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# UNITED STATES PATENT OFFICE

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## PRODUCTION OF PATTERN EFFECTS UPON TEXTILE FABRICS OR OTHER MATERIALS

George Holland Ellis, Spondon, near Derby, England, assignor to Celanese Corporation of America, a Corporation of Delaware

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This invention relates to a new process for the production of pattern or discharge or resist effects upon textile fabrics or other materials, the new process being of particular value in the treatment of fabrics or other materials made of or containing cellulose acetate or other organic esters of cellulose or made of or containing cellulose ethers.

According to the new process of the present invention, in the production of azo colouring matters on textile fabrics or other materials by diazotizing amines or amino colouring matters on the material and developing, "discharge" or "resist" effects are produced by treating the materials locally before diazotization and development so as to render the amines or amino colouring matters in selected areas incapable of forming colouring matters by diazotization and development. The developer components may be applied before the diazotization, for example together with the amines or amino colouring matters, so that upon diazotization development is effected simultaneously.

I have found that chlorates, chromates or other oxidizing discharges may be applied to the materials so as to render amines or amino colouring matters incapable of forming colouring matters by diazotization and development. Such a treatment of amines or amino colouring matters is entirely novel and constitutes a remarkable and valuable advance in the art of discharge printing.

On account of the ease with which amines may be incorporated in cellulose esters and ethers the processes of the invention are of particular value as applied to materials containing such cellulose derivatives. The invention is however applicable to the "discharge" of amino colouring matters and to the production of the pattern effects upon materials other than cellulose derivatives.

As examples of amino bases and amino colouring matters on the one hand, and developers or coupling components on the other hand, which may be used for the purpose of the present invention, the following may be instanced, though the listing of these examples implies no limitation of the invention thereto.

*Amino bases and amino colouring matters*

Metanitraniline
Paranitraniline
Paranitroorthotoluidine
Metanitroparatoluidine
Paranitroorthoanisidine
Metanitroorthoanisidine
Aminoazobenzene
Aminoazotoluene
Paraaminobenzeneazodimethylaniline
Paraaminobenzeneazoalphanaphthylamine
Orthomethoxybenzeneazoalphanaphthylamine
Dimethylaminobenzeneazoalphanaphthylamine
Benzidine
Tolidine
Dianisidine
Diaminodiphenylmethane
Diazamine Bordeaux B (Sandoz.)
Chlorazol black BH (Colour Index No. 401)

*Developers or coupling components*

Xylidines, cresidines, anisidines, phenetidines, metatoluidine, metaphenylenediamine, nitrometaphenylenediamine, alkyl-, aryl- or aralkylanilines, phenols, cresols, resorcinol, aminophenols or alkylamino-phenols, such as dimethylmetaaminophenol, α-or β-naphthylamines or alkyl derivatives thereof, or naphthylamine ethers, ω-oxy-ethyl-α-naphthylamine, γ-chlor-β-oxy-propyl-α-naphthylamine, (condensation of α-naphthylamine and epichlorhydrin), aminonaphthoic acids, amino-naphthols, or any compounds obtained by the acetylation or other acidylation of amino-groups in the said coupling components.

The aminoazo colouring matters to be used for discharge purposes according to the present invention may of course be applied as such or they may be produced on the material itself before the application of the discharge.

As oxidation discharges we find that chlorates or mixtures of chlorates and chromates give the best results. Any chlorates, for example alkali chlorates, such as sodium or potassium chlorate, or chlorates of other bases, for instance alumina, may be employed, preferably in conjunction with accelerators or catalysts, for example salts of iron, e. g. prussiates, or salts of vanadium. Assistants, for instance tartaric acid, citric acid, sodium citrate and the like, may also be employed. The concentration of the discharges and the conditions under which they are applied will be adjusted in accordance with the requirements of the particular amino base or amino colouring matter to be discharged. In general more vigorous conditions are required than those necessary to produce the ordinary oxidation discharges known in the art.

To obtain coloured discharges, colouring matters, which resist the action of the discharges sufficiently and also the diazotizing and development processes, may be incorporated in the discharge pastes or like compositions. As instances

of such resistant colours for oxidation discharges, particularly on cellulose esters and ethers, the following may be mentioned:—colouring matters of the pigment type (insoluble in water but soluble in oils, soaps, fats or the like), of the mineral pigment type and vat dyes of the anthraquinone series, e. g. m-nitraniline→Naphthol AS (β-hydroxy naphthoic acid anilide), p-nitraniline→β-naphthol or Naphthol AS, p-nitro-o-toluidine→β-naphthol or Naphthol AS, and p-nitro-o-anisidine→β-naphthol or Naphthol AS, Methylene blue (Color Index No. 922), Rhodamine 6 G extra (color Index No. 752), Chrome yellow (Color Index No. 1270), Lemon Chrome yellow, Guignet's green (Color Index No. 1292), and Vermilion (Color Index No. 1280). The vat dyestuffs of the anthraquinone series may be incorporated in the pastes or other compositions in the form of esters of their leuco compounds, while the mineral pigment colours may be applied in conjunction with albumens or the like. Many of the colouring matters commonly used for the colouration of cellulose ester materials, particularly colouring matters of the nitro-diarylamine series or of the amino anthraquinone series, may likewise be used. Care should be exercised, however, in the choice of dyestuffs of the α-amino anthraquinone series since some members of this class having a substituent, particularly hydroxyl or amino, in the para position to the α-amino group or insufficiently resistant to the action of oxidizing discharge preparations.

It has further been found that the acidylamino-anthraquinone colouring matters, owing to their resistance to the action of oxidizing agents, are particularly useful for incorporation in oxidizing discharge preparations, whether these preparations contain chlorates or chromates or any other oxidation discharges. The acidylamino-anthraquinones may contain in addition to acidylamino groups other substituent groups or atoms, such as hydroxy groups, alkoxy groups and halogen atoms. Of this group of colouring matters the aliphatic acidylamino-anthraquinones are of especial interest for use in coloured discharge preparations owing to their good affinity for cellulose ester and ether materials. The following are examples of such aliphatic acidylamino anthraquinones and the colourations yielded by them on cellulose esters and ethers:—

1-acetylamino-anthraquinone.....Yellow
1-propionylamino-anthraquinone.....Yellow
1-acetylamino-2-methyl anthraquinone..... Yellow (less green)
1 acetylamino-4-dyhroxy anthraquinone..... Golden orange
1-propionylamino-4-methoxy anthraquinone..... Golden yellow
1:4-di-(propionylamino) anthraquinone... Red
1-methylamino-4-acetylamino anthraquinone..... Reddish violet
1:4-di-(acetylethylamine) anthraquinone... Red
1:5-di-(acetylamino)-4:8-dihydroxy-anthraquinone..... Red
1-propionylmethylamino-4:5-dihydroxy-anthraquinone..... Red
1:4-di-(acetylmethylamino)-5:6-di-hydroxy-anthraquinone..... Violet
2-propionylamino-anthraquinone.....Pale greenish yellow

As indicated above the developer may be applied to the fibre together with the amino base or the like before the local application of the discharging agent, the final development being by means of nitrous acid. The materials before treatment with nitrous acid are preferably dried and aged or steamed.

The discharge effects may be obtained with any suitable means of local application, for example machine or hand-block printing, spraying, stencilling or the like.

As indicated above the most valuable results may be obtained according to the present invention on materials containing organic esters of cellulose, for example cellulose acetate, cellulose formate, propionate or butyrate, or the products obtained by the treatment of alkalized cellulose with esterifying agents (e. g. the product known as "immunized cotton" obtained with para-toluene sulpho-chloride) or containing cellulose ethers, for instance methyl, ethyl or benzyl cellulose or the corresponding condensation products of cellulose and glycols or other polyhydric alcohols. However, in addition to obtaining pattern effects on materials comprising cellulose esters and/or ethers, the processes of the present invention may be used to obtain effects on materials made of or containing other fibres, for instance cotton or the cellulosic type of artificial silk.

Effects may moreover be produced on mixed goods containing, for example, cellulose acetate or other cellulose esters and/or ethers in association with other fibres, for instance cotton or the cellulosic type of artificial silk. Furthermore, such mixed goods may be dyed differentially by utilizing the property of the cellulose ester portion of absorbing amines substantively from solution, in preference to their absorption by the other components. Differential or uniform shades may be obtained by means of colours having an affinity for the non-ester portion but which resist cellulose esters. According to the effect desired, such colouring matter for the non-ester portion of the mixed goods may be so chosen that they are either discharged by or resist the discharging agents employed; further they may if desired be selected so that they either resist or respond to the diazotization and development operations.

The following examples are intended to illustrate the invention but not to limit it in any way:—

*Example 1*

A fabric composed of cellulose acetate yarns is treated in a bath of volume ratio 50:1 with 0.5% of its weight of para-nitro-ortho-anisidine, previously dispersed by heating with sodium sulphoricinoleate. The dyeing is allowed to proceed for 1½ hours at 80° C. after which the fabric is washed and dried at a low temperature and further prepared for printing as desired. It is then printed by roller printing machine with a paste composed as follows:—

| | |
|---|---|
| 500 | grams gum arabic 1:1 |
| 190 | grams aluminium sulphate 1:1 |
| 90 | grams sodium chlorate |
| 120 | grams water |
| 25 | grams potassium ferricyanide |
| 75 | grams water |
| 1000 | |

After printing the material is dried and steamed in the "cottage" steamer for 15 minutes with steam at 5 lbs. pressure after which it is diazotized for half an hour in a cold 50:1 bath containing 5% of its weight of sodium nitrite and 16% of its weight of hydrochloric acid 28° **Tw.**

When diazotization is complete the fabric is washed well in cold water and developed with 2% of its weight of betaoxynaphthoic acid, after which it is rinsed, soaped lightly and otherwise treated and finished as desired or requisite. A white pattern is thus obtained on a deep pink ground.

*Example 2*

A fabric composed of cellulose acetate yarns is treated in a bath of volume ratio 50:1 containing 1% of its weight of dianisidine dispersed prior to adding to the dyebath in sodium sulphoricinoleate. After treating at 80° C. for 1½ hours the fabric is washed and dried and further prepared for printing as desired. It is then printed by a roller printing machine with a paste composed as follows:—

500 grams gum arabic 1:1
190 grams aluminium sulphate 1:1
90 grams sodium chlorate cryst:
120 grams water
25 grams potassium ferricyanide
75 grams water

1000

After printing the material is dried and steamed in the "cottage" steamer for 3 minutes with steam at 5 lbs. pressure, or given an equivalent steaming in the "rapid ager", after which it is diazotized for half an hour in a cold 50:1 bath containing 5% of its weight of sodium nitrite and 16% of its weight of hydrochloric acid 28° Tw. After diazotization the material is well washed in cold water and developed by known methods with 3% of its weight of betaoxynaphthoic acid. It is then rinsed, soaped lightly and otherwise treated and finished as desired or requisite.

The unprinted portions are deep blue and the printed portions discharged.

*Example 3*

A fabric composed of cellulose acetate yarns is treated in a bath of volume ratio 50:1 with 0.5% of its weight of aminoazotoluene sulphate, rendered slightly alkaline with ammonia after dissolving. The dyeing is continued for 1½ hours at 80° C. and the fabric is then washed and dried at a low temperature and further prepared for printing as desired. It is then printed by roller printing machine or hand-block with a paste consisting of the following:—

500 grams gum arabic 1:1
190 grams aluminium sulphate 1:1
90 grams sodium chlorate cryst:
120 grams water
25 grams potassium ferricyanide
75 grams water

1000

After printing, the material is dried and steamed in the "cottage" steamer for 15 minutes at 5 lbs. pressure, after which it is diazotized in a bath containing 5% of its weight of sodium nitrite and 16% of its weight of hydrochloric acid of 28° Tw strength. After diazotizing for ½ hour the fabric is washed well in cold water and developed in known manner with 2% of its weight of betaoxynaphthoic acid. It is finally rinsed, soaped lightly and otherwise treated and finished as desired or requisite. A white pattern on a bluish red ground is thus obtained.

*Example 4*

A fabric woven from cellulose acetate yarns is dyed in a mixture of 0.5% of o.methoxybenzeneazoalphanaphthylamine and 1% of Naphthol AS.BS, calculated on the weight of material. (The Naphthol AS.BS is dissolved in aqueous caustic soda and poured into the dyebath prepared with 2 ccs. of sodium sulphoricinoleate per litre. The bath is now just neutralized with dilute acetic acid and the solution of the above amine, previously dispersed by heating with aqueous sodium sulphoricinoleate, added.) Dyeing is continued for 1½ hours at 80° C. and the material well washed, dried and otherwise prepared for printing as desired. It is then printed with a paste composed as follows:—

400 grams gum arabic 1:1
190 grams aluminium sulphate 1:1
90 grams sodium chlorate
30 grams potassium ferricyanide
290 grams water

1000

After printing and drying, the material is given a very short steaming, e. g. 2 minutes in the cottage steamer at 3 lbs. pressure or an equivalent steaming in the continuous ager. The fabric is then treated cold for 1½ hours in a bath containing 4 grams per litre of sodium nitrite and 6 grams per litre of acetic acid, after which it is rinsed and soaped and otherwise treated as desired or requisite. The result is a tinted discharge on a navy blue ground.

*Example 5*

A fabric composed of cellulose acetate yarns is treated, as in dyeing, with 1% of its weight of dianisidine, the latter being dispersed by heating with three times its weight of aqueous sodium sulphoricinoleate before being added to the bath. The treatment is continued for 1½ hours at 80° C. the material being then washed well, dried and prepared for printing as desired. It is then printed by roller printing machine with a paste of the following composition:—

400 grams gum arabic 1:1
190 grams aluminium sulphate 1:1
40 grams sodium chlorate
50 grams sodium bichromate
30 grams potassium ferricyanide
290 grams water

1000

After printing the material is dried and steamed in the cottage steamer for 3 minutes with steam at 5 lbs. or given an equivalent steaming in the rapid ager at 100° C. After steaming the fabric is diazotized for 20 minutes in the cold in a bath containing 2% of sodium nitrite and 7% of hydrochloric acid 28° Tw. calculated on the weight of the material. After diazotization is complete the fabric is washed well in cold water and developed in known manner with 1% of its weight of betaoxynaphthoic acid, after which it is rinsed, soaped lightly and otherwise treated as desired or requisite. The result is a greenish tinted discharge on a deep blue ground.

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

1. Process for the production of discharge effects on materials, comprising applying a diazotizable amino compound to a material comprising

an organic derivative of cellulose, applying to the material locally an oxidizing discharge and treating the amino compound so that it is rendered incapable of diazotization in the selected areas, and finally diazotizing and developing.

2. Process for the production of discharge effects on materials, comprising applying a diazotizable amino compound to a material comprising cellulose acetate, applying to the material locally an oxidizing discharge and treating the amino compound so that it is rendered incapable of diazotization in the selected areas, and finally diazotizing and developing.

3. Process for the production of discharge effects on materials, comprising applying a diazotizable amino compound to a material comprising an organic derivative of cellulose, applying to the material locally a chlorate discharge and treating the amino compound so that it is rendered incapable of diazotization in the selected areas, and finally diazotizing and developing.

4. Process for the production of discharge effects on materials, comprising applying a diazotizable amino compound to a material comprising cellulose acetate, applying to the material locally a chlorate discharge and treating the amino compound so that it is rendered incapable of diazotization in the selected areas, and finally diazotizing and developing.

5. Process for the production of discharge effects on materials, comprising applying a diazotizable amino compound to a material comprising an organic derivative of cellulose, applying to the material locally an oxidizing discharge, drying and ageing to render the amino compound incapable of diazotization in the selected areas, and finally diazotizing and developing.

6. Process for the production of discharge effects on materials comprising applying a diazotizable amino compound to a material comprising cellulose acetate, applying to the material locally an oxidizing discharge, drying and ageing to render the amino compound incapable of diazotization in the selected areas, and finally diazotizing and developing.

7. Process for the production of discharge effects on materials, comprising applying a diazotizable amino compound together with a developer component to a material comprising an organic derivative of cellulose, applying to the material locally an oxidizing discharge and treating the amino compound so that it is rendered incapable of diazotization in the selected areas, and finally diazotizing.

8. Process for the production of discharge effects on materials, comprising applying a diazotizable amino compound together with a developer component to a material comprising cellulose acetate, applying to the material locally an oxidizing discharge and treating the amino compound so that it is rendered incapable of diazotization in the selected areas, and finally diazotizing.

GEORGE HOLLAND ELLIS.