This invention relates to new or improved artificial effect filaments, yarns, threads, cords, ribbons, knitted, woven or other fabrics or other materials made of or containing cellulose esters.

The present invention comprises new effect materials, for example filaments, yarns, threads or knitted, woven or other fabrics, made of or containing cellulose esters, for example cellulose formate, cellulose propionate or cellulose butyrate.

The invention further comprises the above material after differential saponification, e.g., after treatment so that part of the cellulose ester is saponified and part remains unsaponified. The invention in addition comprises processes for the manufacture of such materials and for their treatment and particularly their colouration.

I have found that very desirable effects may be produced by weaving, knitting, twisting or otherwise making up filaments, yarns or threads of cellulose acetate or other cellulose esters having different degrees of resistance to saponification. By differential saponification of the products, materials may be produced which while consisting substantially of cellulose esters nevertheless are capable of yielding cross-dyed effects. By including yarns or threads of other fibres for example wool, silk, cotton, viscose or other artificial silk, still further effects may be produced upon colouring the materials. The portion of the cellulose ester which is saponified acquires an affinity for the direct or substantive colours, while according to the degree of saponification the saponified portion of the cellulose ester may or may not lose its affinity for the dispersed insoluble type of dye, e.g., the “GRA” colours. The saponification may be conducted so that the less or least resistant portion only is saponified, or so that part is completely saponified and part only partially saponified. Again if three types of cellulose ester are employed in the fabric or other material having three different degrees of resistance to saponification, the least resistant may be completely saponified, another portion may be partially saponified while the most resistant may remain substantially unsaponified.

The filaments, yarns, threads, etc. of cellulose acetate or other cellulose esters having different degrees of resistance to saponification may be produced by any suitable process. Different esters having the desired difference in resistance may be employed, or degrees of resistance may be produced in any one ester by suitable variation of the initial acyl content or of the conditions of spinning or other factors. For example I have found that by varying the solvent, e.g., acetone, content of the evaporative medium in the immediate vicinity of the spinning nozzles in a dry-spinning process filaments of various degrees of resistance to saponification may be produced. Thus in the case of dry-spinning a concentrated acetone solution of cellulose acetate, e.g., 25% concentration or more, by carrying out the spinning in such a way that the concentration of acetone in the region of the spinning nozzles is higher than 1%, e.g., 2 or 3% or more, filaments are produced which are more resistant to saponification than filaments produced by spinning into air in which the concentration of acetone is less than 1%. The solvent concentration in the vicinity of the spinning nozzles may be varied in any desired manner. For example it may be increased by injection of solvent vapour, mixed if desired with a proportion of air or other inert gas or vapour, or by decreasing the rate of flow of the evaporative medium. Again the reverse effect may be obtained by decreasing the solvent concentration, e.g., by injection of air or other inert gas in the region of the nozzles or by increasing the rate of flow of the evaporative medium.

The invention further comprises filaments having a periodically or intermittently varying resistance to saponification. Such filaments may be produced for example by periodically or intermittently varying the solvent concentration in the region of the nozzles of the dry-spinning apparatus, e.g., by intermittent injection of solvent vapour and/or air or other inert gas or by intermittent increase and decrease of the rate of flow of the evaporative medium. New yarns, threads, cords, knitted, woven or other fabrics or other materials may be made by associating, twisting, cording, weaving, knitting or otherwise making up such filaments of periodically or intermittently varying resistance to saponification. Doubled yarns or cords exhibiting novel effects upon subsequent colouration may be produced by twisting or otherwise associating yarns of periodically or intermittently varying resistance to saponification so that the parts of a definite degree of resistance to saponification do not register with each other. For example a yarn showing periodicity of two different degrees of resistance to saponification may be twisted with a similar yarn so that the less resistant portion of one yarn registers with the more resistant portion of the other, or so that the resistant portion of one yarn registers with half the resistant portion and half the unresistant portion of the other yarn. Upon subsequently dyeing the...
latter doubled yarn or cord a periodic increase and decrease of colouration is obtained while with the former doubled yarn or cord speckled or pale colouration effects are obtainable. Effects may moreover be produced by twisting, knitting, weaving or otherwise making up the above intermittently or periodically varying filaments with filaments, yarns or threads of unvarying resistance to saponification and/or with other fibres such as silk, wool, cotton or the cellulose type of artificial silk. Again such intermittently or periodically varying filaments in obtaining yarns or threads produced therefrom, may be made up with two or more types of cellulose ester filaments, yarns or threads, having different but unvarying degrees of resistance to saponification.

As indicated above the invention includes the processes of differentially saponifying the above materials and includes the products so produced.

For the purpose of producing this differential saponification the concentration of the saponifying solution or reagent, and/or the conditions under which it is applied are so chosen that various degrees of saponification are produced in different types of cellulose ester. As a broad indication it may be stated that a fabric composed of cellulose acetate filaments produced by dry spinning into air containing less than 1% of acetone vapour spinning into air containing 2 to 3% of acetone vapour may be satisfactorily differentially saponified by treatment for 1/4 to 21/2 hours at about 70 to 80° C. with a solution containing 0.5 to 1.0 grams of caustic soda per litre or 2.5 to 5.0 grams of sodium carbonate per litre. Any other suitable saponifying agent may be employed for the purpose of the present invention, for example caustic potash, potassium carbonate, sodium silicate, tri-sodium phosphate and the like. Buffer salts, for example sodium chloride or soaps, may be added to the saponification baths or reagents. Furthermore swelling agents for the cellulose esters, for example ethyl or methyl alcohol, may be added. The addition of such swelling agents may affect the degree and type of saponification produced. For example with suitable swelling agent in the saponifying bath the saponification may be rendered uniform throughout the filaments as opposed to superficial. Swelling agents are also useful in the treatment of a portion of any particular portion of the cellulose ester material. In the case of treating materials containing two different cellulose esters, e.g. cellulose acetate and cellulose benzoate, the swelling agent may be so chosen that it swells and promotes saponification of only one of the esters.

The new cords, fabrics or other materials of the present invention may be coloured by any suitable process before or after saponification.

The invention is of particular importance in connection with differentially coloured materials obtainable by colouring after differential saponification. Depending on the degree to which they have been saponified, the cellulose ester materials retain or lose their affinity for the dispersed insoluble colours, e.g. the "SRA" colours. Successfully or completely saponified materials acquire an affinity for the substantive cotton colours, while uniformly partially saponified materials do not in general acquire such an affinity. A large variety of effects may therefore be obtained by varying the method of saponification or by employing appropriate dyestuffs. Dyeing may further take place simultaneously with saponification, for example by incorporating a cotton dye-stuff in a saponification bath. As already indicated further effects may be produced by associating other fibres with the cellulose esters of various degrees of resistance to saponification and applying suitable colouring materials.

The following examples show the best methods known to me for carrying the invention into effect but they are not to be considered as limiting it in any way:

**Example 1**

A fabric is knitted or woven or a yarn or cord doubled from a yarn made from cotton or such other fibres as 60% acetyl content (calculated as acetic acid) and from a yarn of cellulose acetate of 50% (or under) acetyl content.

**Example 2**

An acetone soluble cellulose acetate is dissolved in acetone to form a 25% solution and the solution spun by dry spinning methods while maintaining a concentration of acetone vapour in the immediate vicinity of the jet of about 1% or less. The same cellulose acetate solution is then spun while maintaining in the region of the jet an acetone concentration of about 3% so as to form a second yarn. The two yarns are then doubled to form a doubled yarn or cord or are knitted, woven or otherwise made up to form a fabric.

A yarn showing a periodically varying resistance to saponification is obtained by dry spinning the same cellulose acetate solution and by periodically injecting acetone vapours into the region of the nozzle so that the acetone concentration in this vicinity varies from 1 to 3%. The yarn thus obtained may be knitted or woven with itself or with either of the yarns produced according to Example 1 or with any other suitable yarns to form a doubled yarn or cord or to form a fabric.

**Example 3**

Differential saponification of any of the products obtained according to Examples 1 and 2. A saponification bath is made up containing 0.05% of caustic soda and 0.1% soap. The yarn, cord or fabric produced according to Example 1 or 2 is entered into a bath of about 80 times its weight and the saponification continued at about 80° C. for a period of 2 to 3 hours. If desired the goods may be simultaneously dyed by addition to the bath of a cotton dyestuff in a concentration of 1% of the weight of the goods.

Instead of caustic soda sodium carbonate may be used, the quantity being approximately five times the weight of caustic soda used.

What I claim and desire to secure by Letters Patent is:

1. Process for the production of improved textile materials, which comprises producing filaments of an organic ester of cellulose by a dry spinning operation in the course of which the solvent content of the evaporative atmosphere is varied to produce local differences in the resistance to saponification of the filaments, and subsequently treating said filaments with a saponifying liquid at a temperature and for such time that local differences in the degree of saponification are produced.

2. Process for the production of improved textile materials, which comprises producing filaments of cellulose acetate by a dry spinning operation in the course of which the solvent content of the evaporative atmosphere is varied to produce local differences in the resistance to saponification of the filaments, and subsequently treat-
5. Process for the production of improved textile materials, which comprises producing filaments of an organic ester of cellulose by a dry spinning operation, in the course of which the solvent content of the evaporative atmosphere is intermittently varied to produce filaments having the same acetyl content along the length thereof and having local differences in the resistance to saponification of the filaments, and subsequently treating said filaments with a saponifying agent of such strength, at such temperature and for such time that local differences in the degree of saponification are produced.

4. Process for the production of improved textile materials, which comprises producing filaments of cellulose acetate by a dry spinning operation, in the course of which the solvent content of the evaporative atmosphere is intermittently varied to produce filaments having the same acetyl content along the length thereof and having local differences in the resistance to saponification of the filaments and subsequently treating said filaments with a saponifying agent of such strength, at such temperature and for such time that local differences in the degree of saponification are produced.

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