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COLORED CELLULOSE MATERIAL

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The U. S. Patent 1,448,251 discloses a process for the manufacture of salts of acid sulphuric acid esters of leuco vat dyestuffs. These ester salts are water soluble, stable derivatives, easily 5 reconvertible into the corresponding vat-dye-
stuffs by means of acid oxidation. They are already being used for dyeing and printing textile fibres and other materials (see for instance U. S. Patent 1,575,958 and others).

10 The present invention refers to a process for the direct production of dyed, regenerated cellulose known as viscose in any form (threads, ribbons, film, etc.) basing on the principle of dyeing same with ester salts of leuco-vat dyestuffs.

15 Viscose, a kind of artificial silk, results, when cellulose, by treatment with caustic soda lye and carbon disulphide, is transformed into an aqueous alkaline solution of sodium cellulose-xanthogenate and this solution is pressed together with any 20 required addition through a spinning apparatus into an acid bath for coagulating purposes, whereby the wholly or partially hydrated cellulose is regenerated in the form of a thread or any other form. According to the present invention 25 the solution of an estersalt of a leuco vat dyestuff is added to said aqueous, alkaline sodium cellulose-xanthogenate mass (viscose mass) as a rule in any phase of the process previous to coagulation.

30 The mass is well kneaded and the dyeing in the regenerated cellulose mass developed after or during the coagulation process, by means of acid oxidation. This development of the dyeing may be performed in different ways:

35 (a) The viscose mass contains the ester salt. First the cellulose is regenerated in the coagulation bath. Afterwards in a second bath the dyeing is developed by means of acid oxidation.

(b) The viscose mass contains the ester salt. 40 Coagulation and development are performed by adding the oxidizing agent already to the acid coagulation bath simultaneously in the same bath.

45 (c) To the viscose mass is added besides the ester salt of a leuco vat dyestuff, at the same time, a suitable oxidizing agent, inactive in an alkaline medium, but active in an acid medium, such as for instance sodium nitrite. In the coagulation bath therefore coagulation of the cellulose and development of the dyeing take place simultaneously.

50 The production of dyed cellulose material by adding dyestuffs directly to the viscose mass has already been suggested. Such processes are of little practical importance, since not all dyestuffs are sufficiently resistant against the alkali present in the viscose mass, or against the rather strong acid treatment—even at high temperatures—in the coagulation bath. It was therefore necessary 55 to make a selection. The remaining and to-day

employed dyestuffs do not possess the fastness properties of vat dyestuffs. With regard to the use of vat dyestuffs in the vatted form, such an addition to the viscose mass would meet with difficulties. Thus, for instance a premature oxidation of the leuco vat dyestuff in the alkaline viscose mass or the use of an excess of a reducing product like hydrosulphite, in order to obviate premature oxidation, would have a detrimental effect during the coagulation process.

5 10 In the case of the present process, the above mentioned difficulties do not exist. The ester salts resist the various treatments with strong alkalies and acids etc. A cellulose material dyed with vat dyestuffs shows the wellknown fastness properties.

15 The present process allows the production of special dyeing effects. When artificial silk is spun, as a rule several individual filaments are united to a thread of the desired standard. 20 These individual filaments may be dyed with different ester salts, or dyed and white individual filaments may be united. In this way particular effects are obtained.

25 As the ester salts are soluble in water, it is possible to remove same superficially from a cellulose material of any form (thick thread or ribbon etc.) containing undeveloped estersalt, by means of a suitable treatment with water. During the subsequent development of the dyestuff 30 by oxidation, there results, as a strange effect, that the cellulose material is either dyed stronger in the inside than on the surface, or not at all on the surface and only in some parts inside. Such effects cannot be obtained when working 35 according to the dyeing process known so far. It is, of course, also possible to completely remove an ester salt from the cellulose material by such a water treatment. According to the present process further effects should be obtainable with 40 the help of the wellknown printing-reserve-discharge-process for ester-salts of leuco vat dyestuffs.

45 The invention is illustrated, but not limited by the following examples:

Example 1

A solution of the ester salt of leuco indigo corresponding to 20 grs. of indigo and sodium cellulose-xanthogenate corresponding to 1 kg. of spun 50 viscose fibre are thoroughly kneaded together until a uniform mixture is obtained. This mass is pressed by means of the ordinary spinning apparatus into a coagulation bath which contains sulphuric acid of 18° Bé. and is kept at a temperature of 40—50° C. The thus obtained viscose threads—cellulose-material—are wrung out and treated in a bath containing 35 grs. of sulphuric acid of 66° Bé. and 4 grs. of sodium-nitrite per litre, at ordinary temperature for 1/4—1/2 minute, 55 60

whereby development of the dyeing takes place. The dyed goods are rinsed, after-treated in a bath containing alkali, rinsed again and finished.

5 *Example 2*

In a similar way, as described in Example 1, a solution of an ester salt of leuco-6:6'-diethoxythioindigo is mixed thoroughly with the viscose mass. This mass is pressed through the spinning apparatus into a bath containing sulphuric acid of 18° Bé. and 4 grs. of sodium nitrite per litre and which is kept at a temperature of about 40° C. Coagulation of the mass and development of the orange-dyeing takes place simultaneously. 10 The dyed goods are rinsed, after-treated in an alkaline bath, rinsed again and finished.

15 *Example 3*

20 As described in Example 1, a solution of the estersalt of leuco-indigo is kneaded with the viscose mass. This mass in form of a thick thread or a ball is brought to coagulation. By washing with cold water the undeveloped ester salt can 25 be removed completely up to a desired depth of the material (this can be ascertained by trials). After development in an acid oxidizing bath the surface of the material will appear colorless and transparent, whereas the inner part is dyed.

30 *Example 4*

35 5 grs. of a paste containing 18% of the easily soluble ester salt from 3:3'-dichloro-1:2:2':1'-dianthrquinoneazine (see U. S. Patent No. 1,999,477) are dissolved in 30 litres of a viscose mass, the mass is spun as usual and the threads are coagulated. During coagulation the threads 40 become red-violet shaded. The spinning cakes obtained are developed either by a passage through a weak bichromate bath, or by treatment in a nitrite bath.

45 (a) *Development with bichromate.*—The constitution of the developing bath may for instance be the following one:

	Grams
Sodium bichromate	0.5
Sulphuric acid of 66° Bé	36
50 Ammonium vanadate solution (1:1000)	20
Oxalic acid cryst	2
Per litre of water.	

The threads are treated in this bath for 1 minute at about 40° C.

55 (b) *Development with nitrite.*—The constitution of the developing bath may be the following one:

	Grams
60 Sulphuric acid of 66° Bé	36
Sodium nitrite cryst	3
Ammonium vanadate solution (1:1000)	20
Oxalic acid cryst	2
Per litre of water.	

The threads are treated in this bath for 1 minute at 35-45° C.

5 The dyeing is completely developed and one obtains a bright, light blue. The dyestuff may easily be over-oxidized and thus produce a somewhat greenish shade. However, in the subsequent operations, necessary for finishing the goods, as for instance desulphuration, which may take place in a bath, having a slightly reducing effect, the over-oxidized dyestuff is reduced again 10 to normal and finally one obtains the desired, bright, pure, light blue shade.

15 The ester salt used in this example can be replaced by the ester salt from 1:2:2':1'-dianthrquinoneazine. In this case the resulting threads are dyed in the shade of indanthrene.

20 In a similar manner cellulose threads may be dyed with ester salts from other anthraquinone-azo compounds, such as for instance those obtained from diazotized β -aminoanthraquinone as 25 azo-compound, and β -naphthol or the various anilides of β -oxynaphthoic acid as coupling compounds.

What I claim is:—

1. A process for manufacturing colored cel- 25 lulose material, which consists in adding to an alkali cellulose-xanthogenate solution in any phase previous to coagulation a solution of an ester salt of a leuco vat dyestuff, performing the coagulation in a known manner and developing 30 the dyeing in the regenerated cellulose by acid oxidation.

2. A process for manufacturing colored cel- 35 lulose material, which consists in adding to an alkali-cellulose-xanthogenate solution previous to coagulation a solution of an ester salt of a leuco vat dyestuff, performing simultaneously coagulation of the mass and development of the dyeing in the regenerated cellulose in an acid bath 40 containing an oxidizing agent.

3. A process for manufacturing colored cel- 45 lulose material, which consists in adding to a sodium-cellulose xanthogenate solution a solution of an ester salt of a leuco vat dyestuff, performing coagulation in a known manner and developing the dyeing in the regenerated cellulose by treating the latter in a bath containing bichromate and acid.

4. A process for manufacturing colored cel- 50 lulose material, which consists in adding to a sodium cellulose xanthogenate solution a solution of an ester salt of a leuco vat dyestuff, pressing the mixture into a bath containing sulphuric acid and sodium nitrite, whereby simultaneously co- 55 agulation of the cellulose and development of the dyeing therein take place.

5. The herein described colored cellulose material obtained by adding to an alkali-cellulose-xanthogenate solution a solution of an ester salt of a leuco vat dyestuff, performing coagulation in a known manner and developing the dyeing in the regenerated cellulose by acid oxidation.

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