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[54] PROCESS OF LEVEL DYEING OF FIBROUS POLY-ACRYLONITRILE TEXTILES WITH CATIONIC DYESTUFFS

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[51] **Int. Cl.**....................D06p 3/70
[58] **Field of Search**....................8/177, 177 AB

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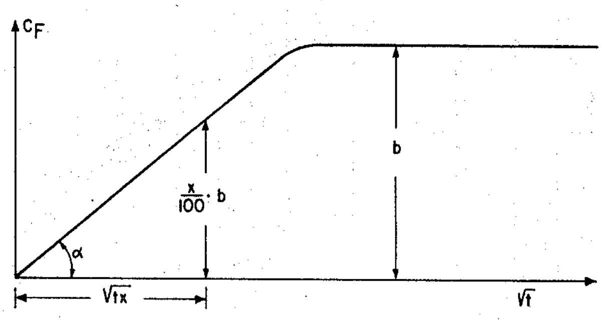
[57] **ABSTRACT**

A method of dyeing a fibrous textile material composed of an acrylonitrile polymer in level shades with a cationic dye from an aqueous liquor by carrying out the dyeing at a predetermined temperature *T* which is dependent upon definite liquor exhaustion rates, a constant *a* which denotes the change in temperature which halves or doubles the liquor exhaustion rate measured at a dyeing temperature of 100° C and a constant *b* which denotes the depth of color to be achieved in milligrams of dye per gram of fibrous material.

3 Claims, 2 Drawing Figures



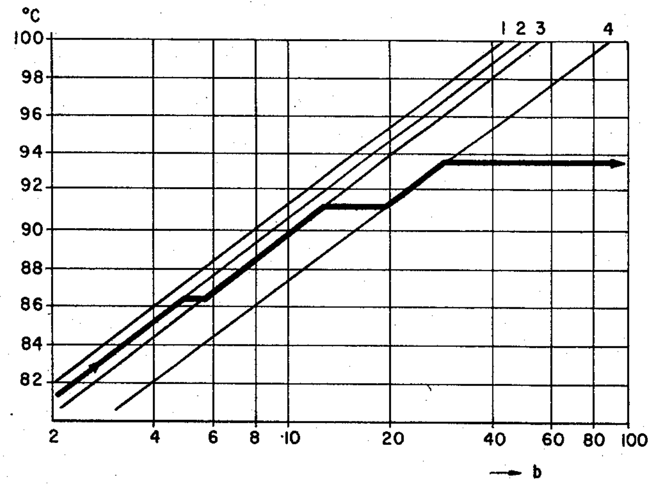


FIG. 1

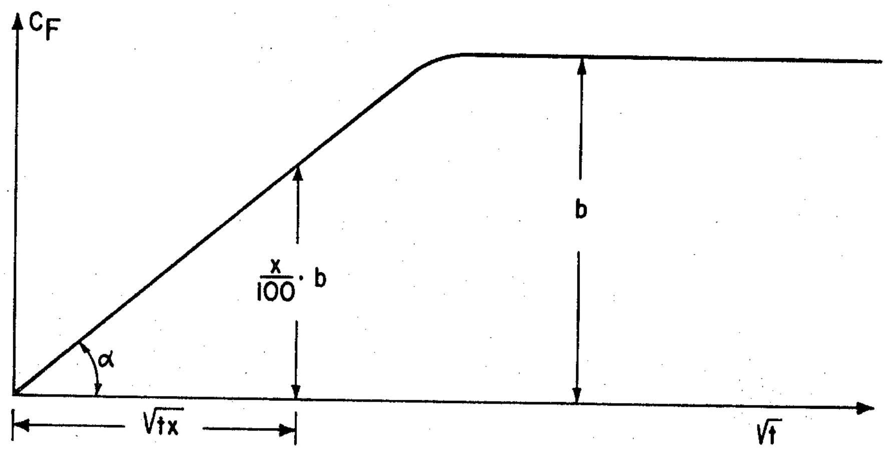
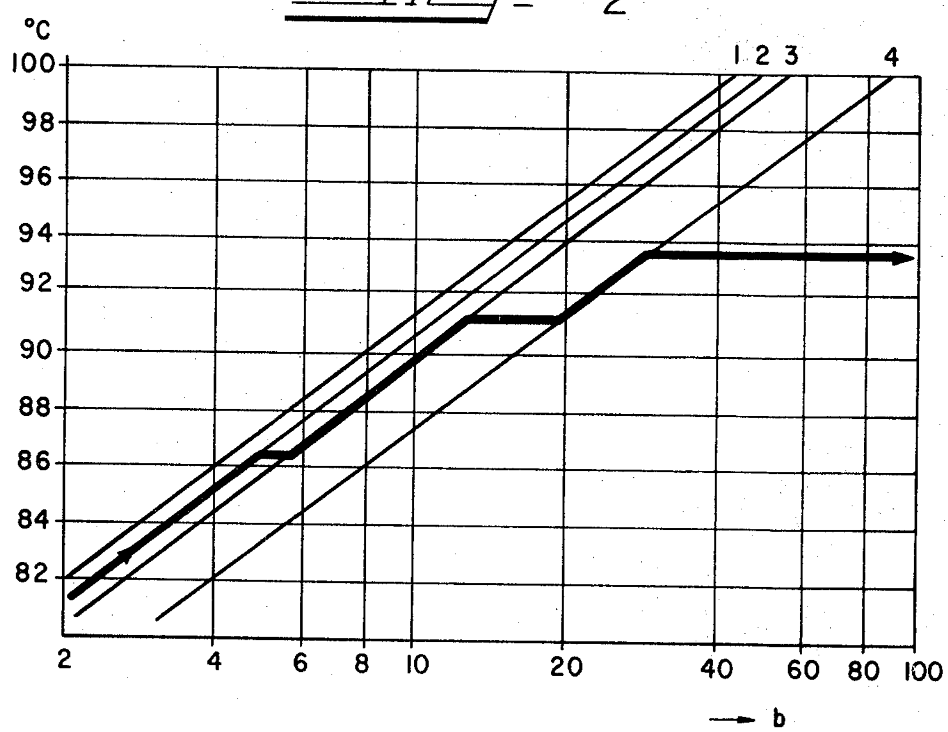


FIG. 2



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PROCESS OF LEVEL DYEING OF FIBROUS POLYACRYLONITRILE TEXTILES WITH CATIONIC DYESTUFFS

This invention relates to a new process for dyeing acrylonitrile polymers.

According to conventional methods of dyeing acrylonitrile polymers, an acid, a salt and a dye and, if necessary, a retarding agent are added to the dye liquor which is rapidly brought to a temperature corresponding to the glass temperature of the fiber generally from 70° to 85°C. The temperature is thereafter raised slowly and uniformly to 100°C and the liquor is held at boiling temperature until it is exhausted and good penetration of the fiber has been achieved.

In this method it is a disadvantage that a long heating up period is necessary and that the temperature has to be increased with great care in order to prevent unevenness.

In the rapid-dyeing method described in Melliand Textilberichte, 49, 195 et seq. (1968) the difficulties occuring during the heating up period are avoided by adding acid and salt to the liquor, rapidly bringing it to boiling temperature and only then adding the dye and any retarder needed. The entire dyeing process thus takes place at the boiling temperature. This method is only suitable however for dyeing equipment in which there is a particularly rapid liquor circulation because it is only thus that dye added at the boiling temperature can be quickly and homogeneously distributed in the dye liquor.

Another method of dyeing acrylonitrile polymer fibers is that known as the constant-temperature method. The retarder can be dispensed with in this method. Acid and salt are added to the liquor and it is brought to a temperature T which lies between 80° and 100°C, depending on the depth of color required. As soon as this temperature is constant, the dye is added and allowed to be absorbed.

The disadvantage of this method is that the experimental methods of determining T are so inexact that it is not possible to give a specific temperature but only a wide temperature range. The inaccuracy of the methods of determining T is also shown by the fact that it is not possible to differentiate between dyes having different tinctorial behavior and that the experimental results make it seem that there is a linear dependence of the dyeing temperature on the depth of color to be achieved.

The rate of absorption of cationic dyes is in fact so dependent on temperature that it is doubled or halved as a rule by a change in temperature of only 4°C. It follows from this that in the constant-temperature method the usual indication of a temperature range is not exact enough and does not ensure reliable results.

We have now found that acrylonitrile polymer and copolymer textile material can be dyed level shades with cationic dyes by heating the liquor to the dyeing temperature T and carrying out the dyeing at this temperature at a defined rate of exhaustion, the temperature T being derived from the equation:

$$T = 100 - \frac{a}{\log 2}\left(\log tg\alpha(100^\circ\text{ C.}) - \log b - \log\left(\frac{X}{\sqrt{t_x}}\right)_T + 2\right) \quad (1)$$

where:

a is the change in temperature which halves or doubles

$tg\alpha$(100°C is the depth of color to be achieved in mg of commercial dye per g of fibrous materal

dye per g of fibrous material

X is the exhaustion of the liquor as a percentage

t_x is the dyeing time in seconds appertaining to the liquor exhaustion X

$(X/\sqrt{t_x})T$ is the rate of liquor exhaustion at the temperature T, and

$tg\alpha$(100°C) is equal to $C_F/\sqrt{t}$

C_F being the concentration of commercial dye in the fiber in mg per g which is present after the time t at a dyeing temperature of 100°C.

The term commercial dye refers to a dye of commercial purity. Acrylonitrile polymers and copolymers for the purposes of this invention are e.g. the polymerization products of acrylonitrile which are modified so that they are dyeable with cationic dyes.

Fibers consisting of such polymers are readily available in the commercial market. The textile material to be dyed according to the invention may be present in the form of fibers, flock, or non-woven, woven or knitted fabrics.

Cationic or basic dyes for the purposes of the invention are those, in which the cation is the chromophor portion. For a definition of basic dyes see e.g. Color Index, Volume 1, p. 1617 (1956).

Within the group of cationic dyes the compounds having an azacyanine system are of special importance.

There are several variants for dyeing at a defined rate of liquor exhaustion. For example the dye liquor to which acid (with or without salt) has been added and which already contains the textile material to be dyed may be heated to the dyeing temperature calculated according to equation (1) and then the dissolved dye added.

To avoid disturbances caused by temporary differences in concentration during addition of the dye, it may be advantageous to remove the textile material from the liquor, to add the dye and, as soon as it has been homogeneously dispersed, to return the textile material. To compensate for any fall in temperature occurring by heat radiation of the textile material, the liquor can be raised to an appropriately higher temperature prior to removal of the textile material.

For the single bath bulking and dyeing of high bulk yarn according to the new process, the liquor to which acid (with or without salt) has been added may be heated rapidly to boiling point and kept boiling until the yarn has been bulked. It is then cooled to the calculated temperature T, the dye is added and dyeing is carried out.

Finally it is also possible, as in the conventional methods, to add acid, salt and dye at a low temperature, to heat the liquor to the temperature T calculated according to equation (1) and to carry out dyeing at this temperature.

When the dyeing process at the temperature T calculated according to equation (1) is substantially over, the liquor may either be cooled immediately, or it may be heated to a higher temperature, for example 100°C, to improve liquor exhaustion and penetration of the fiber.

Unevenness arises from the fact that at different parts of the fibrous material the dye goes on at different rates owing to temperature and concentration differences of the dye in the liquor.

Unevenness is therefore the better prevented the more rapidly the liquor circulates in the equipment used. The probability of obtaining a level dyeing under given dyeing conditions is therefore dependent on the type of machine used. For example level dyeings may easily be obtained in cheese dyeing machines in which liquor circulation is good, but in the case of hank dyeing machines having slow liquid circulation it is often necessary to take special precautions to obtain a good result.

The new process offers the advantage over prior art methods that the liquor exhaustion rate can be adjusted for all dyeings with cationic dyes to an optimum value for given equipment. This value depends especially on the circulation of the liquor in the machine and can be so adjusted that the liquor is exhausted for example in 20, 30, or 90 minutes or two hours.

Another advantage of this process arises from the fact that the probability of obtaining a level dyeing is the same for all dyeing recipes provided dyeing is carried out at the same liquor exhaustion rate. When it has been established that in a particular machine a liquor exhaustion time of for example 60 minutes results in level dyeings, this liquor exhaustion time can be relied on to give level shades in all subsequent batches.

The equation (1) which is necessary according to the new process for ascertaining the dyeing temperature T is determined as follows:

In dyeing polyacrylonitrile fibers it is necessary to distinguish between liquor exhaustion rate and rate of absorption. The rate of absorption is given by the equation (2):

$$C_F/\sqrt{t} = \text{constant}\ \sqrt{D} \quad (2)$$

C_F being the concentration of dye in the fiber in mg of commercial dye per g of fibrous material; constant denoting fiber constant;

D denoting diffusion coefficient and

t denoting time in seconds.

If in a coordinate system the concentration C_F is plotted against $\sqrt{t}$, a straight line is obtained whose inclination:

$$\text{tg}\alpha = \text{constant}\ \sqrt{D}$$

is a clear measure of the rate of absorption of the dye concerned. As may be seen from the equation, tgα is independent of the concentration in the dye liquor and accordingly independent of the depth of color to be achieved.

In FIG. 1 of the drawing the absorption process for a dyeing whose depth of color is to be variable and is denoted by b is represented by such a straight line (see FIG. 1).

Since the amount of dye cannot exceed the value b, C_F rises linearly with $\sqrt{t}$ and finally becomes a straight line proceeding parallel to the abcissa at a distance b.

If the amount of dye in parts absorbed is given by the expression $(X:100)\cdot b$ and the dyeing time appropriate to this amount of dye is given by t_x, the equation (3) holds good according to FIG. 1:

$$tg\alpha = \left(\frac{X}{\sqrt{t_x}}\right)_T \cdot \frac{b}{100} \quad (3)$$

where p1 X = liquor exhaustion in %

t_x = time for liquor exhaustion X

b = depth of color to be achieved in mg of commercial dye per g of fiber

$(X/\sqrt{t_x})$T = rate of liquor exhaustion at a temperature T, i. e. the extent (in %) to which the liquor is exhausted after a certain time.

Equation (3) establishes a quantitative relation between absorption rate tgα and liquor exhaustion rate $(X/\sqrt{t_x})$T. Having regard to the fact that tgα is a dye constant independent of quantity, equation (3) shows that the liquor exhaustion rate has to decrease as the depth of color b increases, which agrees with experience in practice.

The rate of absorption of cationic dyes by polyacrylonitrile fibers is very dependent on temperature above the glass temperature. With some types of fiber a lowering of the temperature by only 3°C is enough to halve the tgα value. If the temperature is lowered by 6°C, the tgα value is quartered and upon lowering the temperature by 9°C one eighth of the tgα value results.

In order to find a quantitative expression for the dependence on temperature of the value tgα to be determined at 100°C, the question may be asked how often tgα has to be halved in order to obtain the lower value tgα (T), and this question formulated by an equation. Equation (4) follows from this:

$$\frac{tg\alpha(100°\ \text{C.})}{2^n} = tg\alpha(T) \quad (4)$$

n = the number of times tgα has to be divided in half in the lowering of the temperature from 100°C to T°C. Since a single halving of tgα is brought about by a reduction in temperature of 1 × 3°C (with a fiber having a temperature factor of 3°C), a second halving by a reduction in temperature of 2 × 3°C, halving by n times by a reduction in temperature of n × 3°C,

$$\Delta T = n \times 3°\text{C} \quad (5)$$

The value n in equation (4) may therefore be replaced by $\Delta T/3$ and equation (6) is then obtained:

$$\frac{tg\alpha(100°)}{2^{\frac{\Delta T}{3}}} = \frac{tg\alpha(100°)}{2^{\frac{100-T}{3}}} = tg\alpha(T) \quad (6)$$

Having regard to equation (3), equation (7) is then obtained:

$$\frac{tg\alpha(100°)}{2^{\frac{100-T}{3}}} = \left(\frac{X}{\sqrt{t_x}}\right)_T \cdot \frac{b}{100} \quad (7)$$

which can be generalized by replacing the number 3 by a, equation (8) being obtained:

$$\frac{tg\alpha(100°)}{2^{\frac{100-T}{a}}} = \left(\frac{X}{\sqrt{t_x}}\right)_T \cdot \frac{b}{100} \quad (8)$$

a = reduction in temperature which halves the tgα value of any given fiber.

By solving for T, equation (1) is obtained from equation (8):

$$T = 100 - \frac{a}{\log 2}\left(\log tg\alpha(100°) - \log b - \log\left(\frac{X}{\sqrt{t_x}}\right)_T + 2\right)$$

By means of this equation it is possible to find for any given depth of color b a temperature T at which the liquor exhaustion rate $(X/\sqrt{t_x})$T corresponds to the optimum value for given equipment. It is merely necessary to determine by experiment the value tgα (100°).

Equation (1) shows that at a given liquor exhaustion rate, parallel straight lines having an inclination of a/log 2 must be obtained if the dyeing temperature T is plotted against the depth of color b on the logarithmic scale. By means of these straight lines the temperature T may be determined for any combination of dyes.

A combination of

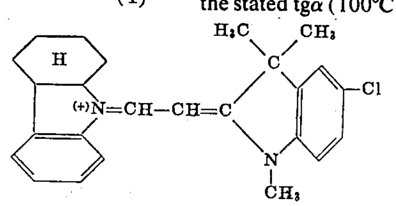
0.5 percent of dye 2 (5mg of dye/g of fiber)

0.7 percent of dye 3 (7mg of dye/g of fiber)

0.9 percent of dye 4 (9mg of dye/g of fiber)

will be given as an example with reference to FIG. 2 of the drawing.

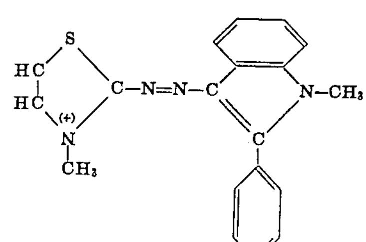
The dyes have the following structural formulas and the straight lines in FIG. 2 hold good for a fiber having a = 4 and the stated tgα (100°C) values:



$Cl^{(-)}$

Dye 2

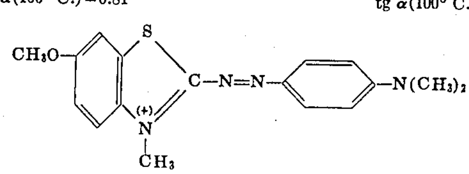
tg α(100° C.) = 0.81



$CH_3SO_4^{(-)}$

Dye 3

tg α(100° C.) = 0.93



$CH_3SO_4^{(-)}$

Dye 4

tg α(100° C.) = 1.48

The temperature value for a 0.5 percent dyeing with dye 2 is first found and this value is located on the straight line belonging to dye 3. A move is then made on the abscissa about 0.7 percent further and the temperature value obtained is entered on the straight line for dye 4 and then 0.9 percent is added to the abscissa. The ordinate value obtained is the dyeing temperature for the combination.

It is assumed that with respect to the liquor exhaustion rate 0.5 percent of dye 2 corresponds to 0.56 percent of dye 3, and 1.26 percent of dye 3 corresponds to 1.97 percent of dye 4 so that there is not objection to one dye being substituted for another.

In the same way as for dyes, it is possible in the case of cationic retarders or auxiliaries of similar constitution (which can be regarded as colorless dyes) to determine via the tgα value at 100°C a straight line which illustrates in dependence on the amount used the temperature required at a given liquor exhaustion rate.

From this it follows that it is also possible to determine the temperature to be chosen for a combination of dye and retarder or cationic auxiliary at which a particular liquor exhaustion rate is present.

By means of this straight line it is also possible to determine what amount of a cationic auxiliary has to be used as a thermoregulator with a given dye combination in order to obtain a defined liquor exhaustion rate at a given dyeing temperature. This is of great importance when dyeing equipment having automatic temperature control is used because the number of temperature-time programs required can be kept low.

For example if it is certain that a liquor exhaustion rate of equation (9)

$$\left(\frac{X}{\sqrt{t_x}}\right)_T=\frac{100}{60}=1.67 \tag{9}$$

at which the liquor is exhausted after 60 minutes is sufficient for level dyeing, then equation (10) holds good for all dyes and all depths of color:

$$T=100-\frac{a}{\log 2}\left(\log \operatorname{tg} \alpha(100°)-\log b-\log 1.67+2\right) \tag{10}$$

For the general case, not starting from an established liquor exhaustion rate of 100/60, equation (11) holds:

$$T=100-\frac{a}{\log 2}\left(\log \operatorname{tg} \alpha(100°)-\log b-\log\left(\frac{X}{\sqrt{t_x}}\right)_T+2\right) \tag{11}$$

When equation (11) is substracted from equation (12):

$$T_w=100-\frac{a}{\log 2}\left(\log \operatorname{tg} \alpha(100°)-\log b-\log\left(\frac{X}{\sqrt{t_x}}\right)_{T_w}+2\right) \tag{12}$$

equation (13) is obtained:

$$T_w-T=\frac{a}{\log 2}\left(\log\left(\frac{X}{\sqrt{t_x}}\right)_{T_w}-\log\left(\frac{X}{\sqrt{t_x}}\right)_T\right) \tag{13}$$

Equation (12) gives the dependence of liquor exhaustion rate

$$\left(\frac{X}{\sqrt{t_x}}\right)_{T_w}$$

on an arbitrarily chosen temperature T_w.

Equation (13) is of considerable practical importance. By means of this equation it is possible to determine how many °C an arbitrarily chosen temperature T_w is below or above the optimum temperature T when the liquor is exhausted at a rate

$$\left(\frac{X}{\sqrt{t_x}}\right)_{T_w}$$

which can be determined.

Equation (13) can therefore be used to discover the temperature at which the optimum liquor exhaustion rate is present, by means of a preliminary experiment in which the liquor exhaustion rate at the temperature T_w is determined.

In practice it has proved to be particularly favorable to determine the dyeing temperature for dye combinations by calculation, and it is most advantageous to reduce the amounts of dye to be used to a common reference magnitude. A straight line which reproduces the dyeing temperature in dependence on the amount used and which has been determined for a thermoregulator is outstandingly suitable as a reference magnitude. For any given thermoregulator there is for every dye a factor by which the amount of dye has to be multiplied in order to discover the amount of thermoregulator corresponding to it in terms of the liquor exhaustion rate. In the case of combination dyeings it is only necessary to add the amounts of dye expressed as amounts of thermoregulator in order to obtain (with reference to the straight line which is specific for the thermoregulator) the dyeing temperature required for a given liquor exhaustion rate.

The invention is illustrated by the following Examples. Parts and percentages in the Examples are by weight.

EXAMPLE 1

One hundred parts of an acrylonitrile polymer cloth having a value $a=4$ is dyed in an aqueous liquor containing four parts of dye 3 having a tgα (100°C) value of 0.93 and three parts of acetic acid at a liquor ratio of 12:1 and a temperature T of 98° C.

The temperature T = 98° C. results from the equation

$$T=100-\frac{4}{\log 2}(\log 0.93-\log 40-\log 1.67+2)$$

The value 1.67 is the value of the quotient of the liquor exhaustion rate ($X/\sqrt{t_x}$) assuming that a 100 percent liquor exhaustion is achieved after 1 hour.

The liquor is first heated to 98°C after which the dye solution is added. After a dyeing time of 60 minutes, the liquor is exhausted and is cooled. The dyeing is excellently level.

EXAMPLE 2

One hundred parts of acrylonitrile polymer flock having a value $a = 3$ is dyed in an aqueous liquor which contains two parts of dye 4 having a tgα (100°C) value of 1.66, three parts of acetic acid and 10 parts of Glauber's salt at a liquor ration of 15:1 and a temperature T of 92°C calculated according to the equation:

$$T=100-\frac{3}{\log 2}(\log 1.66-\log 20-\log 1.36+2)$$

The value 1.36 corresponds to a liquor exhaustion rate of $100/\sqrt{90.60}$, i.e. a dyeing time of 90 minutes.

The liquor is heated to 92°C and then the dissolved dye is added. Ninety minutes later the whole is heated to 100°C within 10 minutes and the liquid is kept at the boil for another 20 minutes. An excellently level dyeing is obtained.

EXAMPLE 3

One hundred parts of an acrylonitrile polymer cloth ($a = 4$) is dyed in an aqueous liquor which contains:
0.5 part of dye 2 having a tgα (100°C) value of 0.81,
0.7 part of dye 3 having a tgα (100°C) value of 0.93,
0.9 part of dye 4 having a tgα (100°C) value of 1.48 and three parts of acetic acid at a liquor ratio of 20:1 and a temperature of 93.5°C. The temperature is ascertained from the graph in FIG. 2 by the method described above.

The liquor is heated rapidly to 95.5°C, the yarn is taken out from the liquor and the dissolved dyes are added; as soon as the dyes have homogeneously dispersed, the yarn is reintroduced. The liquor cools down to 93.5°C. Dyeing is continued for 60 minutes at this temperature and the whole is then cooled. The dyeing obtained is excellently level.

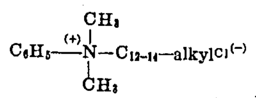
EXAMPLE 4

One hundred parts of a high-bulk acrylonitrile polymer yarn ($a=4$) is dyed in an aqueous liquor which contains 0.5 part of dye 2 having a tgα (100°C) value of 0.81, 0.7 part of dye 3 having a tgα (100°C) value of 0.93, and three parts of acetic acid at a liquor ratio of 30:1 and a temperature of 91° C. The temperature is ascertained graphically analogously to Example 3.

The liquor is rapidly brought to 100°C and the yarn is bulked for 5 minutes at this temperature. The whole is then cooled and the temperature is adjusted at 91°C. The dissolved dyes are then added to the liquor. After a dyeing time of 60 minutes the exhausted liquor is cooled. The dyeing is excellently level.

EXAMPLE 5

One hundred parts of an acrylonitrile polymer cloth ($a = 4$) is dyed in an aqueous liquor which contains 1.3 parts of a thermoregulator 1 having the formula



and having a tgα (100°C) of 0.70. 1 part of dye 4 having a tgα (100°C) value of 1.48 and three parts of acetic acid at a liquor ratio of 20:1 and at a temperature of 95°C. The temperature is determined graphically analogously to Example 3.

The solution of dye and auxiliary is added to the liquor at 95°C. Sixty minutes later the whole is cooled and an excellently level dyeing is obtained.

EXAMPLE 6

One hundred parts of a mixture of 50 parts of an acrylonitrile polymer fiber ($a = 4$) and 50 parts of cotton is dyed with 1 part of a dye having a tgα (100°C) value of 0.93 and three parts of acetic acid at a liquor ratio of 50:1 and at a temperature of 93°C calculated according to the equation:

$$T=100-\frac{4}{\log 2}(\log 0.93-\log 20-\log 1.36+2)$$

and a liquor exhaustion rate of 1.36.

The liquor has acetic acid and dye added at 60°C and is then heated to 93°C. After dyeing for 90 minutes at 90°C the temperature is raised rapidly to 100°C and kept there for 20 minutes. An excellently level dyeing is thus obtained.

EXAMPLE 7

One hundred parts of a fibre mixture of 50 parts of acrylonitrile polymer ($a=4$) and 50 parts of polyester is dyed with 0.2 part of dye 2 having a tgα (100°C) value of 0.81, 0.2 part of dye 3 having a tgα (100°C) value of 0.93 and three parts of acetic acid at a liquor ratio of 40:1 and at a temperature of 89°C. The temperature is ascertained graphically as in Example 3.

The dyes and acid are added to the liquor adjusted to 89°C. After 60 minutes the exhausted liquor is cooled. The dyeing is excellently level.

EXAMPLE 8

One hundred parts of an acrylonitrile polymer cloth ($a=5$) is dyed with two parts of dye 4 having a tgα (100°C) value of 2.4 and three parts of acetic acid at a liquor ratio of 40:1 and at a temperature of 87°C. The temperature is obtained from the following equation for a liquor exhaustion rate of 100/40.60=2.05:

$$T=100-\frac{5}{\sqrt{\log 2}}(\log 2.4-\log 20-\log 2.05+2)$$

The dye liquor has acetic acid and dye added to it at 60°C and is then heated to 87°C. Dyeing is continued for 40 minutes at this temperature and the penetration of the fiber is improved by heating the liquor for 10 minutes at 100°C. An excellently level dyeing is thus obtained.

EXAMPLE 9

In dyeing 100 parts of acrylonitrile polymer fibers ($a = 3$) with

0.2 part of dye A having an unknown tgα (100°C) value,
1.7 parts of dye B having an unknown tgα(100°C) value,
0.6 part of dye C having an unknown tgα (100°C) value and
three parts of acetic acid

it is determined in a preliminary test that the liquor exhaustion rate at an arbitrarily chosen temperature T_w=90°C is 100/$\sqrt{150.60}$=1.05.

For the desired liquor exhaustion rate of 100/$\sqrt{60.60}$ = 1.67 a value of T results from equation (13) as follows:

$$T=90+\frac{3}{\log 2}(\log 1.67-\log 1.05)=92°\text{ C.}$$

EXAMPLE 10

To determine the a value of an acrylonitrile polymer fiber of unknown origin, 100 parts of this fibrous material is dyed at 100°C and at 90°C with 3 parts of dye 3 having a tgα (100°C) value which is not known for this fiber and three parts of acetic acid. From the measured liquor exhaustion rates $(X/\sqrt{t_x})$ 100 C and $(X/\sqrt{t_x})$90 C of 2.4 and 0.32 and by means of the equation:

$$a=\frac{(T_{w1}-T_{w2})\log 2}{\log\left(\frac{X}{\sqrt{t_x}}\right)_{T_{w1}}-\log\left(\frac{X}{\sqrt{t_x}}\right)_{T_{w2}}}$$

the value for a is found to be:

$$a=\frac{(100-90)\cdot\log 2}{\log 2.4-\log 0.32}=3.4$$

What we claim is:

1. A process for the level dyeing of an acrylonitrile polymer fibrous textile material with a cationic dye in an aqueous liquor which comprises heating the liquor to a predetermined dyeing temperature T and dyeing the textile material with said cationic dye at this temperature at a defined liquor exhaustion rate, the temperature T being determined by the equation

$$T=100-\frac{a}{\log 2}\left(\log tg\alpha(100°\text{ C.})-\log b-\log\left(\frac{X}{\sqrt{t_x}}\right)_T+2\right)$$

wherein:

a denotes a constant for each specific fiber of about 3 to 5 which is the change in temperature which halves or doubles to α (100°C);
b denotes the depth of color (in mg. of said cationic dye per g of fibrous material) to be achieved;
X denotes the liquor exhaustion in %;
t_x denotes the dyeing time in seconds which corresponds to the liquor exhaustion X;
$(X/\sqrt{t_x})$T denotes the liquor exhaustion rate at the temperature T; and
tg α (100°) = $C_F/\sqrt{t}$ wherein C_F denotes the concentration of said cationic dye in the fiber in mg per g which is present in the fiber after the time t at a dyeing temperature of 100°C.

2. A process as claimed in claim 1 which includes the step of using the value of T, where the value of tgα (100°) of a cationic dye for a specific fiber is not known, by dyeing said specific fiber with the cationic dye at an arbitrarily chosen temperature T_w and then determining the temperature T from the equation

$$T=T_w+\frac{a}{\log 2}\left(\log\left(\frac{X}{\sqrt{t_x}}\right)_T-\log\left(\frac{X}{\sqrt{t_x}}\right)_{T_w}\right)$$

where $(X/\sqrt{t_x})T_w$ denotes the liquor exhaustion rate at the temperature T_w to be measured and $(X/\sqrt{t_x})$T is defined as in claim 1.

3. A process as claimed in claim 1 which includes the step of determining the value of the constant a of a specific fiber by dyeing with said cationic dye at two arbitrarily chosen temperatures T_{w1} and T_{w2} and using an a from the equation

$$a=\frac{(T_{w1}-T_{w2})\log 2}{\log\left(\frac{X}{\sqrt{t_x}}\right)_{T_{w1}}-\log\left(\frac{X}{\sqrt{t_x}}\right)_{T_{w2}}}$$

in which

$$(X/\sqrt{t_x})T_{w1} \text{ and } (X/\sqrt{t_x})T_{w2}$$

denote the liquor exhaustion rates which are measured at the arbitrarily chosen temperatures T_{w1} and T_{w2} and where X and t_x are defined as in claim 1.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,658,461 Dated April 25, 1972

Inventor(s) Udo Mayer and Herbert Fleischer

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, lines 65 to 67,
"tg α(100°C is the depth of color to be achieved in mg of commercial dye per g of fibrous materal
dye per g of fibrous material"
should read
-- tg α(100°C)
b is the depth of color to be achieved in mg of commercial dye per g of fibrous material --.

Column 8, line 24, "100 C" should read -- 100° C --; line 24, "90 C" should read -- 90° C --; line 54, claim 1 "to α" should read -- tg α --.

Signed and sealed this 3rd day of October 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents