acid. These include the reaction products of ortho titanic acid with ethyl amine, methyl amine, butyl amine, decyl amine, palmityl amine, oleyl amine, cetyl amine, aniline, benzyl amine, naphthyl amine, etc.

Organic derivatives of metatitanic may also be used to produce the condensation polymers of this invention.

The condensation polymers range from crystal-clear viscous fluids to white waxy solids. They are soluble in substantially anhydrous organic solvents including anhydrous alcohols, hydrocarbons, ketones, etc. The polymers may be formed by adding the requisite amount of water slowly to the anhydrous titanium monomer with constant agitation. However, for ease of working, the polymerization is preferably carried out in an anhydrous solvent which may advantageously be an excess of the solvent used in making the monomer. The polymer prepared in the solvent medium is then used in the form of a solution without freeing it from the solvent.

The process of this invention provides a method for treating fabricated asbestos fibers in the form of paper, rope, batts, cloth, etc. to increase its wet strength to a remarkable degree and to improve the tear resistance of the paper in both the wet and dry states. The invention is applicable to woven asbestos sheets as well as to felted asbestos paper such as Quinterra paper.

It is obvious that variations may be made in the prod-

ucts and processes of this invention without departing from the spirit and scope thereof as defined by the appended claims.

What is claimed is:

1. A fabricated composition comprising asbestos fibers bonded with the polymeric water-insensitive reaction product of water and a straight-chain polymer of a tetraorgano derivative of orthotitanic acid.

2. A composition as in claim 1 wherein the straight-chain polymer is a polymer of a tetra alkyl ester of orthotitanic acid.

3. A composition as in claim 1 wherein the straight-chain polymer is a polymer of a mixed anhydride of an organic acid and orthotitanic acid.

4. A composition as in claim 1 wherein the straight-chain polymer is a polymer of a tetra amide of orthotitanic acid.

5. A composition as in claim 1 wherein the straight-chain polymer is a polymer of tetrabutyl orthotitanate.

6. A process for increasing the wet strength of asbestos paper which comprises impregnating the paper with an anhydrous solvent solution of a water-reactive straight-chain polymer of a tetraorgano derivative of orthotitanic acid, removing the solvent and exposing the impregnated paper to a humid atmosphere in order to condense and insolubilize the polymer.

7. A process as in claim 6 wherein the water-reactive condensation polymer is a polymer of a tetra alkyl orthotitanate.

8. A process as in claim 6 wherein the water-reactive condensation polymer is a polymer of a mixed anhydride of an organic acid and ortho titanic acid.

9. A process as in claim 6 wherein the water-reactive condensation polymer is a polymer of a tetra amide of ortho titanic acid.

10. A process as in claim 6 wherein the water-reactive condensation polymer is a polymer of tetrabutyl orthotitanate.

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