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PRODUCTION OF COLORATIONS ON MATERIALS

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This invention relates to the coloration of textile materials and more particularly to the production of dark colorations thereon. The invention is of special value in connection with the production of such colorations on materials consisting of or containing cellulose esters or ethers.

The production of satisfactory blacks and other dark colorations on textile materials by direct dyeing methods is a matter of some difficulty. In the first place there is a decided lack of direct dyeing dyestuffs of satisfactory fastness properties, and in the second place, in order to produce shades of sufficient depth, it is generally necessary to employ proportions of dyestuff relative to the material which are very high compared with those usually sufficient for the production of pale and medium shades. As a consequence the deep dyeings produced by direct dyeing methods frequently lack fastness to rubbing in addition to lacking fastness to other agencies. Further, the use of such high proportions of coloring matters involves considerable expense. Consequently if satisfactory deep shades are required it has generally been found expedient to employ indirect dyeing methods such as dyeing with vat dyestuffs or with azo dyestuffs produced on the material. These latter methods however suffer from the grave disadvantage that they require exceptional skill and that the matching of shades to a given sample is a matter of some difficulty.

The aforesaid difficulties are particularly pronounced in the case of cellulose ester or ether materials owing to the substantial absence of any direct dyeing unitary dyestuffs capable of yielding black or other very dark shades thereon. If therefore it is desired to produce such dark shades by direct dyeing methods, it has been essential to employ very large proportions of mixtures of brightly dyeing dyestuffs. Thus, black shades have been produced by the application of a mixture of direct dyeing blue, red and orange or yellow dyestuffs in which the blue predominates. Such dyeings are particularly prone to lack fastness to rubbing.

I have now found that by incorporating in textile materials a dark colored pigment of such character and in such proportion as to yield thereon a grey, drab or other dark shade, valuable materials may be produced. By subsequently dyeing these materials by direct dyeing methods a wide range of valuable dark colorations may be produced using only relatively small quantities of the direct dyeing dyestuffs.

This new method is of especial value for the

production of dark shades upon artificial filaments of cellulose esters or ethers, for, as indicated above, there is for these materials a marked lack of direct dyeing dyestuffs inherently capable of yielding deep shades thereon. Further, the incorporation of the pigment is particularly easy in the case of these materials, as the operation may readily be effected by way of the spinning solutions from which the materials are produced.

The pigments employed are preferably such as impart to the materials neutral shades, that is yield materials which absorb a proportion of light of each wave-length and do not to any great extent preferentially reflect light of any particular wave-length. Such a result is obtainable for instance by employing carbon black or magnetic oxide of iron as the pigment. These neutral shades are of particular value in that by applying relatively small quantities of different dyestuffs thereto, an extremely wide range of deeply colored materials may be produced from a single material pigmented to a definite degree. Thus, in order to produce black shades, small amounts only of blue, red and yellow need be applied to the pigmented material. Again, by the subsequent application to the same material of green or a mixture of blue and yellow dyestuffs, there may be produced a series of olive greens, khakis, drabs and the like. Where yellows, oranges and reds are applied shades varying from yellow-brown to chocolate may be obtained, while purple, violet, and the like produce deep wine shades such for example as bordeaux, maroon, etc. All of these shades are produced more economically than they would be produced by the use of the requisite proportions of direct dyeing dyestuffs only, while the reduction in the amount of dyestuff necessary reduces danger of the dyed material not being fast to rubbing. Moreover, as the dyeing process proper is a direct one, the matching of the dyeings to given samples is easy.

It will be appreciated from the foregoing that for commercial requirements it is not essential, in order to obtain a satisfactory range of deep shades, to manufacture more than a very limited number of pigmented materials. In fact one or two materials pigmented to suitable greys or like neutral tints will be found sufficient to cover practically all commercial requirements as regards dark shades.

As previously indicated the invention is of particular importance in connection with the production of deeply colored cellulose ester and ether

materials, more particularly on account of the lack of inherently dark dyestuffs for these materials. As examples of such cellulose esters or ethers especial mention may be made of cellulose acetate and of other organic acid esters of cellulose, for example cellulose formate, propionate and butyrate, also ethers of cellulose e. g. ethyl and benzyl cellulose. The invention is not, however, limited to the treatment or production of cellulose ester or ether textile materials, as it may be applied to cellulose esters or ethers in other forms, for example as ribbons, straws, or films or like products having a large surface in relation to their mass. The processes of the invention may also be applied to textile materials generally, whether natural or artificial, and especially to such artificial filaments as may be prepared by extrusion of appropriate solutions for example regenerated cellulose filaments prepared from viscose.

The pigments incorporated in the materials may be of either organic or inorganic character. Again the desired shade may be secured either by the use of substances inherently possessing the desired hue or by the use of mixtures of substances of such character and in such proportion that the mixtures have the desired hue. For example the pigments may be colloidal metals or metal compounds or finely divided carbon. Again, they may be azo compounds, for example unsulphonated azo compounds obtainable from diazo compounds and arylamides of hydroxy carboxylic acids of the benzene, naphthalene or other series, or insoluble sulphur dyestuffs or vat dyestuffs of the anthraquinone or other series, or aniline black, or other pigment dyestuffs such as have little or no direct affinity for cellulose esters or ethers. As indicated previously magnetic oxide of iron and carbon black have been found of particular value for they yield desirable shades and possess in a high degree the property, very desirable in these pigmenting materials, of resistance to chemical agencies. Thus they are unaffected by bleaching or stripping operations, or by oxidizing or reducing discharges such as are used for the production of pattern effects upon textile materials.

These substances may be incorporated in the materials at any convenient stage of the production of the latter. Thus for example not only may they be incorporated in the spinning solutions from which the filaments are spun, but they may be applied for example as fine dispersions to the finished materials prior to dyeing. Such dispersions may contain any other desired ingredients such for example as solvents or swelling agents to soften and/or swell the material. Again, the pigments may be actually formed in the material. Thus for example a material may be colored a grey color by the oxidation of aniline, p-amino-diphenyl-amine, or other suitable aromatic compound thereon. Inorganic pigments may similarly be formed in the materials by appropriate reactions.

As indicated previously, the proportion of pigment employed is such as to yield a grey, drab or other dark shade. In order to produce cellulose acetate filaments suitable for coloration in deep shades of brown, green or navy, about 0.5-0.75% of carbon black or 3-4% of magnetic oxide of iron based on the weight of the cellulose acetate may be employed. Again, for materials to be colored in substantially black shades, about 0.8-1.5%, e. g. 0.8-1.0%, of carbon black may be employed. In the latter case the pigmented ma-

terial is of a deep grey shade and readily yields a variety of reddish-blacks, greenish-blacks, bluish-blacks etc., by direct dyeing or printing with relatively small proportions of suitable direct dyeing dyestuffs.

If desired, waste cellulose derivative materials which already contain suitable pigments, e. g. materials dyed with aniline black or with insoluble azo dyestuffs obtained from diazo compounds and arylamides of hydroxy carboxylic acids, may be dissolved in a suitable solvent such for example as acetone, the pigment concentration of the solution adjusted if requisite by the addition of new cellulose acetate or otherwise, and the solutions spun to form filaments. These filaments or materials made therefrom may then be dyed in the same way as the pigmented materials already described.

For the production of black or other dark colorations on the pigmented materials the requisite blue, red and yellow or orange or other dyestuffs may be water soluble and applied to the materials directly from aqueous solution or water insoluble and applied from aqueous dispersions. The aqueous dispersions where employed may be prepared in any desired manner, for example with the aid of dispersing agents. These dispersions may contain assistants, swelling agents or any other desired ingredients to aid the coloration of the materials.

The coloring matter may be applied either uniformly or locally according to the effects required. Further if desired discharge effects may be produced with the aid of appropriate discharging agents applied before or after the coloring matter. The discharges may contain coloring matters which will, in conjunction with the pigment of the material if the latter resists the discharging agent, yield dark shades different from the ground shades.

Textile fabrics may, in accordance with the invention consist of pigmented filaments of uniform shade or of pigmented filaments of different shades or in part of pigmented filaments and in part of non-pigmented filaments. Thus for example, grey pigmented filaments may be twisted with uncolored filaments and/or with filaments of another shade of grey and the yarns so obtained woven into a fabric. On dyeing, cross dyed effects may be obtained. Similarly grey yarn may be woven with uncolored yarn of the same or different material to form a fabric which when dyed exhibits still other cross dyed effects.

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

Example 1

A cellulose acetate spinning solution is prepared containing 25% of cellulose acetate and 0.6-0.7% of a carbon black (based on the weight of the cellulose acetate) of an average particle size of 1-2 microns. This solution is spun into filaments by a dry-spinning process and in this manner material of a grey color is obtained.

This grey material is then dyed from a 30:1 soap bath containing in dispersion coloring matters having direct affinity for cellulose acetate. The material is entered into the bath at a relatively low temperature and the temperature is then gradually raised to 70-80° C., dyeing being continued until the desired shade is achieved. The materials are then withdrawn from the dye-bath, washed, dried and finished in the usual

manner. The following table shows some shades obtainable:

	Dyestuff	Shade obtained
5	(a) 0.10 to 0.15% 1-amino-2-methylantraquinone	Nigger brown
	(b) 0.60% 4-nitro-2-methoxy-benzene-azo-di-ethylaniline	Deep Maroon
10	(c) 0.50% 1:4-di-(methyl-amino)-anthraquinone and 0.35% benzeneazo-benzeneazo phenol	Deep bottle green
15	(d) 2.0% 1-amino-4-anilido-5-oxyanthraquinone (see U. S. application S. No. 655,614 filed 7th February, 1933)	Deep navy blue

Example 2

Cellulose acetate yarn is prepared in the manner described in Example 1, but for the carbon black is substituted 3.5% of very finely divided magnetic oxide of iron (based on the weight of the cellulose acetate).

The yarn so obtained or a fabric prepared therefrom is then dyed in a 30:1 soap bath containing 0.45% of para-nitro-benzene-azo-paraxylidine in a state of fine dispersion. Dyeing is commenced at a low temperature and gradually raised to 70-75° C., being continued until the desired shade has been obtained. In this manner the material assumes a rich brown shade, whereas the azo dyestuff employed normally yields bright orange shades on cellulose acetate.

Example 3

Cellulose acetate yarn containing carbon black or magnetic oxide of iron is prepared in the manner described in Example 1 or 2. This yarn is then woven into a warp of artificial silk prepared from viscose.

The resulting mixed fabric is then dyed in a solid shade of deep brown very suitable for lining purposes by means of a mixture of 1-amino-2-methyl anthraquinone and Chlorazol Nigger brown. By substituting for the aforementioned dyestuff mixture a mixture of 4-amino-1-oxy anthraquinone and Chrysophenine G, the same fabric is dyed in two colors, the cellulose acetate deep puce and the viscose yellow.

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

1. Process for the production of deeply colored cellulosic filaments, which comprises incorporating in a cellulosic spinning solution particles of a pigment of such nature and in such proportion as to impart to the filaments formed therefrom a neutral shade, spinning such solution into filaments and thereafter coloring the filaments with dyestuffs.

2. Process for the production of deeply colored organic derivative of cellulose filaments, which comprises incorporating in an organic derivative of cellulose spinning solution particles of a pigment of such nature and in such proportion as to impart to the filaments formed therefrom a neutral shade, spinning such solution into filaments and thereafter coloring the filaments with dyestuffs.

3. Process for the production of deeply colored cellulose acetate filaments, which comprises incorporating in a spinning solution of cellulose acetate finely divided magnetic oxide of iron in proportion sufficient to impart a grey color to the filaments formed therefrom, spinning such solution into filaments, and thereafter dyeing said filaments with dyestuffs having direct affinity therefor.

4. Artificial filaments having a deep color due to the presence therein of a dyestuff having a direct affinity for the filaments and of particles of a pigment uniformly distributed throughout said filaments and of such nature and in such proportion as to impart a neutral shade to the filaments in the absence of the dyestuff.

5. Artificial filaments of organic derivatives of cellulose having a deep color due to the presence therein of a dyestuff having a direct affinity for the filaments and of particles of a pigment uniformly distributed throughout said filaments and of such nature and in such proportion as to impart a neutral shade to the filaments in the absence of the dyestuff.

6. Process for the production of deeply colored filaments of organic derivatives of cellulose, which comprises spinning filaments of organic derivatives of cellulose from solutions containing particles of an inorganic pigment of such nature and in such proportion as to impart to the filaments a grey shade and thereafter coloring the filaments with dyestuffs having direct affinity therefor.

7. Process for the production of deeply colored cellulose acetate filaments, which comprises spinning cellulose acetate filaments from solutions containing particles of an inorganic pigment of such nature and in such proportion as to impart to the filaments a grey shade and thereafter coloring the filaments with dyestuffs having direct affinity therefor.

8. Process for the production of deeply colored cellulose acetate filaments, which comprises spinning filaments from a solution of cellulose acetate containing finely divided carbon in proportion sufficient to impart a grey color to the filaments and thereafter dyeing said filaments with dyestuffs having direct affinity therefor.

9. Artificial filaments having a deep color due to the presence therein of a dyestuff having direct affinity therefor and of particles of carbon in such proportion as to impart a grey shade to the material in the absence of the dyestuff.

10. Cellulose acetate artificial filaments having a deep color due to the presence therein of a dyestuff having direct affinity for cellulose acetate and of particles of carbon in such proportion as to impart a grey color to the material in the absence of the dyestuff.

11. Cellulose acetate artificial filaments having a deep color due to the presence therein of a dyestuff having direct affinity for cellulose acetate and of particles of magnetic oxide of iron in such proportion as to impart a grey color to the material in the absence of the dyestuff.

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