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# UNITED STATES PATENT OFFICE

HENRY DREYFUS, OF LONDON, ENGLAND

## TREATMENT OF CELLULOSE DERIVATIVES

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This invention relates to the dyeing, printing or stencilling of cellulose ethers such as methyl cellulose, ethyl cellulose and benzyl cellulose in the form of artificial silk, yarn, fabric, film or other form, alone or mixed with other fibres, threads or materials artificial or natural, such as cotton, silk, wool, or viscose.

I have found that cellulose ethers (i. e. cellulose ethers which are insoluble in hot or cold water) can be dyed, printed or stencilled with coloring matters or organic compounds which are insoluble or practically insoluble in water or are of relatively low solubility in water (all hereinafter in the claims included in the term "relatively water-insoluble coloring compounds"), the said coloring matters or organic compounds being applied in form of aqueous dispersions. Such aqueous dispersions may be obtained for example by grinding (e. g. in colloid mills), by dissolving in a solvent and pouring into water containing or not containing protective colloids, or by pretreating the coloring matters or compounds with one or more solubilizing agents. As examples of such solubilizing agents may be specified bodies having oily or fatty characteristics, namely higher fatty acids or sulphonated or other derivatives thereof containing salt-forming groups such as sulphonicinoleic acid or other sulphated fatty acids or salts of such acids or bodies, for instance their alkali or ammonium salts; carbocyclic compounds containing in their structure one or more salt-forming groups such as naphthenic acids or other carboxylic or sulphonic acids of the cycloparaffins, phenols, sulphonic acids, carboxylic acids, phenolsulphonic acids, sulphonated naphthalene-formaldehyde condensation products or other derivatives of the benzene, naphthalene or anthracene series or other derivatives of the saturated or nonsaturated hydrocarbons containing one or more salt-forming groups or sodium or other salts of any such compounds; Twitchell reagents, i. e. sulpho-aromatic fatty acids such as sulphobenzene stearic acid or derivatives thereof such as sulphophenol stearic acid or sulpho naphthalene stearic acid, sulpho naphthalene ricinoleic acid or salts of such bodies; sulphite-cellulose lye or constituents thereof, such as lignin sulphonic acid or sodium or other salts thereof; and soluble resin soaps or sodium or other soluble salts or soaps of resin acid. Such solubilizing agents may be employed either singly or two or more in admixture or in succession. All of these substances are included in the term "bodies of oily or fatty characteristics" in the appended claims.

Further if desirable, auxiliary solvents may be used in conjunction with the aforesaid bodies of oily or fatty characteristics or salts thereof for solubilizing or converting into more soluble modifications any water-insoluble or insufficiently water-soluble coloring matters or organic compounds, greatly improved results being obtained in many cases. As examples of auxiliary solvents I may mention alkyl or alkylene halides, such as tetrachlorethane or trichlorethylene; paraffins such as cyclohexane, heptane, triethylmethane, A-nonane, nonane; simple or "mixed" derivatives of the cyclic or aromatic series containing one or more amino, chlor or hydroxy groups such as cresols, alkylanilines, toluidines, chlorphenols, mono or poly chlor benzenes or chlor naphthalenes; aromatic hydrocarbons such as benzene, toluene, xylene, cumene, $(C_6H_5CH(CH_3)_2)$, propylbenzene, orthomethylethylbenzene, mesitylene, diphenyl methane, naphthalene; hydrogenated derivatives of aromatic compounds such as hexahydrophenol, hexahydrocresols, 1.4-hydrobenzene, dekahydronaphthalene, tetrahydronaphthalene and the like; compounds from petroleum such as dekanaphthene, undekanaphthene, dodekanaphthene, tetradekanaphthene, pentadekanaphthene, duodecylene (which occurs in Canadian petroleum); terpenes, such as turpentine, pinene, sylvestrene, unsaturated bodies and cyclic compounds such as butylethylene, methylcyclopentene, tetramethylethylene, cyclopentene, cymene $C_{10}H_{14}$, 1.1.2-trimethylcyclopentene and the like; or commercial liquids containing mixtures of the aforesaid compounds, such for instance as turpentine (which contains the relevant terpenes) and petroleum, solvent naphtha and commercial benzol which contain mixtures of paraffin and aromatic hydrocarbons). Any other bodies having a similar effect of giving an enhanced solubilizing action in conjunction with the bodies of oily or fatty characteristics may however be employed.

One or more auxiliary solvents may be used in conjunction with one or more of the aforesaid bodies of oily or fatty characteristics for the solubilization of insoluble or insufficiently soluble coloring matters or organic compounds. This process of using auxiliary solvent is of especial use in the solubilization of highly insoluble coloring matters or compounds, which would otherwise require very large and excessive quantities of the bodies of oily or fatty characteristics or salts thereof for their solubilization and practical application although it is to be understood that it may be applied to the dyeing, or otherwise coloring of cellulose ethers with any insoluble or practically insoluble or relatively insoluble coloring matter or compound.

Any insouble or relatively insoluble coloring matter or compound may be used for the present invention. Thus for instance I may employ unsulphonated or other relatively insoluble derivatives of the "azo" class, simple amino bases, unreduced indophenols (aryl or substituted aryl benzo- or naphthoquinone mono-imides) or insoluble or relatively insoluble coloring matters of the following classes:—polyarylmethane, oxazine, azine, thiazine, unreduced indigoid or basic derivatives of the anthraquinone series, e. g. rosaniline base or its alkylated or arylated derivatives, pararosaniline base, malachite green base, amino- and aminohydroxyanthraquinones or their derivatives such as 1-paratolylamino-4-hydroxy-anthraquinone, 1-paratolylamino-4-methylamino-anthraquinone, safranine base and so forth; insoluble or relatively insoluble pyrazolone derivatives, for example unsulphonated azo derivatives of pyrazolone compounds, such as those obtained by coupling 1-phenyl-3-methyl-5-pyrazolone, or 1.3-dimethyl-5-pyrazolone with diazotized amino compounds e. g. aniline, para-anisidine or para-aminobenzene-azo-dimethylaniline; unreduced vat dyestuffs of the anthraquinone series such as those sold under the registered trade marks Indanthrene, Cibanone, Algol and Helindone; insoluble or relatively insoluble nitro derivatives of diarylamines, such as 2.4-dinitro-diphenylamine or its 3′-methoxy or hydroxy or 4′-chlor, amino, dimethyl-amino or hydroxy derivatives, or 4-nitrodiphenylamine or its 4′-methyl, chlor, or nitro derivatives; unsulphonated coloring matters or compounds of the stilbene group, for example stilbene disazobisphenol, stilbene disazobismetatoluidine, stilbene disazobisalphanaphthylamine, amino-stilbene-azo-metaphenylenediamine, or aminostilbene-azometatoluidine; or insoluble or relatively insoluble acidyl derivatives of amino anthraquinones or of substituted amino anthraquinones, containing one or more aliphatic acidylamino groups, e. g. acetyl-, propionyl-, oxalyl, or succinyl-amino groups with or without other substituent groups such as amino, hydroxy, chlor and the like, for example 1-acetylamino-anthraquinone or its 4-oxy, 4-methoxy, 4-amino, 4-methylamino or 4.5.8-triamino derivatives.

The insoluble or relatively insoluble coloring matters or compounds for use in the present invention will usually contain no strongly acidic groups such as the sulpho group and when basic coloring matters or compounds are employed they are always used in the form of the base and not in the form of salts such as the hydrochloride.

When dispersions are to be produced by using solubilizing agents the insoluble or relatively insoluble coloring matter or compound may be mixed or ground with one or more solubilizing agents, in the presence or absence of water, and the whole heated if necessary, the solubilized modifications being filtered if desired before addition to the dyebaths or other preparations for dyeing or otherwise coloring the goods containing cellulose ethers. If auxiliary solvents are to be used one or more of the insoluble or insufficiently soluble or relatively insoluble coloring matters or organic compounds may be treated with one or more bodies of oily or fatty characteristics or salts thereof and one or more auxiliary solvents, in any order separately or together in admixture, at any suitable temperature or pressure in presence or absence of water.

The dyeing or otherwise coloring of the goods may be effected in the usual manner.

If the coloring matter or compound contains diazotizable amino groups, it may be diazotized and developed on the material in the usual manner to form a further dyestuff or dyestuffs.

When dyeings or colorings are to be produced by the azoic or development process the insoluble or relatively insoluble component (whether base or developer or both) may be solubilized, as described, and the dyeing or development conducted as usual, either component being applied first to the material.

For printing or stencilling cellulose ethers, an aqueous dispersion of one or more coloring matters or compounds may be thickened by the use of such substances as starches, flour, gums and the like and applied in the usual manner, followed by such after-treatment as may be required.

Mixed goods may be dyed or otherwise colored in uniform or contrasting effects with or without employment of other dyestuffs or components according to the character of the non-ether portion of the goods, said other dyestuffs or components being applied if desired before or after the application of the aforesaid insoluble or relatively insoluble dyestuffs or compounds, or when not deleteriously affected thereby, they may be applied in conjunction therewith.

The cellulose ethers may be either fully etherified products or the lower ethers or partially etherified products.

The following examples are intended to illustrate the invention but in no way to limit it:—

*Example 1.*—1 part of a 20% aqueous paste of 2.4-dinitro-4′-hydroxy-diphenylamine is ground up with 2 parts of 50% aqueous sodium sulphoricinoleate and the mass is heated and stirred until as homogeneous as possible. Boiling water is then added to make the liquor to a total of 24 parts. The stirred liquor is added to a bath containing 400 parts of soft water. The dyebath is raised to 40–50° C. and 20 parts of insoluble ethyl cellulose artificial silk yarn in hank form are entered, the dyeing temperature being raised to 65–75° C. during half an hour and maintained at that temperature for 1 hour. The goods dyed a yellow shade are lifted, rinsed and dried or otherwise finished as desired.

*Example 2.*—A dyebath is prepared as follows:—1 part of a 20% paste of stilbene disazo phenol is pasted with 1 part of a compound obtained by sulphonating a mixture of naphthalene and castor oil. The paste is diluted with 40 parts of boiling soft water and added, through a sieve if necessary to 500 parts of cold water.

20 parts of insoluble methyl cellulose film are entered into the dyebath at about 60° C. and the temperature slowly raised to 90° C., the dyeing being continued until the requisite shade of yellow is obtained. The goods are then rinsed and dried.

*Example 3.*—1 part of 2.4-dinitrobenzene-azo-diethylaniline is pasted with a solution in a sufficient quantity of water of 8 parts of naphthenic acid rendered slightly alkaline with caustic soda. The mass is heated and poured into 100 parts of 2½% soap solution, the whole being stirred to produce a good dispersion. The liquor is then filtered into a dyebath and 100 parts of insoluble ethyl cellulose artificial silk yarn in the form of hanks are entered into the dyebath at about 40° C. The temperature is raised during ¾ hour to about 75–80° C. and maintained at this temperature for a further ¾ hour, after which the goods, now dyed red, are lifted, rinsed and finished as desired.

*Example 4.*—1 part of 1-acetylamino-4-oxyanthraquinone is dispersed in 9 parts of water containing 2 parts of glue by means of a colloid mill. The paste is added to 3000 parts of water containing 8 parts of glue. 100 parts of insoluble ethyl cellulose artificial silk yarn in hank form are entered into the cold well stirred dyebath and the temperature raised to 80–90° C. during 1 hour, dyeing being continued for a further ½ hour. The goods dyed an orange shade may then be lifted, rinsed and dried.

*Example 5.*—1 part of 2.4-dinitro-4′-hydroxy-diphenylamine is ground up with about 6 parts of 50% sodium sulphoricinoleate and heated; 4 parts of hexahydrophenol are then added and the heating continued until the mass becomes clear, when it is diluted with 500 parts of cold soft water. The dispersion is then added to a dyebath containing 2000 parts of water. 100 parts of insoluble ethyl cellulose artificial silk yarn in the form of hanks are entered into the bath at about 40° C. and the temperature raised during 1 hour to about 90° C., at which temperature dyeing is continued for a further ½ hour. The goods, dyed a yellow shade, are lifted, rinsed and dried or otherwise finished as desired.

*Example 6.*—1 part of a 25% paste of 4-nitro-2-methoxybenzene-azo-diethylaniline is intimately mixed with 1 part of turpentine and 3 parts of 50% Turkey red oil and sufficient boiling soft water is then added to make a thin paste. The paste is heated to 80° C. and diluted to 25 parts with boiling soft water, and the solution obtained poured into 750 parts of soft water containing 0.5 parts of olive oil soap in solution. 30 parts of insoluble ethyl cellulose artificial silk yarn in hank form are entered into the dyebath at about 40° C. and the dyeing proceeded with as in the previous example. The goods are dyed a yellow-red shade.

The term dyeing in the claims is to be understood to include printing and stencilling and further the term coloring compound in the claims includes, in addition to coloring matters or dyestuffs, organic compounds which are capable of forming coloring matters or dyestuffs upon the material, for example the components (base or developer or both) used in the azoic or development process of dyeing.

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

1. Process for dyeing material comprising a cellulose ether, comprising dyeing the material with an aqueous dispersion of a relatively water-insoluble coloring compound,

said dispersion being prepared by pretreating the compound with a solubilizing agent comprising a sodium salt of sulpho-ricinoleic acid and with xylene.

2. Process for dyeing material comprising ethyl cellulose, comprising dyeing the material with an aqueous dispersion of a relatively water-insoluble coloring compound, said dispersion being prepared by pretreating the compound with a solubilizing agent comprising a sodium salt of sulpho-ricinoleic acid and with xylene.

In testimony whereof I have hereunto subscribed my name.

HENRY DREYFUS.