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PROCESS OF DYEING ARTIFICIAL TEXTILE MATERIALS FROM CELLULOSE DERIVATIVES

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The present invention relates to the dyeing of artificial textile material from organic cellulose derivatives and more particularly to the dyeing of such textile material with diazo compounds and naphthol derivatives, especially those of the Naphthol AS series.

It is an object of the present invention to provide a process by which cellulose ester or ether silk may be dyed in deep tints with diazo and azo components, at least one of which has insufficient affinity for cellulose ester or ether silk.

A further object of the invention is to dye or print artificial textile materials or films from organic cellulose derivatives which contain polymeric or resinous additional components of hydrophil nature. Further objects will be apparent from the detailed specification following hereafter.

It is known that artificial textile materials, particularly fibres produced from organophilic highly polymeric bodies, above all those from cellulose derivatives, cannot be dyed directly with many valuable azo- and diazo-component in the manner usual for other fibres. The components of the Naphthol AS-series penetrate but little into the structure of for instance acetate artificial silk. This is also true for the diazonium salts of which only certain representatives, for instance the diazonium salt from 4-methoxy-4'-amino-diphenylamine yield feeble dyeings which have hitherto had practically no value. There have been various proposals for improving the affinity of these materials for naphthols. Thus, it has been found that a series of naphthols of comparatively low molecular weight are better adsorbed in the form of their acyl compounds, for example the acetyl compounds or the dialkylamino-carbaminyl compounds, by hydrophobe fibres such as acetate artificial silk, whereupon they may be coupled with diazo compounds produced on the fibres. In this manner strong tints of yellow to blue are obtained, but the number of useful combinations remains limited. Especially is it impossible to obtain green dyeings with derivatives of commercial naphthols. There is a known process by which the affinity of the naphthols is considerably improved by the addition of organic bases, for example guanidine. However, in this new process, which gives very good results, the choice of components is still limited; in particular it is impossible to substitute for diazonium compounds produced on the fibre diazo salts in solution. The use of the process in printing, therefore, presents difficulties. To a certain extent acetate artificial silk may be saponified in order to improve its affinity for Naphthol AS components. In this case, however, the total dyeing behaviour of the fibre is profoundly altered, so that this process must in most cases be excluded. The dyeing character is indeed much less altered if the saponification is effected in permutoid manner, for example with gaseous ammonia. In this case, however, there is the disadvantage that the wet tenacity is considerably diminished without, on the other hand, attaining by moderate saponification a sufficient adsorptic capacity of the fibre.

The present invention is based on the observation that very good dyeings and printings can be obtained even when the relative wet tenacity is considered, if the structure used contains embedded in a relatively hydrophobe fundamental material such as acetyl cellulose or ethyl cellulose a hydrophil substance, i. e., an additional component of highly polymeric and or resinous nature, which has a high swelling capacity. In particular, such resinous substances are effective which contain salt-forming acid groups, especially carboxyl groups, in abundance. Products having basic residues stable to alkali are less effective in alkaline medium unless hydrophil radicals like hydroxyl or carboxyl groups are present. Quaternary derivatives obtainable by alkylating behave more favorably. Also such resinous additional components which owe their hydrophil character merely to the presence of hydrophil groups which do not form salts, especially hydroxyl groups, are not to be excluded. The hydrophil additional components may be pre-formed in the fibre or they may be formed or liberated subsequently by an after-treatment. In this connection reference may be made to my United States patent applications Ser. Nos. 41,500, filed September 20, 1935, 47,638, filed October 31, 1935, 57,524, filed January 4, 1936, in which the production of artificial fibres containing additional substances which are suitable for the purpose of this invention is described. Those fibres have been found especially useful which contain basic groups in addition to acid groups. The following list contains a few additional substances useful for the process of this invention.

1. *Bodies having acid groups.*—Polymerization products from unsaturated acids or mixed polymerizates with acid components, for example acrylic acid or maleic acid or maleic acid with vinyl compounds capable of polymerization, for instance vinyl esters, vinyl ethers, vinyl ketones,

acrylic acid esters, acrylic acid nitrils, acrylic acid amides; ester acids of cellulose, for example mixed ester from acetyl and methyl cellulose with maleic acid, phthalic acid, diglycolic acid, strongly acid alkyd resins. Especially suitable are the mixed polymerizates which contain maleic anhydride or other β-unsaturated carboxylic anhydrides, since these substances can be spun particularly easily with other highly polymeric bodies, for example acetyl cellulose.

2. *Bodies with basic groups.*—Polyacrylic acid-ω-diethyl-amino-ethylamide alkylated on the fibre; basic especially quaternary derivatives of polyglycide, polyvinyl chloracetate which has been caused to react on the fibre with bases such as pyridine or trimethylamine.

3. Products without salt-forming groups which in themselves or owing to the action of an alkaline saponifying agent are hydrophil and effective in the sense of this invention are, for example, formic acid esters of cellulose or mixed esters and mixed ethers with formic acid esters, cellulose nitro-acetate, cellulose nitro-ethylether, polyvinyl formate, polyvinyl ethylether. In so far as saponification of such substances comes into question, this may occur before or during the dyeing, there being preferably added a saponifying agent which has a certain affinity for the fibre, for example cyclo-hexylamine. In the case of nitro-compounds, sulfides of amines or mercapto-alkyl amines are applicable.

The new process for dyeing and printing is of general application. With correct adjustment of the hydrophobe and hydrophil constituents practically all naphthols and salts thereof and also the stabilized diazo compounds to be found on the market and their mixtures with naphtholates may be used.

The dyeings obtainable partly have an astonishing depth of tone, for example by printing with naphthols in a ground printing process on acetate artificial silk containing 54.5 per cent of bound acetic acid with an addition of 10 per cent of the mixed polymerizate from vinyl methyl-ether and anhydride the same depth of tint is obtained as in the case of viscose, so that mixed fabrics of these fibres in the warp and viscose crepe in the weft can be printed in uniform tints by this very important process with a high utilization of the dyestuff, which it is known is not possible with ordinary acetate artificial silk unless the goods have been profoundly saponified previously. In the necessary steaming which follows in the process the acetate silk in the added polymerizate remains lustrous, whereas acetate artificial silk without such addition suffers in its lustre and indeed may become matt. This phenomenon is generally undesired, since matt articles are preferably produced from material which is dyed during the spinning owing to the fact that the quality of the final product is better ensured by this process. Interesting effect possibilities are afforded by the combination of the two materials for reason of this difference in behaviour. Thus, not only effects graded in depth of shade or color-white effects, but also matt-lustre patternings, are possible. This, however, does not exhaust the possibilities at the disposal for patterning. For example, by including basic dyestuffs multi-color effects, if desired in matt and lustre, may be obtained.

The dyeing process follows the usual prescriptions. In general it is recommended that known textile assistants, for example oleyl polyglycol should be used in the developing baths; in the case of artificial textile materials with acid groups additions of urea and urea derivatives, for example thiourea, ethylene thiourea, and of pyridine bases have been found useful. Also a pretreatment with such substances or even a preliminary soaping has proved remarkably advantageous, especially when rapid and thorough reaction is necessary.

According to the suggestion mentioned above (page 1, lines 45 to 55) it is possible to add to the solutions of naphthol organic bases, which facilitate the adsorption of the components of the fibers, especially if the proportion of the hydrophil component viz. the number of hydrophil groups is comparatively small. In principle, however, these additions are not essential.

The dyeings obtainable according to the invention with the components of the Naphthol AS series exhibit generally very good fastness properties especially with regard to washing, fulling, topdyeing and irradiation. The dyeings upon acetate artificial silk containing acid components, e. g., a mixed polymerizate from vinyl alkylether and maleic anhydride are as a rule faster to light than the same combinations upon cotton like the correspondent dyeings on wool.

In textile material from cellulose derivative fibres containing hydrophil components with acid groups, very good results are obtained if the goods—preferably after an alkaline pretreatment—are treated in the first phase with solutions of diazonium salts and are then—if desired after the impression of a reserve or pattern-like exposure to light—developed with azo-components of substantive character. In this manner photographic prints may be obtained in various shades, a feature which hitherto was impossible or at least only limitedly possible with acetate silk or similarly hydrophobe fibres. According to the suggestions of the prior art, which require diazotizing on the fibres, it was impossible to obtain a clear white in the light parts. According to the present process this is attained without difficulty.

The following examples illustrate the invention:

Example 1

A satin fabric consisting of acetate artificial silk having an addition of 12.5 per cent of polyvinyl chloracetate which has been treated for 8 hours at 70° C., with 3 mols of pyridine vapour calculated on the halogen present is printed simultaneously with a corresponding viscose artificial silk fabric with:

Schultz, Farbstofftabellen, 7th edition

8% Rapidogen Yellow G, Vol. II, page 181,
8% Rapidogen Orange IRR, Vol. II, page 181,
8% Rapidogen Scarlet IL, Vol. II, page 181,
6% Rapidogen Red violet RR,
4.5% Rapidogen Violet B, Vol. II, page 181,
4.5% Rapidogen Blue B, Vol. II, page 181,
6% Rapidogen Green B, supplement volume, page 123,
6% Rapidogen Brown JB, supplement volume, page 123,

pure and diluted 1:1. In all cases deep tints are obtained which in the case of the last four dyestuffs come near to the depth on viscose. In the case of the first four dyestuffs the prints are indeed weaker but always of good useful depth.

Similar but more brilliant prints are obtained if acetate artificial silk is used which contains 7 per cent of polyvinyl chloracetate aminated with

pyridine on the fibre and 7 per cent of the mixed polymerizate from 1 mol vinyl ethylether and 1 mol maleic anhydride.

Example 2

A satin fabric from ordinary acetate artificial silk and a satin fabric from an acetate silk having an addition of 5 per cent of the mixed polymerizate from vinyl methylether and maleic anhydride (1:1) are grounded with 12 grams per liter of Naphthol AS (Schultz, Farbstofftabellen, 7th edition, see Fast Scarlet GG. Base, Vol. I, page 30) after the usual de-sizing with soap without intermediate acidifying and then printed with Fast Orange Salt GC new (Schultz, Farbstofftabellen, supplement volume, page 92) (50 grams per kilo of paste), Fast Red Salt TR (Schultz, Farbstofftabellen, 7th edition, Vol. I, page 694) (50 grams per kilo of paste) and Variamine Blue Salt B (Schultz, Farbstofftabellen, 7th edition, Vol. II, page 224) (20 grams per kilo of paste). In all cases, even in dilution of 1:3, deep dyeings which practically agree in depth with those upon viscose are obtained. The comparison dyeings on ordinary acetate silk have only a fraction of the depth.

When a fabric having only 2.5 per cent of the mixed polymerizate is used under the same conditions, there is still obtained a quite deep tint which comes close to that upon viscose. If the last named goods are acidified after de-sizing the depth of the print falls off, but it always exceeds considerably that of the print on ordinary acetate silk. The improvement achieved, therefore, is quite considerable.

Example 3

A satin fabric which consists in the warp of alternate stripes of ordinary acetate artificial silk and stripes of an acetate artificial silk having an addition of 10 per cent of the mixed polymerizate from vinyl methylether and maleic anhydride (1:1) is grounded as described in the preceding example with Naphthol AS (Schultz, Farbstofftabellen, 7th edition, see Fast Scarlet GG. base, Vol. I, page 30), Naphthol ASOL (Schultz, Farbstofftabellen, 7th edition, Vol. I, page 30) and Naphthol ASD (Schultz, Farbstofftabellen, 7th edition, Vol. I, page 30), each 12 grams per liter. The grounded fabrics are then printed with Fast Orange Salt GC new (Schultz, Farbstofftabellen, 7th edition, supplement volume, page 92) (50 grams per kilo of paste), Fast Red Salt TR (Schultz, Farbstofftabellen, 7th edition, Vol. I, page 694) (50 grams per kilo of paste), and Variamine Blue Salt B (Schultz, Farbstofftabellen, 7th edition, Vol. II, page 224) (20 grams per kilo of paste), and in the case of Naphthol ASD also with Fast Orange Salt RD (Schultz, Farbstofftabellen, 7th edition, supplement volume, page 92) (50 grams per kilo of paste). The prints on the stripes with added polymerizate correspond in depth of tint fully with those of comparison prints on viscose. Ordinary acetate artificial silk is only feebly colored and, moreover, on steaming becomes matt. Thus, there is obtained simultaneously graded effects of depth of print and a matt-lustre effect, both in the white and in the colored portion.

Example 4

An acetate artificial silk made from 92.5 parts of acetyl cellulose having an acetic acid content of 51.5 per cent and 7.5 per cent of partially saponified polyacrylic acid methylester by the dry spinning process in a solution of acetone and methanol 60:40 is preliminarily washed with 2 grams of the sodium salt of oleyl-methyl-taurine per liter at 20° C. for 10 minutes and then grounded in liquor ratio 1:30 with a solution prepared by the cold dissolving process of 3 grams of Naphthol ASOL (Schultz, Farbstofftabellen, 7th edition, Vol. I, page 30) per liter. For developing the silk is immersed for 10 minutes in a solution cooled to 10° C. of 11 grams of the commercial dyeing salt of 20 per cent strength from Fast Red AL-Base (Schultz, Farbstofftabellen, 7th edition, Vol. II, page 95). The goods are finally soaped and treated with acid. In this case deep dyeings are obtained. The dyeing is still somewhat deeper if the silk is soaped before grounding. Comparative samples of ordinary acetate artificial silk simultaneously treated are dyed only quite insufficiently.

Example 5

An acetate artificial silk containing 12.5 per cent of the mixed polymerizate from vinyl formate and maleic anhydride is preliminarily soaped and dyed in manner similar to that described for the silk used in Example 4. The dyeing is still more intense. An acetate silk having an addition of 7.5 per cent of polyacrylic acid diethyl-amino-ethylamide simultaneously dyed in the same manner is only comparatively little more colored than ordinary acetate artificial silk, because the hydrophil character of the fibre in an alkaline medium is only slight.

Example 6

A satin ribbon made from an acetate artificial silk containing 85 per cent of cellulose acetate having 54.5 per cent of bound acetic acid and 15 per cent of cellulose acetate-isononylene-succinic acid ester is thoroughly de-sized with 7 grams of soap per liter for 2 hours at 75° C. and then grounded with 3 grams of Naphthol AS (Schultz, Farbstofftabellen, 7th edition, see Fast Scarlet GG. Base, Vol. I, page 30) per liter for 15 minutes at 20° C. On development with 5 per cent of the commercial dyeing salt of 40 per cent strength from Fast Blue BB-Base (Schultz, Farbstofftabellen, 7th edition, Vol. II, page 91) at 10° C. there is produced a deep blue dyeing which becomes more greenish on soaping.

Example 7

A film of polyvinyl formal having a content of 20 per cent of the mixed polymerizate from vinyl methylether and maleic anhydride in ratio of 1:1 is grounded with 4 grams of Naphthol ASD (Schultz, Farbstofftabellen, 7th edition, Vol. I, page 30) per liter for 15 minutes at 20° C. After cold rinsing the film is developed at 10° C. in a liquor containing per liter 2 grams of the commercial dyeing salt of 40 per cent strength from Fast Red 3 GL Base (Schultz, Farbstofftabellen, 7th edition, Vol. II, page 94). Finally, the goods are soaped at 30° C. and soured.

Example 8

An acetate artificial silk having a content of 10 per cent of monomethyl-cellulose-nitrate is denitrated in the usual manner and grounded with 3 grams of Naphthol AS (Schultz, Farbstofftabellen, 7th edition, see Fast Scarlet GG Base, Vol. I, page 30) per liter at 20° C. for 10 minutes and finally rinsed cold. By developing with a a solution of the commercial dyeing salt of 20 per cent strength from Fast Red KB Base (Schultz,

Farbstofftabellen, 7th edition, Vol. I, pages 45 and 694) (12 grams per liter) there is produced a deep and fast red dyeing.

Example 9

An acetate artificial silk fabric containing 10 per cent of the mixed polymerizate from vinyl methylether and maleic anhydride in ratio of 1:1 is grounded with 3 per cent of the commercial salt of 40 per cent strength from Fast Red 3 GL Base (Schultz, Farbstofftabellen, 7th edition, Vol. II, page 94) for 30 minutes at 10° C., rinsed and cautiously dried. By printing the various commercial naphthols deep brilliant dyeings or printings are obtained.

Example 10

An acetate artificial silk having a content of 10 per cent of the fibre of denitrated monomethyl-cellulose-nitrate is preliminarily dyed with 2 per cent of 5-chloro-2-toluidine at 30–65° C., 20 per cent of sodium acetate being added at the finish. The fabric is then immersed in liquor containing per liter 4 grams of 2:3-hydroxy-naphthoic acid-5-chloro-ortho-toluidide and finally diazotized in the usual manner. There is obtained a deep red dyeing.

Example 11

A tightly woven satin fabric of an acetate artificial silk having 10 per cent of the mixed polymerizate from vinyl methylether and maleic anhydride in the ratio of 1:1 is grounded with 4 per cent of the commercial diazonium salt of 40 per cent strength from Fast Blue BB Base (Schultz, Farbstofftabellen, 7th edition, Vol. II, page 91) in the liquor ratio 1:50 for 10 minutes at 10° C. As a sensitizer the solution contains per 100 cc. 2.5 per cent of a solution of 0.01 per cent strength of Rhodamine B Extra (Schultz, Farbstofftabellen, 7th edition, Vol. I, page 365). After cautious drying the material is exposed at a low temperature under a photographic negative rich in contrast and the print is then developed with a solution of 4 grams of Naphthol AS per liter. Instead of the dyeing operation the diazo-salt solution may be applied by the padding process and the goods continuously dried. In this manner half-tone prints in any of the tints accessible with Naphthol AS components may be produced.

Example 12

100 grams of an acetate artificial silk from 90 parts of acetyl cellulose having an acetic acid content of 54.8 per cent and 10 parts of polyvinyl chloracetate which has been caused to react with 1 mol of pyridine in the gaseous phase, calculated on 1 atom chlorine (U. S. pat. appl. Ser. No. 41,500 filed September 20, 1935), are treated for half an hour at 50–60° C. with a dispersion containing per 2000 cc. of water 10 grams of the sodium salt of 2:3-hydroxy-naphthoic acid ortho-toluidide, 30 grams of pyridine, 16 cc. of concentrated ammonia and 10 grams of glue. After thoroughly centrifuging, the dyeing is developed with a solution buffered with sodium bicarbonate which contains 3 grams of 4-methoxy-diphenyl-amine-4-diazonium-chloride per liter for 1 half hour at 40–50° C. The usual soap follows.

There is produced a deep reddish blue dyeing which is considerably stronger than a comparative dyeing on usual artificial silk from acetyl cellulose of the above named content of acetic acid. The dyed acetate artificial silk may be used for example as effect threads.

The term "Naphthol AS compounds" includes the derivatives of beta-hydroxynaphthoic anilide. (The Condensed Chemical Dictionary, sec. edition, 1930, page 320).

What I claim is:

1. A process of dyeing textile materials comprising an organic hydrophobe cellulose derivative and having incorporated and fixed therein at least one hydrophil polymeric component selected from the group consisting of polymerized vinyl ethers, polymerizates and mixed polymerizates containing α-β-unsaturated acids, mixed polymerizates from maleic acid anhydride and vinyl compounds, alkyd resins containing free acid groups, ester-acids of polymeric hydroxy-compounds, polymerizates of the vinyl series containing basic nitrogen, basic amides of polymerized acrylic acids, polymeric alkylene imines, and mixtures of these substances—which process comprises treating said material with an azo- and a diazo-component of which at least one has insufficient affinity for said acid hydrophobe cellulose derivative.

2. A process of dyeing textile materials, which comprises impregnating a textile material from an organic hydrophobe cellulose derivative having incorporated and fixed therein as an additional component at least one hydrophil polymeric compound selected from the groups consisting of polymerized vinyl ethers, polymerizates and mixed polymerizates containing α-β-unsaturated acids, mixed polymerizates from maleic acid anhydride and vinyl compounds, alkyd resins containing free acid groups, ester-acids of polymeric hydroxy-compounds, polymerizates of the vinyl series containing basic nitrogen, basic amides of polymerized acrylic acids, polymeric alkylene imines, and mixtures of these substances with a Naphthol AS compound, and developing the dyestuff by treating said textile material with a liquid containing a diazo-compound.

3. A process of dyeing a textile material consisting substantially of an organic hydrophobic cellulose derivative having incorporated and fixed therein as an additional component a polymeric hydrophil compound selected from the group consisting of polymerized vinyl ethers, polymerizates and mixed polymerizates containing α-β-unsaturated acids, mixed polymerizates from maleic acid anhydride and vinyl compounds, alkyd resins containing free acid groups, ester-acids of polymeric hydroxy-compounds, polymerizates of the vinyl series containing basic nitrogen, basic amides of polymerized acrylic acids, polymeric alkylene imines, and mixtures of these substances, which process comprises treating said material with an alkaline agent, impregnating said material with the solution of a diazonium salt, and developing the coloring with a Naphthol AS compound.

4. A process of dyeing a textile fabric comprising fibers consisting substantially of an organic hydrophobe cellulose derivative and having incorporated and fixed therein an additional polymeric hydrophil component selected from the group consisting of polymerized vinyl ethers, polymerizates and mixed polymerizates containing α-β-unsaturated acids, mixed polymerizates from maleic acid anhydride and vinyl compounds, alkyd resins containing free acid groups, ester-acids of polymeric hydroxy-compounds, polymerizates of the vinyl series containing basic nitrogen, basic amides of polymerized acrylic acids, polymeric alkylene imines, and mixtures of these substances, which process comprises im-

pregnating said fabric with a diazonium salt, exposing said fabric to light in pattern-like manner, and developing the coloring with a liquid containing a Naphthol AS compound.

5. A process of dyeing textile materials, which comprises impregnating an acetate artificial silk having incorporated and fixed therein as an additional component a mixed polymerizate of maleic acid anhydride and a vinyl alkyl ether with a diazonium compound, and developing the coloring with a liquid containing a Naphthol AS compound.

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