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PROCESS FOR PRODUCING LUSTROUS
TITANIUM IMPREGNATED YARNSFrederick Roy Millhiser, Richmond, Va., assignor
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mington, Del., a corporation of DelawareNo Drawing. Application September 18, 1946,
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7 Claims. (Cl. 117—102)

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This invention relates to cellulosic materials of reduced flammability, and more particularly to the production of improved films, fibers, and fabrics of cellulose and its derivatives which are lustrous yet contain substantial quantities of insoluble titanium compounds.

It is well known that the flammability of cellulosic materials may be reduced by incorporating suitable organic or inorganic materials therein. Though water-soluble impregnants suffice for some purposes, insolubility in water is frequently required. Water-insoluble compounds are usually incorporated by impregnating the cellulosic material with a water-soluble compound of an element which is subsequently precipitated in the form of one of its insoluble compounds, for example as an oxide, silicate, phosphate, or tungstate. Titanium compounds have been found useful for this purpose but their utility has been limited by attendant, undesired delustering of the impregnated material. This ability of titanium compounds to deluster is well known and it is possible at times to take advantage of it. Thus, many textile materials are delustered by introducing titanium compounds before or after spinning. For many purposes, however, the luster and transparency of cellulosic materials must be preserved. Brightness and luster are frequently required in textile materials and to an even greater extent in films and foils. Many titanium compounds are free from color, chemically inert, difficultly soluble, and non-flammable, all of which make them attractive as flame-retarding agents provided they can be incorporated in substantial quantity without delustering the cellulosic material.

In accordance with copending application Serial No. 692,386, filed August 22, 1946, lustrous films, fibers, and fabrics of regenerated cellulose and cellulose esters and ethers containing titanium are produced by impregnating such cellulosic materials with a soluble titanium compound, removing superficial impregnant from the treated product, and then precipitating a water-insoluble titanium compound within impregnated cellulosic material. More specifically the invention disclosed in Serial No. 692,386, filed August 22, 1946, comprises producing a lustrous regenerated cellulosic material of substantially reduced flammability containing at least 3% by weight of titanium, by impregnating said material with a relatively concentrated solution of a water-soluble, inorganic compound of titanium, such as titanyl sulfate, removing excess impregnant from the treated material by thoroughly

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rinsing with an alcohol, and then precipitating a water-insoluble titanium compound within the rinsed cellulosic product.

In accordance with one adaptation of the invention disclosed in copending application Serial No. 692,386, filed August 22, 1946, regenerated cellulosic yarn or fabric is suitably impregnated by immersion, preferably in a titanyl sulfate solution containing from about 50 to 150 grams per liter of TiO_2 for a relatively short period of time and at room temperature or temperatures ranging from 0° C. to 80° C., care being exercised not to utilize elevated temperatures at which hydrolysis would occur. After such impregnation, excess impregnant is removed as thoroughly as possible by conventional hydro-extraction, draining or wringing. These and similar mechanical operations are insufficient in themselves, however, to prevent undesired delustering of the cellulosic material in the subsequent operations necessary to insolubilize or fix the titanium. When materials treated in this manner are immersed in aqueous alkali, phosphate solution, water at ordinary temperature, or other media for fixing the titanium, precipitation occurs on the surface as well as precipitation within the cellulosic material. The cellulosic material becomes coated with a rough, adherent, delustering deposit of titanium compound. This deposit is relatively easy to remove from films but is exceedingly difficult, if not altogether impossible to remove from textile materials by mere washing. Seemingly, the deposition is due to incomplete removal of impregnating agent from the surface of the cellulosic material prior to fixation of the titanium as the oxide or other insoluble compounds. To overcome this and avoid such deposition, a thorough rinsing of the impregnated material in preferably an alcohol is resorted to. Ethyl alcohol is particularly preferred, since it does not extract titanyl sulfate from within the fiber yet appears to remove the titanyl sulfate from the surface of the fiber. The rinsed product can then be washed with water to insolubilize the titanium sulfate within the fiber and to render the yarn sulfate-free, but preferably it is treated with a suitable neutralizing agent, such as a 3% solution of sodium carbonate, followed by water washing to accomplish the same purpose.

By the process of the invention described above lustrous, regenerated cellulosic material containing a delustering concentration of a titanium compound may be produced as a new product. The thorough removal of superficial impregnant, that is, excess titanyl sulfate, is essential to pre-

vent undesired delustering. The rinsing steps effectively used are rinsing with an alcohol, or aqueous mixtures of an alkali and a polyhydric alcohol or with water at a temperature not above 10° C. While these procedures are effective and useful, more efficient rinsing steps have been sought to permit more economic operation of the process commercially both in respect to time and quantity of materials consumed.

The present invention has as an object the improvement of the production of lustrous, regenerated cellulose material containing a delustering concentration of a titanium compound. A further object is the provision of inexpensive, efficient means for the rinsing of cellulosic material impregnated with soluble titanium compounds. Other objects will appear hereinafter.

These objects are accomplished by rinsing cellulosic materials impregnated with soluble titanium compounds with aqueous solutions of inorganic, neutral salts.

The following examples, which are merely illustrative and are not to be considered as limitative, are given to provide a clearer understanding of the invention.

Example I

Twelve pounds of gel skeins of 150 denier-40 filament Bright yarn were impregnated by immersion at room temperature in a solution of titanyl sulfate for 30 minutes. The titanyl sulfate solution was composed so as to be equivalent to 150 grams of TiO_2 per liter. The skeins were then washed at room temperature with 10% aqueous solution of sodium sulfate. Washing was effected by the shower method and was continued until the washings were acid free. The skeins were then washed with soft water at room temperature to remove sodium sulfate. The following steps were then taken in turn at room temperature: a wash using a 5% aqueous solution of sodium carbonate, a soft water wash until the yarn was alkaline-free, a wash using a 3% aqueous solution of phosphoric acid and finally a soft water wash until the yarn was acid free. The treating cycle with the sodium carbonate and phosphoric acid was one hour. The soft water washing treatments were conducted for the length of time required to reach a neutral pH. This generally involved about eight hours. After washing, the yarn was finished with a solution of a sulfonated vegetable oil for 30 minutes at 50° C. After centrifuging and drying, the yarn was analyzed and it was found that the minimum amount of TiO_2 was 7.9%; the maximum was 12.5% and the average was 9.9%.

Example II

A gel skein of 150 denier-40 filament Bright yarn was immersed in a solution of titanyl sulfate equivalent to 150 grams of TiO_2 per liter for one-half hour at room temperature, after which treatment it was allowed to drain for one-half hour in order to remove excess titanyl sulfate. The skein was then washed in 10% sodium chloride solution at room temperature until acid-free. Washing was accomplished by immersing the skein in sodium chloride solution for 5 minutes, and then centrifuging for 2 minutes to remove excess solution and to facilitate the washing operation. The skein was then immersed in fresh sodium chloride solution and the above operation repeated until the skein was acid free. This required seven two-liter washes for a 75 gram skein.

Next the skein was washed with soft water to remove sodium chloride, then with 5% sodium

carbonate solution, washed alkaline free with soft water, treated with 3% phosphoric acid solution and then washed acid-free with soft water. All treatments were conducted at room temperature. After washing, the skein was finished with a solution of sulfated vegetable oil for one-half hour at 50° C., centrifuged and dried.

TiO_2 analyses on a skein of Bright yarn treated in the above manner were as follows: minimum amount of TiO_2 was 7.27%; the maximum was 8.26% and the average was 7.77%.

Although the invention has been described above as applied to certain preferred embodiments thereof, it will be obvious that due variance therefrom may be made without departing from its underlying principles and scope. Thus, although it is particularly applicable to the treatment of textile materials such as cellulosic threads, yarns, or fabrics, the invention is not limited thereto. It may, for example, be applied to films, foils, sheets and even to plastic compositions and molded objects. The materials treated may consist of or contain cellulose acetate or other derivatives of cellulose, for example, cellulose nitrate, cellulose nitro-acetate, cellulose formate, cellulose propionate, cellulose butyrate, hydroxyethyl cellulose, ethyl cellulose and other esters, ethers, and ester-ethers of cellulose. The titanium may be introduced during spinning or casting, as for example by incorporating titanyl sulfate in an acid regenerating bath, or at any suitable stage during subsequent processing or fabrication.

It is usually possible to introduce up to 20% by weight of titanium (calculated as TiO_2) into films and up to 13% by weight into textile materials. The amount of titanium introduced may be relatively small, e. g., as low as 0.5% by weight. At least 3% by weight of titanium is required to materially reduce flammability. The reduction in flammability is directly related to the quantity of titanium introduced and larger quantities (preferably from 5% to 10% by weight) are frequently desirable when the cellulosic material has a large surface area, as in the case of brushed rayon fabrics. Preferably, also, the titanium is precipitated within the cellulose structure as the oxide, phosphate or phytate.

As noted above, titanyl sulfate is advantageously employed as the preferred impregnating agent by virtue of its high solubility in water, its relatively non-injurious effect on cellulose, and its ability to introduce large quantities of titanium. It is usually employed in aqueous solutions at a concentration equivalent to, say, from 50 to 150 grams of TiO_2 per liter, though higher concentrations (up to 200 or 300 grams per liter) can also be used, i. e., from 5% to 30% TiO_2 in solution. Excess sulfuric acid above that required for stoichiometric equivalence with titanyl ion sometimes facilitates introduction of the titanium though less than 100% excess is preferred.

The soluble titanium compound may be incorporated in a variety of ways, as for example by a bath treatment, by padding or by spraying. Any soluble titanic, titanous, or titanyl salt may be used though the sulfates, chlorides, oxalates, and acetates are particularly suitable. The titanium may be precipitated within the fibers by a variety of agents, for example, phosphates, phytates, silicates, tannates, borates, etc. Though water is preferred as the impregnating and precipitating medium, all or part of the water may be replaced with alcohols, acetone, dioxane, and the like.

It is not essential to pre-swell the cellulosic

structure but this is usually helpful and may be accomplished by soaking in water or other swelling medium or, in the case of regenerated cellulose, by employing so-called gel cellulose which has not been dried after regeneration. The rate of incorporation of titanium may sometimes be increased by raising the temperature of the impregnating solution, but, as already noted, care must be exercised to avoid hydrolysis. The time of impregnation may vary from a few seconds to a minute or more in case of yarns, fabrics, and films continuously passed through an impregnating bath up to 15 minutes or longer in batchwise impregnations.

The aqueous salt wash may be carried out at any convenient temperature and pressure, though operation at or near room temperature is generally expedient. While sodium sulfate is a preferred agent for use in this step, other water soluble, neutral salts may be used. For example, sodium chloride, potassium chloride or potassium sulfate may be employed with comparable efficiency. So also may the nitrates of lithium, sodium and potassium. In general, any salt which does not precipitate an insoluble titanium compound may be used. These salts may be used in dilute or concentrated solutions. In general, however, concentrations ranging from 5% to 20% are preferred, concentrations of 10% generally being employed.

The temperature of the salt solutions may be varied from 0° C. to 50° C. However, washing of the desired effectiveness is obtained at room temperatures. There is no need to cool the aqueous solutions since the hydrolysis action of the water is sufficiently retarded by the presence of the salt. Advantages in cost are taken by the operativeness of the wash at room temperature and temperatures in the neighborhood of 25° C. are preferred.

Other advantages attend the process of this invention. Very inexpensive materials are used in the washing step, thereby avoiding the necessity and cost of recovery steps. Further, the amount of wash material needed to produce the same end condition is materially reduced. For example, about 45 gallons of alcohol are required to wash each pound of final yarn produced, whereas only 15 to 20 gallons of the less expensive washing solutions of this invention are required per pound of yarn. This means also that the total time consumed in the operation of the process is materially reduced. The economic advantages attendant are obvious.

Processing subsequent to rinsing depends upon the particular titanium compound to be precipitated. If titanium oxide is to be precipitated, the especially rinsed materials are simply washed with water until sulfate-free or, since this is slow, neutralized with alkali, preferably 3% aqueous sodium carbonate, and washed with water. If it is desired to precipitate another insoluble titanium compound, the rinsed material may be immersed in a dilute solution of a compound containing the desired anion, as, for example, a water solution containing a phosphate, a phytate, or the corresponding free acids. Acids which extract titanium, for example, hydrochloric and sulfuric, should be avoided.

If desired, the process may be used to reduce the flammability of previously delustered materials when it is desirable to avoid further reduction in luster, clarity, or surface deposition of inorganic material.

As many apparently different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A process for producing a lustrous regenerated cellulosic product which comprises impregnating a regenerated cellulosic material with a water-soluble titanium compound; rinsing the resultant impregnated material with an aqueous solution of a water-soluble alkali salt selected from the group consisting of sulfates, nitrates and chlorides to remove superficial impregnant of the soluble titanium compound; and then precipitating a delustering concentration of a water-insoluble titanium compound ranging from 3% to 20% of titanium by weight within the rinsed cellulosic material by reacting the remaining impregnated soluble titanium compound with a precipitating agent.

2. A process in accordance with claim 1 wherein said salt is a sulfate.

3. A process in accordance with claim 1 wherein said salt is a chloride.

4. A process in accordance with claim 1 wherein said salt is a nitrate.

5. A process in accordance with claim 1 wherein said salt is sodium sulfate.

6. A process for producing a lustrous regenerated cellulosic product which comprises impregnating a regenerated cellulosic material with a water-soluble titanium compound; rinsing the resultant impregnated material with a 5% to 20% aqueous solution of sodium sulfate at 0° C. to 50° C. to remove superficial impregnant of the soluble titanium compound; and then precipitating a delustering concentration of a water-insoluble titanium compound ranging from 3% to 20% of titanium by weight within the rinsed cellulosic material by reacting the remaining impregnated soluble titanium compound with a precipitating agent.

7. A process in accordance with claim 6 wherein said aqueous solution is a 10% solution of sodium sulfate and the temperature is room temperature.

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