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54 **Novel compositions.**

57 Aqueous finish compositions containing a nitrogen-containing textile finish compound for treatment of synthetic fibers are disclosed, characterized in that they further contain a nitrosamine inhibitor. The use of such compositions for treating synthetic fibers to thereby reduce the level of nitrosamine on their surface and fibers so treated are further disclosed.

**EP 0 623 701 A1**

This invention relates to new finish compositions for synthetic fibers, synthetic fibers treated with such finish compositions and the use of such compositions for reducing the amount of nitrosamine on the surface of such fibers. More particularly, this invention relates to an aqueous finish composition comprising a nitrogen-containing textile finish compound for treatment of synthetic fibers characterized in that it further  
5 contains a nitrosamine inhibitor. This invention relates further to the use of such compositions for treating synthetic fibers to thereby reduce the level of nitrosamine on their surface and fibers so treated.

#### Background of the Invention

10 The production and downstream treatment of synthetic or man-made fibers entails contacting the fiber at various stages with a finish composition to impart various properties, e.g. lubrication and antistatic properties. Synthetic fiber production employs textile finishes during spinning, drawing, crimping and cutting of the fiber, and downstream of the fabric production, e.g. ring-, open-end- and air-jet-spinning, knitting, weaving, dyeing and finishing. These finish compositions are typically aqueous and often contain a  
15 nitrogen-containing textile finish compound and are per se known in the art. Such compositions typically also contain one or more additional agents such as emulsifiers, dispersants, surfactants, lubricants, softening agents, wetting agents, antimicrobials, cohesive agents, slickening agents, dyeing assistants and the like.

A drawback of known textile finish compositions, however, is that the nitrogen-containing textile finish  
20 compounds they contain can form nitrosamines at the high temperatures employed typically during the drawing, crimping and drying processes, as well as in the downstream heat-requiring steps, e.g. thermobonding processes. The nitrogen-containing textile finish compounds are believed to react with nitrous oxides (NO<sub>x</sub>) in the hot air stream and/or the atmosphere to form nitrosamines at the fiber surface. Although these nitrosamines are typically present only in minute quantities on the surface of the fiber, e.g. 10-200 parts per  
25 billion (ppb) it is nevertheless highly desirable to inhibit or completely eliminate their formation as nitrosamines are believed to play a role in causing cancer and other diseases.

It is known in the art to use certain compounds such as polyethylenimines or tocopherols to inhibit nitrosamine formation or as antioxidants in the context of certain polymer production (cf. e.g. S.F. Laermer,  
30 R. Nabholz, "The use of biological antioxidants as polypropylene stabilizers", *Plastics & Rubber Processing & Application*, 14 (1990), pp. 235-239; JP 4082910 A (1992)). Such applications, however, are neither concerned with aqueous compositions, nor treatment of synthetic fibers.

It is also known to treat various synthetic fibers with aqueous emulsion lubricant solutions containing  $\alpha$ -tocopherol and an organic phosphite (CA 92: 139712m (1980); JP 55022024 (1980)). These solutions, however, do not contain nitrogen-containing textile finish compounds and do not concern themselves with  
35 the suppression or elimination of nitrosamine formation.

The use of tocopherol and/or ascorbic acid is also known in the cosmetic and food industry, and in particular, in oil and water emulsions for such end uses (cf. e.g. DE 3939474 A1 (1989), E. Kamp et al. "Vorkommen und Entstehung von Nitrosaminen in Koerperpflegemitteln", GIT Supplement 2/89 Lebensmittelchemie und -Technologie.

40 It has now been found that nitrosamine inhibiting compounds can be added to known aqueous compositions comprising nitrogen-containing finish compounds for synthetic fibers with the effect of substantially reducing or eliminating the formation of nitrosamine on the fiber surface. This result is particularly surprising when one considers that the nitrosamine is typically present at the fiber surface in only trace amounts (e.g. 10-200 ppb) and yet a very small amount of the nitrosamine inhibiting compound  
45 (e.g. as low as about 50 parts per million (ppm)) will have the effect of lowering the amount of nitrosamine to levels approaching zero.

The efficiency of the effect is also surprising when one considers that some of the nitrosamine inhibiting compounds of the invention are insoluble or only slightly soluble in the compositions of this invention (since they tend to be water insoluble or only slightly water soluble). One would not expect that the water  
50 insoluble/slightly soluble nitrosamine inhibiting compounds would uniformly treat the surface of the fibers.

In addition, as it is known that even slight changes in finish compositions can have a deleterious effect on the friction and other properties of a composition, it is surprising that the compositions of this invention, while inhibiting nitrosamine formation, retain the desirable properties of a finish composition.

Detailed Description of the Invention

As used herein, certain terms have the following meanings.

"Synthetic fiber" refers to known classes of man-made fibers including polyester, polyamide, polyaramid, elasthan, polyethylene, polypropylene, polytetrafluorethylene and regenerated cellulose. The composition is suitable, too, in the area of general textile finishing, including finishing of natural fibers.

"Aqueous compositions" refer to solutions, emulsions and dispersions that contain an aqueous component. Such compositions will typically contain about 75 to 99 % by weight water, although they may be formulated as concentrates and later diluted to the desired concentration for end use.

A "nitrogen-containing textile finish compound" refers to the various known such compounds found in textile finish solutions which typically serve to lubricate and provide anti-static and other desirable properties to the fiber. Compounds of this type include alkylamines and alkanolamines both of which may be primary, secondary or tertiary, arylamines and heteroarylamines, amides, ammonium salts and aminosilicones. Specific examples of these compounds are diethanolamine and triethanolamine.

Nitrogen-containing textile finish compounds typically comprise 1% to 100% by weight of the non-aqueous component (oil-base) of the finish composition of this invention.

A "nitrosamine inhibitor" refers to various known compounds which inhibit nitrosamine formation. These compounds are believed to compete with the nitrogen-containing textile finish compounds for the ambient  $\text{NO}_x$  and in reacting with the  $\text{NO}_x$  form harmless compounds. Suitable nitrosamine inhibitors according to the invention include the heat-stable tocopherols and derivatives thereof, e.g. d,l-alpha-tocopherol (vitamin E); d,l-2-carboxy-6-hydroxy-2,5,7,8-tetramethylchroman (water soluble vitamin E, e.g. TROLOX, available from Hoffmann-La Roche); l(+)-ascorbic acid (vitamin C) and derivatives; polyethylenimine and derivatives and mixtures of these.

Further inhibitors include various phenolic compounds, e.g. vanillin, hydroquinone, thymol, tannin, and metal salts and derivatives thereof which show a suitable electrochemically reversible redox potential for nitrosamine inhibition.

Particularly preferred nitrosamine inhibitors according to the invention are d,l-alpha-tocopherol (vitamin E) and l(+)-ascorbic acid (vitamin C).

Nitrosamine inhibitors are typically present in the finish composition in an amount ranging from 50 ppm to 0.1 % by weight of the non-aqueous (oil-base) component of the composition, more particularly from 250 to 750 ppm.

A further common component of textile finish compositions is a fatty acid or ester or amide thereof. Typical such fatty acids have carbon backbones of 8 to 23 carbons. Preferred such fatty acids are oleic acid and lauric acid.

As previously mentioned, the aqueous textile finish solution according to the invention may also include other typical additives known in the art such as emulsifiers, dispersants, surfactants, lubricants, softening agents, wetting agents, antimicrobials, cohesive agents, slickening agents, dyeing assistants and the like.

Finish compositions are as indicated in the examples below. The polyester fibers are melt spun in a conventional manner through a commercial multi-hole spinneret. The molten filaments are solidified in a conventional manner using a cross-flow air quenching apparatus. A primary (spin) finish composition is applied to the freshly solidified undrawn filaments by means of a conventional rotating finish roll which is partly immersed in a pan containing the spin finish. The composition of this 1% aqueous primary (spin) finish is the same laid down in spin cans. The polyester spin tow is drawn in a conventional manner using a multi-stage drawing process. The tow (fiber) is mechanically crimped in a commercial manner and heated in a drying oven at 75-85°C for annealed textile manufacturing processes and 100-180°C for relaxed textile manufacturing process, before cutting.

In a preferred aspect of this invention, polyester staple (cut) fibers are provided containing about 0.05 to 1% by weight of finish on tow based on the dry weight of treated fibers.

50 Examples

The finish compositions of this invention are preferably applied as a diluted aqueous mixture, e.g., 0.04-5% by weight. Preferably, the fibers in form of a tow are treated during crimping by spray application with 0.05-1% by weight of the finish composition based on the weight of the dry, heated tow, more preferably about 0.1% by weight. While it is preferred to apply the compositions of this invention in an aqueous form, it should be appreciated that, except for equilibrium amounts, the water will subsequently be removed by evaporation occurring during heating steps. In the below given examples which serve to illustrate the invention further, all parts are by weight and all percentages are by weight based on the total weight of the

composition, except in the case of nitrosamine inhibitor, whose amount is given based upon the weight of the non-aqueous (oil-base) component.

5 Examples 1-9 are prepared to show that the finish compositions of this invention will process in the normal range regarding friction properties in comparison with control finishes (Examples 1 and 5). Examples 3 and 4 are prepared with purified triethanolamine to demonstrate that a decrease of diethanolamine will result in no significant change of friction properties. Using more purified triethanolamine is believed to also inhibit nitrosamine formation because reaction time of triethanolamine with NO<sub>x</sub> appears to be much slower than for diethanolamine.

10 Examples 7-9 are prepared to show that several nitrosamine inhibitors can be used together. Particularly good results are obtainable where one of the nitrosamine inhibitors is water soluble.

For friction testing the finish examples are metered onto 70/34 continuous polyester filament yam at 0.08% by weight for characterization. The following compositions are used to prepare the 12.55 aqueous textile finish compositions for friction testing:

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EP 0 623 701 A1

|    | <u>Example No.</u> | <u>Ingredient</u> | <u>Weight %</u> | <u>Amount (g)</u>     |
|----|--------------------|-------------------|-----------------|-----------------------|
| 5  | 1                  | A                 | 34.5            | 4.32                  |
|    |                    | B                 | 57.5            | 7.21                  |
|    |                    | C                 | 8.2             | 1.03                  |
|    |                    | water             |                 | 87.44                 |
| 10 | 2                  | A                 | 34.5            | 4.32 + 500 ppm vit. E |
|    |                    | B                 | 57.5            | 7.21                  |
|    |                    | C                 | 8.2             | 1.03                  |
|    |                    | water             |                 | 87.44                 |
| 15 | 3                  | D                 | 34.5            | 4.32                  |
|    |                    | B                 | 57.5            | 7.21                  |
|    |                    | C                 | 8.2             | 1.03                  |
|    |                    | water             |                 | 87.44                 |
| 20 | 4                  | D                 | 34.5            | 4.32 + 500 ppm vit. E |
|    |                    | B                 | 57.5            | 7.21                  |
|    |                    | C                 | 8.2             | 1.03                  |
|    |                    | water             |                 | 87.44                 |
| 25 | 5                  | E                 | 66.66           | 8.37                  |
|    |                    | B                 | 33.33           | 4.18                  |
|    |                    | water             |                 | 87.45                 |
| 30 | 6                  | E                 | 66.66           | 8.37 + 500 ppm vit. E |
|    |                    | B                 | 33.33           | 4.18                  |
|    |                    | water             |                 | 87.45                 |
| 35 | 7                  | A                 | 34.5            | 4.32 + 500 ppm vit. E |
|    |                    | B                 | 57.5            | 7.21 500 ppm vit. C   |
|    |                    | C                 | 8.2             | 1.03                  |
|    |                    | water             |                 | 87.44                 |
| 40 | 8                  | D                 | 34.5            | 4.32 + 500 ppm vit. E |
|    |                    | B                 | 57.5            | 7.21 500 ppm vit. C   |
|    |                    | C                 | 8.2             | 1.03                  |
|    |                    | water             |                 | 87.44                 |
| 45 | 9                  | E                 | 66.66           | 8.37 + 500 ppm vit. E |
|    |                    | B                 | 33.33           | 4.18 500 ppm vit. C   |
|    |                    | water             |                 | 87.45                 |
| 50 |                    |                   |                 |                       |

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A = Mixture of 85% triethanolamine and 15% diethanolamine.

5 B = Diethanolamine salt of mono and diacid phosphate esters of blend 20% C<sub>12</sub>, 30% C<sub>10</sub>, 50% C<sub>8</sub> alcohols.

C = Oleic acid obtained from catalytic hydrogenation of tall oil.

10 D = 100% triethanolamine impurified with < 1.0% diethanolamine.

E = Ethoxylated ester/amide of lauryl acid

15 vit. E = vitamin E

vit. C = vitamin C

20 ppm = parts per million based upon the non-aqueous component of the composition

25 Generally, finish composition preparation requires a special procedure, otherwise, it cannot be guaranteed that the vitamin E is completely soluble in the composition as is demonstrated by adding vitamin E directly to the clear 2.55% aqueous control finish compositions (Examples 1 and 5): a slight clouding after vitamin E addition indicates its insolubility, whereas for example addition of water-soluble vitamin C dissolves easily.

For Examples 1 and 3, the following procedure is suitable:

- 30 - A mixture of the indicated amounts of A or C with D is prepared.  
 - The mixture is heated at 60 °C under agitation.  
 - The indicated amount of B is added at 60 °C.  
 - The mixture is agitated for 15 minutes at 60 °C at the highest agitation rate.  
 - The indicated amount of water is added at 60 °C.  
 35 - The mixture is diluted with water to form a 2.5 weight % aqueous composition.

For Examples 2 and 4, the above procedure is followed with the exception that 500 ppm of vitamin E is added in the first step to the mixture of A or C with D, prior to heating and agitating.

40 For Examples 7 and 8, the procedure set forth for Examples 2 and 4 is followed, with the exception that prior to dilution with water to a 2.5 weight % aqueous composition, 500 ppm vitamin C based on the non-aqueous component is added to the mixture, which is then agitated for 10 minutes at 60 °C at a high agitation rate.

For Example 5, the following procedure is suitable:

- 45 - The indicated amount of E is heated to 60 °C.  
 - The indicated amount of B is added at 60 °C and the mixture is agitated for 30 minutes at 60 °C at highest agitation rate.  
 - The indicated amount of water is added at 60 °C.  
 - The mixture is diluted with water to a 2.5 weight % aqueous composition.

For Example 6, the procedure of Example 5 is followed with the exception that 500 ppm Vitamin E is added to E in the first step and agitated at 60 °C.

50 For Example 9, the procedure of Example 6 is followed with the exception that prior to dilution with water to a 2.5 weight % aqueous composition, 500 ppm vitamin C based on the non-aqueous component is added to the mixture, which is then agitated for 10 minutes at 60 °C at a high agitation rate.

The friction data of Examples 1-6 obtained as averages of duplicates are more variable than normal but, however, indicate that the modified finishes will process in the normal range.

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**Claims**

- 5
1. An aqueous textile finish composition comprising a nitrogen-containing textile finish compound for treatment of synthetic fibers characterized in that the composition further contains a nitrosamine inhibitor.
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  2. An aqueous textile finish composition according to claim 1 wherein the nitrosamine inhibitor is selected from the group consisting of the heat-stable tocopherols and derivatives thereof; l(+)-ascorbic acid and derivatives; polyethylenimine and derivatives thereof.
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  3. An aqueous textile finish composition according to claim 2 wherein the nitrosamine inhibitor is selected from the group consisting of d,l-alpha-tocopherol and d,l-2-carboxy-6-hydroxy-2,5,7,8-tetramethylchroman.
  - 20
  4. An aqueous textile finish composition according to claim 1 comprising a nitrogen-containing textile finishing compound, a fatty acid or an ester thereof, and a nitrosamine inhibitor.
  5. An aqueous textile finish composition according to claim 1 comprising a nitrogen-containing textile finishing compound selected from the group consisting of diethanolamine and triethanolamine and a nitrosamine inhibitor selected from the group consisting of d,l-alpha-tocopherol and d,l-2-carboxy-6-hydroxy-2,5,7,8-tetramethylchroman.
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  6. A synthetic fiber treated with a finish composition according to claims 1 to 5.
  7. A method for reducing the amount of nitrosamine on the surface of a synthetic fiber comprising treating the fiber with a finish composition according to claims 1 to 5.

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EUROPEAN SEARCH REPORT

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| DOCUMENTS CONSIDERED TO BE RELEVANT   |  |   |  |
|---|--|---|--|
| Category  | Citation of document with indication, where appropriate, of relevant passages  | Relevant to claim   | CLASSIFICATION OF THE APPLICATION (Int. Cl.5)  |
| D, A  | DE-A-3 939 474 (EISENBRAND)<br>* the whole document *<br>---   | 1   | D06M13/184<br>D06M13/224<br>D06M13/328<br>D06M13/325<br>D06M13/368<br>D06M13/152<br>D06M13/322 |
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|   |  |   | C10M<br>D06M   |
| Place of search   | Date of completion of the search   | Examiner  |  |
| THE HAGUE   | 08 OCTOBER 1993  | BLAS V.   |  |
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