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[54] **TEXTILE FINISHING**

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[57] **ABSTRACT**

The flame-resist properties of natural and synthetic polyamide fibres, especially wool and wool blends, are improved by depositing in the fibres an organic chelate or fluoride complex of titanium, preferably to the extent of 0.2 – 2.5% calculated as titanium dioxide. The complexes may be dissolved as such in an aqueous medium and applied by spraying, padding or by exhaustion from a bath. Alternatively the complexes may be formed in situ in the aqueous medium by adding a complexing agent to a water-soluble titanium compound or on the fibre, as by treating with a fluoride solution fibres already treated with a titanium compound, which may itself be a chelate complex. Where the titanium complex is applied from a bath a dye can be applied to the fibres from the same bath, either simultaneously or as a separate step.

6 Claims, No Drawings

TEXTILE FINISHING

The present invention relates to textile finishing, and more especially to the improvement in the properties of natural and synthetic polyamide fibres.

Naturally occurring polyamide fibres, for example the wool of sheep, display a high degree of natural flame retardancy because of their relatively high nitrogen and moisture content, high ignition temperature (570°–600°C), low heat of combustion, low flame temperature and high limiting oxygen index.

The performance of wool fabrics in the various test methods currently in use depends on the specified test method and fabric construction. A horizontal test method is much less severe than a 45° or a vertical test. Most wool fabrics will pass a horizontal test but may not pass some 45° or vertical tests. The influence of fabric construction is also very important, the denser and heavier the fabric the lower the flammability. For example a conventional wool carpet will pass the American tablet test (DOC FF 1-70, DOC FF 2-70), while an open shag pile or Flokati carpet will not pass the same test.

It follows that wool in some cases needs a flame-resist treatment in order to pass a particular flammability specification and test method. Curtains and wall coverings in public buildings, aircraft furnishings and blankets, furnishings and curtains in general transport, protective clothing and very low density carpets (shags), are products which may require treatment.

It is known that titanium compounds, especially titanium tetrachloride, when when applied to textile fibres, especially natural cellulosic fibres such as cotton, improve their fire-resist properties. However, in these prior art methods the titanium compound has to be applied in undesirably high amounts, up to 20% by weight, and the high proportion of mineral incorporated into the fibre or made-up textile sheet has an undesirable effect on the mechanical properties, for example, the handle thereof. Furthermore, the titanium compound forms a weakly adherent coating on the surface of the fibre, and is, therefore, not fast to washing or even to repeated mechanical deformation.

The present invention provides a process for improving the flame-resist properties of natural or synthetic polyamide fibres which comprises applying to the fibres a complexed titanium compound, usually as a solution, wherein the complex is formed with an organic chelating agent or with fluoride ions. In order to produce a fully satisfactory effect, the amount of titanium compound applied to the wool should preferably be at least 0.2%, especially 0.2 – 2.5% by weight calculated as titanium dioxide on the weight of fabric (o.w.f.). The complexed titanium compound is normally applied in aqueous solution.

The invention may be applied to the treatment of synthetic polyamide fibres, for example nylon, but is especially valuable for the treatment of natural polyamide fibres. Preferably the fibres are of sheep's wool, but they can also be derived from alpaca, cashmere, mohair, vicuna, guanaco, camel hair, silk, and llama, or of blends of these materials with sheep's wool. Fabrics consisting of a blend containing major proportion of wool and a minor proportion, generally 30% or less, of synthetic fibres, or natural cellulosic fibres, for example polyamide, polyester or cotton fibres, may also be treated. The treatment may be applied to the fibres at any desired stage during textile processing, and the fibres may, for example, be in the form of fleeces, tops, card sliver, noils, yarns, threads, woven or knitted fabrics, non-woven fabrics, pile fabrics or garments. Preferably the material to be treated is scoured to a residual methylene chloride extract of not more than 0.8% in order to remove spinning additives or natural waxes which can contribute to the flammability of the product.

The titanium compound may be applied using conventional machinery for treating textiles and garments with liquors including dollies, winches, beam dyeing equipment, package dyeing machinery, hank dyeing machinery, top dyeing equipment, washing and laundering equipment and dry-cleaning machinery for batchwise treatments, and including pad mangles, lick rollers, spray units, continuous cloth washing units, backwashing machines and solvent scouring machines for continuous or semi-continuous treatments.

The complexed titanium compound may be added directly to the treatment liquor or alternatively it may be formed in situ. Compounds which may be added directly to the treatment liquor include fluorotitanates oxalates and titanium citrates, or alkali metals or ammonia. Alternatively a complex may be formed in situ by treating a soluble titanium salt, for example titanium tetrachloride with a source of fluoride ions or with an organic chelating agent, for example oxalic, or preferably citric or tartaric acid. Compounds which may be used as sources of fluoride ions include sodium and potassium fluorides or bifluorides and ammonium bifluoride. A water soluble fluoroborate, e.g. ammonium fluoroborate, may also be used as the source of fluoride ions.

The treatment can be carried out at temperatures in the range 20°–130°C and at pH of less than 4 and preferably less than 3.5. The pH value can readily be adjusted by adding a strong mineral acid, for example hydrochloric acid, or an acidic substance such as ammonium bifluoride. Although treatment with fluoride complexes can be carried out with good results at room temperature, it is preferred in the case of organic chelate complexes to work at an elevated temperature. By applying titanium complexes of hydrocarboxylic acids by exhaustion from a hot liquor, and preferably at the boil, a high degree of penetration of the titanium complex is thereby achieved, with an enhanced flameproofing effect.

The titanium complex can be applied to the fibres to be treated by any conventional method, i.e. by any method heretofore known or described in the literature for applying water-soluble compounds, for example by the "pad-dry," "pad-steam," "stray-nip-dry," "drip-nip-dry" or "exhaustion" methods. The term pad-dry as used herein means the method of applying a liquor or paste to fibres to be treated either by passing them through a bath and subsequently through squeeze rollers (including the method in which the fibres are passed vertically downwards through horizontally disposed nip rollers having a bath of liquor formed above their point of contact) or by passing them, through squeeze rollers, the bottom one of which is immersed partly in a bath of the liquor, and subsequently drying them. The term spray-nip-dry means the method of spraying a liquor onto the fibres to be treated, passing them through a nip, and subsequently drying them. The term exhaustion means the method of treating the fibres in a bath with a solution of the active substance until the substance is substantially completely taken up, and subsequently drying the fibres. The term pad-steam means the application of the treating liquor by the previously described padding technique followed by steaming at 100°–120°C. The term drip-nip-dry means the method of immersing the fibres into the treating bath, passing them through a nip, and subsequently drying them.

Other flame-retardant agents previously known or described in the literature may be applied provided that they do not interfere with the titanium treatment. For example, antimony trifluoride and antimony potassium tartarate can be applied to the wool by exhaustion. Aluminium compounds may also be applied to the wool.

The present process may be carried out at the same time as dyeing, provided that the dye is capable of exhausting onto wool with level results at pH values below 5. Acid levelling, 1:1 pre-metallised dyes and certain reactive dyes can be used and there is no need to add additional formic or sulphuric acid as is conventional when using these dyes since the pH of the dyebath is already sufficiently low. Glauber's salt should preferably not be added to the solution since it interferes with the exhaustion of the titanium complex, but organic non-ionic levelling agents, for example Avolan SC or Albegal B can be used. Acid milling and 1:2 premetallised dyes cannot be applied satisfactorily at the same time as the titanium treatment. When using an acid milling dye, the dye can first be exhausted preferably at the boil from the dyebath, the temperature of the dyebath is then reduced to, for example 70°C, the complexed titanium compound is then added, and the bath is then further heated until the titanium complex has exhausted onto the wool. When dyeing with chrome dyes, the dyeing operation must be carried out after the titanium treatment, otherwise complex formation between titanium in solution and the dye can give rise to a color change.

The acid dyes which can be used are water-soluble compounds of, for example, the monazo type or a triphenylmethane or anthraquinone derivative.

Acid milling dyes form a class of dyestuffs which have greater molecular weight and fewer solubilizing groups than the acid levelling dyes. There is no rigid distinction between the milling class of dyes and the levelling class, and many dyes have intermediate properties. Milling dyes are generally applied at a pH of 4–5.

The premetallised dyes comprise a class of dyes having 0,0'-dihydroxy azo, 0-amino-0'hydroxy azo or 0-carboxyl-0'hydroxy azo groups which are coordinated to a metal atom, for example chromium or cobalt. The dyes may be used as 1:1 complexes.

The dyes that may be employed include reactive dyes, e.g. those that react with the fibres and become covalently bonded to them, and such dyes give a high degree of fixation on the fibres. Dyestuffs falling within this class can incorporate the following groups:

epoxy-, ethylene-imino-, isocyanate-, isothiocyanate-, carbamic acid aryl ester-, propiolic acid amido-, mono-chloro-, and dichloro crotonylamino-, chloroacrylamino-, acrylamino, sulpho halo-, sulphuric acid ester, sulphoxy-, labile halogen atoms, trichloropyridazino-, dichloroquinoxalino-, allylsulphonyl-, and certain reactive ammonium or hydroxonium residues.

Especially good results are obtainable with highly reactive dyes, for example, those incorporating a 2:4 -dichlortriazinyl-, vinyl sulphonyl-, 2:3 -dichloroquinoxalino-, or bromo-acrylamido group.

Large numbers of dyes of these various classes are commercially available and can be found, for example, in the color index.

The treatment according to the invention has the further advantage that it is compatible with fluorocarbon oil-and-water repellent treatments for upholstery fabrics for use, for example, on aircraft seats. Fluorocarbon resins, for example FC-214, FC 208, FC 218, all available from the 3M Company can be applied preferably in the presence of an extender, for example Phobotex FTN (CIBA). The titanium and fluorocarbon can be applied simultaneously by padding followed by drying at a temperature of at least 100°C., further heating for a period and at a temperature sufficient to cure the resin, washing and drying. The titanium treatment can be also applied before or after the water and oil-repellent treatment.

The mechanical properties of wool treated with titanium by the present process are closely similar to the properties of wool dyed with acid dyes. This can be seen from the tests set forth in Table I which relates to yarns and Table II which relates to upholstery fabrics.

Table I

Mechanical and flammability properties of yarns with various treatments

Sample	Tensile Strength	Extension at break	Yellowness index	Ash Content	Tablet test on a shag pile carpet		
					Initial	After 10 washings[1]	After 10 dry cleanings[2]
Untreated	2.61 kg	12.1%	0.09	0.06%	Fails	Fails	Fails
Flame-resist treated	2.38	10.3	0.14	0.53	Passes	Passes	Passes
Dyed only	2.37	10.4	—	0.06	Fails	Fails	Fails
Dyed - Flame-resist treated	2.34	10.4	—	0.48	Passes	Passes	Passes

[1] 10 washings at 60°C, 15 min. 1:20 in accordance with the Federal Specification DOC FF 1-70

[2] 10 dry cleanings with Perklone in the Launderometer. Each dry cleaning for 30 minutes, 30°C. 1:20.

Table II

Mechanical and flammability properties of a flame-resist treated upholstery fabric

Sample	Abrasion Resistance	Tensile Strength		Extension at break		Tear Strength		Vertical test[1]		
		Warp	Weft	Warp	Weft	Warp	Weft	Initial	After 10 washings[2]	After 10 dry cleanings[3]
Untreated	4,900	55.3 g	50.6 g	27.2%	24.6%	5.9 kg	5.5 kg	Fails	Fails	Fails
Treated	4,800	55.5 g	49.8 g	31.3%	29.3%	5.4 kg	5.1 kg	3.3 sec. 2.9 ins.	2.5 sec. 1.7 ins.	4.3 sec. 2.5 ins.

[1] Average of three samples in warp and three in weft direction
[2] 10 washings at 40°C. 15 min. using the Philips automatic washing machine. Woolmark programme
[3] 10 dry cleanings with Perklone in the Launderometer. Each dry cleaning for 30 minutes, 30°C. 1:20.

Undyed wool which has been treated in accordance with the invention, exhibits a pale yellow color. Such a discolouration is a disadvantage when it is desired to produce a natural-wool-colored or pastel-colored product, and can be reduced or prevented according to the invention by after-treatment of titanium treated fibres with a fluoride solution, a solution containing, for example, alkali metal or ammonium fluoride or bifluoride. The fibres are first treated with a titanium complex which can be titanium citrate, potassium titanium oxalate or a complex formed in situ between titanium tetrachloride and a chelating agent, especially oxalic, citric or tartaric acid. It is conveniently applied to the fibre in a liquor ratio of 1:20 and preferably not more than 1:30 by exhaustion at a pH of less than 4, preferably less than 3.5. When using titanium tetrachloride in association with citric acid, the citric acid is preferably at a concentration of 4%. Exhaustion of the titanium compound is normally complete after boiling for a period of 5–30 minutes, generally about 15 minutes. A dyestuff can be applied to the fibre in admixture with the titanium compound provided that it exhausts at a pH of less than 4 with level results, otherwise the titanium treatment should be carried out as a pretreatment before dyeing. Chrome dyestuffs in particular should always be applied after flame-resist treatment since they complex in solution with the titanium compounds and may then give rise to a color change. The fibre is then treated with a solution of a fluoride preferably ammonium bifluoride. The treatment is preferably carried out in acid solution, conveniently at a pH of about 4. When sodium fluoride is used the pH is adjusted to 4 by addition of an acid, for example formic acid. The concentration of the ammonium bifluoride is preferably 0.2 to 20 g/litre and the solution is left in contact with the fibre for 5–30 minutes. The treated fibre is then rinsed with water, hydroextracted by passing it through a nip and dried.

When the desired product is an undyed wool, it is convenient to mix the fluoride with a reducing agent. A suitable aqueous fluoride solution contains 4% w/v ammonium bifluoride and 4% w/v sodium metabisulphite or 4% sodium formaldehydesulphoxylate and can provide substantially complete removal of the yellow colour.

Table 1 below illustrates the effect of treating carpet yarns firstly by exhaustion with a solution containing potassium titanium oxalate or titanium tetrachloride and oxalic, citric or tartaric acids and subsequently with a solution containing ammonium bifluoride. The results show that with increasing titanium concentration the yellowness index increases, the increase being most marked when using oxalic acid and least marked when using citric acid. In order to obtain minimum yellowing of the fibre it is preferred to apply a mixture of titanium tetrachloride and citric acid to the fibres, and subsequently to treat them with ammonium bifluoride.

Table 1

Treatment	After Treatment	Yellowness Index
Untreated	—	0.070
4% PTO* + 4% Oxalic acid	—	0.238
4% PTO + 4% Tartaric acid	—	0.216
4% PTO + 4% Citric acid	—	0.197
1.5% PTO + 4% Citric acid	—	0.151
1.5% $TiCl_4$ (50%) + 4% Citric acid	—	0.136
1.5% $TiVl_4$ (50%) + 4% A12 $(SO_4)_3$ + 4% Citric acid	—	0.120
4% PTO + 4% Citric acid	1% $NH_4F.HF$	0.171
4% do.	2% do.	0.120
4% do.	3% do.	0.112
4% do.	4% do.	0.108
1.5% PTO + 4% Citric acid	4% do.	0.096
1.5% $TiCl_4$ (50%) + 4% Citric acid	4% do.	0.091

*PTO - potassium titanium oxalate
All treatments by exhaustion - 45 min. at 100°C, liquor ratio 1:20
After-treatments at 45°C, 15 min. liquor ratio 1:20

TEST METHODS

The following tests have been used in the Examples or have been referred to elsewhere in this specification.

a. Exhaustion

The degree of exhaustion of the titanium compound used for the flame-resist treatment can be foolowed by the reaction between titanium solutions and hydrogen peroxide to form a yellow color. The reaction is assumed to be due to the formation of pertitanic acid H_4TiO_5.

A 10 ml sample of the bath solution, if necessary freed from the dyestuff, is treated with 3 ml of 3% hydrogen peroxide. A yellow color develops which indicates the amount of titanium present in the solution. When this test was performed during the exhaustion treatment, the degree of exhaustion was estimated using quantitive colorimetric estimation at a wavelength of 410 m.

The amount of titanium and aluminium exhausted on wool during the flame-resist treatment can be estimated as ash content (metal oxides). As wool always contains some inorganic matter the ash content of the untreated wool should always be estimated and the difference between the ash content of flame-resist treated and untreated wool indicates the total amount of metal oxides exhausted on wool during the treatment. This method is especially useful when the flame-resist treatment is performed simultaneously with dyeing and the dyestuff can interfere with the titanium hydrogen peroxide reaction.

b. Flame-resistance

The flame-resistance of textile fabrics can be measured by the Vertical Flame Test (A.A.T.C. Test Method 34-1969, Fire Resistance of Textile Fabrics) which involves suspending a conditioned (65% relative humidity) strip of the fabric to be tested in a flame of a Bunsen burner for twelve seconds and determining the length of the charred portion of the fabric and the burning time. The flame-resistance of carpets can be measured by the Tablet Test (U.S. Federal Specification DOC FF 1–70 which involves drying a specimen of the carpet at 105°C for 2 hours, igniting a standard time-burning "Methanamine" (Hexamethylenetetramine) tablet on the surface of the carpet, and observing the spread of flame over the surface of the carpet. It is an object of the present invention to provide textile materials which pass these tests, hereinafter referred to as the "Vertical Flame Test" and "Tablet Test" respectively.

EXAMPLE I

A wool carpet yarn was treated in hank form in an aqueous bath with the following composition:

Titanium tetrachloride (50%)	3.0% o.w.f.
Citric acid	4.0% o.w.f.
Aluminium chloride	4.0% o.w.f.

The yarn and treating agent were mixed together at 40°C, after which the mixture was boiled for 45 minutes. During the process the titanium compound formed a chelate with the citric acid and was then presumably decomposed to form a basic titanium compound within the wool fibres.

After the treatment the yarn was then removed from the bath, washed, dried, and formed into a carpet. The latter was then tested according to the Tablet Test (U.S. Federal Specification DOC FF 1-70) and was found to possess excellent flame-resistance.

EXAMPLE II

This Example illustrates the simultaneous treatment of loose wool stock with a flame-resist agent and also the application of dye.

A loose wool stock was boiled for 45 minutes in a package dyeing machine with a solution containing:

Potassium titanium oxalate	4% o.w.f.
Tartaric acid	3% o.w.f.
Neopolar Yellow 4GL	3% o.w.f.

Neopolar Yellow 4GL is an acid levelling dye. The loose stock was then rinsed, dried, spun to a yarn and converted into a carpet having a 2-inch pile and a weight of 36 oz/sq.yd.

The carpet was then tested for flame-resistance according to the Tablet Test previously referred to, both after dyeing and after it had been cleaned 10 times according to the procedure described in DOC FF 1-70.

The carpet was found to have excellent resistance both before and after cleaning, thus showing that the effect of the treatment has considerable resistance to removal by the cleaning step.

EXAMPLE III

This example illustrates the application of a flame-resist treatment to a previously manufactured carpet.

The pile of a carpet having a 2-inch pile and a weight of 36 oz/sq.yd. was sprayed with a solution containing potassium titanium oxalate (80 g/litre), tartaric acid (10 g/litre), antimony trifluoride (20 g/litre), and Tergitol Speedwet (Union Carbide; 1 g/litre), until the pile increased 50% by weight.

The pile was then pressed lightly to ensure penetration of the yarns by the solution, after which it was dried. The treated carpet was then found to pass the Tablet test described above.

EXAMPLE IV

The following composition was applied to a woollen fabric as an aqueous solution by means of a pad mangle:

Titanium tetrachloride (50% aqueous solution)	3% on the weight of wool (o.w.w.)
Ammonium bifluoride	1.5% o.w.w.
Formic acid (80% aqueous solution)	2% o.w.w.

The fabric was dried. It was subsequently rinsed for 15 minutes in water at 30°C at a liquor ratio of 1:20, hydroextracted and dried. The fabric was tested for flame-resistance by means of the Vertical flame test (A.A.T.C. Test Method 34-1969, Fire Resistance of Textile Fabrics) and exhibited a satisfactory flame-resistance. The test involves suspending a conditioned (65% relative humidity, 20°C) strip of the fabric to be tested in the flame of a Bunsen burner for 12 seconds and determining the length of the charred portion of the fabric and the burning time. The treatment was found to be fast to at least 10 washings (45°C, 15 minutes, Philips automatic washing machine, Woolmark programme), and at least 10 dry cleanings (28°C, 15 minutes, liquor ratio 1:20, Perklone, launderometer).

EXAMPLE V

The following composition was applied to a woollen textile fabric as an aqueous solution by means of a pad mangle:

Titanium tetrachloride (50% aqueous solution)	1.5% o.w.w.
Ammonium bifluoride	1.0% o.w.w.
Formic acid (85% aqueous solution)	2.0% o.w.w.

The treated fabric was then dried, then washed with aqueous sodium bicarbonate hydroextracted and dried. It exhibited satisfactory flame resistance in the Vertical Flame Test (see Example 1). The treatment was fast to 10 washings (each 15 min. 45°C, Philips automatic washing machine, Woolmark programme). After 10 washings the char length in the Vertical flame test was 40% shorter, indicating that the flame-resistance increases on washing.

EXAMPLE VI

The following composition was applied to a woollen textile fabric as an aqueous solution by means of a pad mangle:

Titanium tetrachloride (50% aqueous solution)	1.5% o.w.w.
Antimony trichloride	1.5% o.w.w.
Ammonium bifluoride	1.5% o.w.w.
Formic acid (85% aqueous solution)	2% o.w.w.

The fabric was subsequently treated as in Example V. In the Vertical Flame test it exhibited a char length 20% less than the fabric of Example V. The treatment was fast to washing by the test method described in Example V. After 10 minutes the char length was 40% shorter, indicating that the flame-resistance increases on washing.

The presence of antimony trichloride in the treatment composition is especially applicable to lightweight fabrics (less than 200 g/m^2).

EXAMPLE VII

The following composition was sprayed onto a ready-made shag-pile carpet:

Titanium tetrachloride (50% aqueous solution)	3% o.w.w.
Ammonium bifluoride	1.5% o.w.w.
Formic acid (85% aqueous solution)	2% o.w.w.

The treated carpet was passed through a nip and then dried. The flammability measured by the Tablet test (U.S. Federal Specification DOC FF 1-70) was satisfactory. (The Tablet test for carpets involves conditioning a specimen of the carpet at 105°C for 2 hours, igniting a time-burning "Methenamine" (hexamethylenetetramine) tablet on the surface of the carpet, and observing the spread of flame over the surface of the carpet). The carpet pile did not burn away and no spread of flame over the surface fuzz of the unworn treated carpet was observed. The treatment was fast to 10 washings (each 15 min., 60°C, liquor ratio 1:20, Hotpoint washing machine). In addition to the flame proofing action, the composition imparts a soil-repellency which is believed to be due to the presence of titanium compounds on the fibre surface.

Sodium or potassium bifluorides can be used in place of the ammonium bifluoride, and can be applied to the carpet as described herein.

EXAMPLE VIII

Wool top (100 lbs) was treated by exhaustion with $TiCl_4$ (50%) — 3% o.w.w. and citric acid (4% o.w.w.) simultaneously with dyeing [Xylene light yellow 29 (Sandoz acid levelling dyestuff)]. The titanium tetrachloride and the dyestuffs were completely exhausted after 30 min. boiling. The dyestuff exhaustion was approximately 5–10% higher than with the same dye; without the addition of $TiCl_4$ and the dyeing was level. The wool top was spun into a yarn. A very open shag pile carpet made from the treated and dyed yarn easily passed the Tablet test. Color fastness to light, water, perspiration and washing (40°C) is the same as with the dyed but untreated yarn.

EXAMPLE IX

The procedure of Example VIII was repeated with a sample of undyed wool and in the absence of a dyestuff in admixture the titanium. A shag pile carpet made from the treated yarn easily passed the Tablet test. A conventional carpet test by the Air Registration Board Specification 8 had a char width of 2 ins. (untreated 3 ins.). The same carpet without any backing tested by the Vertical Test had a char length of 1 in. and burning time — 0 sec. (untreated — char length 2.7 ins., burning time — 23 sec.).

EXAMPLE X

This example illustrates the simultaneous application to wool of a flame-resist treatment and a water- and oil-resist treatment.

The following composition was applied to a wool fabric by a pad mangle to 100% wet pick up:

Isopropanol (wetting agent)	0.5% o.w.w.
FC-214 (Fluorocarbon resin made by the 3M Company)	2.0% o.w.w.
Phobotext FTN (CIBA)	0.5% o.w.w.
Titanium tetrachloride	5.0% o.w.w.
Ammonium bifluoride	2.5% o.w.w.
Formic acid (85% aqueous solution)	2.0% o.w.w.

The fabric was then dried at 120°C for a period of 3 minutes and then maintained at 165°C for 4 minutes to cure the fluorocarbon resin. The fabric was then rinsed on a winch at 20°C with water at a liquor ratio of 1:30 for a period of 15 minutes, and then dried at 120°C for 3 minutes.

The dried fabric was tested by the Vertical test and had a char length of 2.6 ins. and a burn time of 5 seconds. It exhibited satisfactory resistance to water and oils as tested by the spray- and oil-rating test.

EXAMPLE XI

This example illustrates the application of a flame-resist treatment by the pad-steam technique to a previously manufactured shag pile carpet.

The carpet was impregnated with the following solution to a pick-up of 400%.

10 g/l $TiCl_4$ (50%)
5 g/l Ammonium bifluoride
4 g/l Irgapadol P (foaming agent) (ciba-Geigg)
3 g/l Solvitose OFA (thickening agent) (Scholten)
1 g/l Tergitol Speedwet (wetting agent) (Union Carbide)

The impregnated carpet was steamed in a horizontal position for 10 minutes at 106°C, rinsed in two separate bowls with water and dried.

The Tablet test revealed that the treated carpet easily passed the specification, while the untreated one failed to meet the specification.

After 10 commercial shampooings the treated carpet passed the Tablet test.

EXAMPLE XII

This example illustrates the application of a flame-resist treatment by the drip-nip-dry technique of a wool sheep-skin used as floor-covering and car seat cover.

The sheep-skin was impregnated with the following solution:

20 g/l Ammonium bifluoride
40 g/l $TiCl_4$ (50%)
20 g/l Formic acid 80%
1 g/l Tergitol speedwet.

After proper wetting the sheep-skin was squeezed to a wet pick-up of 150% between rollers and dried at 50°C in order to not damage and harden the skin. After dyeing the sheep-skin was rinsed with water at 25°C for 15 minutes in order to remove the residual chemicals, which could impair the soft wool handle. After rinsing, the sheep-skin was hydroextracted and dried at 50°C.

The treated sheep-skin passed the Tablet test. The difference between the flammability properties of the treated and untreated sheep-skins was very significant, because of the very open pile construction and loose fibre being readily available. With the untreated sheep-skin no single fibre remained after the Tablet test, while with the treated sheep-skin only a surface flash of 2 ins. in diameter appeared followed by immediate self-extinguishing of the flame-resist treated wool fibre.

EXAMPLE XIII

This example describes the application of the dip-nip-dry technique for the continuous flame-resist treatment of loose wool stock in the last bowl of the raw wool scouring machine (leviathan).

The solution of the last (fifth) bowl of a commercial scouring machine had the following composition:

60 g/l $TiCl_4$ (50%)
30 g/l $NH_4F.HF$
40 g/l $HCOOH$ (85%)

Loose wool stock passed continuously through this bowl for 7 minutes at 30°C, was squeezed to a 60% wet pick-up and continuously dried.

The Tablet test showed a significant degree of flame-resistance when compared with the same untreated wool fibres.

As in some cases the residual chemicals interfered with the processability of the treated wool, part of the treated loose stock was rinsed in a separate bowl with water for 15 minutes at 25°C and dried. The treated and rinsed loose wool stock passed the Tablet test.

EXAMPLE XIV

This example illustrates the exhaustion treatment of a wool-nylon (80/20) blend knitted garment. The garment was treated in a side-paddle dyeing machine with the following chemicals for 45 minutes at the boil:

5% $TiCl_4$ (50%) o.w.w.
6.5% citric acid o.w.w.

After boiling the titanium complex was exhausted to 90% and the garment was rinsed and dried. The Vertical Flame Test showed a burning time of 1 sec. and char length of 3.5 ins., values easily meeting the specification (Max. burn time 15 sec., max. char length 8 ins.).

EXAMPLE XV

A wool blanket containing 15% of cotton in warp direction was treated by the exhaustion treatment on a winch with the following chemicals:

4.5% $TiCl_4$ (50%) o.w.w.
6% citric acid o.w.w.

The temperature of the bath was brought to the boil at a rate of 40°C/min. and boiled for 45 minutes. After checking the exhaustion of the titanium citrate complex the blanket was rinsed and dried.

No difference is handle or mechanical properties between the treated and untreated blanket was noticed. The treated blanket easily met the specification when tested in both warp and weft direction, by the Vertical Flame Test, while the untreated blanket failed to meet the specification in both directions.

EXAMPLE XVI

A wool-polyester (80/20) yarn was treated in hank form by the exhaustion technique with the following chemicals:

4% $TiCl_4$ (50%) o.w.w.
5% citric acid o.w.w.

The citric acid was dissolved in warm water in bucket and the titanium tetrachloride solution was added to the dissolved citric acid in the bucket while stirring. The titanium citrate complex prepared in situ was added to the bath, which was brought to the boil and kept at the boil for 45 minutes. After rinsing and drying a knitted fabric was prepared from the treated yarn and tested by the Vertical Flame Test. The burning time (1 sec.) and char length (2.5 ins.) indicated a sufficiently effective flame-resist effect.

EXAMPLE XVII

A furnacemans cloth (pure wool, woven, 600 g/m^2) was treated by the exhaustion technique with the following chemicals at the boil for 45 minutes:

Titanium tetrachloride (50%)	5% o.w.w.
Citric acid	6½% o.w.w.

After exhaustion of the titanium complex the fabric was rinsed and dried.

As in actual foundry conditions resistance to radiant heat is much more important than resistance to flame the treated and untreated fabric was tested by ASTM E-162-66T surface flammability of materials using a radiant heat energy source. Under the conditions of this test the fabric is exposed to a temperature of 800°C for 15 minutes and the char length is measured. The results were as follows:

Untreated	Char length	43 cm.	(full length)
Treated	do.	15 cm.	

The results of this test show that the flame-resist treated fabric is more resistant to heat than the untreated one.

EXAMPLE XVIII

Carpet wool (100 lbs) in hank form was treated by exhaustion with $TiCl_4$ (50%) — 3% o.w.w. and citric acid (4% o.w.w.) simultaneously with dyeing [Xylene light yellow 29 (Sandox acid levelling dyestuff)]. The titanium tetrachloride and the dyestuffs were completely exhausted after 30 min. boiling. The dyestuff exhaustion was approximately 5–10% higher than with the same dye; without the addition of $TiCl_4$ and the dyeing was level. A very open shag pile carpet made from the treated and dyed yarn easily passed the Tablet test. Color fastness to light, water, perspiration and washing (40°C) is the same as with the dyed but untreated yarn. 20 lb. of a blended yarn 80/20 (Wool/nylon) was simultaneously treated. The color shade was darker because of the nylon, but the shag pile carpet made from this yarn also easily passed the Tablet test. Nevertheless, the burning rate was slightly higher than with 100% wool.

EXAMPLE XIX

The procedure of Example XVIII was repeated with a sample of undyed wool and in the absence of a dyestuff in admixture the titanium. After the titanium treatment the yarn was treated with 4% ammonium bifluoride o.w.w. for 15 min. at 50°C. The after-treatment completely removed the slight yellow color. A shag pile carpet made from the fluoride after-treated yarn easily passed the Tablet test. A conventional carpet test by the Air Registration Board Specification 8 had a char width of 2 ins. (untreated 3 ins.). The same carpet without any backing tested by the Vertical Test had a char length of 1 in. and burning time — 0 sec. (untreated — char length 2.7 ins., burning time — 23 sec.).

A simultaneous after-treatment with 4% $NH_4F.HF$ and 4% sodium metabisulphite or 4% sodium formaldehyde - sulphoxylate completely eliminated the yellowness, without affecting the flame-resist properties.

EXAMPLE XX

A carpet yarn was treated in hank form with an aqueous solution containing:

Sodium fluoroborate	2% o.w.f.
Titanium tetrachloride (5% aqueous solution)	3% o.w.f.
Hydrochloric acid (37%)	3% o.w.f.

The solution was then boiled for 45 minutes and the treated yarn was rinsed twice, hydroextracted and dried. It was fabricated into a very open shag pile carpet which easily passed the Tablet test.

What I claim is:

1. A process for improving the flame resistance of natural and synthetic polyamide fibres which comprises wetting the fibres with an aqueous solution of a complex compound of titanium consisting essentially of titanium complexed with fluoride ions, a di- or polycarboxylic acid organic chelating agent or hydroxycarboxylic acid organic chelating agent having a pH less than about 4 until the fibres have taken up at least 0.2% by weight of the complex compound of titanium, calculated as titanium dioxide, from said solution.

2. The process of claim **1** wherein the amount of complex compound taken up on said fibres is 0.2% to 2.5% by weight, calculated as titanium dioxide.

3. The process of claim **1** wherein the complex titanium compound containing fibres are treated with an aqueous solution containing fluoride ions to reduce the yellowing thereof.

4. The process of claim **1** carried out at 20°–130°C.

5. The process of claim **4** carried out at room temperature where the titanium compound is a complex of titanium and fluoride ions.

6. The process of claim **4** carried out by immersing the fibres in the solution at the boil until the titanium complex has exhausted thereon.

* * * * *

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,857,727 Dated December 31, 1974

Inventor(s) LADISLAV BENISEK

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

The face of the patent should indicate the assignment

-- I. W. S. Nominee Company Limited. --.

Signed and sealed this 15th day of April 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks

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