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3,600,121

## METHOD FOR OBTAINING LEVEL DYEING ON CELLULOSIC FIBERS USING POLYETHYLENE GLYCOL CARBOXYLIC ACID ESTERS AS UNSTABLE RETARDING AGENT

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17 Claims

### ABSTRACT OF THE DISCLOSURE

Dyeing methods employing polyethylene glycol carboxylic acid esters as unstable retarding agents in alkaline dyebaths containing vat or sulfur dyestuffs provide level dyeing and permit substantial exhaustion of dyebath and close control over the dyeing process.

This invention relates to the dyeing of cellulosic fibers to obtain level dyeings and permit substantial exhaustion of the dyebath. More particularly, the invention relates to the use of carboxylic acid esters of polyethylene glycols and closely related compounds as retarding agents in alkaline dyebaths for cellulosic fibers, this mixture with other fibers and yarns and fabrics made from them.

Dyeing defects such as light shoulders, white spots, light selvages occur, for instance, often in package and beam dyeing even with vat dyes which are generally classified as level dyeing. It is not difficult to understand that there is a close relation between flow rate, the rate of exhaustion and levelness of dyeing.

Unevenness caused by variations of flow rate within a package can be counteracted either by increasing the flow or by reducing the rate of exhaustion.

It has been known for many years that many water soluble nonionic compounds which have a hydrophobic group and a polyethylene glycol chain as a solubilizing group are retarding agents. The first such agent was probably Peralgal O of I. G. Farben-industrie which is made by the addition of ethylene oxide to a fatty alcohol. Compounds of this type are completely stable to caustic and thus are stable in vat or sulfur dyebaths which are generally strongly alkaline. It is generally assumed that the nonionic compounds form a bond with the leuco form of the vat dyestuff and so compete for it with the cotton. If this mechanism is accepted then it must be expected that the exhaustion will be incomplete if the concentration of the nonionic agent is too high and that there will be a severe upper limit on the concentration of retarding agent which can be used without preventing exhaustion of a substantial part of the dyestuff. This puts a severe limit on the degree of retarding that can be obtained. In addition, this permissible concentration of retarding agent will vary with the dyestuff and with temperature and concentration of other chemicals present in the dyebath. Thus, the retarding of dyestuff mixtures is made especially impractical.

It is to be expected that the levelness of dyeing of yarn packages, for instance, will be improved by reducing the rate of exhaustion. If this rate is sufficiently low the dye concentration in the solution will change only a little during passage through the yarn package so that the dye concentration is almost the same at every point in the package at any given time during the dyeing process. Combined with the generally practiced periodic reversal of flow, this will lead to a level dyeing except for any non-uniformity of the yarn itself.

It is necessary for the leuco compound-retarder complex to stay in solution so that it circulates freely through the package. It should not form a precipitate which would

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filter out on the surface of the package even if the precipitate would release the dyestuff gradually because this would be equivalent to feeding the dyestuff slowly into the dyebath without using a retarder and would of course lead to unlevel dyeing.

Fatty alcohol ethers of polyethylene glycol and fatty amine-ethylene oxide condensation products and numerous other polyoxyethylated compounds have been employed heretofore as retarding agents. Schoeller et al. patent, U.S. Pat. 1,970,578, discloses agents of this type as well as polyoxyethylated fatty amines. The group of compounds disclosed and claimed in U.S. Pat. 1,970,578 includes also the polyglycol esters of fatty acids but the use of these esters in dyeing under conditions where they are unstable is not considered or recommended there. None of the numerous examples on the use of the esters deals with dyeing. Since the issuance of this patent in 1934 the textile industry has accepted and used to some extent the fatty alcohol ethers of polyethylene glycol and other polyoxyethylated compounds which are stable in the dyebath. The fatty acid esters, however, are unstable in the dyebath and have not been used. It has been and is still generally believed that a retarding agent or levelling agent must be substantially stable in the dyebath and that materials which are unstable in the dyebath are unsuitable.

It has been found that carboxylic acid esters of polyethylene glycol, which are unstable in alkaline dyebaths, provide excellent levelling action during dyeing and permit substantially complete exhaustion of the dyebath when conditions most favorable to decomposition, i.e., saponification, such as increased temperature and/or pH, are applied. It has also been discovered that the rate of saponification is controllable and can be utilized to control the rate of dyeing and extent of exhaustion. For example, this rate initially can be selected by the proper selection of the carboxylic acid portion of the ester and, to some degree by the chain length of the polyethylene glycol portion. Moreover, during the dyeing process the rate of saponification can be controlled through regulation of temperature and/or pH, both of which have a profound effect on the rate of saponification in the dyebath.

The present invention, therefore, comprises an improvement in the method of dyeing cellulosic fibers or yarns with a vat or sulfur dyestuff in which the alkali soluble or reduced form of the dyestuff is applied to the fiber or yarn in an aqueous alkaline medium. The improvement of this invention comprises contacting the alkali soluble leuco form of the dyestuff with an unstable retarding agent comprising a carboxylic acid ester of polyethylene glycol, hereinafter referred to as PEG, before the alkali soluble form is contacted with the fiber or yarn and before the ester is saponified. Thereafter, the cellulosic fibers or yarns are immersed in the dyebath containing the leuco-form of the vat or sulfur dyestuff and as retarding agent, the PEG ester and dyeing of the fiber or yarn is carried out under conditions providing a rate of saponification of the ester-dye complex in the dyebath to provide the desired rate of exhaustion of the dyestuff and to substantially complete the exhaustion in the desired period of time. The saponification rate can be readily controlled by the temperature or pH of the dyebath and by the choice of the retarding agent employed.

The rate of dyeing or exhaustion of the dyebath appears to be substantially directly related to the rate of saponification of the PEG ester. The dye in its reduced state, e.g., leuco or alkali soluble form, probably forms a complex with the retarding agent and this slows down greatly or may even prevent the absorption of the dye on the fiber. Then, as the PEG ester decomposes, the dye form is released and dyes the fiber. The present invention permits a close control over the rate of dyeing during the dyeing operation, by selection of the particular PEG

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ester used, as explained more fully hereinafter, and/or by the regulation of normal dyeing conditions such as temperature and/or pH. Thus, the initial and/or major portion of the dyeing operation can be conducted at a given temperature and pH which provides a relatively slow saponification rate resulting in a slow rate of release of dyestuff and consequently a level dyeing. This is particularly important in dyeing beams and packages where it is desired to prevent the dyebath from being markedly exhausted before it reaches the inner portions of the beam or package. Then, when the desired shade is approached, the dyebath can be substantially fully exhausted by increasing the rate of saponification as by increasing the temperature and/or pH. The close control over the dyeing operation provided by the present invention promises a far-reaching effect on industrial dyeing by making it possible to use in package and beam dyeing dyestuffs which were not suitable because it was not possible, heretofore, to obtain level dyeings with them.

The present invention also makes it possible to obtain level dyeings of a desired shade by using mixtures of dyestuffs which differ widely in their dyeing properties and their response to retarding agents.

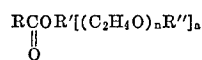
Another embodiment of the invention comprises the use, as retarding agent, of mixtures of two or more PEG esters, one of which saponifies at a relatively high rate and the other of which saponifies at a relatively low rate. This embodiment of the invention is based on the unexpected discovery that the saponification rate of the PEG ester and ester-dye complexes formed therefrom, in general, largely depends upon the molecular weight and structure of the carboxylic acid portion and to a lesser extent on the molecular weight of the polyethylene glycol chain. In the case of fatty acids it has been unexpectedly found that the lower the molecular weight of the acid portion the faster the rate of the saponification. To a lesser extent the rate of saponification is faster for the PEG esters having longer polyethylene glycol chains. There is an upper limit on the chain length of the polyethylene glycol as explained in more detail hereinafter. In addition, PEG esters made from tertiary carboxylic acids and ester-dye complexes formed therefrom are characterized by lower saponification rates than PEG esters made from primary acids of the same molecular weight and ester-dye complexes formed therefrom. Similarly, polyoxyethylated compounds in which the carboxylic acid is esterified with a secondary hydroxyl group, and the ester-dye complexes thereof, are characterized by lower saponification rates than corresponding PEG ester wherein the ester is formed with a primary hydroxyl.

By use of two or more PEG esters of different saponification rates, it is possible to attain level dyeing and substantially complete exhaustion within a practical period of time without increasing the temperature or pH, although such increase can be made, if desired.

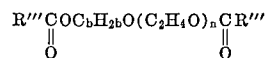
The PEG esters employed as retarding agents in this invention are made from mono-carboxylic acids which are water insoluble and contain 1 or more polyoxyethylene chains having a total of no more than about 25 ethylene oxide units. The polyoxyethylene chain or chains impart water solubility to the PEG ester and may be directly connected through an oxygen bond, to the acyl group derived from the mono-carboxylic acid or said chain or chains may be connected through an organic linking group derived from an organic polyhydric alcohol, e.g., 1,2-propylene glycol, sorbitan, glycerol, etc. Such PEG esters must be soluble in the alkaline dyebath containing the vat or sulfur dyestuff. Upon saponification, the polyoxyethylene chain or chains and connected linking group, if any, form an alcohol, i.e., a mono-ol or a polyol which should not hold the dye in solution in the dyebath.

The PEG esters employed as retarding agents in this invention include monoesters of the formula:

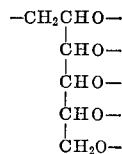
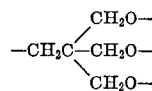
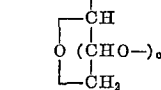
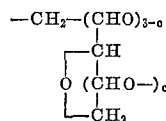
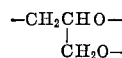
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and the diesters of the formula:



wherein R is a monovalent hydrocarbon group having 6 to 25 carbon atoms, R' is a polyvalent group selected from the class consisting of:

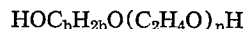


wherein b and c are each an integer of 2 to 3, and R'' is hydrogen or monovalent hydrocarbon having 1 to about 4 carbon atoms, R''' is a monovalent hydrocarbon group having 6 to 18 carbon atoms, a is an integer equal to the valence of R' minus 1, and n is an integer, preferably 4, or more such that the total number of C<sub>2</sub>H<sub>4</sub>O units does not exceed about 25 per molecule. Preferably, the monovalent hydrocarbon groups represented by R and R''' contain 10 to 18 carbon atoms and n is 6 to 18.

Upon saponification in alkaline medium the PEG esters of the type described should form alcohols of the formula:

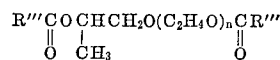


in the case of the monoesters or



in the case of the diesters, and such alcohols should be soluble in the dyebath and should not be capable of holding the dye in solution. The carboxylic acids from which the above-described PEG esters are formed should be water-insoluble. The PEG ester itself, of course, should be soluble in the dyebath.

Typical examples of PEG diesters suitable for use in this invention are polyethylene glycol dilaurate, dicaprate, dimyristate, didodecylate, didecylate, diphenylacetate, diesters of the formula:



where the



groups are respectively lauroyl, caproyl and phenylacetyl and the like. Typical PEG monoesters are polyethylene glycol monostearate, monolaurate, monopalmitate, monooleate, monolinoleate, mononeoheptanoate, monolinolenate, monoarachidate, monolignocerate, monocaproate, monomyristate, monerucate, monovaccenate, monododecylate, monodecylate, monopalmitoleate, and the methyl, ethyl propyl and the butyl ethers of these monoesters. Further examples are polyoxyethylene sorbitan

monolaurate (Tween 20), polyethylene sorbitan mono-palmitate (Tween 40), polyoxyethylene sorbitan mono-oleate, and the like. The monoesters as listed above are advantageous in that fewer ethylene oxide units are needed than in the case of the diesters for providing comparable solubility in the dye bath.

PEG esters having a total of more than about 25 ethylene oxide units have been found to have the disadvantage that their saponification products prevent full exhaustion with some dyes. Thus, PEG esters containing a total of more than about 25 ethylene oxide units are of limited use in this invention.

veniently expressed in terms of "half-life" which is determined by measuring the slope of the straight line of the plot.

The half-lives of several PEG esters were measured in the above-described manner and are set forth in Table I below. The PEG ester in each case was made from the acids listed in Table I and the methyl monoether of polyethylene glycols (PEG ether) having the average molecular weights as listed in the table. The molecular weight range corresponding to the listed average molecular weight of 350 is 335 to 365, of 550 is 525 to 575, and of 750 is 715 to 785.

TABLE I.—RATE OF SAPONIFICATION OF PEG ESTERS

| Measurement No. | Average mol. wt., PEG ether | Acid                          | Temp., ° C. | NaOH, norm. | Half-life   |
|-----------------|-----------------------------|-------------------------------|-------------|-------------|-------------|
| 1.....          | 750                         | Stearic-palmitic <sup>1</sup> | 55          | 0.10        | 51 min.     |
| 2.....          | 550                         | Stearic.....                  | 55          | 0.10        | 73 min.     |
| 3.....          | 750                         | Isostearic <sup>2</sup>       | 55          | 0.10        | 63 min.     |
| 4.....          | 750                         | Oleic (red oil)               | 55          | 0.10        | 69 min.     |
| 5.....          | 750                         | do.....                       | 60          | 0.10        | 51 min.     |
| 6.....          | 750                         | do.....                       | 75          | 0.10        | 24 min.     |
| 7.....          | 750                         | do.....                       | 55          | 0.05        | 147 min.    |
| 8.....          | 750                         | do.....                       | 55          | 0.15        | 33 min.     |
| 9.....          | 750                         | do.....                       | 55          | 0.20        | 21 min.     |
| 10.....         | 750                         | do.....                       | 40          | 0.10        | 135 min.    |
| 11.....         | 550                         | do.....                       | 55          | 0.10        | 78 min.     |
| 12.....         | 550                         | do.....                       | 40          | 0.10        | 148 min.    |
| 13.....         | 550                         | do.....                       | 75          | 0.10        | 20 min.     |
| 14.....         | 550                         | Tall oil FA <sup>3</sup>      | 55          | 0.10        | 57 min.     |
| 15.....         | 750                         | Myristic.....                 | 55          | 0.10        | 35 min.     |
| 16.....         | 750                         | do.....                       | 65          | 0.10        | 18 min.     |
| 17.....         | 750                         | do.....                       | 55          | 0.20        | 11 min.     |
| 18.....         | 550                         | do.....                       | 55          | 0.10        | 47 min.     |
| 19.....         | 750                         | Lauric.....                   | 55          | 0.10        | Very short. |
| 20.....         | 750                         | do.....                       | 55          | 0.05        | 10 min.     |
| 21.....         | 750                         | do.....                       | 40          | 0.10        | 10 min.     |
| 22.....         | 550                         | do.....                       | 40          | 0.10        | 12 min.     |
| 23.....         | 350                         | do.....                       | 40          | 0.10        | 23 min.     |
| 24.....         | 350                         | Neohexanoic <sup>4</sup>      | 55          | 0.10        | 26 min.     |
| 25.....         | 750                         | Phenylacetic.....             | 55          | 0.10        | Very short. |
| 26.....         | 350                         | do.....                       | 40          | 0.10        | Do.         |

<sup>1</sup> A commercial fatty acid sold under the trade name GROCO 59D comprising a mixture of stearic and palmitic acids.

<sup>2</sup> Isostearic acid is a mixture of branched isomers of stearic acid.

<sup>3</sup> Acinol FAs.

<sup>4</sup> Neohexanoic acid is a tertiary hexanoic acid.

Theoretically, the retarding action depends on the strength of the bond between the PEG esters and the particular alkali soluble dye form, e.g., leucodye, of the complex and on the rate at which the PEG ester is hydrolyzed. The latter factor is subject to measurement and the progress of the saponification in an alkaline bath can be followed by periodically determining the monocarboxylic acid salt set free from the PEG ester. The saponification rate, of course, should be determined in the range of concentration in which the glycol ester would be used in the dye bath, e.g. of the order of  $\frac{1}{200}$  mol per liter. The saponification of the PEG esters in alkaline solution is not reversible. Sodium hydroxide is used in large excess over the ester concentration so that the sodium hydroxide concentration will remain practically constant during the reaction. A particularly satisfactory method for measuring the saponification rate rapidly is to take samples at given intervals and determine the amount of acid salt by titration with an inorganic acid, e.g., HCl.

Under conditions of high sodium hydroxide concentration the hydrolysis of the PEG esters behaves formally as a first order reaction as described by the formula

$$\frac{dc}{dt} = KC$$

wherein  $c$  is the PEG ester concentration,  $t$  is the corresponding time,  $C$  is the corresponding glycol ester concentration and  $K$  is a constant which depends only on temperature and OH concentration. When the logarithms of the measured ester concentrations are plotted against the times at which the ester concentration is measured a straight line is obtained. The saponification rate is con-

The most surprising findings shown by Table I are the great differences in rates found for esters of different fatty acids. The half-life for the 750 oleate at 55° C. in 0.05 normal NaOH (Measurement No. 7) is 147 minutes, while a half-life of only 10 minutes is found for the 750 laurate at the same temperature and NaOH concentration, a half-life ratio of 1 to 15. Generally, the half-life rises (saponification rate decreases) with the molecular weight of the fatty acid used to make the PEG ester. The molecular weight of the PEG or PEG monoether used to make the PEG ester also affects the half-life although not as much as the fatty acid. Generally, the half-life of the ester is longer (saponification rate is lower) for the PEG ester of the PEG or PEG monoether having a lower molecular weight, for instance, 78 minutes for the 550 oleate (Measurement No. 11) and 69 minutes for the 750 oleate (Measurement No. 4) at 55° C. in 0.10 N NaOH. Either an increase in temperature or in NaOH concentration considerably lowers the half-life (increases the saponification rate).

The tertiary acid, neohexanoic acid, esterified with the 350 glycol monoether forms a PEG ester which has a much longer half-life than a PEG monoether ester with the corresponding primary acid. Tertiary acids, such as abietic acid, therefore, can be used to make PEG esters of long half-life for use in dyeing at high temperatures and/or high caustic concentrations.

Any suitable dyeing procedure can be used wherein the alkali soluble or reduced form of the dye is contacted with the PEG ester before it contacts the fiber to be dyed and before the PEG ester is saponified. When dyeing beams and packages with vat or sulfur dyes the following procedure (hereinafter referred to as the DR procedure) is convenient. The textile material is immersed in water and then caustic and hydro (sodium sulfoxylate)

in the case of vat dyestuffs, or sodium sulfide and sodium carbonate and/or sodium hydroxide in the case of sulfur dyestuffs, are added first and in machine dyeing the resulting aqueous solution is circulated. A solution is prepared outside, containing the dye in dispersed form and the PEG ester retarding agent, and this solution is then added to the dyebath in the machine and circulation is continued. By this procedure the dye is apparently reduced in the expansion tank and on the way to the packages or beams and the PEG ester retarding agent passes with the dyestuff in the intended ratio. Feeding and circulation of the dyebath to the machine is conducted in any desired manner. When it is desired to accelerate the dyeing operation, the temperature of the dyebath may be raised and/or additional caustic may be added to raise the pH. The dyebath is circulated through the package to substantially full exhaustion.

Another procedure (hereinafter called the S procedure) is to first prepare an aqueous solution of the dyestuff, caustic and hydro, in the case of vat dyestuffs, or of the dyestuffs, sodium sulfide and sodium carbonate in the case of sulfur dyestuffs, and to add the retarding agent with vigorous stirring and then introduce without delay the textile material, a yarn skein for instance. It is preferred in this procedure to begin at a relatively low temperature such as ambient or room temperature and after the dyebath has been fully constituted to increase the temperature gradually while dyeing.

Another dyeing procedure (hereinafter called the CH procedure) consists in contacting with the textile material first a solution of the dispersed dye and the retarding agents. (In machine dyeing the resulting solution is circulated in the machine.) Thereafter either an aqueous solution of caustic and hydro (or sodium sulfide and sodium carbonate and/or sodium hydroxide in the case of sulfur dyes) is added with vigorous agitation or the alkali is first added and then quickly hydro (or sodium sulfide in the case of sulfur dyes) with vigorous agitation. This procedure is least suitable for those PEG ester retarding agents that are characterized with a high rate of saponification.

The proportion of PEG ester retarding agent employed in the dyebath is not narrowly critical. There should be sufficient PEG ester to retard the dyeing sufficiently to obtain level dyeings, this will, of course, depend greatly on conditions such as flow rates, uniformity of package winding, nature and concentration of dyestuff, temperature, pH, etc.

Cellulosic fibers which can be dyed utilizing the retarding agents of the present invention include 100 percent cotton fibers, 100 percent rayon fibers as well as fiber blends made from cotton fibers and rayon fibers together or from cotton and/or rayon fibers blended with synthetic fibers, including polyester fibers, such as, Fortrel (registered trademark of Fiber Industries, Inc.), which comprises a polymerized polycondensate of terephthalic anhydride and ethylene glycol; nylon; polymers containing at least 80% polymerized acrylonitrile, such as those available commercially under the trade names Orlon and Acrilan, and so on.

#### EXAMPLE 1

This example illustrates the advantages of this invention in dyeing packages in a machine. The shade selected for this example was 0.5% Blue BF dyestuff C.I. 69825/6, which in dyeing light shades notoriously provides unlevel dyeings. In order to create strikingly unfavorable conditions from a levelness standpoint, the flow in the machine was throttled down to a greatly reduced rate.

In this example, 1585 grams of cotton yarn in a package were placed in a package dyeing machine and wet out and rinsed in the regular manner. A liquor ratio of 1/7.5 was used in the dyeing. 60 g. sodium hydroxide and then 60 g. hydro was added and circulated through the package at 130° F. for 10 minutes. Then, while the solution was being circulated on the out-to-in-flow (7 mins.), there

was added an aqueous mixture of 0.5% based on the yarn Blue BF double paste and 2.5% based on the yarn of the methyl monoether of polyethylene glycol monomyristate (550 PEG myristate) made from a methyl monoether polyethylene glycol having an average molecular weight of 550. The flow was reversed to in-to-out. The dyeing operation was continued for 30 minutes, at 130° F. periodically reversing the flow.

The package was taken apart and in spite of conditions severely adverse to levelness, the dyeing was found to be level throughout with the only exception of a light outside, a well known defect of dyeing Blue BF in the light shades. Packages dyed with the same amount of Blue BF according to standard dye-house procedure without any PEG ester retarder contained large undyed areas extending through the package.

In order to obviate the light outside effect, packages were dyed as described in detail above using 550 PEG oleate instead of 550 PEG myristate. There resulted a level dyeing throughout and the outside of the package was only slightly light, resulting in a very significant reduction in the light outside effect. This illustrates that the use of a PEG ester having a slower rate of saponification can be used to overcome even minor levelness problems under the severest conditions.

#### EXAMPLE 2

This example illustrates the advantages of this invention in the machine dyeing of packages with mixtures of dyes having different properties. The dye employed in this example comprises 1% Olive T, (C.I. 69525) 0.28% Blue RA (C.I. 59815) and 0.06% Jade Green (C.I. 59825/6) based on the weight of the yarn.

In this example 1600 grams of cotton yarn in a package were placed in a dyeing machine and wet out in the usual manner for 20 minutes at 180° F. and then rinsed for 5 minutes. An aqueous solution containing the above mentioned dye mixture and 5%, based on the yarn, of the methyl monoether of polyethylene glycol laurate (550 PEG laurate) made from a methyl monoether polyethylene glycol having an average molecular weight of 550, was formed in the machine. The solution was circulated on the out-to-in cycle for 6 minutes and then the flow was reversed for the in-to-out cycle for 4 minutes. Then, 5 grams sodium hydroxide and 2.5 grams hydro per liter of dye solution were added. The dyeing operation was carried out by alternating the direction of flow in 6-4 cycles, that is out-to-in flow for 6 minutes and in-to-out flow for 4 minutes. The first 10 minutes of dyeing was carried out at 40° C., the second 10 minutes was carried out at 550° C., the third 10 minutes was carried out at 60° C. and the remaining dyeing time was carried out at 70° C. Thereafter the package was finished in the usual manner.

Fabrics made from yarns from the inside, middle and outside of the package confirmed the excellent levelness of the dyeing. Moreover, the desired gray shade was obtained indicating that each dye of the mixture exhausted to the proper extent for producing the desired gray shade. The dyebath had exhausted more than about 85% after one hour of dyeing.

The present invention permits the selection of a wide range of degrees of retarding and permits dyeing at any desired speed while permitting the attainment of the desired shade, even though mixtures of dyes, having widely different properties, are used. Moreover, the present invention makes it possible to select a desired degree of retarding by the proper selection of the PEG ester as described herein and permits the attainment of the same shades at widely different dyeing speeds as desired.

#### EXAMPLE 3

A dye solution was prepared which contained 2.00 grams Olive Green BD (C.I. 69500), 5 grams sodium hydroxide and 5 grams sodium sulfoxylate per liter. Six dye vessels of a laboratory skein dyeing machine were

charged each with 250 ml. of this dye solution so that each dye vessel contained 0.50 gram of the dyestuff. The dye solutions were heated in the machine to 55° C. Cotton yarn skeins weighing 10.0 grams each were wet out, rinsed, squeezed, and fastened on skein holders. Now 0.5 gram of methoxypolyethylene glycol 550 oleate dissolved in 5 ml. water was added to a dye vessel stirred slowly and then a skein inserted which was kept in constant motion by the machine. Retarding agent and skeins were put into 5 more vessels following exactly the same procedure. After having been dyed for the times indicated in Table No. 2, the skeins were withdrawn and the remaining dye solution transferred to screw top jars and held for colorimetric determination of the dye concentration. A Bausch and Lomb Spectronic 20 spectrophotometer was used for this and well known procedures were followed.

Table 2

| Time:      | Dye concentration, percent |
|------------|----------------------------|
| Zero       | 100                        |
| 2 minutes  | 67                         |
| 5 minutes  | 58                         |
| 10 minutes | 45                         |
| 20 minutes | 37                         |
| 60 minutes | 16                         |
| 85 minutes | 12                         |

When the retarding agent was omitted but the same procedure followed, otherwise there was only 19% of the dye left after two minutes and only 10% after five minutes. This demonstrates that the retarding agent has slowed down the exhaustion of the dye greatly while not preventing it from completion in objectionable way. At the liquor ratio of 25/1 used here over 5% of the dye remains in solution in absence of a retarding agent.

## EXAMPLE 4

The procedure in Example 3 was repeated exactly except that the dyeing was done at 40° C.

Table 3

| Time:      | Dye concentration, percent |
|------------|----------------------------|
| Zero       | 100                        |
| 2 minutes  | 91                         |
| 5 minutes  | 83                         |
| 10 minutes | 76                         |
| 20 minutes | 67                         |
| 40 minutes | 55                         |
| 60 minutes | 45                         |

At 40° C. the exhaustion of the dye is still much slower than at 55° in Example 1. This is largely due to the lower rate of saponification of the retarding agent at the lower temperature. It will be a very good procedure to start at 40° C. and gradually raise the temperature to complete exhaustion.

## EXAMPLE 5

Skeins were dyed with 2% Olive Green BD at 55° C. following the same procedure as in Example 3 but using "Siponic L 12" as retarding agent, a product said to be an adduct of 12 moles ethylene oxide to a lauryl alcohol.

The product is similar to the ethers named in U.S. Pat. 1,970,578 as leveling agents for vat dyes and is completely stable in the alkaline dye bath. Instead of determining the dye concentration in the dye bath colorimetrically the shade of the dyed skeins was estimated visually by comparison with skeins dyed with known percentages of the dyestuff. The results are given in Table No. 4.

Table 4

| Time:      | Percent of full shade |
|------------|-----------------------|
| 2 minutes  | 15                    |
| 5 minutes  | 20                    |
| 10 minutes | 30                    |
| 20 minutes | 40                    |
| 40 minutes | 50                    |
| 60 minutes | 50                    |

It is seen that the retarding agent retained half of the dyestuff in the dyebath permanently.

## EXAMPLE 6

Skeins were dyed with 2% (on the weight of the yarn) of Blue RA (C.I. 59815) following the procedure described in Example 4. 5% Carbowax 750 Laurate was used as retarding agent where Carbowax 750 is a methoxy polyethylene glycol of molecular weight 750. Table No. 5 gives the results.

Table 5

| Time:      | Dye concentration, percent |
|------------|----------------------------|
| Zero       | 100 (87)                   |
| 10 minutes | 95                         |
| 30 minutes | 76 (50)                    |
| 60 minutes | 40 (10)                    |
| 90 minutes | 33                         |

The exhaustion is slower than may be desired, but when the dyeing was run the same way, except that the concentration of sodium hydroxide was increased from 5 to 10 grams/liter, the figures in the third column were obtained. This demonstrates how increase in pH raises the exhaustion by raising the rate of saponification of the ester retarding agent. When the retarder was omitted in the dyeing performed with 5 grams/liter sodium hydroxide the exhaustion was complete in much less than ten minutes and too rapid for measurement by the procedure.

## EXAMPLE 7

The procedure in Example 6 was repeated except that Carbowax 550 Decanoate was used as retarding agent and the results of Table 6 were obtained.

Table 6

| Time:      | Dye concentration, percent |
|------------|----------------------------|
| Zero       | 100                        |
| 5 minutes  | 74                         |
| 10 minutes | 53                         |
| 20 minutes | 36                         |
| 30 minutes | 25                         |
| 45 minutes | 17                         |
| 60 minutes | 13                         |

Carbowax 550 Decanoate proves to be a very good retarding agent for Blue RA at 55° C. with 5 grams/liter sodium hydroxide in the dye bath. It is saponified more rapidly than the Carbowax 550 Laurate (see Table 5) and therefore, permits more rapid dyeing.

## EXAMPLE 8

The procedure of Example 3 was used for dyeing skeins with 2% Blue BF (C.I. 69825/6) and Tween 40 (5% on the weight of the yarn) as retarding agent. Tween 40 is a polyoxyethylene sorbitan monopalmitate. Dyeings were made at 40° C. and at 55° C. and the results are shown in Table 7. The course of the dyeing was followed here not by colorimetric determination of dye concentration in the dye bath but by estimating the depth of shade by visual comparison with skeins dyed with known amounts of Blue BF.

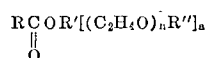
TABLE 7

| Time            | Percent of full shade |           |
|-----------------|-----------------------|-----------|
|                 | At 40° C.             | At 55° C. |
|                 | Zero                  | Zero      |
| 5 minutes.....  | 35                    | 55        |
| 10 minutes..... | 45                    | 60        |
| 20 minutes..... | 55                    | 65        |
| 47 minutes..... | 65                    | 75        |
| 60 minutes..... | 70                    | 100       |

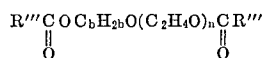
When the dyeing was done at 55° C. in absence of a retarding agent the exhaustion was complete in five minutes, and at 40° C. it was complete in ten minutes. The example shows clearly that with the ester retarding agents the exhaustion of the dye can be greatly slowed down by starting the dyeing at low temperature and still made complete in a reasonable time by raising the temperature later.

What is claimed is:

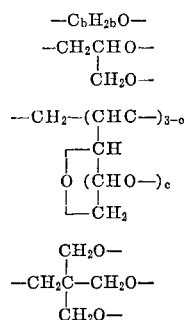
1. In dyeing cellulosic fibers with a vat dyestuff or a sulfur dyestuff wherein said dyestuff is reduced to its alkali soluble form which is applied in alkaline dyebath to said fiber, that improvement comprising, contacting said alkali soluble form with an ester soluble in said dyebath and selected from the class consisting of monoesters of the formula:



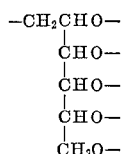
and diesters of the formula:



wherein R is a monovalent acyl group having 6 to 25 carbon atoms, derived from a water insoluble mono-carboxylic acid, R' is a polyvalent group selected from the class consisting of:



and



wherein *b* and *c* are each an integer of 2 to 3, and R'' is member of the class consisting of hydrogen and lower alkyl having 1 to about 4 carbon atoms, R''' is a monovalent acyl group having 6 to 18 carbon atoms derived from a water insoluble mono-carboxylic acid, *a* is an integer equal to the valence of R' minus 1, and *n* is an integer of 1 to about 25, each ethylene oxide chain, (C<sub>2</sub>H<sub>4</sub>O)<sub>*n*</sub>, being bonded to oxygen of said polyvalent group, said ester being contacted with said alkali soluble form prior to contacting said reduced form with said

fiber and prior to saponification of said ester contacted with said reduced form, and the concentration of alkali in said dyebath being in large excess over the concentration of said ester and sufficient to maintain the pH of the dyebath substantially constant.

2. Improvement as claimed in claim 1 wherein the monovalent acyl groups as represented by R and R''' contain 10 to 18 carbon atoms and *n* is 6 to 18.

3. Improvement as claimed in claim 1 wherein said dyestuff is a vat dyestuff.

4. Method as claimed in claim 3 wherein said ester is the dilaurate of a polyethyleneglycol of an average molecular weight of about 400 to 1000.

5. Method as claimed in claim 3 wherein said composition is methyl monoether of polyethylene glycol monostearate containing 6 to 18 oxyethylene units.

6. Method as claimed in claim 3 wherein said ester is methyl monoether of polyethylene glycol mono-oleate containing 6 to 18 oxyethylene units.

7. Method as claimed in claim 3 wherein said ester is methyl monoether of polyethylene glycol monomyristate containing 6 to 18 oxyethylene units.

8. Method as claimed in claim 3 wherein said ester is methyl monoether of polyethylene glycol monolaurate containing 6 to 18 oxyethylene units.

9. Method as claimed in claim 3 wherein said ester is in a mixture of monoesters of methyl monoether of polyethylene glycol containing 6 to 18 oxyethylene units and stearic acid and palmitic acids.

10. Method claimed in claim 3 wherein said ester is in a mixture of monoesters of methyl monoether of polyethylene glycol containing 6 to 18 oxyethylene units and branched isomers of stearic acid.

11. Method as claimed in claim 3 wherein said ester is methyl monoether of polyethylene glycol monophenylacetate containing 6 to 18 oxyethylene units.

12. Method as claimed in claim 3 wherein said ester is methyl monoether of polyethylene glycol mononeoheptanoate containing 6 to 18 oxyethylene units.

13. Method as claimed in claim 3 wherein said ester is polyoxyethylene sorbitan monolaurate containing 6 to 18 oxyethylene units.

14. Method as claimed in claim 3 wherein said ester is polyoxyethylene sorbitan monooleate containing 6 to 18 oxyethylene units.

15. Method as claimed in claim 3 wherein said ester is polyoxyethylene sorbitan monopalmitate containing 6 to 18 oxyethylene units.

16. Method of dyeing cellulosic fibers as claimed in claim 1 comprising immersing the fiber to be dyed in said alkaline dyebath containing said dyestuff and two or more of said esters dissolved in said dyebath.

17. Method as claimed in claim 16 wherein said dyestuff is a vat dyestuff.

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