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# UNITED STATES PATENT OFFICE

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## PRODUCTION OF ARTIFICIAL MATERIALS

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7 Claims. (Cl. 18—54)

This invention relates to the production or treatment of artificial filaments, threads, yarns, ribbons, fabrics, films or other materials, and is more particularly concerned with new or improved processes for the production of filaments, threads, fabrics or other materials having a reduced, subdued or modified lustre.

According to the present invention, artificial materials having a subdued, reduced or modified lustre are produced by incorporating therein organic substances in a quantity greater than is soluble in the base, for example cellulose acetate, of which the filaments, ribbons, films or other materials consist or which they contain. The organic substances are preferably insoluble or substantially insoluble in the base, and, moreover, are preferably insoluble in water and in dilute acids or alkalies or other reagents with which the materials are liable to be treated in commercial practice. Furthermore considerable advantages result from the use of substances insoluble in the common organic solvents.

I have found that the best results are obtainable by means of organic substances which are of high or very high melting point, for example above about 240°–260° C. Substances which I have found particularly suitable are symmetrical α-dinaphthyl urea, β-tetranaphthyl urea, β-dinaphthyloxamide, succinc α-naphthalide, para-nitrophenylphthalimide, anthraquinone, 2.6-dichloranthraquinone or other derivatives of anthraquinone having a high melting point and acenaphthenequinone. Substances of lower melting point, e. g. of from about 200° to 240° C., may be used, but their use is less advantageous. Such substances are, for example, anthracene, carbazole, symmetrical-α-dinaphthyl thiourea and diphenyl oxamide. All these substances are substantially insoluble in water and aqueous liquids and in organic solvents, and for this reason their incorporation in artificial materials yields products having a subdued, reduced or modified lustre of great permanence.

The organic substances may be incorporated in the materials by any convenient method. I prefer to incorporate them in the spinning solutions used for the manufacture of the artificial filaments, threads, yarns, ribbons, films, etc. and this method of incorporation forms an important feature of the present invention. The organic substances are particularly advantageous for incorporation in spinning solutions, e. g. acetone solutions of cellulose acetate, since it is found that, even though they are insoluble therein, stable suspensions or dispersions are readily obtainable from which the dispersed or suspended substances do not readily settle.

As stated above, the organic substances are preferably insoluble in water and in organic solvents, and they may be incorporated in the spinning solution in a state of dispersion or fine sub-division. Preferably, the degree of sub-division is such as to enable the spinning solutions to be spun without obstructions being caused in the spinning pumps, spinning dies, or other parts of the apparatus. The substances may be sufficiently finely divided or dispersed to enable them to pass through the filters, so that they may be incorporated in the spinning solutions before their filtration.

Organic substances may be employed which, while being insoluble or substantially insoluble in the cellulose acetate or other base, are soluble in the spinning solution. Such substances may of course be incorporated in the spinning solutions by simple solution therein or by solution in the solvent or part of the solvent used for making up the spinning solution.

The incorporation of organic substances insoluble in the spinning solutions may take place by any convenient method. For example, an aqueous paste containing the organic substance in the desired state of sub-division may be worked with the solvent to be used for making up the spinning solution, for example acetone in the case of cellulose acetate, or with a small proportion of the spinning solution itself, preferably dilute, e. g. a dilute solution of cellulose acetate in acetone. Alternatively, an aqueous suspension or dispersion containing the organic substance may be added directly to the spinning solution or to the solvent before solution of the cellulose derivative or other base. Again if the organic substance employed be insoluble in the spinning solution but soluble in another solvent, it may be dissolved in such other solvent and the solution added to the solvent used for making up the spinning solutions or better still to the spinning solution itself.

In some cases, the organic substance may be obtained in a very fine state of sub-division by actually forming it in the spinning solution itself or otherwise in the presence of the cellulose derivative or other base of the spinning solution or by forming it in the solvent used for making up the spinning solution. For example, leuco anthraquinone or the leuco compounds of anthraquinone derivatives may be dissolved in a suitable organic solvent, which may be the solvent to be used in the spinning solution, and the leuco com-

pound oxidized to the anthraquinone or derivative thereof so as to obtain a fine suspension or dispersion of the anthraquinone or derivative thereof in the solvent. Such a formation of the anthraquinone or anthraquinone derivative or other organic solvent may furthermore take place in the presence of the cellulose acetate or other base of the spinning solution; for example the leuco compound of anthraquinone or a derivative thereof may be dissolved in the spinning solution and then oxidized. Again, the organic substance may be formed in the presence of the cellulose acetate or other base apart from the solvent employed in the spinning solution. For example it may be formed in an acetylation or esterification mixture before or after ripening but before the precipitation of the cellulose acetate or other ester.

As indicated above, the organic substance or substances employed are preferably insoluble or substantially insoluble in the cellulose acetate or other base used for forming the materials, and in such cases the quantity of organic substance incorporated may be of the order of ½–1 or 2% of the organic substance relative to the cellulose derivative or other base. The invention is, however, not limited to such quantities, since lower or higher quantities, for example 5–10% or more, may be employed. In the case of using substances which are somewhat soluble in the cellulose derivative or other base, the higher proportions may be necessary to produce the required effect, and the invention contemplates the employment of such organic substances in a quantity greater than that which will dissolve in the cellulose derivative or other base.

The substances employed are preferably white or substantially white, so that any desired colouration may be imparted to the materials in the usual manner. In certain cases, however, improved results may be obtained by incorporating a small proportion of a black or other dark-coloured substance, which may be either organic or inorganic, in addition to a white organic substance. For example, a black or dark organic colouring matter may be added, e. g. in a proportion of about 1–2%, to a white or substantially white organic substance and the whole incorporated in the materials in the desired proportion as described above.

The invention is more particularly applicable to the production of filaments, threads, yarns, ribbons or other products from solutions containing cellulose acetate or other cellulose esters or ethers, for example cellulose formate, cellulose propionate, cellulose butyrate, methyl cellulose, ethyl cellulose or benzyl cellulose, and such solutions may be spun by either the dry-spinning method or the wet-spinning method. The invention is, however, also applicable to the production of filaments or other products of reduced, subdued or modified lustre from solutions of other bases, for example viscose or other base used for the manufacture of filaments or other products of the cellulosic type.

The following examples illustrate the invention but are not to be considered as limiting it in any way:—

*Example 1*

β-tetranaphthyl urea is ground in a ball mill with water so as to obtain a thin paste containing some 60 to 75% of water. The thin aqueous paste is then further worked with acetone until a smooth acetone paste of the tetranaphthyl urea is obtained. Preferably the grinding is continued until the particles have an average size of 1–3 or 1–5 microns or less (i. e. .001 to .003 or .005 millimeter). The acetone-aqueous paste is then thoroughly mixed with a 25 to 30% solution of cellulose acetate in acetone. Preferably the mixing is first effected with a relatively small amount of the acetone solution of cellulose acetate and the resulting dispersion thereafter added to the main bulk of the spinning solution in such a proportion that the tetranaphthyl urea is present in a ratio of 1 to 4% calculated on the cellulose acetate. The resultant spinning solution may thereafter be spun by any suitable method.

*Example 2*

80 parts of a 10% aqueous paste of anthraquinone containing the anthraquinone in a sufficiently finely divided state to pass the spinning dies and filters are homogeneously incorporated in a solution of 260 parts of cellulose acetate in 740 parts of acetone. The resultant spinning solution may be spun according to known methods.

*Example 3*

20 parts of a 25% aqueous paste of 2.6-dichloranthraquinone are ground first with 20 parts of acetone until a smooth paste is obtained and then with a further 40 parts of acetone, and the resulting paste is added to 1000 parts of a 25 to 30% solution of cellulose acetate in acetone, and the spinning solution obtained is spun in known manner.

In a similar manner the above or any other suitable organic substances may be incorporated in organic solutions of any other cellulose derivatives. Again the organic substances may be incorporated in spinning solutions used for the production of the cellulosic type of artificial silk, for example viscose. In such a case an aqueous paste containing the organic substance in the desired state of sub-division may be added to or worked directly with the aqueous spinning solution.

The term "organic substances" as used in the description and claims is to be understood as comprising only purely organic compounds and not substances containing metallic radicles, such as salts of organic acids.

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

1. In a process for the manufacture of artificial filaments, threads, yarns, ribbons and similar materials of subdued luster by the extrusion of a spinning solution into a setting medium, the step of incorporating in such spinning solution a proportion of a finely divided substantially white crystalline aromatic compound having a melting point above 200° C. in a proportion greater than is soluble in the substance of the materials and sufficient to impart a subdued luster to artificial materials spun from said solutions, said aromatic compound containing at least one amido group in which hydrogen is substituted by a naphthalene residue.

2. In a process for the manufacture of artificial filaments, threads, yarns, ribbons and similar materials of subdued lustre by the extrusion of a cellulose acetate spinning solution into a setting medium, the step of incorporating in said cellulose acetate spinning solution finely divided β-tetranaphthyl urea in an amount equal to at least ½% based on the weight of the cellulose acetate present.

3. An organic derivative of cellulose solution for use in the manufacture of artificial filaments, threads, yarns, ribbons and similar materials of subdued lustre comprising an organic derivative of cellulose and a finely divided substantially white crystalline aromatic compound having a melting point above 200° C. and which is substantially insoluble in the organic derivative of cellulose, said aromatic compound containing at least one amido group in which hydrogen is substituted by a naphthalene residue and being present in an amount sufficient to impart a subdued luster to artificial materials spun from said solution.

4. A cellulose acetate spinning solution for use in the manufacture of artificial filaments, threads, yarns, ribbons and similar materials of subdued luster comprising cellulose acetate and finely divided β-tetranaphthyl urea in an amount equal to at least ½% based on the weight of the cellulose acetate present.

5. Artificial filaments, threads, yarns, ribbons and similar materials of subdued luster containing a finely divided substantially white crystalline aromatic compound having a melting point above 200° C. in a proportion substantially greater than is soluble in the substance of the materials and sufficient to impart a subdued luster to the artificial materials, said aromatic compound containing at least one amido group in which hydrogen is substituted by a naphthalene residue.

6. Artificial filaments, threads, yarns, ribbons and similar materials of subdued luster having a base of cellulose acetate and containing a finely divided substantially white crystalline aromatic compound which has a melting point above 200° C. and which is substantially insoluble in the substance of the materials, said aromatic compound containing at least one amido group in which hydrogen is substituted by a naphthalene residue and being present in an amount sufficient to impart a subdued luster to the artificial materials.

7. Artificial filaments, threads, yarns, ribbons and similar materials having a base of cellulose acetate and containing finely divided β-tetranaphthyl urea in an amount equal to at least ½% based on the weight of the cellulose acetate present.

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