

PATENT SPECIFICATION

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(54) METHOD FOR DYEING HYDROPHOBIC FIBER MATERIAL WITH MIXTURES OF DISPERSE DYE

(71) We, SUMITOMO CHEMICAL COMPANY LIMITED, a Corporation organised under the laws of Japan, of 15 Kitahama-5-chome, Higashi-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method for dyeing hydrophobic fiber materials uniformly with a blend of disperse dyes in a short period of time.

There are two methods for obtaining levelness in dyeing synthetic fibers with disperse dyes. One method comprises regulating a dyeing rate of a dye according to a mechanical dyeing ability of dyeing equipments to distribute the dye as uniformly as possible on the fibers from the initial stage of dyeing. The other method makes use of the fact that disperse dyes have a high degree of migration as compared with ionic dyes. In the latter method, levelness is obtained by the migration dye while the bath is being kept at the dyeing temperature, even though the dye distribution is somewhat non-uniform at the initial stage of dyeing. The commercial dyeing is, in fact, carried out by spending a long period of time safely but wastefully by combining the both methods.

In order to attain levelness as rapidly as possible with disperse dyes conventionally used in industry, it is most efficient to regulate the dyeing rate of dye. When a single dye is used for dyeing, levelness is attained relatively easily by properly regulating the dyeing rate by controlling the condition of temperature-increase programme or by using dyeing assistants. In the usual commercial dyeing, however, it is very rare to carry out the dyeing with a single dye. In most cases, a blend of several dyes is used for dyeing in order to obtain dyed materials having a wide range of color shade and it is usual to use a blend of three primary dyes, i.e., yellow dyes, red dyes and blue dyes. When the dyeing rates of each component dye in the three primary dyes are different from one another, the dyeing operation becomes troublesome because it is necessary to regulate the dyeing conditions such as temperature-increase programme, depending upon the separate dyeing rate of the respective component dyes. Further, it takes a long period of time for dyeing as compared with dyeing using a single dye. Accordingly, it is desired that the dyeing rates of each component dye are similar to one another and that the combination of the dyes has good dyeing compatibility enough to be treatable as a single dye. However, various combinations of a wide range of color shade, each of which is satisfactory in the dyeing compatibility, can hardly be obtained only by varying a proportion of a component dye in a fixed set of three primary dyes, as is well known from Textile Chemist and Colorist, Vol. 2, No. 20, 350 (1970) and Senshoku Kogyo, Vol. 21, No. 3, 139 (1973).

In dyeing synthetic fibers with disperse dyes, the dyeing rate depends upon the dyeing concentration, in other words, the dyes are exhausted at a relatively low temperature in a pale shade dyeing while they are exhausted at a higher temperature as the dyeing concentration becomes higher as is shown in Figs. 1, 2 and 3. Further, in a combination dyeing, the dyeing rate of the combination is similar to that of each component dye as is shown in Figs. 4, 5 and 6. Consequently, the range of color shade obtained with good compatibility from the combination of a fixed set of three primary dyes is limited in principle. For example, in the combination dyeing using C.I. Disperse Yellow 51, C.I. Disperse Red 60 and C.I. Disperse Blue 56 as three primary dyes, relatively good dyeing compatibility is obtained when the dyes are blended in

such a proportion as to produce a gray color as in Fig. 5. While the compatibility becomes poor when the dyes are blended so as to produce color shades other than a gray color as is shown in Figs. 4 and 6.

At present, therefore, in order to obtain the blends of disperse dyes having good dyeing compatibility over a wide range of color shade, it is common, as is described in *Senshoku Kogyo*, Vol. 2, No. 3, 137-146 (1973), to previously prepare several kinds of the combination from various sets of three primary dyes having different dyeing rates from one another and to select one combination from them which produces a desired color shade with good compatibility.

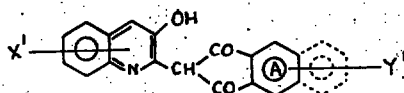
When dyeing factories employ this method, however, they meet with economical and technical difficulties, because they should have various kinds of three primary dyes and because dye selection for color matching is troublesome. Consequently, this method is only used in practice by a few well-controlled, biggest dyeing factories. In most factories, at present, it is common to use the dye blends of poor compatibility and to spend a long period of time to obtain levelness.

In the case of cationic or acid dyes, good compatibility can be obtained over a wide range of colour shade by dyeing with a mixture of a yellow dye, a red dye and a blue dye, each dye having a similar dyeing rate. However, with disperse dyes, it is not possible to obtain good compatibility over a wide range of colour shades (for example, for all colour shades from brown to grey) by dyeing with a mixture of a yellow dye, a red dye and a blue dye.

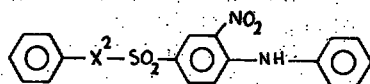
According to the present invention there is provided a method for dyeing a hydrophobic fiber material, which comprises contacting said fiber material with a dye bath containing a combination of at least nine disperse dyes having chemical structures different from one another to the extent that any blend of two of the dyes has a eutectic point.

Using the method of the present invention, good compatibility can be obtained even if the mixing ratio of the component dyes is widely varied to obtain a specific colour shade.

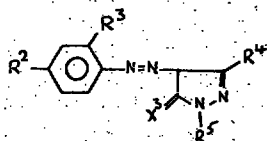
All disperse dyes which are commercially available and known from any literature can be employed in the method of the present invention. Examples of the commercially available dyes are those listed in the section, "Disperse Dye", of *Colour Index*, 3rd edition (published by Society of Dyers and Colourists). Of these, the disperse dyes favorably used in the present method include those having the following formulae:



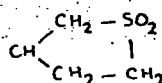
wherein X^1 is hydrogen or halogen, Y^1 is hydrogen, $\text{C}_1 - \text{C}_4$ alkyl, $\text{C}_1 - \text{C}_4$ alkoxy or $-\text{COOR}^1$ in which R^1 is $\text{C}_1 - \text{C}_4$ alkyl, and A is benzene or naphthalene nucleus,



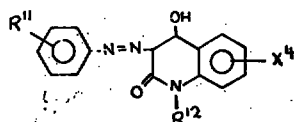
wherein X^2 is $-\text{NHCH}_2-$ or $-\text{NH}-$,



wherein R^2 and R^3 may be the same or different and are each hydrogen, halogen, $-\text{CN}$, $-\text{NO}_2$, $\text{C}_1 - \text{C}_4$ alkyl, $-\text{SO}_2\text{R}^4$ or $-\text{COOR}^4$ in which R^4 is $\text{C}_1 - \text{C}_4$ alkyl, R^4 is $\text{C}_1 - \text{C}_4$ alkyl, phenyl unsubstituted or substituted by halogen, $\text{C}_1 - \text{C}_4$ alkyl, $\text{C}_1 - \text{C}_4$ alkoxy, $-\text{COOR}^5$ in which R^5 is $\text{C}_1 - \text{C}_4$ alkyl, $-\text{NH}_2$ or $-\text{NHCOOR}^6$ in which R^6 is $\text{C}_1 - \text{C}_4$ alkyl, R^5 is hydrogen, $\text{C}_1 - \text{C}_4$ alkyl,

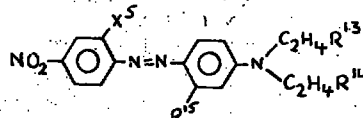


—CH₂CH(OR⁹)CH₂OR¹⁰ in which R⁹ is hydrogen, C₁—C₄ alkyl or —COCH₃, and R¹⁰ is C₁—C₄ alkyl or phenyl unsubstituted or substituted by C₁—C₄ alkyl, C₁—C₄ alkoxy or halogen, and X³ is oxygen or imino,



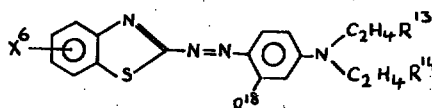
(4)

wherein R¹¹ is hydrogen or —NO₂, R¹² is hydrogen or C₁—C₄ alkyl, and X⁴ is hydrogen or halogen,



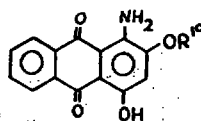
(5)

wherein R¹³ and R¹⁴ may be the same or different and are each hydrogen, hydroxy, cyano, C₁—C₃ alkyl, C₁—C₄ alkoxy, —OCOR¹⁶, —OCOOR¹⁶ in which R¹⁶ is C₁—C₄ alkyl or phenyl, or phenyl unsubstituted or substituted by halogen, hydroxy, C₁—C₄ alkyl or C₁—C₄ alkoxy, R¹⁵ is hydrogen, C₁—C₄ alkyl or —NHCOR¹⁷ in which R¹⁷ is C₁—C₄ alkyl or phenyl, and X⁵ is halogen or cyano,



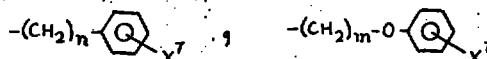
(6)

wherein R¹³ and R¹⁴ are as defined above, R¹⁸ is C₁—C₄ alkyl, and X⁶ is 1 to 3 halogens or nitro groups or a group of the formula —SO₂CH₃ or —SCN,

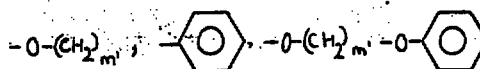


(7)

wherein R¹⁹ is C₁—C₆ alkyl, hydroxy-C₁—C₆ alkyl,



wherein *n* is an integer of 1 to 4, *m* is an integer of 1 to 4 and X⁷ is hydrogen, hydroxy, halogen, C₁—C₄ alkyl, C₁—C₄ alkoxy or hydroxy-C₁—C₄ alkyl, or phenyl unsubstituted or substituted by halogen, hydroxy, C₁—C₄ alkyl, C₁—C₄ alkoxy, hydroxy-C₁—C₄ alkyl, OCOOR²⁰ in which R²⁰ is C₁—C₆ alkyl, —(CH₂)_{*n*}—COOR²¹, —O—(CH₂)_{*n*}—COOR²¹ in which R²¹ is C₁—C₄ alkyl and *n*' is an integer of 1 to 4,



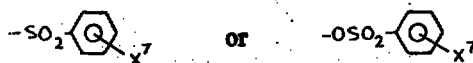
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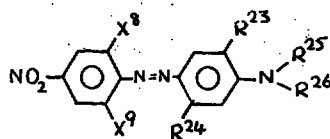
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in which m' is an integer of 1 to 4, $-\text{S}-(\text{CH}_2)_{n'}\text{OR}^{22}$, $-\text{SO}_2\text{NH}(\text{CH}_2)_{n'}\text{OR}^{22}$ in which R^{22} is hydrogen or C_1-C_4 alkyl, and n'' is an integer of 1 to 4,



in which X^7 is as defined above,

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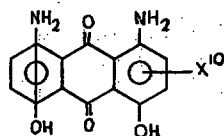


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wherein R^{23} is hydrogen, C_1-C_4 alkyl or C_1-C_4 alkoxy, R^{24} is $-\text{NHCOR}^{27}$ in which R^{27} is C_1-C_4 alkyl or phenyl, R^{25} and R^{26} may be the same or different and are each hydrogen, C_1-C_6 alkyl, hydroxy- C_1-C_6 alkyl, $-(\text{CH}_2)_{n''}\text{OR}^{28}$, $-(\text{CH}_2)_{n''}\text{OCOR}^{28}$, $-(\text{CH}_2)_{n''}\text{OCOOR}^{28}$ in which R^{28} is hydrogen, C_1-C_4 alkyl or phenyl and n'' is an integer of 1 to 4, $-(\text{CH}_2)_{m'''}\text{CH}(\text{OR}^{29})(\text{CH}_2)_{m'''}\text{OR}^{30}$ in which R^{29} is hydrogen, C_1-C_4 alkyl or phenyl, R^{30} is hydrogen, C_1-C_4 alkyl or phenyl, and n''' and m''' are each an integer of 1 to 4, X^8 is halogen, cyano or nitro, and X^9 is cyano, halogen or nitro,

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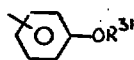
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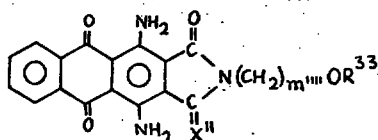
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wherein X^{10} is halogen or

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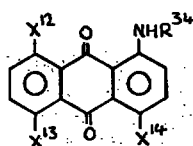
in which R^{31} is C_1-C_4 alkyl, acyl, $-\text{COR}^{32}$ or $-\text{CONHR}^{32}$ in which R^{32} is C_1-C_4 alkyl or phenyl,



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wherein R^{33} is C_1-C_6 alkyl, hydroxy- C_1-C_6 alkyl or phenyl, X^{11} is oxygen or imino, and m''' is an integer of 1 to 6,

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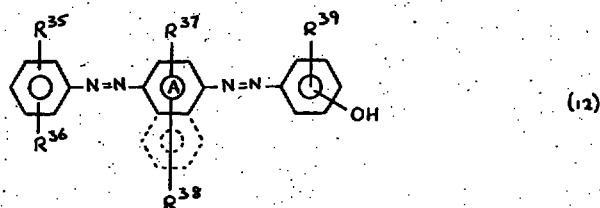


(11)

wherein R^{34} is C_1-C_4 alkyl or phenyl unsubstituted or substituted by halogen, C_1-C_4 alkyl, C_1-C_4 alkoxy or hydroxy- C_1-C_4 alkyl, and X^{12} , X^{13} and X^{14} may be the same or different and are each hydrogen, hydroxy, amino, nitro or NHR^{34} in which R^{34} is as defined above, and

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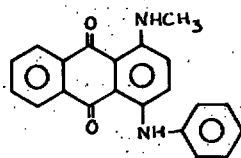


wherein R^{35} and R^{36} may be the same or different and are each hydrogen, hydroxy, C_1-C_4 alkyl, C_1-C_4 alkoxy, nitro or halogen, R^{37} , R^{38} and R^{39} may be the same or different and are each hydrogen, C_1-C_4 alkyl or C_1-C_4 alkoxy, and A is as defined above.

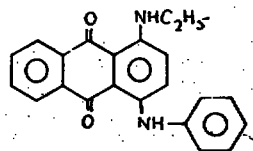
In carrying out the method of the present invention, at least nine dyes may be added separately to a dyeing bath, or may be blended to prepare a blended dye composition. The combinations of up to thirty dyes provides commercially satisfactory results.

In the present invention, when two dyes have chemical structures which have the same basic skeleton but are slightly different locally, for example, the terminal substituents connecting to the basic skeleton are slightly different from each other (e.g. difference in the number of carbon atoms constituting an alkyl or alkoxy group is only about one), and moreover when a blend of the two dyes has an eutectic point, the two dyes are regarded as separate ones, while when the eutectic point is not present, they are regarded as one dye in a pair.

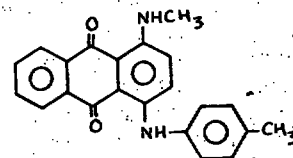
For example, a combination of the following Dye I and Dye II has no eutectic point and therefore they are regarded as one dye even if mixed together, while the combination of Dye II and Dye III has an eutectic point and therefore they are treated as separate ones.



(Dye I)



(Dye II)



(Dye III)

It is course possible to use a blend of Dye I and Dye II in practice as one dye.

In the present invention, it is preferred to use three primary dyes to obtain a wide range of color shade. As the three primary dyes, brilliant yellow, red and blue dyes are generally used in most cases. In the present invention, however, orange dyes and yellowish brown dyes are used as a yellow component in addition to the three primary dyes. Similarly, rubine dyes and reddish brown dyes are used as a red component and dark blue dyes, olive dyes and bluish gray dyes are used as a blue dye, in addition to the three primary dyes. An intermediate color dyes such as olive dyes and brown dyes which are prepared previously by blending two or more dyes can be used. The present invention will be illustrated hereinafter with reference to the combination of three primary dyes which is most widely applied.

The yellow component of the three primary colors is preferably prepared by blending at least three yellow dyes having different chemical structures from one another and such that articles dyed therewith, to a depth of shade similar to that of JIS L 0818, have a dominant wavelength of from 560 to 600 nm when measured with CIE illuminant C in the 1931 CIE system as a light source. Similarly, the red component of the three primary colors is preferably prepared by blending at least three red dyes having different chemical structures from one another and articles dyed therefrom have a dominant wavelength of from 600 to 770 nm and a complementary wavelength of less than 560 nm. Further, the blue component of the three primary colors is preferably prepared by blending at least three blue dyes having different chemical structures from one another and articles dyed therefrom have a dominant wavelength of 495 to 380 nm and a complementary wavelength of 495 to 380 nm and a complementary wavelength of more than 560 nm. When the yellow, red and

blue components thus prepared are used for color matching as three primary dyes, at least nine dyes are finally present in the dyeing bath, and good dyeing compatibility is always obtained for every color shade within a wide color shade range obtainable by blending these three primary dyes.

In blending at least nine dyes to prepare a blended dye composition according to the method of the present invention, a combination of disperse dyes alone having a high sublimation resistance (so-called high energy type dyes) produces compositions which have high sublimation resistance, good compatibility and good levelness. While a combination of levelling type disperse dyes (so-called low energy type dyes) produces compositions which have good covering property, good migration property and good compatibility, and permit easy dyeing with extremely superior reproducibility.

Further, when the high energy type dyes and low energy type dyes are blended for every three primary color while being well balanced, there are obtained general-purpose three primary dyes having good compatibility, good levelness and a level of fastness which is easy to use in practice.

In blending at least nine dyes to obtain an intermediate color shade, a proportion of one dye which occupies the largest proportion is 60% by weight or less, based on the weight of the composition, and each proportion of the other dyes which occupy the second largest proportion and the third largest proportion therein is 45% by weight or less and 30% by weight or less, respectively, based on the weight of the composition. Also, the sum of the proportions of dyes which occupy the ninth proportion and the subsequent proportions is at least 1% by weight based on the weight of the composition.

In blending three primary dyes according to the method of the present invention, any blending ratio of the dyes may be employed. However, a proportion of one dye in one of the three primary dyes is usually less than 70% by weight based on the weight of the composition and further it is preferred to limit the subtotal of two dyes, wherein one of them occupies the largest proportion and the other occupies the second largest proportion, to less than 90% by weight based on the weight of the composition.

In the present invention, it is a matter of course that the three primary dyes, yellow, red and blue dyes, may be replaced by at least one kind of a mixed dye having an intermediate color shade prepared by blending at least three dyes having extremely different colors from one another, and good dyeing compatibility is also attained, although the range of matchable color shade is somewhat limited as compared with the combination of three primary dyes. Further, it is of course possible to blend at least nine dyes having a similar color.

The fiber materials to be dyed according to the present method include synthetic fiber materials dyeable with conventional disperse dyes, for example, polyester, triacetate, diacetate, polyamide and polyacrylonitrile fibers. Particularly, the method of the present invention is applied effectively to high temperature dyeing and carrier dyeing method for polyester fibers.

According to the method of the present invention, good dyeing compatibility is always obtained irrespective of the blending ratios of component dyes, and the following effects can be obtained.

(1) Levelness is easily obtained and moreover rationalization of dyeing process, for example, short-period dyeing, becomes possible.

(2) Uneven dyeing is difficult to occur as compared with a blend of poor compatibility.

(3) Uneven dyeing is difficult to occur even when the dyeing conditions are somewhat non-uniform.

(4) The dyed materials have only a slight variation in color and depth, when the dyeing is carried out repeatedly, i.e. the reproducibility of dyeing is very good. In the dyeing industry, accomplishment of the combination of dyes having good dyeing compatibility has a very important meaning.

The method of the present invention, which provides the combination of at least nine disperse dyes having constantly good dyeing compatibility irrespective of the blending ratio of the dyes, is a surprising finding which is beyond conventional common sense and at the same time has a very high industrial value.

Fig. 1 to 9 show a relationship between a dyeing condition (temperature and time) and a ratio of exhaustion on a polyester fiber.

The curves in Figs. 1 to 9 show the rates of dyeing of various dyes in the temperature-increase type dyeing process. Figs. 1, 2 and 3 show the rates of dyeing of C.I. Disperse Yellow 51, C.I. Disperse Red 60 and C.I. Disperse Blue 56, respec-

tively. The numerals, (1), (2), (3) and (4), in each Figure mean the cases of 0.1%, 0.5%, 1.0% and 2.0% o.w.f., respectively.

Figs. 4, 5 and 6 show the cases of the combination dyeings, No. 4, No. 5 and No. 6, respectively, in Example 1. The curves, (5), (6) and (7), are obtained with C.I. Disperse Yellow 51, C.I. Disperse Red 60 and C.I. Disperse Blue 56, respectively.

Figs. 7, 8 and 9 show the cases of the present combination dyeings having good compatibility, No. 1, No. 2 and No. 3, respectively, in Example 1. The curves, (8), (9) and (10), are obtained with yellow A, red A and blue A, respectively.

The method of the present invention will be illustrated with reference to the following examples, in which all parts are expressed by weight unless otherwise indicated.

Example 1.

As three primary dyes having good dyeing compatibility, yellow A, red A and blue A were prepared according to the following recipes.

Yellow A:

C.I. Disperse Yellow	5	17.0 parts
"	49	16.6 "
"	50	16.6 "
"	42	16.6 "
"	64	16.6 "
"	192	16.6 "

Total

100 parts

Red A:

C.I. Disperse Red	54	17.0 parts
"	205	16.6 "
"	60	16.6 "
"	116	16.6 "
"	65	16.6 "
"	132	16.6 "

Total

100 parts

Blue A:

C.I. Disperse Blue	56	17.0 parts
"	26	16.6 "
"	73	16.6 "
"	257	16.6 "
"	301	16.6 "
"	165	16.6 "

Total

100 parts

Using the three primary dye blends thus obtained, Tetoron (Trade Mark) textured fabrics were dyed by high-temperature dyeing process according to the following recipes. Every recipe of the three primary dye blends showed good compatibility. The curves in Figs. 7, 8 and 9 show the dyeing rates of the respective recipes.

TABLE 1

Dyes	No. 1	No. 2	No. 3
Yellow A	1.0% owf	0.5% owf	0.5% owf
Red A	0.5% owf	0.5% owf	0.3% owf
Blue A	0.2% owf	0.5% owf	2.0% owf

For comparison, Tetoron textured fabrics were dyed by high-temperature dyeing process according to the following recipes. In the recipes, C.I. Disperse Yellow 51, C.I. Disperse Red 60 and C.I. Disperse Blue 56 are those which are widely used as levelling type three primary dyes for polyester fibers. As a result the recipe No. 5 had slightly good dyeing compatibility but the other two recipes had very poor dyeing compatibility. The curves in Figs. 4, 5 and 6 show the dyeing rates of the respective recipes.

TABLE 2

Dyes	No. 4	No. 5	No. 6
C.I. Disperse Yellow 51	1.0% owf	0.5% owf	0.5% owf
C.I. Disperse Red 60	0.5% owf	0.5% owf	0.3% owf
C.I. Disperse Blue 56	0.2% owf	0.5% owf	2.0% owf

Polyester spun yarn cheese was dyed by cheese dyeing process using the recipe No. 1. The dyeing conditions were as follows:

Amount of flow: 30 l/kg/min
 Direction of circulation of bath liquor: one-way flow in→out
 Increase in temperature: 50°C→130°C, 2°C/min
 Holding of temperature: 130°C×30 min

As a result, it was found that the differences in depth and color between the dyed yarns in the inner part of the cheese and those in the outer part of the cheese were very slight and therefore level dyeing was obtained. Also, when the cheese dyeing was carried out using the recipe No. 4, the differences in depth and color between the dyed yarns in the inner part and those in the outer part were very large. It meant that unlevel dyeing occurred.

Example 2.

As three primary dyes having good compatibility, yellow B, red B and blue B were prepared according to the following recipes.

Yellow B:		
C.I. Disperse Yellow	5	20 parts
"	42	20 "
"	64	20 "
"	66	15 "
"	83	15 "
"	103	10 "
Total	100 parts	

Red B:		
C.I. Disperse Red	43	20 parts
"	60	20 "
"	73	15 "
"	88	20 "
"	92	10 "
"	135	15 "
Total	100 parts	

5	Blue B:		
	C.I. Disperse Blue	26	10 parts
	"	27	20 "
	"	56	15 "
	"	87	20 "
	"	128	15 "
	"	139	20 "
Total		100 parts	

10 Tetoron textured fabrics were dyed by high-temperature dyeing process in the following blending ratios of these dye blends. As a result, good compatibility and levelness were obtained in every case. 10

TABLE 3

No.	Yellow B	Red B	Blue B	Color at 90°C during dyeing	Color after dyeing at 130°C×30 min	Compatibility
7	2.0%	1.0%	0.5%	Khaki	Khaki	Good
8	2.0%	0.5%	1.0%	Olive	Olive	Good
9	1.0%	2.0%	0.5%	Reddish brown	Reddish brown	Good
10	0.5%	1.0%	2.0%	Dark blue	Dark blue	Good
11	1.0%	1.0%	1.0%	Yellowish gray	Yellowish gray	Good

15 For comparison, combination dyeings were carried out using C.I. Disperse Yellow 64, C.I. Disperse Red 60 and C.I. Disperse Blue 56 which are widely used as three primary dyes for high-temperature dyeing of polyester fibers. As described below, the No. 16 (gray-recipe) alone gave good compatibility, but other recipes gave poor compatibility. 15

TABLE 4

No.	Disperse Yellow 64	Disperse Red 60	Disperse Blue 56	Color at 90°C during dyeing	Color after dyeing at 130°C×30 min	Compatibility
12	2.0%	1.0%	0.5%	Bluish gray	Khaki	Poor
13	2.0%	0.5%	1.0%	Bluish gray	Olive	Poor
14	1.0%	2.0%	0.5%	Bluish gray	Reddish brown	Poor
15	0.5%	1.0%	2.0%	Bluish gray	Dark blue	Slightly poor
16	1.0%	1.0%	1.0%	Bluish gray	Gray	Good

20 Polyester textured fabric was dyed in a jet type dyeing machine under the following conditions using the recipe No. 8. 20

25 Dyeing conditions: 90 m/min
 Cloth circulation speed: 2.7 min/cycle
 Circulation time: 50°C→100°C, 3°C/min
 Increase in temperature: 100°C→130°C, 1°C/min
 Holding of temperature: 130°C×30 min 25

As a result, the dyed material had good uniformity and levelness. For comparison, the dyeing procedure was carried out in the same manner as above using the recipe No. 13 having poor compatibility. As a result, the dyed material having spots and poor levelness was only obtained.

The dyeing procedure was carried out in the same manner as in Example 2 except that yellow B, red B and blue B were replaced by yellow B', red B' and blue B' prepared as follows, respectively. In this combination of the three primary dyes, yellow B', red B' and blue B', eight dyes having a single chemical structure are only present in the dyeing bath. As a result, the effect of the present invention was not obtained and dyeing compatibility was poor.

Yellow B':		
C.I. Disperse Yellow	5	30 parts
"	42	40 "
"	66	30 "

Red B'		
C.I. Disperse Red	43	50 parts
"	135	50 "

Blue B':		
C.I. Disperse Blue	27	40 parts
"	87	30 "
"	139	30 "

Example 3.

As three primary dyes having good dyeing compatibility, yellow C, red C and blue C were prepared according to the following recipes.

Yellow C:		
C.I. Disperse Yellow	192	50 parts
"	60	40 "
"	42	10 "
Total		100 parts

Red C:		
C.I. Disperse Red	190	40 parts
"	191	30 "
"	54	30 "
Total		100 parts

Blue C:		
C.I. Disperse Blue	73	40 parts
"	301	30 "
"	56	30 "
Total		

Tetoron textured fabrics were dyed by the high-temperature dyeing process in the following blending ratios of these dye blends. As a result, good compatibility and levelness were obtained in every case.

TABLE 5

No.	Yellow C	Red C	Blue C	Color at 90°C during dyeing	Color after dyeing at 130°C×30 min	Compatibility
17	2.0%	1.0%	0.5%	Khaki	Khaki	Good
18	2.0%	0.5%	1.0%	Olive	Olive	Good
19	1.0%	2.0%	0.5%	Reddish brown	Reddish brown	Good
20	0.5%	1.0%	2.0%	Dark blue	Dark blue	Good
21	1.0%	1.0%	1.0%	Gray	Gray	Good

Example 4.

As a dye for combination dyeing having good compatibility, a mixed brown dye was prepared by the following recipe.

5	Brown A:					5
	C.I. Disperse Yellow	64	18 parts			
	"	42	10 "			
	C.I. Disperse Orange	13	8 "			
	"	30	20 "			
10	C.I. Disperse Red	54	10 "			10
	"	190	10 "			
	"	74	8 "			
	C.I. Disperse Blue	72	6 "			
	"	73	8 "			
15	"	54	2 "			15
	Total		100 parts			

The brown dye thus obtained was blended with the three primary dyes obtained in Example 3 according to the following recipes and used for dyeing polyester fabrics. As a result, good compatibility was obtained in every case.

20	No. 22	{ Brown A 0.8% Blue C 0.4% }	(gray)	20
	No. 23	{ Brown A 0.3% Yellow C 0.2% Blue C 0.3% }	(olive)	
	No. 24	{ Brown A 1.3% Yellow C 0.5% Red C 0.2% }	(khaki)	

Example 5.

The following dye compositions were prepared respectively using each dye having

the formula described below which had been processed in a commercially available disperse dye.

Yellow D:

C.I. Disperse Yellow	160	25 parts
C.I. Disperse Yellow	42	25 "
"	8	25 "
"	5	25 "

Red D:

C.I. Disperse Red	54	50 parts
"	88	25 "
"	60	25 "

Blue D:

C.I. Disperse Blue	224	25 parts
"	56	25 "
"	60	25 "
"	64	25 "

Polyester spun yarn cheese was dyed under the following dyeing conditions to obtain a uniform brown dyeing. Compatibility was good, so that the color shade from beginning to end was consistent, and no difference in color was observed between the inside and outside of the cheese.

Dyeing conditions:

Blend Yellow D	1.0%	o.w.f.
Red D	0.5%	"
Blue D	0.25%	"

Assistant Sumipon TF (anionic surfactant produced by Sumitomo Chemical Co. Ltd.)

1 g/l

pH 5

(Sodium acetate 1 g/l
Acetic Acid 0.25 g/l)

Bath ratio 1:15

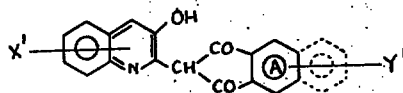
Temperature from room temperature to 100°C:3°C/min.
from 100°C to 130°C:1°C/min.

Circulation of bath liquor 30 l/kg/min.

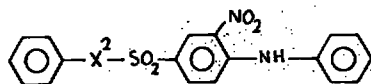
WHAT WE CLAIM IS:—

1. A method for dyeing a hydrophobic fiber material, which comprises contacting said fiber material with a dye bath containing a combination of at least nine disperse dyes having chemical structures different from one another to the extent that any blend of two of the dyes has a eutectic point.

2. A method according to Claim 1, wherein the combination comprises at least nine disperse dyes selected from disperse dyes of the formulae (1) to (12), the formula (1) being



wherein X¹ is hydrogen or halogen, Y¹ is hydrogen, C₁—C₄ alkyl, C₁—C₄ alkoxy or —COOR¹ in which R¹ is C₁—C₄ alkyl, and A is benzene or naphthalene nucleus, the formula (2) being





the formula described below which had been processed in a commercially available disperse dye.

Yellow D:

C.I. Disperse Yellow	160	25 parts
C.I. Disperse Yellow	42	25 "
"	8	25 "
"	5	25 "

Red D:

C.I. Disperse Red	54	50 parts
"	88	25 "
"	60	25 "

Blue D:

C.I. Disperse Blue	224	25 parts
"	56	25 "
"	60	25 "
"	64	25 "

Polyester spun yarn cheese was dyed under the following dyeing conditions to obtain a uniform brown dyeing. Compatibility was good, so that the color shade from beginning to end was consistent, and no difference in color was observed between the inside and outside of the cheese.

Dyeing conditions:

Blend Yellow D	1.0%	o.w.f.
Red D	0.5%	"
Blue D	0.25%	"

Assistant Sumipon TF (anionic surfactant produced by Sumitomo Chemical Co. Ltd.)

1 g/l

pH 5

(Sodium acetate 1 g/l
Acetic Acid 0.25 g/l)

Bath ratio 1:15

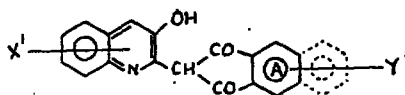
Temperature from room temperature to 100°C:3°C/min.
from 100°C to 130°C:1°C/min.

Circulation of bath liquor 30 l/kg/min.

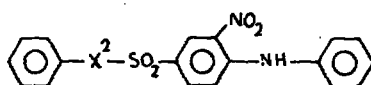
WHAT WE CLAIM IS:—

1. A method for dyeing a hydrophobic fiber material, which comprises contacting said fiber material with a dye bath containing a combination of at least nine disperse dyes having chemical structures different from one another to the extent that any blend of two of the dyes has a eutectic point.

2. A method according to Claim 1, wherein the combination comprises at least nine disperse dyes selected from disperse dyes of the formulae (1) to (12), the formula (1) being



wherein X¹ is hydrogen or halogen, Y¹ is hydrogen, C₁—C₄ alkyl, C₁—₄ alkoxy or —COOR¹ in which R¹ is C₁—C₄ alkyl, and A is benzene or naphthalene nucleus, the formula (2) being





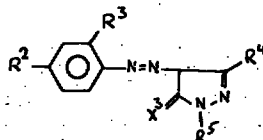
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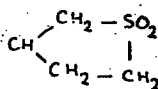
wherein X^2 is $-\text{NHCH}_2-$ or $-\text{NH}-$, the formula (3) being



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wherein R^2 and R^3 may be the same or different and are each hydrogen, halogen, $-\text{CN}$, $-\text{NO}_2$, C_1-C_4 alkyl, $-\text{SO}_2\text{R}^6$ or $-\text{COOR}^6$ in which R^6 is C_1-C_4 alkyl, R^4 is C_1-C_4 alkyl, phenyl unsubstituted or substituted by halogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, $-\text{COOR}^7$ in which R^7 is C_1-C_4 alkyl, $-\text{NH}_2$ or $-\text{NHCOOR}^8$ in which R^8 is C_1-C_4 alkyl, R^5 is hydrogen, C_1-C_4 alkyl,

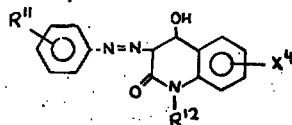
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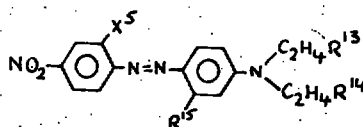
$-\text{CH}_2\text{CH}(\text{OR}^9)\text{CH}_2\text{OR}^{10}$ in which R^9 is hydrogen, C_1-C_4 alkyl or $-\text{COCH}_3$, and R^{10} is C_1-C_4 alkyl or phenyl unsubstituted or substituted by C_1-C_4 alkyl, C_1-C_4 alkoxy or halogen, and X^3 is oxygen or imino, the formula (4) being

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wherein R^{11} is hydrogen or $-\text{NO}_2$, R^{12} is hydrogen or C_1-C_4 alkyl, and X^4 is hydrogen or halogen, the formula (5) being

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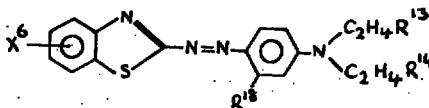


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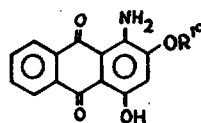
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wherein R^{13} and R^{14} may be the same or different and are each hydrogen, hydroxy, cyano, C_1-C_8 alkyl, C_1-C_4 alkoxy, $-\text{OCOR}^{16}$, $-\text{OCOOR}^{16}$ in which R^{16} is C_1-C_4 alkyl or phenyl, or phenyl unsubstituted or substituted by halogen, hydroxy, C_1-C_4 alkyl or C_1-C_4 alkoxy, R^{15} is hydrogen, C_1-C_4 alkyl or $-\text{NHCOR}^{17}$ in which R^{17} is C_1-C_4 alkyl or phenyl, and X^5 is halogen or cyano, the formula (6) being

20



wherein R^{13} and R^{14} are as defined above, R^{18} is C_1-C_4 alkyl and X^6 is 1 to 3 halogens or nitro groups, or a $-\text{SO}_2\text{CH}_3$ or $-\text{SCN}$ group, the formula (7) being



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wherein R^{19} is C_1-C_6 alkyl, hydroxy- C_1-C_6 alkyl,

25

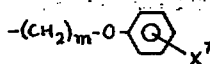
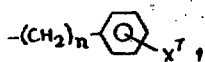
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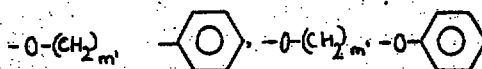
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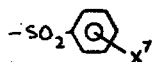
wherein n is an integer of 1 to 4, m is an integer of 1 to 4 and X^7 is hydrogen, hydroxy, halogen, C_1-C_4 alkyl, C_1-C_4 alkoxy or hydroxy- C_1-C_4 alkyl, or phenyl unsubstituted or substituted by halogen, hydroxy, C_1-C_4 alkyl, C_1-C_4 alkoxy, hydroxy- C_1-C_4 alkyl, $-OCOOR^{20}$ in which R^{20} is C_1-C_6 alkyl, $-(CH_2)_n-COOR^{21}$, $-O-(CH_2)_n-COOR^{21}$ in which R^{21} is C_1-C_4 alkyl and n' is an integer of 1 to 4,

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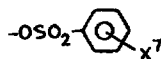


in which m' is an integer of 1 to 4, $-S-(CH_2)_n-OR^{22}$, $-SO_2NH(CH_2)_n-OR^{22}$ in which R^{22} is hydrogen or C_1-C_4 alkyl, and n'' is an integer of 1 to 4,

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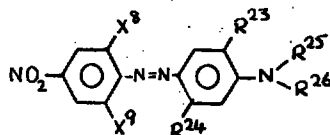


or



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in which X^7 is as defined above, the formula (8) being



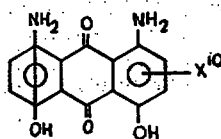
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wherein R^{23} is hydrogen, C_1-C_4 alkyl or C_1-C_4 alkoxy, R^{24} is $-NHCOR^{27}$ in which R^{27} is C_1-C_4 alkyl or phenyl, R^{25} and R^{26} may be the same or different and are each hydrogen, C_1-C_6 alkyl, hydroxy- C_1-C_4 alkyl, $-(CH_2)_n-OR^{28}$, $-(CH_2)_n-OCOOR^{28}$, $-(CH_2)_n-OCOOR^{28}$ in which R^{28} is hydrogen, C_1-C_4 alkyl or phenyl and n''' is an integer of 1 to 4, $-(CH_2)_n-CH(OR^{29})(CH_2)_m-OR^{30}$ in which R^{29} is hydrogen, C_1-C_4 alkyl or phenyl, R^{30} is hydrogen, C_1-C_4 alkyl or phenyl, and n''' and m''' are each an integer of 1 to 4, X^8 is halogen, cyano or nitro, and X^9 is cyano, halogen or nitro, the formula (9) being

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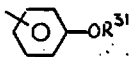
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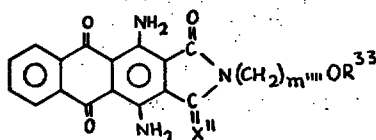
wherein X^{10} is halogen or

25



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in which R^{31} is C_1-C_4 alkyl, acyl, $-COR^{32}$ or $-CONHR^{32}$ in which R^{32} is C_1-C_4 alkyl or phenyl, the formula (10) being





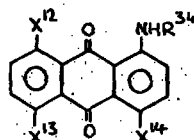
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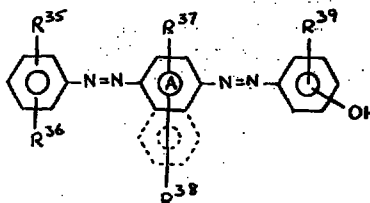
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wherein R^{33} is C_1-C_6 alkyl, hydroxy- C_1-C_6 alkyl or phenyl, X^{11} is oxygen or imino, and m''' is an integer of 1 to 6, the formula (11) being



5 wherein R^{34} is C_1-C_4 alkyl or phenyl unsubstituted or substituted by halogen, C_1-C_4 alkyl, C_1-C_4 alkoxy or hydroxy- C_1-C_4 alkyl, and X^{12} , X^{13} and X^{14} may be the same or different and are each hydrogen, hydroxy, amino, nitro or NHR^{34} in which R^{34} is as defined above, and

5



10 wherein R^{35} and R^{36} may be the same or different and are each hydrogen, hydroxy, C_1-C_4 alkyl, C_1-C_4 alkoxy, nitro or halogen, R^{37} , R^{38} and R^{39} may be the same or different and are each hydrogen, C_1-C_4 alkyl or C_1-C_4 alkoxy, and A is as defined above.

10

3. A method according to Claim 1 or Claim 2, wherein the combination comprises three primary yellow, red and blue dyes, which comprise at least three yellow, red and blue disperse dyes, respectively.

15

4. A method according to Claim 3, wherein said at least three red dyes are such that the material, after dyeing has a dominant wavelength of from 600 to 770 nm and a complementary wavelength of less than 560 nm.

20 5. A method according to Claim 3 or Claim 4, wherein said at least three yellow dyes are such that the material, after dyeing, has a dominant wavelength of from 560 to 600 nm.

20

25 6. A method according to any of Claims 3 to 5, wherein said at least three blue dyes are such that the material, after dyeing has a dominant wavelength of from 495 to 380 nm and a complementary wavelength of more than 560 nm.

25

7. A method according to any of the preceding Claims, wherein a proportion of one of at least nine disperse dyes which occupies the largest proportion in the combination is 60% by weight or less, based on the weight of the combination, each proportion of the other dyes which occupy the second largest proportion and the third largest proportion therein is 45% by weight or less and 30% by weight or less, respectively, based on the weight of the combination, and the sum of the proportions of dyes which occupy the ninth and subsequent proportions is at least 15% by weight based on the weight of the composition.

30

8. The method according to Claim 3, wherein a proportion on one dye in one of the three primary yellow, red and blue dyes is less than 70% by weight based on the weight of the three primary yellow, red and blue dyes, respectively, and a proportion of two dyes which occupy the largest and the second largest proportions in one of the three primary dyes, is less than 90% by weight based on the weight of the three primary yellow, red and blue dyes, respectively.

35

9. The method according to any of the preceding Claims, wherein the contacting is conducted under conditions employed in high-temperature dyeing and carrier dyeing.

40

10. A dye composition comprising at least nine disperse dyes having chemical structures different from one another to the extent that any blend of two of the dyes has a eutectic point.

45 11. A method according to Claim 1 and substantially as herein described.

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12. A method according to Claim 1 and substantially as described in any of the Examples.

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13. A dye composition according to Claim 10 and substantially as herein described.
14. A dye composition according to Claim 10 and substantially as described in any of the Examples.

5 15. A hydrophobic fiber material whenever dyed by a method as claimed in any of Claims 1 to 9, 11 and 12 or using a dye composition as claimed in any of Claims 10, 13 and 14. 5

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ERRATUM

SPECIFICATION No. 1,541,929

Page 15, line 32, for 15% read 1%

THE PATENT OFFICE

28th August, 1979

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