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(54) Title: ABRASION-RESISTANT WATER-BASED SOL GEL COATINGS FOR FIBROUS SUBSTRATES

(57) Abstract: A coating for fibrous substrate materials used in high temperature applications. The coating is formed by applying a composition comprising a water-soluble metal alkoxide or a precursor thereof and optionally a coupling agent in aqueous solution on the surface of the substrate. The cured coating provides protection of the fibrous surface at high temperature, thereby preventing degradation of the fibrous material, while increasing its flexibility and use life.

ABRASION-RESISTANT WATER-BASED SOL GEL COATINGS FOR FIBROUS SUBSTRATES

TECHNICAL FIELD AND INDUSTRIAL APPLICABILITY OF THE INVENTION

The present invention relates to coatings applied on fibrous substrates that are used in high temperature applications. In particular, the invention relates to sol-gel coatings for application to fibrous substrates that are used in a variety of high temperature filtration applications, such as the filtration of particulates during combustion processes. As such, the coatings are suitable for use in pollution control or particulate manufacturing operations. The coating imparts an abrasion-resistant effect to the fibrous substrate and renders it more flexible. Accordingly, materials treated with the coatings of this invention exhibit improved durability at high temperatures.

BACKGROUND OF THE INVENTION

It is generally known that reinforcing fiber materials such as glass can be used in fibrous substrates, and that such fibers have wide application in situations where a strong yet flexible reinforcing material is desired. In particular, reinforcing fiber materials can be used in woven or nonwoven fabrics, or in the construction of flexible sheeting materials. Glass fiber-reinforced fabrics or sheeting materials are particularly used in high temperature applications, because of their flame resistance. For example, fabrics made of glass are used to filter particulate substances released from combustion processes, or during the manufacture of certain particulate compounds. In either case, the high processing temperatures preclude the use of conventional filters made from combustible substances such as paper or natural fibers. It is generally known that at temperatures in excess of 500°F (260°C), most materials commonly used to manufacture filters or fabrics, such as natural or polymeric fibers, will degrade. By the term "degrade" it is meant that these materials either burn, fuse, melt or otherwise undergo deterioration that makes them unsuitable for use in high temperature applications.

High-temperature operations such as those described above require filtration materials made out of a material that can withstand very high temperatures. Conventionally in the art then, it has been known to use fabrics made of glass reinforcing

fibers in such applications. One outstanding benefit of using glass in such applications is that it is highly heat resistant and, as a result, it is therefore less susceptible to combustion or other temperature- related decomposition. One example of such a high temperature use is a woven fabric containing glass fibers that is used to make filter bags for use in high temperature atmospheres where it is desirable to capture particulate contaminants such as fly ash. Alternatively, the glass-reinforced fabric may be used to provide filters in manufacturing operations where particulate products are manufactured and purified at high temperatures. One such example is the process for manufacturing carbon black. The operations may also require use of a fibrous substrate that has been impregnated or otherwise treated with a catalyst to enhance the reaction.

Certain drawbacks, however, are known to be associated with the use of glass-based fabrics. One of these problems is that the fibers are inherently abrasive, and as such are susceptible to abrasion and scratching. The strength of glass fibers is sensitive to the characteristics of the fibers' surfaces. As a result, when the fibers contact each other, breakage or strength degradation may occur. This behavior is exacerbated at high temperatures, particularly at temperatures where conventional coatings no longer survive. Self-abrasion is therefore a contributing factor in the degradation of fabrics and other fibrous articles made from glass fibers at high temperatures.

Degrading of the glass fiber materials also affects the durability of the substrate. In this regard, strength and flexibility are important characteristics of the fibrous material, and are particularly relevant considerations in the making of glass fiber fabrics that are used in filter bags. Filter bags typically require periodic cleaning, which usually takes one of two forms. In the first method of cleaning, the bags are mechanically shaken, for example using strong agitation. In the other method, blasts of air are periodically pulsed through the bags. In either method, the fabric is subjected to rigorous flexing. It is therefore desirable that the fabric has a long flexural fatigue resistance (flex-life). However, high use temperatures compromise the flex life of the fabric because of the tendency of the fibers to degrade.

Another difficulty results from the ability of the filtered material to react with the surfaces of the fibers in the filter fabric. For example, in the manufacture of carbon black, carbon particles exhibit the tendency to fuse with the surface of the glass fibers in the filtration material, where such fibers are left untreated. Accordingly, it is desirable to treat the surface of the fibers or the woven fabric itself with a protective agent that reduces

reactivity with the particulate filter residue.

To address these recognized needs for abrasion resistance, flexibility and surface protection over the usable life of articles made using woven glass fabrics, attempts have been made to devise a coating to be applied to the fibers. For example, TEFLON ®, a polytetrafluoroethylene material, has been used as a coating for fibers in a filter bag. While this material does increase the fabric's resistance to abrasion, it is generally not suitable for long term, high temperature applications such as filtration at temperatures at or above 662°F (350°C). Neither is such a material generally suitable as a support or undercoat for catalytically active materials.

Typically in the art, sol-gel coatings for woven glass fabrics have been made using a solvent-based coating system, in which a sol-gel coating is suspended or dissolved using an organic solvent. Exemplary coatings of this nature are described in U.S. Patent No. 4,970,097. The organic solvent solution is deposited onto the fibrous surface of the fabric material, then allowed to air dry. After air drying, the coating is exposed to heat to effect the cure. The organic carrier solvent used is routinely selected by those skilled in the art. For example, $C_1 - C_8$ alcohols such as isopropanol, ethanol and diacetone alcohol may serve as the organic solvent.

There are certain drawbacks, however, to using organic solvent-based compositions as coatings for fibrous substrates. One major problem is that solvent vapors present a health hazard to personnel handling the coatings, because of the risk of fire or explosion. Another disadvantage is that the solvent vapor emitted during manufacture of the coating is a source of volatile organic chemicals (VOCs), which are recognized as hazardous environmental contaminants.

A need exists therefore for a coating formulation for treating reinforcing fibers to reduce self-abrasion at high temperatures, and to reduce the tendency of the fibrous substrate to react with the material being filtered. Also needed is a coating formulation that is solvent-free, and which, accordingly, is environmentally safe, as well as safe for handling by industry personnel. Further, it is desirable that the woven fabrics made with the fibrous reinforcing substrate be sufficiently flexible to allow manipulations such as shaking or flexing, and thereby improving the flex life of the material, without deterioration of the fibrous material.

SUMMARY OF THE INVENTION

Applicants have surprisingly discovered water-based coatings suitable for application to fibrous substrates used in high temperature processing application. The coatings of this invention are effective in preventing deterioration of the fibrous substrate and indeed cause the substrate to become abrasion resistant. Further, the coatings of the invention increase the flex life of the fibers contained in these materials. The terms "abrasion resistant", and "abrasion resistance", as they are used herein, include resistance to abrasion of fibers in the substrate resulting from contact with other materials or substances, as well as a reduced tendency to undergo the phenomenon of self-abrasion at high temperatures. As further advantages, the coatings of the invention are environmentally safe, and they greatly minimize the risk that personnel may be exposed to harmful vapors.

The coating composition of the invention is a water-based sol gel formulation comprising a metallic compound which reacts to form a metallic oxide in the sol-gel coating. The term "metallic compound" as it is used herein, is defined to mean an inorganic or metallo-organic material that may be selected from several categories of compounds having functional groups capable of reaction to form metal oxides. Such compounds may be selected from the group consisting of inorganic metallic compounds, metallic alkoxides, semi-metallic alkoxides, or metallic or semi-metallic alkoxide precursor compounds and mixtures thereof. These compounds are capable of reacting to form metal oxides upon exposure to a high temperature oxidizing environment. Specifically, the metallic compound may be applied directly in the coating composition, whereupon, when heat is applied, the conversion to the corresponding metal oxide occurs. Where, for example, a precursor compound such as a metallic alkoxide precursor is employed, the reaction to form the metal oxide precursor first occurs when the coating is prepared, and the resulting product is then cured to form the desired oxide. Alternatively, a mixture of one or more of the aforementioned metallic compounds may be used in the coating formulation.

In particular, the inventors have surprisingly discovered that certain water-soluble metallic compounds may be used to form the solvent-free coatings of the present invention. Prior to this invention, an organic solvent was often necessary to sufficiently solubilize metallic or semi-metallic ingredients used in sizing formulations, because those materials known to be useful were not water-soluble. Further, typical coupling agents

used in coatings, such as organosilanes, were known to be insoluble or only slightly soluble in water. However, as expressed herein, the inventors have now discovered that particular metallic and semi-metallic alkoxides, metal chlorides and other metallic compounds with a relatively high degree of solubility in water may be used alone or in combination to form an effective protective coating composition for fibrous glass substrate materials. The water-soluble metallic compounds of this invention may also act as coupling agents to facilitate the bonding of the coating materials to the surface of the fibrous substrate.

The metallic compound is formed from any metal in the Periodic Table of Elements that is capable of forming an aqueous solution that can be cured to form the corresponding metal oxide. Further, the metallic compound may form a water-soluble alkoxide in solution, that may later be cured to form the metal oxide. Such elements include a large number of metals and metalloids. For example, the water-soluble alkoxides of this invention may be formed from a tetral metal belonging to periodic group IV A, or a transition metal element.

Alternatively, the alkoxide is formed *in situ* by the addition of a metallic alkoxide precursor compound. The precursor compound may be an organometallic compound, a transition metal compound or a semi-metallic compound. The organometallic, transition metal or semi-metallic compounds suitable for use in the invention are those that are capable of conversion to metal oxides upon heating. Accordingly, the coating may contain a water-soluble alkoxide that is added directly to the coating composition at the time it is made, or alternatively, the alkoxide may be formed from an added precursor.

It is also an object of this invention to provide a method for forming a coating on a fibrous substrate that provides abrasion resistance and extends the flex life of the substrate. Accordingly, the method of the invention comprises the steps of:

a) preparing a composition comprising a metal alkoxide or a metal alkoxide precursor compound and a coupling agent;

b) coating the surface of a fibrous substrate with the coating composition;

c) drying the coated surface; and

d) curing the coating with heat at an elevated temperature.

Hereinafter, the term "fibrous substrate" is intended to mean fibrous materials in the form of fibers, strands or rovings, woven or nonwoven fabrics, sheets or any other material comprising reinforcing fibers. This includes fibers that can be used in high temperature

applications, preferably above 500°F (260°C). Examples of fibrous substrates that may suitably be coated with the composition of this invention include glass fiber reinforcements, ceramic fibers, glass-carbon hybrid fibers, polymeric fibers that are stable at high temperatures, and mixtures thereof.

Preferably, the fibrous substrate is a woven material or article in the form of a fabric bag or cloth that is used in filtering operations. In a preferred embodiment, the fibers that compose the fibrous substrate are of glass. The term "glass" in the context of this invention means glass, ceramic or ceramic-glass formulations including fibers made from minerals, such as rock. Preferably, conventional glass fibers are used, such fibers being one or more of many formulations well known in the art. Desirably, the glass will be an alkaline earth aluminosilicate formulation. Most preferably, in high temperature filtration applications the fibers are of an S-type glass, however other glass compositions such as the alkaline earth borosilicate compositions found in E-glass may also be used. Glass is a particularly preferred fiber in woven fabrics used in the high temperature applications of this invention because the glass surfaces provide a surface rich in hydroxyl functional groups. These hydroxyl groups in turn promote adhesion by reacting with the alkoxide. The resulting coating is a hydrolyzed alkoxide coating that is chemically linked to the glass fiber surface.

The invention further comprises coated articles having the aforementioned coating.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

The coating formulations of the invention comprise a metallic compound as defined above, which may be either an inorganic or metallo-organic material that may be selected from several categories of compounds having functional groups capable of reaction to form metal oxides, a water-soluble metal alkoxide or a metallic alkoxide precursor salt that forms an alkoxide during curing of the coating, together with a coupling agent. The combination of the alkoxide with the coupling agent produces a coating that, upon cure, forms a layer that effectively reduces or inhibits the degrading of the reinforcing fibers in the fibrous substrate that may be due to surface flaws. These surface flaws, which normally intensify at high temperatures and result in self-abrasion

and loss of flexibility, are effectively diminished by application of the coatings of this invention.

The water-soluble metallic compound may be formed from any metallic or semi-metallic element of the Periodic Table of Elements that is capable of forming a water-soluble alkoxide and/or which is capable of forming a metal oxide on the surface of the fibrous when it is heated. Preferably, the element is a tetral element belonging to the Group IV A or IV B series of the Periodic table. Further, the water-soluble metallic compound is preferably selected from organometallic compounds or transition metal compounds that can be converted to an alkoxide upon exposure to heat, preferably at temperatures above 752°F (400°C). Preferred metals include titanium, tin and silicon.

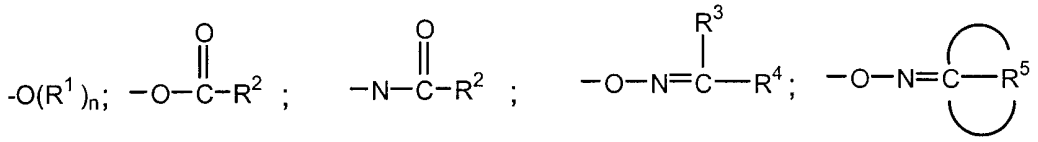
The metallic compound may, for example, be selected from the group consisting of metallic or organometallic salts, such as organic or inorganic chlorides. For example, the metallic compound may be an organotin chloride compound such as monobutyl trichlorotin, which is a water-soluble organic salt. Alternatively, the metallic compound may be an inorganic salt such as tin chloride, $SnCl_4$.

Alternatively, the metallic compound may be an alkoxide capable of dissolving in water to form an aqueous solution. Such alkoxides are generally of the formula $M(OR)_x$, where M denotes an atom or metal; R is an alkyl group having from 1 to 5 carbon atoms, and x represents an integer from 1 to 4. A mixture of one or more of these alkoxides may be used in the coating formulations of this invention. Exemplary alkoxides useful in the practice of this invention include titanates such as titanium alkoxides, which are commercially available, for example, under the trade name TYZOR from DuPont Inc. Examples of these titanates include TYZOR TPT, TYZOR TE, and TYZOR 131, all of which are titanium alkoxides. The amount of the alkoxide that may be used in the coating composition ranges from about 3 percent weight to about 20 percent weight, and preferably, is from about 5.5 percent weight to about 14 percent weight. Most preferably, the amount of metal alkoxide is about 9 percent weight. However, in the case of certain alkoxide solutions, the preferred concentrations may be higher since they contain additional water in the pre-mix solution.

The amount of water-soluble metallic compound may range from about 0.1 percent weight to about 5 percent weight. Preferably, the concentration of this ingredient is from about 0.5 percent weight to about 2 percent weight, and most preferably, from about 0.5 percent weight to about 1.5 percent weight.

The semi-metallic alkoxides preferably used in this invention are water-soluble compounds having hydrolyzable groups that can react with the glass surface to remove unwanted hydroxyl groups, as well as one or more groups that can react with a film-forming matrix polymer in the coating to chemically link the polymer with the glass surface. In this context, these alkoxides also serve as coupling agents in the coating formulations in which they are included. Preferably, the coupling agent is one that has 1-3 hydrolyzable functional groups that can interact with the surface of the glass fibers, and one or more organic groups that are compatible with the polymer matrix. Such organosilanes are disclosed in U.S. Patent No. 5,709,715.

Examples of hydrolyzable groups associated with these organosilanes include vinylic, amino and imino groups such as:.



and the monohydroxy and/or cyclic $C_2 - C_3$ residue of a 1,2- or 1,3-glycol, wherein R^1 is H or C_1-C_3 alkyl; R^2 is H or C_1-C_4 alkyl; R^3 and R^4 are independently selected from H, C_1-C_4 alkyl or C_6-C_8 aryl; and R^5 is C_4-C_7 alkylene; and n is an integer from 1 to 3. The organosilanes of this invention are preferably those which produce 1-3 hydroxyl groups for bonding at the inorganic glass surface to form O-Si-O bonds, and which also possess at least one organic group for binding to the matrix resin. Further, while many organosilanes demonstrate some degree of water solubility and therefore could theoretically be used in this invention, silanes having a high level of water solubility are most efficient and cost-effective, and therefore are particularly preferred. Examples of suitable water-soluble organosilanes that may be used in this invention include trimethoxy aminopropylsilane, which is commercially available as Y11777; bis-(triethoxy silyl) ethane, which is commercially available as Y9805; 1-triethoxy silyl, 2-methyl diethoxy silyl ethane, available as Y11620; and aminopropyl silane, which is available as A-1170. These silanes are manufactured and sold by OSi, which is a division of Witco Chemical Co. The Y11777 is particularly effective because of its low organic content, which facilitates formation of a defect free coating.

Further, the organosilane may react with one or more of the other metallic compounds described above, such as a titanate or organotin compound, to produce a

metallate:silicate coating upon cure. It is believed that this mixed metal coating contributes to the protective effects associated with the coating. Where such a mixture is used, the organosilane is present in the coating compositions in a concentration of from about 3 percent weight to about 25 percent weight. Preferably, the coupling agent is present from about 9 percent weight to about 20 percent weight, and most preferably, from about 11 percent weight to about 15 percent weight. For example, in the formulations according to this invention, a water-soluble organosilane or a mixture thereof such as was hereinbefore described, may be used in an amount ranging from about 11 percent weight to about 15 percent weight.

Optionally, the high temperature filtering operations may also involve the use of a catalyst. Accordingly, the coating is desirably compatible with a catalyst that may be included on the surface of the fibrous substrate, or alternatively, mixed in with the coating composition. In this circumstance, the woven fabric is first coated with the water-based coating according to the process of this invention. The abrasion resistant, long flex-life coating so formed can then be overcoated with catalytically active materials. Exemplary catalytically active materials may include vanadium-aluminum catalysts or iron oxide-based catalysts.

The coating formulations of the invention may also contain one or more ingredients typically used in coating treatments for reinforcing fiber substrates. For example, one or more film formers, thickening agents, lubricants, chelating agents and/or wetting agents may be added. These materials are generally added to aid in the coating process, to promote adhesion of the coating and wettability of the fiber surface, or to otherwise improve the quality of the coating.

Film formers selected for the practice of this invention include conventional resins known in the art for coating glass fiber materials, and may be either thermoplastic or thermosetting in nature. The film formers play an important role in forming and adhering the coating material to the fibrous surface, after which they typically burn off at the high temperatures required to convert the metallic compounds to oxides. Such film formers may be selected from the group consisting of polyvinyl acetates, polyvinyl alcohols and polyvinyl pyrrolidones, however, any film former that can be used to improve the coating quality and integrity during handling is useful. A preferred film former is a polyvinyl pyrrolidone. Typically, the concentrations of the film formers are low, so as to minimize defects that may occur upon burn-out.

A chelating agent may be necessary to aid solvation or hydrolysis of the metal compound. Examples of chelating agents include carboxylic and other organic acids, and carboxylic esters such as acetoacetic acid esters. For example, an acetic acid solution may be mixed with the metal compound. Examples of wetting agents suitable for use in the invention include TRITON-X 100™, which is a non-ionic surfactant, polyvinyl pyrrolidone (PVP) and polyvinyl alcohol (PVA).

The coating compositions of the present invention may be formulated by first mixing the water-soluble metal alkoxide or the metallic alkoxide precursor compound with a chelating agent such as an organic acid. The resulting mixture may then be diluted with water and thoroughly blended. The coupling agent may then be added to the aqueous solution, along with other ingredients, such as film formers, wetting agents, thickening agents and lubricants. The coating composition may be diluted to a desired concentration with water. The concentration of the metal compound or the coupling agent in the coating composition may vary, however an overall molarity of from about 0.1 M to about 0.75 M for the metal compound, and from about 0.1 to about 0.75 M of the coupling agent, may be used. Where a mixture of an organosilane and another metallic compound is used, preferably, the weight ratio of the other metallic compound to the organosilane is about 1:1. Preferably, the concentration of either the other metallic compound or the organosilane should be in the range of about 0.1 to about 0.75 molar.

The coating composition may be applied to the fibrous substrate by any method known to those skilled in the art, such as spraying, immersion, flooding, roller-or pad-coating. In an exemplary embodiment, the composition is applied to a woven fabric of glass fibers by dipping, padding or spraying. A single coat or a plurality of coats may be applied to the fibrous substrate. For example, the aqueous coating composition may be applied to the surface of a fibrous fabric using a flood-and-extract technique, in which an excess of the coating composition is flooded over the surface of the fabric to submerge it, and the impregnated fabric is then removed and allowed to dry. Alternatively, a non-aqueous composition of the ingredients may be applied to the surface, then immediately after, a water mist may be applied. The coating is then dried.

After the coating composition containing the metallic compound is applied, it must further be exposed to high heat to cure the coating and form the metallic oxide. In one preferred embodiment, the coating composition is applied to the surface of a woven glass fabric and dried, after which the coating is fired to temperatures of about 248°F

(120°C) to about 752°F (400°C) to solidify it and to remove the water and residual coating solution and any residual organic compounds, including hydrolysis by-products such as alcohols or acetic acid. Preferably, firing is carried out at a temperature range of from about 572°F (300°C) to about 707°F (375°C). During cure, the precursor compound is converted to the alkoxide. The alkoxide, whether applied directly or formed *in situ*, cures to form a metal oxide which reacts with the coupling agent in the coating. For example, where a titanate is used as the alkoxide in combination with an organosilane coupling agent, the titanate forms a titanium oxide, TiO_2, during cure, while the silane reacts to form a silicate. The resulting coating, it is believed, comprises a silicate:titanate coating in a crystalline lattice or amorphous structure.

Where a single coat of the composition is applied to the fibrous substrate, a higher concentration of the ingredients in the aqueous formulation is preferred. For example, when a silane-titanate coating formulation is used, the concentrations of the organosilane and the titanate compound may each be increased up to about 0.5M. Where a single coat is applied, a higher concentration of the ingredients in the aqueous formulation is preferred. Excellent results may preferably be achieved, however, using multiple coats of a more dilute coating composition. Accordingly, when multiple coats are to be applied, lower concentrations of the alkoxide and the coupling agent, for example on the order of about 0.1M each, may be used. Further, where multiple coatings are applied, it is desirable to allow each layer of coating to dry in between application of the successive layers.

Fibrous substrates treated with the coating of this invention are preferably in the form of fabrics or cloths. These fabrics may be used in a wide range of applications. For example, glass fabrics may be used as filters or filter bags in high temperature filtration operations where a temperature-stable, non-reactive porous filter material is required. Alternate fibrous substrates such as individual fiber strands or wool can also be treated with the coatings of this invention. The resulting fibers exhibit improved durability in high temperature environments such as exhaust silencers, thermal insulation blankets or filters in corrosive environments.

A particularly desirable aspect of the invention is that the coating is water-based, and is therefore both environmentally safe and non-toxic. Accordingly, personnel are not exposed to organic solvents during the steps of formulating and applying the coating.

Further, use of the coating does not result in the release of large quantities of toxic solvent vapors into the atmosphere.

EXAMPLES

The coatings of the invention were prepared by formulating aqueous coating compositions including an alkoxide or alkoxide precursor in combination with an organosilane coupling agent. One or more coats of the resulting solution was coated onto fabrics comprised of glass fibers and the coating was then cured. Subsequently, physical parameters such as burst strength, tear resistance and flexibility were determined. Exemplary formulations representative of the invention are described below:

Examples 1-7

Examples 1-7 were prepared by mixing TYZOR-TPT, a titanium isopropoxide available from DuPont Inc., with acetic acid. The acetic acid was used to provide a chelating effect to aid solvation. The dissolved metallic compound was then mixed with water and the coupling agent added. Optionally, a wetting agent and/or a lubricant such as PVA or PVP were then added to the formulation. The proportions of the ingredients in each of the formulations are set forth below. The concentrations were chosen in part based on the number of coats of the composition that would be applied to the fibrous surface. The composition of each mixture is represented in Table 1.

TABLE 1

Coating Formulation Ingredients	EXAMPLES						
	1	2	3	4	5	6	7
TYZOR (g)	7.1	3.6	7.1	10.7	7.1	11.4	11.4
A-1230 (g)	7.1	10.6	7.1	3.6	7.1	11.4	11.4
Acetic acid (g)	14.2	7.1	14.2	21.3	14.2	22.7	22.7
PVA (g)	2.5					2.0	
PVP (g)		1.25	1.25	1.25	1.25		
TRITON-X (drops)		6	6	6	6	5	2
Water (ml)	50	25	50	75	49.7	80	80
Cure Temp. & Time	707 °F / 4 hr	707 °F / 4 hr	400 °F / 2hr, then 700 °F/ 2 hr	707 °F / 4 hr	707 °F / 4 hr	707 °F / 4 hr	707 °F / 4 hr
No. of coats	2	2	2	4	4	2	3

Examples 8-14

Coating compositions were also prepared using various titanium isopropoxides in combination with an organosilane and optionally, tin tetrachloride as a metallic oxide precursor. Boron nitride was added to the formulation of Example 11 to explore its benefits in providing surface lubricity and reducing fiber-to-fiber abrasion. Where TYZOR TPT or TYZOR-TE was used as the metallic compound, acetic acid was added as a chelating agent. To prepare the compositions, the TYZOR compound was mixed with acetic acid, where necessary, to effect chelation, and stirred until homogenous. The mixture was then added to deionized water while stirring. The composition was then stirred until any agglomerates dissolved. Subsequently, the coupling agent was added to the mixture. Where used, the wetting agent and/or the metallic oxide precursor compound, tin tetrachloride, were then added to the mixture.

The coating compositions were then applied to fabrics made of S-glass fibers in one or more layers. The coatings were applied in either a machine-directional or in a cross-directional pattern. The coated fabrics were then dried and cured under the conditions set forth in Table 2 below.

TABLE 2

Coating Formulation Ingredients	EXAMPLES						
	8	9	10	11	12	13	14
TYZOR-TPT (% wt.)	9	9	8.6	9	9		
TYZOR-TE (% wt.)						18	
TYZOR-131 (% wt.)							42
$SnCl_4$ (% wt.)				1	1	1	1
Boron Nitride HCV (% wt.)			4				
A-1230 (% wt.)	9						
Y-11777 (% wt.)		13	12.5	13	13	13	13
Acetic acid (% wt.)	18	18	17.3	18	18	2	
TRITON-X (% wt.)	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Water (% wt.)	64	60	57.6	59	59	66	44
Cure Temp./ Time	700°F / 2 hr	700°F / 2 hr	700°F / 2 hr	700°F / 2 hr	700°F / 2 hr	700°F / 2 hr	700°F / 2 hr
No. of coats	1	1	1	1	1	1	1

The cure conditions for runs 8-14 included a quick pass at 325°C.

Further, the formulations of Examples 8, 9, 10 and 11, as well as several other formulations of the invention, were tested, using conventional ASTM procedures, to determine the physical properties of the coating. After the samples were applied to the fabric and cured, they were tested to determine tensile strength and the Mullen burst test value. In addition, the trapezoid tear strength and MIT 174 values were determined for each specimen. As a control experiment, a range of values was obtained for each physical property measured using an organic solvent-based coating and compared to the coatings of this invention. The results of the testing are set forth in Table 3.

TABLE 3

Specimen / Property	8m	8c	9m	9c	10m	10c	11m	11c	12m	12c	13m	13c	14m	14c	Solvent Coating Control Samples
Tensile strength (lbs.) ASTM D 5035	306	206	606	657	262	373	669	595	322	243	436	338	240	246	300-400
Trap Tear (lbs.) ASTM D1117	14	25	46	42	19	28	50	41	22	23	31	27	18	16	14-23
MIT Folding Endurance ASTM D2176 (cycles to failure)	174	19	614	285	234	32	874	365	171	27	353	2418	273	23	6-713
Mullen Burst (Psi) ASTM D3786	444		724		477		829		461		729		516		350-770

Key:
m - Test performed in the machine direction
c - Test performed in the cross direction

From the results shown in Table 3, the coatings of Example 11, which included the Y-11777 silane, TYZOR-TPT, tin tetrachloride and surfactant, yielded best physical performance results. Excellent results were also obtained for Example 13, which included the Y-11777 coupling agent and the TYZOR-TE alkoxide, and tin tetrachloride.

It is believed that Applicant's invention includes many other embodiments which are not herein specifically described, accordingly this disclosure should not be read as being limited to the foregoing examples or preferred embodiments.

WHAT WE CLAIM IS:

1. An aqueous composition for coating the surface of a fibrous substrate, comprising a water-soluble metallic compound capable of forming a metallic oxide on the surface of the fibrous substrate.

2. The composition of claim 1, wherein the water-soluble metallic compound comprises one or more compounds selected from the group consisting of inorganic metallic compounds, organometallic compounds, semi-metallic compounds, metallic or semi-metallic alkoxide precursors and mixtures thereof.

3. The composition of claim 2, wherein the water-soluble metallic compound is a compound having a tetral metal, a semi-metal or a transition metal as the metallic element.

4. The composition of claim 3, wherein the water-soluble metallic compound is selected from the group consisting of titanium alkoxides.

5. The composition of claim 3, wherein the water-soluble metallic compound is selected from the group consisting of organosilanes.

6. The composition of claim 3, wherein the water-soluble metallic compound is selected from the group consisting of organometallic halides.

7. The composition of claim 6, wherein the water-soluble metallic compound is an organotin halide.

8. The composition of claim 2, wherein the metallic or semi-metallic alkoxide precursor forms an oxide in the cured coating.

9. The composition of claim 1, further comprising one or more ingredients selected from the group consisting of film-formers, lubricants, catalysts and wetting agents.

10. The composition of claim 1, further comprising a chelating agent.

11. A coating comprising one or more layers, wherein each of said one or more layers comprises a silicate:metal material, and further wherein the silicate:metal material is formed from a composition comprising an inorganic metallic compound, an organometallic compound, a semi-metallic compound, a metallic or semi-metallic alkoxide precursor, or mixtures thereof.

12. The coating of claim 11, wherein the metal in the silicate:metal material is tin or titanium.

13. An article comprising a fibrous substrate coated with the coating of claim 11.

14. A method of coating a woven or nonwoven fabric comprising:

a) preparing an aqueous composition comprising a metal alkoxide or a metallic alkoxide precursor compound or mixtures thereof;

b) contacting the surface of a fibrous substrate with the composition to form a coated surface;

c) drying the coated surface; and

d) curing the coating.

15. The method of claim 14, wherein the step of preparing the aqueous coating composition further comprises the step of adding a water-soluble coupling agent.

16. The method of claim 14, wherein the step of preparing the aqueous coating composition further comprises the step of adding a chelating agent.

17. The method of claim 14, wherein the step of preparing the aqueous coating composition further comprises the step of adding one or more compounds selected from the group consisting of film formers, lubricants, catalysts and wetting agents.

18. A fibrous substrate coated with the composition of claim 1.

INTERNATIONAL SEARCH REPORT

Interna al Application No
PCT/US 00/24224

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03C25/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	US 5 955 177 A (SANOCKI STEPHEN M ET AL) 21 September 1999 (1999-09-21) column 1, line 45 -column 2, line 63 ---	1,2,8,9, 11-18
X	EP 0 784 034 A (MATSUSHITA ELECTRIC WORKS LTD) 16 July 1997 (1997-07-16) example 6 ---	1,2,8,9, 11-18
X	US 5 120 339 A (SCHAFFER ROBERT R ET AL) 9 June 1992 (1992-06-09) the whole document ---	1-18
X	US 5 032 241 A (ROBERTSON MICHAEL K ET AL) 16 July 1991 (1991-07-16) claims ---	1,2,8,9, 11-18
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 December 2000	03/01/2001

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INTERNATIONAL SEARCH REPORT

Interna al Application No
PCT/US 00/24224

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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