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DYED CELLULOSE ETHER PRODUCT AND PROCESS OF MAKING SAME

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It has not been possible previously, to color alkyl celluloses which do not dissolve in water at room temperature or articles made therefrom, with substantive (direct dyeing) or acid dyes or vat dyes or sulfur dyes. Even basic dyes produce only delicate shades of color, usually not very fast. The process of dyeing products made from alkyl celluloses is therefore limited to adding dyes to the solutions of the alkyl celluloses, and then working up these solutions into technical products.

I have made the discovery that alkyl ethers, particularly ethers of cellulose and articles of all kinds made therefrom, as plastic masses, artificial fibres and threads, particularly artificial silk, films, coatings of all kinds or the like, may be dyed either with substantive (direct dyeing) dyes, or with acid dyes, or vat dyes, or sulfur dyes, or mordant dyes, or basic dyes to any desired shade of color, if the following procedure be followed: The article is made of such alkyl derivatives of cellulose or its conversion products as are insoluble in water at 16° C. and above, but which swell or are soluble in water below this temperature, particularly below 10° C. (for example the alkyl celluloses made according to the processes of the patent applications, filed in U. S. on June 10, 1922, No. 567,426 and 567,430, the latter being now Patent No. 1,505,043, Aug. 12, 1924). In dyeing water is allowed to act upon these articles at a temperature at which they just swell to some extent, but do not disintegrate or dissolve, and the swollen articles are treated with dye solutions in the usual manner.

The temperature of the water which is used for causing swelling of the alkyl derivatives of cellulose or its conversion products or the articles made therefrom, preparatory to the dyeing operation, depends on the temperature at which the particular alkyl ether used will swell. Thus, if an ethyl ether of cellulose which swells in water at 5 to 8° C., but which dissolves in water below 5° C., is to be dyed, then water at 5 to 8° C., is used for swelling. If an ethyl ether is to be dyed which swells in water at 1 to 5° C., without dissolving or disintegrating or decomposing, then water at 1 to 5° C., is used for the swelling preparatory to dyeing. The time required for the swelling operations depends on the thickness of the thread, filament, film, coating, body or other article concerned. With very thin fibres or filments, a few minutes will suffice under ordinary circumstances; and the thicker the article, the longer time must the swelling operation be continued.

The dyeing of the swollen article is then accomplished in similar manner to that in which cotton or wool or real or artificial silk or the like (capable of dyeing) are dyed, so that in many cases the customary dyeing recipes may be used.

The present process is not only suited to the dyeing of the artificial fibres or threads made from the alkyl ethers of cellulose or its conversion products, or fabrics made from (or containing) such fibres or threads, but also to plastic masses, films, and coatings of all kinds made therefrom (such as for example, coatings or finishings on fabrics, artificial leather, book cloth and the like), in which such cellulose ethers are present. The dyed articles may also be treated with tanning materials, or with any of the materials which are capable of precipitating albuminous matters (such as tannic acid, tannins, alum, chrome alum, etc.), either before or after the dyeing, according to the process of my application called "tantan" filed in U. S. on June 10, 1922, Serial No. 567,429 (now Patent No. 1,505,044, Aug. 12, 1924). In order to eliminate or decrease their property of swelling in very cold water. The articles need not consist of alkyl celluloses alone. They also may include any admixtures, such as for example other cellulose derivatives (nitrocelluloses, acetyl-celluloses or formyl-celluloses), or other colloids, or also media for making them pliable or plastic (for example camphor or camphor substitutes, naphthalene or its derivatives, high boiling esters (for instance the phosphoric acid esters of the phenols, ethers of the phenols, high boiling hydrocarbons, drying or non-drying oils, fats or the like), or also filling materials (for example China clay, chalk, zinc white, lithopone, or the like).

While the process of the present application has been found to give useful results with all ethers of cellulose or its conversion products which are insoluble in water at 16° C. but which have the property of swelling or becoming stretchable in water at some lower temperature, without disintegrating or dissolving in water at said lower temperature (although they may be soluble in water or may disintegrate in water at a still lower temperature), I have found that the treatment of those ethers which are insoluble in water at 10° C., and above, but which swell in water of some lower temperature, gives particularly satisfactory results.

In executing the present process it must be borne in mind that the desired degree of swelling of the article to be dyed, depends not only upon the temperature of the water, and the thickness of the article, but also upon the time which the article remains in the water. An article (film, filament, thread, fabric coated of filled with cellulose ethers, or the like) made from an alkyl derivative of a cellulosic body displaying the properties stated above, may, brought into the water at some temperature below 16° C., disintegrate, or become friable, or even dissolve if it remains very long in contact with the water, but only swell to the desired extent if it is kept in the water for a shorter time.

As various types of alkyl celluloses exist that are, in the above stated manner, affected by water at below 16° C. particularly at below 10° C., the temperature of the water or aqueous liquid employed for the swelling procedure and the time which the article to be dyed remains in the water will vary considerably.

By way of example, it may be mentioned that an article made from an ethyl or methyl ether of cellulose soluble in water at about 5 to 8° C. and below, but insoluble in water at above 8° C., will require for swelling, water at about 10–12° C., whilst an article manufactured from an ethyl or methyl ether of cellulose only slightly swelling in water at 9 to 10° C., but distinctly swelling in water at between 5 and 8° C., and disintegrating in water at 1 to 5° C., should preferably be soaked in water at 5 to 8° C. An article made from an ethyl or methyl cellulose which shows a distinct swelling only in water between 1 and 5° C., is treated with water preferably at said temperatures, and an article made from an ethyl or methyl cellulose that even in very cold water (1 to 5° C.) swells only to a moderate degree evidenced only by becoming soft or stretchy or both, should preferably be soaked in very cold water. According to the thickness of the article in question, the time which it remains in the swelling bath may vary from a few minutes to many hours.

For the swelling operation either pure water or water containing other substances, for example glycerine, sugars, soaps, Turkey red oil, organic or inorganic acids etc. may be employed. The swelling operation may be performed either before the dyeing or at any stage of the dyeing-procedure. In other words: the dye bath itself may be used as swelling bath for which purpose it must, when the process of swelling is about to be undertaken, preferably at the very beginning, have a temperature at which the cellulose ether or the article made therefrom can swell or soften. After the alkyl cellulose or the article made therefrom or containing it has remained in the dye bath possessing the required low temperature, for the softening or swelling of the article, sufficiently long to produce the desired degree of swelling or softening, the temperature of the dye-bath may be raised to 50 to 100° C., and the article kept in the bath until the former gets the desired shade of color. As some alkyl ethers of cellulose or articles made therefrom in the swelled or softened state take on dyes well also in the cold or at moderate temperatures, the dyeing may, in some cases, be carried out in the cold i. e. either at the actual temperature of the swelling operation or at temperatures not much above the temperature of the swelling. Thus if the dye bath be used also as swelling or softening bath, the swelling and dyeing may, in such cases, be done at the same temperature.

Without restricting myself to details, the following examples are given, by way of illustration:

I.—Dyeing with substantive (direct dyeing) dyes

For dyeing alkyl ethers of cellulose, displaying the aforesaid properties, or articles made therefrom, with substantive dyes, every dye-stuff belonging to this group, or mixtures of dye-stuffs belonging to this group may be employed. Thus, for example, all the so-called Diamin dyes, Dianil dyes, Benzidin or Benzo dyes, Mikado dyes, Columbia dyes, Congo dyes, Chicago dyes, Chloramin dyes, Direct dyes, Phenol dyes, Naphthamin dyes, etc. may be used.

The number of dye-stuffs belonging to this group being enormous, the enumeration of all of them is impossible. By way of example, the following may be stated as typical representatives useful for the dyeing of the alkyl celluloses in question and articles made therefrom, particularly, artificial filaments such as artificial silk or the like:

Black.—Dianil black, Diamin black, Diamin Fast black, Oxydiamin black, Paradiamin black, Columbia black, Patent Dianil black, Pluto black, Benzo black, Benzo Deep black etc.

Brown.—Congo brown, Diamin brown, Benzo brown, Diamin Fast brown, Oxydiamin brown, Diamin Catechin, Benzo Dark

brown, Benzo Light brown, Chloramin brown, Pluto brown, Toluylen brown, Toluylen Fast brown, etc.

Orange.—Mikado orange, Diamin orange, Oxydiamin orange, Benzo orange, Benzo Fast orange, Benzo Light orange, Pluto orange, Pyramin orange, Toluylen orange, Dianil orange, etc.

Yellow.—Chrysamin, Chloramin yellow, Chrysophenin, (Aurophenin), Mikado yellow, Thioflavin S, Diamin yellow, Oxydiamin yellow, Benzo Fast yellow, Thiazol yellow, etc.

Red.—Congo, Benzo Purpurin, Brilliant Purpurin, Brilliant Congo, Diamin red, Diamin Scarlet, Diamin Fast Scarlet, Thiazin red, Oxamin red, Dianil red, Dianil Scarlet, Benzo red, Benzo Fast red, Benzo Fast Scarlet, Benzo Light red, Benzo Light Scarlet, Chloramin red, etc.

Claret and Garnet.—Congo Corinth, Congo Rubin, Diamin claret, Diamin Brilliant claret, Dianil garnet, Benzo Rubin, Benzo claret, Benzo Light claret, Benzo Light Rubin, etc.

Violet.—Diamin violet, Diamin Fast violet, Diamin Brilliant violet, Oxydiamin violet, Diamin Heliotrope, Benzo violet, Benzo Fast violet, Brilliant Benzo violet, etc.

Pink.—Diamin pink, Erica, Geranin, Brilliant Geranin, Benzo Fast pink, etc.

Blue.—Diamin blue, Diamin Pure blue, Oxydiamin blue, Diamineral blue, Diamin Fast blue, Dianil blue, Chicago blue, Naphtamin blue, Azidin blue, Oxamin blue, Eboli blue, Benzo blue, Benzo Fast blue, Benzoazurin, Azo blue, Benzo Light blue, Benzo New blue, Brilliant Azurin, Brilliant Fast blue, etc.

Green.—Diamin Green, Dianil green, Diphenyl green, Chloramin green, Columbia green, Benzo green, Brilliant Benzo green, Benzo Olive, etc.

The dye baths which, of course, are aqueous solutions of the dye-stuffs may have added to them all the ingredients well known in the cotton-dyeing-art, for example sodium carbonate, phosphates, caustic alkali, soaps, Turkey red oil, sodium chloride, sodium sulphate, or other salts, etc. The cellulose ethers or articles made therefrom may be dyed in a weakly alkaline, or a strongly alkaline, or a weakly acid dye bath.

The amount of the dye-stuffs is to be adjusted to the strength of the dye-stuff and the depth of the shade of color desired.

As to the quantities of the dye-stuffs, it may be taken as a rule, to which however, the invention is not limited, that for producing light (or pale) shades of colors about 1 to 2% of the dye stuff, and for dark or deep shades of colors about 3 to 8% of the dye-stuff, calculated on the weight of the cellulose ether or article made therefrom, are employed. The other ingredients, if employed, may be taken in such amounts as are well known in the cotton-dyeing-art.

The alkyl ether of cellulose or article made therefrom and consisting of the cellulose ether alone, or containing other cellulose derivatives (for example a cellulose hydrate, cellulose nitrate, cellulose acetate, or the like), or other colloids (for example albumen, fibroin, koratin or the like), or softening agents (for example drying or non-drying oils, fats, balsams, phosphoric acid esters of the phenols, high boiling aromatic hydrocarbons, phenol ethers, other high boiling ethers or esters, camphor, naphthalene or its derivatives, glycerin, soap or the like) is to be dyed in the swelled or softened state. The swelling or softening of the product to be dyed, for example artificial silk in the shape of threads, or yarn, or woven goods consisting of, or containing the artificial silk, may be effected in a separate bath consisting of water or an aqueous liquid cooled down to the required temperature or in the dye bath itself preferably at the very beginning. The swelling or softening may be effected on the material in a stretched condition. The material to be dyed may, whether previously swelled or softened, be entered into the dye bath while the bath is at a temperature at which the material can swell or soften. If the initial temperature of the dye bath is 16° C. or above, the material must, of course, have been swelled or softened before it is put into the dye bath, while, if the initial temperature of the dye bath is suitable for swelling or softening the material to be dyed, and if the dye bath does not contain substances preventing the swelling or which would make the swelling difficult, the swelling or softening may be effected in the dye bath itself.

As many of the alkyl ethers of cellulose, in the swelled or softened state, take on the dyes very well, the dyeing may, in many cases, be effected in the cold, or hot, i. e. at any temperature lying between 0° and the boiling point of the dye bath. In any case, however, the boiling point of the dye bath will answer the purpose. The swelled or softened material may be entered into the dye bath, boiling or at a lower temperature, and in the latter case the temperature may be slowly raised up to the boiling point. The duration of the dyeing procedure may vary from 10 minutes to 2 hours and depends upon the properties of the cellulose ether from which the material under dyeing is produced, upon the dye-stuff employed, upon the concentration of the dye bath and upon the desired shade of color.

The washing and drying of the dyed material is effected in the usual manner known in the cotton or artificial silk art.

The fastness of the obtained colors may be improved in manner well known in the dyeing art, by a subsequent treatment with metal

salts, for example with copper sulphate in the presence of acetic or formic acid, or with potassium bichromate, alone or in the presence of copper sulphate and acetic acid etc.

The materials dyed with substantive dyes may also be treated (in the manner well known in the dyeing art) with sodium nitrite in the presence of hydrochloric acid and a developer such as β-naphthol, phenol, resorcin, ethyl -β- naphthylamin, m-phenylendiamine, toluylendiamine etc. in order to produce a polyazo dyestuff on the material, and thus to improve the fastness.

II.—Dyeing with acid dyes

The making of alkyl ethers of cellulose or of articles made therefrom accessible to acid dyes i. e. the swelling or softening of them is effected in the same manner as in the previous example dealing with substantive dyes.

The dyeing bath may have various substances added. Thus, acid bodies may be added, for example sulphuric acid, sodium bisulphate, acetic acid, formic acid, lactic acid, or the like. Also salts may be added, for example sodium sulphate, ammonium acetate, ammonium oxalate, ammonium sulphate, etc. These are used in the manner well known in the dyeing art.

As to the amounts of the dye-stuffs, it may be regarded as a rule to which, however, the invention is not limited, that for example 1 to 8% of the dye-stuff, 1–4% of sulphuric acid and 5–20% of sodium sulphate, calculated on the weight of the material to be dyed, are employed.

The swelling or softening is effected like in Example I, the dyeing similar to Example I or in the manner well known in the silk or wool dyeing art.

By way of example the following acid dyestuffs may be stated as useful for dyeing the cellulose ethers in question and articles produced therefrom:

Grey and Black.—Nigrosin, Naphthylamin black, Naphthol Blue black, Silk black, Silk grey, Naphthol black, Palatin black, Agalma black, Acid black, Brilliant black, Guinea black, Amin black, Wool black etc.

Blue and Violet.—Azo Acid blue, Naphthalin blue, Patent blue, Cyanin, Cyanol, Azo Wool blue, Azo Fast blue, Wool blue, Neptune blue, Methyl blue, Alkali blue, Silk blue, Fast blue, Indulin, Cyananthrol, Indigo Carmin, Acid violet, Victoria violet, Guinea Fast violet, Formyl violet, Violamin etc.

Green.—Acid green, Neptune green, Cyanol Fast green, Agalma green, Wool green, Alkali Fast green, Naphthalin green, Guinea green etc.

Red.—Ponceau, Wool Scarlet, Fast red, Fast Ponceau, Fast red, Azo Rubin, Acid Fuchsin, Acid Rhodamin, Azo Carmin, Victoria Scarlet, Brilliant Ponceau, Brilliant Crocein, Naphthol red, Amaranth, Lana Fuchsin etc.

Yellow and Orange.—Naphthol yellow S, Tartrazin, Flavazin, Fast yellow, Chinolin yellow, Acid yellow, Azo Flavin, Metanil yellow, Victoria yellow, Orange II, N, IV, Brilliant orange etc.

III.—Dyeing with sulfur dyes

The swelling or softening of the cellulose ethers or articles made therefrom is effected as in the previous examples, while the dye baths, as well known, contain sodium sulfide besides the dye-stuffs. To the dye baths also may be added, sodium carbonate and sodium chloride or sodium sulphate. The quantity of the sodium sulphide depends upon the dyestuff and in many cases amounts to twice as much as the weight of the dye-stuffs. A small excess of sodium sulphide is harmless, while too large quantities impede the dyeing. An addition of sodium carbonate or sodium hydroxide accelerates solution of many of the sulfur dyes. An addition of Turkey red oil, glucose, glue, or the like promotes the homogeneousness of the coloring.

The amount of the dye-stuffs is to be adjusted to the strength of the dye-stuff and the depth or shade of color desired. 2 to 15% calculated on the weight of the material under dyeing are given as limits, by way of example.

The dyeing is effected as described in Example I or as is well known in the cotton art.

By way of example the following sulphur dyes are mentioned as suitable for the present process:

Sulphur-dyes, Katigen dyes, Thiogen dyes, Immedial dyes, Kryogen dyes, Thion dyes, Pyrogen dyes, Pyrol dyes, Thioxin-dyes, Eclips dyes, Thional dyes, Auronal dyes etc.

IV.—Dyeing with basic dyes

Swelling or softening as in Example I.

The dyeing with basic dyes may be effected either in a dye bath containing acids, for example acetic acid with or without a subsequent treatment with tanning agents such as tannic acid or the like, or on tanning mordants.

In the former cases the dyeing may be effected as in Example I.

In the latter case the swelled or softened material is treated, for say ½ to 1 hour with 1 to 6% of tannic acid or sumac-extract or the like and about 1000% of water calculated on the weight of the material to be dyed. The material treated with tannic acid is squeezed out or centrifuged, treated in well known manner with tartar emetic and a little chalk and rinsed. The dyeing is effected as in Example I.

By way of example the following basic dye-stuffs may be mentioned as answering the purpose:

Black and Grey.—Janus black, Nigrosin, Methylen Grey etc.

Blue.—Methylen blue, New blue, Victoria blue, Nile blue, Meldola blue, Neutral blue, Indazin, Naphthindon, Indoin blue, etc.

Violet.—Methyl violet, Ethyl violet, Crystal violet, Methylen violet, Rosolan, Iris violet etc.

Green.—Malachite green, Brilliant green, Diamond green, New Victoria green, Methylen green etc.

Yellow, Orange and Brown.—Auramin, Thioflavin, Euchryzin, Phosphin, Vesuvin, Chrysoidin, Azophosphin, Flavophosphin, Tannic orange, Bismarck brown, Manchester Brown etc.

Red.—Fuchsin, Rubin, Grenadin, Rhodamin, Safranin, Irisamin, Cerise, Neutral red, Safranin Scarlet, Fuchsin Scarlet etc.

The foregoing examples show that the dyeing of the swelled or softened cellulose ethers or articles produced therefrom with substantive, or acid, or basic, or sulphur dyes, is, in principle, the same as the dyeing procedure of cotton or silk or wool. As this holds good also with vat-dyes (such as Indigo, Indanthren dyes, Algol dyes, Ciba- and Cibanon dyes, Helindon dyes, Thioindigo dyes, Hydron dyes or the like) and with dyes to be dyed on mordants, for example on aluminium compounds, or iron compounds, or chromium compounds or the like (such as Alizarin dyes, Logwood, Fustic, Quercitron, Catechu etc.) and with Naphthol azo dyes, it is sufficient to state that the dyeing of the swelled or softened alkyl derivatives of cellulose or of articles made therefrom is effected in a manner similar to the way in which cotton and cotton goods are dyed with said dyes.

Regardless of the dye-stuff and the method of dyeing employed, the dyed cellulose ethers or articles manufactured therefrom may, in order to increase their resistance to water, be treated with tanning agents or reagents for precipitating albumen, before the dyeing, or at any stage of the dyeing or after the dyeing. The treatment of cellulose ethers not entirely resistant to water with substances capable of precipitating albumens is described in my co-pending U. S. patent application, filed on June 10, 1922, and called "tantan," Serial No. 567,429.

The products made according to the present process are easily to be distinguished from any other dyed cellulose ethers or articles made therefrom. The distinctive mark is their property of considerably softening or swelling or even dissolving in very cold water and the presence of a color. If the products manufactured according to the present process have been made resistant to water by treatment with substances precipitating albumens, for example with tannic acid, then, on acting with even dilute caustic alkali upon this product, the compound is decomposed into the original cellulose ether displaying the characteristic feature of swelling or softening or dissolving in ice cold water and the tanning agent which can easily be found out and identified by the well known analytical methods.

I claim:

1. A process of dyeing alkyl cellulose insoluble in water at 16° C., and above, but capable of substantially swelling in water at some lower temperature, which comprises exposing the article to the action of water at a temperature at which it will swell, and treating the same with a dye solution.

2. A process of dyeing alkyl cellulose insoluble in water at 10° C., and above, but capable of substantially swelling in water at some lower temperature, which comprises exposing the article to the action of water at a temperature at which it will swell, and treating the same with a dye solution.

3. A process of dyeing alkyl cellulose insoluble in water at 5° C., and above but capable of substantially swelling in water at some lower temperature, which comprises exposing the article to the action of water at a temperature at which it will swell, and treating the same with a dye solution.

4. A process of dyeing alkyl cellulose insoluble in water at 10° C. and above but capable of slighty swelling in water at some lower temperature, which comprises exposing the article to the action of water at a temperature at which it will swell, and treating the same with a dye solution.

5. A process of dyeing and treating alkyl cellulose insoluble in water at 16° C., and above, but capable of swelling in water at some lower temperature, which comprises exposing such material to the action of water at a temperature at which it will swell, then treating the same with a solution of a dye, while in a swelled condition, and finally treating the same with a solution of an agent capable of precipitating albuminoid substances, whereby the product is rendered less affected by water.

6. A process of dyeing a material containing an alkyl cellulose insoluble in water at 16° C., and above, but capable of substantially swelling in water at some lower temperature, which comprises exposing the article to the action of water at a temperature at which it will swell, and treating the same with a dye solution.

7. A process of dyeing a formed article containing an alkyl cellulose insoluble in water at 16° C., and above, but capable of substantially swelling in water at some lower temperature, which comprises exposing the article to the action of water at a temperature at which it will swell, treating the same with a dye solution.

8. A process of dyeing a material containing an alkyl cellulose insoluble in water

at 16° C. and above, but capable of substantially swelling in water at some lower temperature, together with other constituents compatible therewith, which comprises exposing the material to the action of water at a temperature at which it will swell, and treating the same with a dye solution.

9. A process of dyeing a material containing an alkyl cellulose insoluble in water at 16° C. and above, but capable of substantially swelling in water at some lower temperature, together with other material capable of influencing the plasticity, suppleness, and softness thereof, which comprises exposing the material to the action of water at a temperature at which it will swell, and treating the same with a dye solution.

10. An article containing a dyed alkyl cellulose insoluble in water at 16° C., but capable of swelling in water at some lower temperature, without dissolving or disintegrating.

11. An article containing a dyed alkyl cellulose insoluble in water at 16° C., but capable of swelling in water at some lower temperature, without dissolving or disintegrating, the dye present in the article being other than a basic dye.

12. An article containing a dyed alkyl cellulose insoluble in water at 16° C., but capable of swelling in water at some lower temperature, without dissolving or disintegrating, the dye present in the article being a substantive dye.

13. An article containing a dyed alkyl cellulose insoluble in water at 16° C., but capable of swelling in water at some lower temperature such alkyl cellulose being combined with a substance capable of precipitating albumen.

14. An article containing a dyed alkyl cellulose insoluble in water at 16° C., but capable of swelling in water at some lower temperature, such alkyl cellulose being combined with a tanning material.

15. An article containing a dyed compound of a tannic acid with an alkyl cellulose insoluble in water at 16° C. but capable of swelling in water at some lower temperature.

16. The process of dyeing cellulose ether which process comprises softening said ether without dissolving the same and dyeing the same while softened.

17. The process of dyeing cellulose ether substantially insoluble in water at room temperature which process comprises swelling said ether without dissolving the same and dyeing said ether while it is swollen.

18. The process of dyeing artificial structures comprising cellulose ether which process comprises softening said ether without disintegrating said structures and dyeing the ether while softened.

19. The process of dyeing artificial structures comprising cellulose ether insoluble in water at room temperature, which process comprises swelling said ether without disintegrating said structures and dyeing said ethers while swollen.

20. The process of coloring artificial structures containing cellulose ether, which process comprises treating said structures in a dye bath until dyed, such treatment being effected at a temperature at which the said structures can absorb dye compound from said bath.

21. The process of coloring artificial structures containing cellulose ether, which process comprises treating said structures in an aqueous dye bath, while at a temperature at which the said structures can absorb dye from said bath, while permitting said structures to remain intact.

22. The process of coloring artificial structures containing cellulose ether, which process comprises treating said structures with a dye bath containing dye compound equal to from 1% to 8% of the weight of the cellulose ether until a strong dyeing is obtained, such treatment being effected at a temperature at which the said structures can absorb dye compound from said bath.

23. The process of coloring solid cellulose ether insoluble in water at room temperature and in a condition in which it is substantially unsusceptible to ordinary dyeing operations, which process comprises treating said ether with a fluid which alters the condition thereof to make it susceptible to a dyeing operation, but without disintegrating or dissolving said ether, and treating said solid ether with dyes, while it is in said susceptible condition.

24. The process of dyeing artificial structures containing cellulose ether insoluble in water at room temperature and normally resistant to dye baths, which process comprises treating said structure with an aqueous liquid under non-disintegrating conditions until said resistance of said ether to dye baths is lessened, and dyeing said structures in the presence of water while said resistance is lessened.

25. The process of dyeing artificial structures containing cellulose ether insoluble in water at room temperature and normally impenetrable to dye, which process comprises treating said structures under non-disintegrating conditions with a penetrant softening liquid compatible with said dye, and treating said structure with dye while said liquid is at least partly penetrated into said structures.

26. The process of dyeing artificial structures containing solid amorphous cellulose ether insoluble in water at room temperature and substantially impenetrable to dye baths, which comprises swelling said structures under non-disintegrating conditions with a penetrant liquid compatible with said baths,

and treating said structures with said baths while the structures are thus swollen.

27. The process of dyeing artificial structures containing cellulose ether insoluble in water at room temperature and normally impenetrable to dye baths, which process comprises treating said structures with a dye bath containing a penetrant liquid acting as at least part of the carrier of the dye under non-disintegrating conditions which permit said liquid to penetrate said structures with said dye.

28. A process which comprises soaking an article containing a cellulose ether, in cold aqueous liquid at a temperature at which such article becomes swollen but not disintegrated nor dissolved, such liquid containing a dissolved dye during the latter part at least of such operation, whereby the dye is absorbed by the said article to an extent sufficient to be properly termed "dyed material" in the ordinary acceptation of said term, and thereafter removing such article from the conditions given.

29. The process of coloring artificial structures containing cellulose ether insoluble in water at room temperature and normally resistant to dyeing, which comprises treating said structures with a modifying liquid under non-disintegrating conditions until said resistance is lessened, treating said structures with a bath containing dyeing material while said resistance is lessened, such latter treatment being continued until said structures take up the dyeing material.

30. A process of dyeing a cellulose ether structure which comprises the step of contacting said structure with a dye bath at a temperature at which such structure absorbs dye from said bath.

In testimony whereof I affix my signature.

LEON LILIENFELD.