Title: METHOD FOR DYEING OR PRINTING TEXTILE MATERIALS

Abstract: A method for dyeing or printing a textile fiber material is disclosed, which comprises the steps of providing a digital data processing device operating reflectance curve data which are associated with the corresponding dye recipes, wherein the reflectance curve data are generated by (a) drawing up a requirement profile for the desired dyeing, (b) selecting a group of dyes that meet the requirement profile that has been drawn up, (c) determining within the colour space the colour position of the said dyes for the desired dyeing, (d) segmenting the colour space of the dyes within a depth of shade plane into triangular areas (e) dividing the triangular areas within a depth of shade arithmetically into a grid.
METHOD FOR DYEING OR PRINTING TEXTILE MATERIALS

The present invention relates to a method for dyeing or printing textile fiber materials comprising the selection of a colour or colour pattern and the preparation of the textile fabrics dyed or printed with the selected colour or colour pattern in one automated process.

Business issues, sociological and economic movements affect the taste and buying pattern of consumers. Accordingly, business success to a large extent is dependent on the time to market, i.e. the period of time required from the idea of a product until its introduction into the market. Since fashion changes rapidly, this applies also to the textile industry. In order to cope with the current market demands methods are required which minimize the time period from the idea of a new fashion colour collection up to the production of the textile fashion fabrics.

Textile professionals, such as designers, merchandisers or product development managers know how critical colour is to the textile business. Since it is important, a precise way to define, select, specify, control and communicate the colour choices is required, whether designing for apparel, accessories, home furnishings or automotive interior.

A problem associated with the definition and communication of colour choices, which serve as colour standards for a fashion colour collection, is that they are generally defined only on one textile material, for example cotton, although the defined colour standard is also used on many other fibres, for example wool, silk, polyester, polyamide, polyacryl, etc. or mixtures thereof. For the dyeing or printing of different fibre materials, however, dyes from different dye classes are used, for example reactive dyes for cotton, acid dyes for silk, wool or polyamide and disperse dyes for polyester. The disadvantage of the customary procedure is that it can result in metamerism, if the dyestuffs used for the garment are not identical with the dyes of the selected colour standard.

The market for textiles calls for specific in-use properties, for example good fastness to light for skiwear or summer clothing or seat covers in the automotive industry, good fastness to chlorine for swimwear, good fastness to perspiration for sportswear and good fastness to washing properties for underwear etc.. In general, however, such specifications are not taken into account when defining the colour standard, with the result that it is possible for
metamerism to occur in that instance also, especially when it is necessary to switch to dyes that take account of in-use properties at a later stage.

Colour standards are generally defined by design professionals who usually have no technical knowledge in the art of industrial dyeing. In some cases, this results in the definition of colour standards which cannot be dyed on certain textile fibers or the recipes for which are not technically optimized or the requisite fastness properties cannot be achieved with the colour standard defined. As a consequence all kinds of problems throughout the textile chain arise, from the designer of the fashion brand through the supplier chain to the dyeing industry, occasionally resulting in considerable financial losses.

In the definition of the standards, too little account is also taken of the colour constancy, which has the result that the colour of an object varies under different sources of illumination, or again results in metamerism if the colour constancy is improved.

Occasionally, a design professional may use a wide variety of objects as colour standard, for example objects made from leather, plastics, metal, paper, flowers, leaves or wood etc. Frequently he will also select his colour standard from colour catalogues. Colour catalogues contain colour samples on a wide variety of materials, for example pigment-dyed paper or dyeings on textile samples of cotton, polyester or wool. In the production of the dyeings that are used to define the colour standard, no account is taken of the fastness requirements for specific uses. Moreover, the number of colours in the colour catalogues that are available is limited, generally from 500 to 2500 different colours. In defining the colour standard using the mentioned objects or colour samples from catalogues, the dye recipes found have to be optimised technically or in respect of the required fastness properties, which can again result in problems of metamerism or colour constancy.

An ideal colour standard does not necessarily have to be a dyeing, but can be represented by a reflectance curve.

According to one aspect of the present invention, the reflectance curve is produced arithmetically, starting from a recipe that has been optimised technically and in respect of the in-use fastness properties and using the stored data of calibration dyeings to calculate the
associated reflectance curve. The reflectance curve, which is thus associated with an application-optimised dye recipe, is rendered visible by means of a suitable device, for example, a calibrated colour screen, and in that manner is used as the defined colour standard.

By first defining the dye recipe in accordance with the requirements of application technology and thereafter calculating the reflectance curve corresponding to the dye recipe, it is possible to avoid the above-mentioned problems.

Providing a convenient and reliable method to textile professionals for the definition of colour standards for a fashion colour collection is one aspect. Another aspect is to shorten the time from the idea of a colour standard to the preparation of the textile fashion fabrics.

Accordingly, the problem underlying the present invention is to provide an integrated technical solution to textile professionals which accounts for the issues indicated above.

The present invention accordingly relates to a method for dyeing or printing a textile fiber material, which comprises the steps of

(i) providing a printing or dyeing apparatus capable of processing digital data;
(ii) providing a digital data processing device organizing reflectance curve data which are associated with the corresponding dye recipes, wherein the reflectance curve data are generated by
   (a) drawing up a requirement profile for the desired dyeing,
   (b) selecting a group of dyes that meet the requirement profile that has been drawn up,
   (c) determining within the colour space the colour position of the said dyes for the desired dyeing,
   (d) segmenting the colour space of the dyes within a depth of shade plane into triangular areas according to shade, wherein the corner points of the triangular areas correspond to the colour position of the dyes in question, and the said dyes define a range of shades delimited by the triangular areas,
   (e) dividing the triangular areas within a depth of shade plane arithmetically into a grid in such a manner that the points of intersection of the grid are distributed evenly
over the triangular areas, where the points of intersection of the grid correspond to
a colour position and a reflectance curve calculated on the basis of a dye recipe is
associated with each of those colour positions;

(iii) providing a device enabling the colour corresponding to the reflectance curve data
to be rendered visible; wherein

the colour of the desired dyeing is defined by browsing the reflectance curve data
organized by the digital data processing device (ii) using device (iii), communicating the
data corresponding to the colour defined from the digital data processing device (ii) to the
printing or dyeing apparatus (i), in which the communicated data are used to control the
printing or dyeing apparatus (i), thereby dyeing or printing a textile fiber material in the
defined colour.

In other words, the problem indicated above is solved by the present invention by providing
a digital catalogue of colour samples that can be reproduced easily and without metamerism
on any desired textile material meeting all the desired in-use properties, the digital catalogue
being equipped with a device enabling the colours organized by the digital colour catalogue to
be rendered visible,

and a printing or dyeing apparatus capable of processing the digital data communicated by the
digital colour catalogue, and
to interconnect the digital colour catalogue with the printing or dyeing apparatus in a manner
that the said components form an integrated operating unit, wherein the textile fiber material
is printed or dyed with the colour or colour pattern defined previously.

A requirement profile drawn up for the desired dyeing according to Step (a) is understood to
mean the definition of the properties or criteria that the dyed substrate is intended to fulfil.
Such properties or criteria are, for example, application-related properties, such as the in-use
fastness properties, for example fastness to light, chlorine, rubbing, wetting, wet rubbing,
washing, water, seawater or perspiration. Suitable substrates are, for example, textile fibre
materials, paper, plastics or metal. Further criteria in drawing up a requirement profile may
also include the dyeing or printing process with which the desired dyeing is to be produced,
the costs, for example of the dyes, or the pricing of the product.
In the context of the present invention, the term "dyeing" is not limited to dyeings in the customary sense, but also includes printing of the fabrics. The terms "dyeing" and "dyed textile fiber material, fabric or garment etc." accordingly include both dyeing processes and printing processes and the coloured substrates produced by means of such processes, respectively.

According to Step (b) in the method according to the invention, a group of dyes is selected that meet the defined requirement profile and cover the colour space as well as possible. A group of dyes is understood to mean, for example, three or more dyes. The selected dyes should also be readily combinable with one another, i.e. they should have similar affinity to the fiber, for example, when dyeing or printing cotton, they should exhibit similar substantivity and reactivity. The number of colours in the colour catalogue according to the invention that can be derived arithmetically is thus dependent inter alia upon the location of the selected dyes in the colour space, that is to say the number increases with the size of the colour space covered by the selected dyes. The selection of the dyes is advantageously made by a person skilled in the field of textile dyeing.

As colour space for the method according to the invention there can be used, for example, the known CIE Lab colour coordinate system, the lightness axis L* being replaced by the depth of shade characteristic FT. The advantage of that procedure is that colour positions of identical depth of shade or of identical colour strength lie in one plane of the colour space. The individual planes of the colour space are defined by the pairs of values a*, b*, which correspond to the values of the same name in the CIE Lab colour coordinate system. The a*, b* value pairs characterise the hue and the colour saturation, which are known to the person skilled in the art from the field of colour communication or colorimetrics and constitute a measure of the shade. Instead of the term "colour saturation", the specialist literature also uses the terms "chroma" or "colour brilliance". In the mentioned FTP*a*b* colour space, colour positions of different depth of shade or colour strength lie one above the other on different planes. When using a depth of shade characteristic based on reflectance measurements, it has proved advantageous to use an additional weighting of the data based on the colour perception of the eye or the impression of colour produced.

As colour space for the method according to the invention, it is also possible to use, for example, the L*C*h colour system, which is based on the same diagram as the CIE Lab colour
coordinate system (L*a*b* system), with polar coordinates being used instead of rectangular coordinates.

A suitable depth of shade characteristic FT is, for example, the standard depth, as described, for example, in P. Rabe and O. Koch, Mellian Textilberichte 38 (1957) pages 173 to 177. The standard depth can be indicated not only in the known 2/1, 1/1, 1/3, 1/6, 1/12 and 1/25 depths, but also further sub-divided, for example in steps of 1/10 standard depth or smaller. Depth of shade characteristics are known to the person skilled in the art of textile dyeing.

As depth of shade characteristic it is also possible to use values from reflectance measurements, obtainable according to instructions in Textilveredlung (1986), pages 299 to 304.

According to the invention, first the colour positions of the selected dyes must be determined according to Step (c), preferably in the FTA*b* colour space, thus defining the colour space for the subsequent Steps. The colour positions of the dyes suitable for the desired dyeing are so selected that they lie on a plane of identical depth of shade, for example on a plane defined by the pairs of values a*, b*. The colour positions are ascertained from calibration data. If the calibration data are not known, these must first be ascertained by measurement using a commercially available colorimetric apparatus, for example a commercially available spectral photometer.

Normally the dyeing behaviour of many dyes in the textile dyeing industry, i.e. their affinity to the fiber, such as their exhaust properties, is non-linear and it is therefore possible in only a small number of cases to infer from a known concentration for a specific depth of shade, for example a 1/1 standard depth, the concentration to use for a different depth of shade. Usually, it is necessary to ascertain the concentration to use for different depths of shade, and from that data to produce a characteristic calibration curve for each selected dye, the desired material to be dyed and the dyeing or printing process applied with the printing or dyeing apparatus indicated under (i).

The depth of shade characteristic FT can be ascertained, for example, from a standard depth colour chart. For that purpose, a standard depth chart or a corresponding concentration curve
is produced in a manner known *per se* for each of the selected dyes, for example for the five dyes indicated in Fig. 1 which follows.

The known depth of shade plane thus establishes the concentration of each dye to use for that depth of shade plane.

The planes of the FTA*b* colour space are segmented into triangular areas according to Step (d), the corner points of the triangular areas corresponding to the colour position of the dyes that were selected for the desired dyeing in accordance with the requirement profile. The individual triangular areas of each depth of shade plane do not overlap. Each colour position in the colour space is defined by a single dye recipe, which consists, for example, of one dye when the desired colour position corresponds to the FTA*b* data of a single dye, or the recipe is a mixture of, for example, two dyes when the desired colour position lies on the usually non-straight line connecting two dyes, or the recipe is a mixture of, for example, three dyes where the ratio of those three dyes corresponds to the point of intersection of a regular grid superimposed arithmetically over the triangular areas according to Step (e).

The dyes selected for the segmentation may themselves already be mixtures of dyes, for example a mixture of two or three dyes, that is to say, for example, that a corner point of the triangular area already corresponds to the colour position of a dye mixture. In that case also, the colour positions of the mixtures must first be ascertained from calibration data.

Once the dyes for a segmentation have been selected and their calibration data have been ascertained in a manner known *per se* from reflectance measurements at different concentrations and thus at different depths of shade and have been stored in a computer, the segmentation of the FTA*b* colour space according to (d) is complete. Using that stored information, according to Step (e) colour positions for the selected dye combination are calculated for a defined depth of shade FT, which colour positions are spaced at regular intervals across the range of shades defined by the a*,b* value pairs, that is to say the depth of shade plane is divided into a grid. Each grid point corresponds to a specific concentration ratio between the selected dyes and thus to a specific dye recipe.
Fig. 1 shows the segmentation of the colour space in a depth of shade plane into three segments, the reference numerals P1 to P5 corresponding to the FTA*b* data of the selected dyes Yellow 1 (P1), Yellow 2 (P2), Red (P3), Blue 1 (P4) and Blue 2 (P5).

Fig. 2 is a further example of the segmentation of the colour space in a depth of shade plane into twelve segments, the reference numerals P1 to P9 corresponding to the FTA*b* data of the selected dyes Yellow 1 (P1), Yellow 2 (P2), Orange 1 (P3), Orange 2 (P4), Red 1 (P5), Red 2 (P6), Blue 1 (P7), Blue 2 (P8) and Blue 3 (P9).

The connecting lines shown in Figs. 1 and 2 are the result of mixing, in each case, two dyes in specific amounts at a predetermined depth of shade, the end points of the connecting lines corresponding to the colour positions of the selected dyes.

Fig. 3 shows a single segment. It is the triangular area produced by points P2, P3 and P4 in Fig. 1. The connecting lines between points P2, P3 and P4 are the colour positions of each of the two-component mixtures. The grid that has been superimposed over the entire triangular area defines colour positions of mixtures having different concentration ratios. Points P2, P3 and P4 define the colour positions of the respective dyes in concentrations C₂, C₃ and C₄. A mixture having the concentrations X₂ x C₂, X₃ x C₃ and X₄ x C₄ (where X₂ + X₃ + X₄ = 1) defines a grid point of the same depth of shade. The grid is produced by interpolating series of mixtures between the single dyes in such a manner that the given spacing of the grid is obtained. For the interpolation, the conversion between K/S values and reflectance values is made using the customary procedure according to Kubelka-Munk, as indicated, for example, in Colour Physics for Industry, Ed. R. McDonald, Society of Dyers and Colourists (1987), Chapter 5, 116 ff. In that procedure, the reflectance spectrum and the concentrations of the dyes are stored for each calculated grid point.

Fig. 4 shows a different segment made up of the dyes P10, P5 and P8. A grid was calculated in the same manner for the triangular area. Points P5 and P8 correspond to points P5 and P8 of Fig. 2.

The spacings between the grid points can be preselected. The smaller the spacings, the more colour positions can be determined within a triangular area. The depth of shade plane defined
by a triangular area corresponds, for example, to a trichromy at a depth of shade, the corner points of the triangular area corresponding to the colour positions selected for the trichromy. It is thus possible to regulate the number of colours per trichromy and thus also the number of colours in the catalogue.

Fig. 5 shows the same segment as Fig. 4, the difference being that the spacing between the grid points is twice as large and thus the number of colour positions determined is reduced to \(\frac{1}{2}\).

Figs. 1 to 5 show a plane of the FTa\(^*\)b\(^*\) colour space. The depth of shade characteristic FT of those planes corresponds, for example, to a 2/3 standard depth. For each colour position in a plane having a specific depth of shade characteristic FT, for example for 1/10, 2/10 or 1/1 standard depth, the reflectance curve and the amounts of dye required to dye a specific substrate in that depth of shade are known. The dye concentration depends, for example, on the dye itself, the depth of shade sought, the application procedure and the substrate to be dyed or printed.

The colour positions corresponding to the points of intersection of the grid are in each case associated with a reflectance curve. Behind each reflectance curve lies a specific dye recipe, that is to say digital instructions for the printing or dyeing apparatus (I) as to the ratio in which the dyes that are to be combined with one another are to be mixed in order to obtain a dyeing that corresponds to the reflectance spectrum ascertained and that meets the requirement profile defined in advance according to (a).

The catalogue which meets the requirement profile defined in advance according to (a) is made up of all the reflectance spectra calculated for all the segments in the given depths of shade.

The reflectance spectra ascertained do not, of course, give the observer any impression of colour. According to the invention, implementation of an operation is required by means of which the reflectance curve is first brought into a format that enables the corresponding colour to be rendered visible using a suitable device. Suitable devices for visualising the reflectance curves are, for example, a colour-calibrated screen, such as a cathode ray tube apparatus or a
liquid crystal flat screen, or a colour-calibrated projection apparatus. It is preferred to use a colour-calibrated screen. For that purpose, the calculated reflectance spectra are formatted in such a manner that they can be imported into a commercially available colour communication system, for example Colorite ImageMaster by Datacolor or Color Talk by GretagMacbeth. In such a system, for example ImageMaster, the spectra can be shown as real colours.

For any dyeing problem it is possible to obtain a comprehensive catalogue of different shades which the user can consult. All that is required is the calibration data of the selected dyes.

The user, for example a colour designer, can then look for colours in the catalogue that come closest to his colour original, which may be an idea of a colour, and that meet the previously defined requirements, and obtains the associated reflectance curves which correspond to specific dye recipes. The recipes obtained are communicated to the printing or dyeing apparatus capable of processing such digital data.

Steps (c), (d) and (e) of the method to generate a digital catalogue of colour samples are advantageously carried with the digital data processing device (ii). The digital data processing device (ii) is also used to store and manage or organize the data obtained and to control the printing or dyeing apparatus (i). The digital data processing device (ii) is e.g. a personal computer.

To make it easy to locate the stored reflectance curves in a data base, they can be provided with a title that contains the dyes used, the substrate and process data and a serial code number. On the basis of that information, the dye recipe associated with the reflectance curves can be recalculated or stored in a recipe data base.

A printing or dyeing apparatus capable of processing digital data according to step (i) of the present invention is, for example, a jet- or spray-dyeing apparatus, an ink-jet printing apparatus or an electrical discharge printing device, preferably a jet- or spray-dyeing apparatus or an ink-jet printing apparatus.

Printing or dyeing is suitably carried out by unwinding a web from a support and passing it through a dyeing or printing unit, wherein the textile fiber is impregnated with at least one
aqueous dyeing composition containing the selected dyestuff, before it is rewound onto another support. After passing the dyeing or printing unit and before being rewinded, the dyed or printed web may continue to travel through a drying and fixing unit, wherein the dyeings or printings are dried or fixed on the web. A pretreatment unit may be arranged before the dyeing or printing unit, wherein the web is pretreated e.g. with an aqueous alkaline liquor in the case of dyeing or printing with reactive dyes. Pretreatment may also be carried out separately. A washing and draining unit may be arranged after the drying and fixing unit in order to remove unfixed dye. Furthermore, a finishing unit may be arranged after the drying and fixing unit or in the absence of a drying and fixing unit, after the dyeing or printing unit, which imparts, for example, softness, water repellency, antimicrobial- or sun protection properties to the fabric.

The dyeing or printing unit comprises at least one dispensing device, which allows the web to be uniformly impregnated with the aqueous dyeing composition over its entire width. As an example there may be mentioned a tube made, for example, of metal, the longitudinal axis of which is directed perpendicular to the moving direction of the web. The tube suitably comprises a multitude of small openings, i.e. nozzles or orifices, being equally spaced along its longitudinal axis, the openings being faced toward the web and distributed in a way that the aqueous dyestuff composition is uniformly distributed in the form of small droplets over the entire width of the web. A further dispensing device which comes into consideration for the process according to the present invention is an ink-jet print head. By means of an ink-jet print head individual droplets of an aqueous ink are sprayed onto the substrate in a controlled manner from a nozzle. Predominantly, the continuous and the drop-on-demand mode of operation are known. In the continuous mode, the droplets are produced continuously and any droplets not required for the printing are conveyed to a collecting vessel and recycled, whereas in the drop-on-demand mode droplets are produced and printed as required; that is to say droplets are produced only when required for the printing. The production of the droplets can be effected, for example, by means of a piezo-inkjet head or by means of thermal energy (bubble jet). Preference is given to printing by means of a piezo-ink-jet head for the method according to the invention.

The dyeing or printing unit may comprise one or more than one, e.g. one, two, three, four, or up to twelve dispensing devices, one being arranged after the other. The dyeing or printing unit may further comprise an arrangement, wherein at least one dispensing device is located
on each side of the web, thereby allowing for complete penetration of the dyeing composition over the entire profile of the web. The dispensing devices on each side of the web can be arranged either directly opposite to one another or laterally displaced with respect to one another. In that case the web is moved along between the dispensing devices.

The position of the dispensing device may be fixed, such as in the case of the tube described above, or it may be installed in a way allowing it to be moved in a direction perpendicular to the moving direction of the web, so that any point over the entire width of the web may be reached, such as in the case for ink-jet printing.

The dispensing device is fed by a reservoir containing the aqueous dyeing composition. The printing or dyeing apparatus capable of processing digital data according to step (i) comprises a reservoir for each of the dyes selected for segmentation of the color space from the group of dyes that meet the requirement profile according to step (b) of the process of generating the digital colour catalogue. In order to obtain a dyeing that corresponds to the reflectance spectra ascertained, the dyes have to be mixed in the corresponding ratio. Mixing may be accomplished by means of an automatic dosing system, a system of valves and pumps, which receives the required commands from the digital data processing device (ii) and, in accordance with the commands received, doses or injects the liquid compositions of the selected dyes into a mixing chamber. The collected, mixed liquids leaving the mixing chamber finally arrive at the dispensing device. Advantageously, mixing is carried out on-line, which means that automatic dosing system and mixing chamber are an integrated part of the supply-line between the reservoir and the dispensing device and only the amounts of liquid dyestuff compositions are fed into the mixing chamber which are actually consumed in the dyeing process. Mixing may also be accomplished directly on the web. In that case, an automatic dosing system and a mixing chamber is not required and each dispensing device is fed by a separate reservoir which allows each dyestuff liquor to be sprayed on the web in the predetermined quantity.

In an interesting embodiment of the present invention there comes into consideration an ink-jet print head as a dispensing device which comprises
- a nozzle layer (ai) defining a plurality of ejection nozzles,
- an ink supply layer (bi) which is formed from a porous material having a multitude of small interconnected pores so as to allow passage of ink therethrough, the ink supply layer featuring a plurality of connecting bores (holes) from the rear surface to the front surface, each connecting bore being aligned so as to connect between a corresponding one of the ejection nozzles and
- a deflection layer (ci), comprising a plurality of transducers related to the connecting bores for ejecting ink droplets out through the nozzles.

The ink-jet print head applied in accordance with the present invention may additionally comprise
- an ink cavity layer (di), associated with the rear surface of the ink supply layer (bi) having a plurality of apertures, each aperture being positioned to correspond to one of the connecting bores of the ink supply layer so as to at least partially define a corresponding ink cavity.

The ink-jet print head applied in accordance with the present invention comprises a layered structure, a key element of which is the ink supply layer (bi) made of a porous material. The ink supply layer (bi) is in direct communication with both the ink reservoir and the individual ink cavities of the connecting bores (holes) and/or the individual ink cavities of the ink cavity layer (di), thereby acting as hydraulic linkage between the ink main supply and the individual ink cavities.

The porous material includes, for example, sintered material, most preferably, sintered stainless steel.

The ink cavity layer (di) may be omitted. In this case, the deflection layer directly adjoins the ink supply layer.

The ink-jet print head used in accordance with the present invention is described in detail in US Patent No. 5,940,099, the disclosure of which is incorporated herein.
The ink-jet print head applied in accordance with the present invention belongs to the category of drop on demand systems, wherein the ink drops are ejected selectively as required.

The transducers are, for example, piezoelectric crystals (piezoelectric type) or thermoelectric elements (thermal bubble jet type), preferably piezoelectric crystals.

The ejection of ink drops using a device according to one embodiment of the present invention is accomplished as follows: A pressure pulse is imparted to a volume of ink in an ink cavity through the deflection of a thin deflection plate, or diaphragm, located on top of the ink cavity. The plate is deflected downward by the action of a piezoceramic crystal whenever a voltage is applied across its electrodes, one of which is in electrical contact with the usually metallic deflection plate. The pressure pulse created by the downward bending of the deflection plate drives the ink towards and through an outlet, having a convergent nozzle at its outlet end, causing the ejection of a drop of a specific size. When the piezoelectric crystal is de-energized, it returns to its equilibrium position, reducing the pressure in the ink cavity and causing the meniscus at the outlet end to retract. The retracted meniscus generates a capillary force which acts to pull ink from an ink reservoir through the porous material of the ink supply layer (bi) into the ink cavity and into the connecting bores (holes) related to the nozzle. The refilling process ends when the meniscus regains its equilibrium position.

The micron grade and the surface area of the porous material which is open for flow into the ink cavity has a crucial impact on the refill time of the ink cavities and hence on the maximum drop ejection rate, or frequency. The ink moves through the interconnected pores and channels of the ink supply layer (bi) with suitable flow resistances in order to realize system performance which allows for high ejection frequencies, for example, 5 to 100 kHz, preferably 10 to 50 kHz and especially 20 to 40 kHz.

Further embodiments of suitable ink-jet print head configurations comprising an ink supply layer which is formed from a porous material are described in US Patent No. 5,940,099.

In a preferred embodiment of the present invention a suitable ink-jet print head comprises
- a nozzle layer (ai) defining a plurality of ejection nozzles,
- an ink supply layer (bi) having a front surface associated with the nozzle layer and a rear surface associated with a cavity layer (di), the ink supply layer being formed with a plurality of connecting bores (holes) from the rear surface to the front surface, each connecting bore being aligned so as to connect between a corresponding one of the ink cavities and a corresponding one of the ejection nozzles, wherein the ink supply layer additionally features (ei) a pattern of ink distribution channels formed in the front surface, and (fi) at least one ink inlet bore passing from the rear surface to the front surface and configured so as to be in direct fluid communication with at least part of the pattern of ink distribution channels, the pattern of ink distribution channels and the at least one ink inlet bore together defining part of an ink flow path which passes from the rear surface through the at least one ink inlet bore to the pattern of ink distribution channels on the front surface, and through the porous material to the plurality of ink cavities.
- a deflection layer (ci), comprising a plurality of transducers related to the connecting bores for ejecting ink droplets out through the nozzles.

The location of ink distribution channels on the front surface ensures that ink flow through the porous material of ink supply layer occurs through the bulk of the layer. Preferably ink distribution channels are distributed over the front surface in such a pattern that each connecting bore is approximately the same distance from its nearest ink distribution channel. In the typical case that the connecting bores define an array on the front surface having two row directions, the pattern of ink distribution channels preferably includes a plurality of channels deployed substantially parallel to one of the row directions and interposed between adjacent rows of the connecting bores. The ink flow path is particularly effective for providing a sufficient and generally uniform ink supply to the porous layer across an entire array of ink cavities.

The ink-jet print head which may be used in accordance with the present invention is a multi-nozzle print head, the individual nozzles of which are advantageously arranged as an array made up of horizontal rows which are horizontally staggered, or skewed, with respect to one another, comprising, for example, 512 nozzles staggered in a 32 x 16 array.
The ink-jet print head which may be used in accordance with the preferred embodiment of the present invention is described in detail in US Patent No. 6,439,702, the disclosure of which is incorporated herein.

Further embodiments of suitable ink-jet print head configurations comprising an ink supply layer which is formed from a porous material are described in US Patent No. 6,439,702.

The dispensing device which may be used in accordance with the present invention comprises at least one of the ink-jet print heads described above. Preferably, the printing device uses at least 3 process colors, for example 3, 4, 5 or 6 process colors, preferably 6 process colors, wherein each color is processed with at least one print head, for example 1, 2, 3, 4, 5, 6 or 7 printing heads, preferably 7 printing heads.

The ink-jet printing device described above allows textile fiber materials to be printed with a speed of at least 50 m²/h, preferably in the range of 100 to 250 m²/h, especially 150 to 250 m²/h.

In the drying and fixing unit, the web is exposed to e.g. infra-red radiation (IR) or elevated temperatures. Fixing can be effected, for example, by means of ultraviolet radiation (UV) or by means of thermal energy or by subjecting the textile fiber material to a steaming process.

Drying is carried out at temperatures of up to 150°C, especially from 80 to 120°C.

In the steaming process, the printed fibrous material is subjected, for example, to treatment in a steamer with steam which is optionally superheated, e.g. at a temperature of from 95 to 180°C, advantageously at from 95 to 130°C, especially using saturated steam.

Fixing can be carried out batchwise at low temperature or at elevated temperatures without passing the web through a drying and fixing unit and rewinding it on a support after having passed the dyeing or printing unit.

Low-temperature fixing takes place by storing the impregnated and wound web at an ambient temperature, for example, at a temperature between 10 and 40°C, in particular between 15 and
35°C. The duration of the low-temperature treatment can depend on the dye used and varies within wide limits, which range from 3 to 24 hours, preferably from 4 to 10 hours, particularly preferably from 6 to 8 hours.

A corresponding fixing treatment at elevated temperature, in which the dye is fixed on the fiber by storage of the wound web at a temperature above 40°C, in particular of up to 70°C, and preferably of up to 60°C, in a storage unit containing the impregnated and wound web, is also possible. The duration of the treatment can depend on the dye used and varies within wide limits. Preferably, the duration of the treatment is up to 3 hours, in particular 0.5 to 3 hours, and preferably 1 to 3 hours.

In particular, the dyes used in the inks for ink-jet printing according to the present invention should preferably have a low salt content, that is to say should have a total salt content of less than 0.5 % by weight, based on the weight of the dyes. Dyes which, as a result of their preparation and/or the subsequent addition of diluents, have higher salt contents can be desalted, for example, by membrane separation processes, such as ultrafiltration, reverse osmosis or dialysis.

The aqueous dye compositions or the inks preferably have a total dye content of from 1 to 35 % by weight, especially from 1 to 30 % by weight and more especially from 1 to 20 % by weight, based on the total weight of the ink. The preferred lower limit is 1.5 % by weight, especially 2 % by weight, more especially 3 % by weight.

The aqueous dye compositions or the inks may comprise water-miscible organic solvents, for example C\textsubscript{1}-C\textsubscript{4} alcohols, for example methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol or isobutanol; amides, for example dimethylformamide or dimethylacetamide; ketones or ketone alcohols, for example acetone, diacetone alcohol; ethers, for example tetrahydrofuran or dioxane; nitrogen-containing heterocyclic compounds, for example N-methyl-2-pyrrolidone or 1,3-dimethyl-2-imidazolidone; polyalkylene glycols, for example polyethylene glycol or polypropylene glycol; C\textsubscript{2}-C\textsubscript{6} alkylene glycols and thioglycols or di, tri or tetramers of C\textsubscript{2}-C\textsubscript{6} alkylene glycols, for example ethylene glycol, propylene glycol, butylene glycol, thioglycol, hexylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol; other polyols, for example glycerol or 1,2,6-hexanetriol; and C\textsubscript{1}-
C$_{2-4}$ alkyl ethers of polyhydric alcohols, for example 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol or 2-[2-(2-ethoxyethoxy)ethoxy]ethanol; preferably N-methyl-2-pyrrolidone, diethylene glycol, glycerol or, especially, 1,2-propylene glycol, usually in an amount of from 2 to 30 % by weight, preferably from 5 to 30 % by weight and especially from 10 to 25 % by weight, based on the total weight of the ink.

The aqueous dye compositions or the inks may also comprise solubilisers, for example epsilon-caprolactam.

The aqueous dye compositions or the inks may comprise thickening agents of natural or synthetic origin, *inter alia* for the purpose of adjusting the viscosity.

Examples of thickeners that may be mentioned include commercially available alginate thickeners, starch ethers or locust bean flour ethers, especially sodium alginate on its own or in admixture with modified cellulose, e.g. methylcellulose, ethylcellulose, carboxymethylcellulose, hydroxyethylcellulose, methylhydroxyethylcellulose, hydroxypropyl cellulose or hydroxypropyl methylcellulose, especially with preferably from 20 to 25 % by weight carboxymethylcellulose. Synthetic thickeners that may be mentioned are, for example, those based on poly(meth)acrylic acids, poly(meth)acrylamides or polyvinyl pyrrolidones.

In a particularly preferred embodiment of the present invention poly C$_2$-C$_4$-alkyleneglycol or the mono- or di-C$_1$-C$_4$-alkyl ether of poly C$_2$-C$_4$-alkyleneglycol is used as a viscosity adjusting agent, the alkylene moieties of which may be straight chained or branched, especially poly C$_2$-C$_3$-alkyleneglycol, such as, polyethylene glycol, polypropylene glycol or a mixed ethylene oxide/propylene oxide copolymerisate, and more especially a mixed ethylene oxide/propylene oxide copolymerisate. The molar mass is, for example, from 1,000 to 35,000 g/mol, preferably from 2,000 to 25,000 g/mol and especially from 3,000 to 20,000. The said compounds are commercially available, for example, as P41-type polyglycols (Clariant).

The aqueous dye compositions or the inks comprise such thickening agents, for example, in an amount of from 0.01 to 2 % by weight, especially from 0.01 to 1 % by weight, based on the total weight of the ink.
The aqueous dye compositions or the inks may also comprise buffer substances, for example borax, borates, phosphates, polyphosphates or citrates. Examples which may be mentioned include borax, sodium borate, sodium tetraborate, sodium dihydrogen phosphate, disodium hydrogen phosphate, sodium tripolyphosphate, sodium pentapolypophosphate, as well as sodium citrate. They are used especially in amounts of from 0.1 to 3 % by weight, preferably from 0.1 to 1 % by weight, based on the total weight of the ink, in order to establish a pH value of, for example, from 4 to 10, especially from 5 to 9.5.

The aqueous dye compositions or the inks may comprise surfactants or humectants as further additives.

There come into consideration as surfactants commercially available anionic or non-ionic surfactants. In the inks according to the invention, there come into consideration as humectants, for example, urea or a mixture of sodium lactate (advantageously in the form of a 50 to 60 % aqueous solution) and glycerol and/or propylene glycol in amounts of preferably from 0.1 to 30 % by weight, especially from 2 to 30 % by weight.

Preference is given to inks having a viscosity of from 1 to 40 mPa·s, especially from 1 to 20 mPa·s and preferably from 1 to 10 mPa·s.

The aqueous dye compositions or the inks may also comprise further conventional additives, for example antifoam agents or, especially, substances inhibiting fungal and/or bacterial growth. Such substances are usually used in amounts of from 0.01 to 1 % by weight, based on the total weight of the ink.

As preservatives there come into consideration formaldehyde-releasing agents, e.g. paraformaldehyde and trioxane, especially aqueous, for example 30 to 40 % by weight formaldehyde solutions, imidazole compounds, e.g. 2-(4-thiazolyl)benzimidazole, thiazole compounds, e.g. 1,2-benzisothiazolin-3-one or 2-n-octyl-isothiazolin-3-one, iodine compounds, nitriles, phenols, haloalkylthio compounds and pyridine derivatives, especially 1,2-benzisothiazolin-3-one or 2-n-octyl-isothiazolin-3-one. As an example for a broad spectrum biocide for the preservation against spoilage from bacteria, yeasts and fungi a 20%
by weight solution of 1,2-benzisothiazolin-3-one in dipropylene glycol (Proxel™ GXL) can be used.

The aqueous dye compositions or the inks may comprise further ingredients such as fluorinated polymers or telomers for example polyethoxy perfluoro alcohols (Forafac® products) in an amount of from 0,01 to 1% by weight based on the total weight of the ink.

The method according to the invention is not limited to specific dyes or specific textile substrates. Dyes of a wide variety of dye classes can be used, irrespective of whether they are water-soluble or disperse dyes. Preference is given to disperse dyes, acid dyes, metal complex dyes, reactive dyes, vat dyes, sulfur dyes, direct dyes and pigments, and also to cationic dyes. Also suitable are natural dyes or developing dyes, such as naphthol dyes.

As an example of the different dye classes, reference may be made to the Colour Index; Colour Index, Third Edition, 1970/1971: Acid Dyes, Volume 1, pages 1001 to 1562; Basic Dyes, Volume 1, pages 1607 to 1688; Direct Dyes, Volume 2, pages 2005 to 2478; Disperse Dyes, Volume 2, pages 2479 to 2743; Natural Dyes, Volume 3, pages 3225 to 3256; Pigments, Volume 3, pages 3267 to 3390; Reactive Dyes, Volume 3, pages 3391 to 3560; Solvent Dyes, Volume 3, pages 3563 to 3648; Vat Dyes, Volume 3, pages 3719 to 3844.

Suitable acid dyes that can be used may belong to a wide variety of dye classes and may contain one or more sulfonic acid groups. They include, for example, triphenylmethane dyes having at least two sulfonic acid groups, heavy-metal-free monoazo and disazo dyes each having one or more sulfonic acid groups, and heavy-metal-containing, namely copper-, chromium-, nickel- or cobalt-containing, monoazo, disazo, azomethine and formazan dyes, especially metallised dyes, that contain two molecules of azo dye, or one molecule of azo dye and one molecule of azomethine dye, bonded to a metal atom, especially such dyes containing mono- and/or dis-azo dyes and/or azomethine dyes as ligands and a chromium or cobalt ion as central atom, as well as anthraquinone dyes, especially 1-amino-4-arylminoanthraquinone-2-sulfonic acids and 1,4-diarylmino- or 1-cycloalkylamino-4-arylminoanthraquinonesulfonic acids.

There come into consideration as anionic acid dyes, for example, dyes of formula
wherein

$R_1$, $R_2$, $R_3$ and $R_4$ are each independently of the others $C_1$-$C_4$alkyl, and

$R_5$ is $C_1$-$C_4$alkyl, $C_1$-$C_4$alkoxy or hydrogen;

wherein

$R_6$ is benzoylamino, phenoxy, chlorophenoxy, dichlorophenoxy or methylphenoxy,

$R_7$ is hydrogen, benzoyl, phenyl or $C_1$-$C_4$alkyl, and

the substituents $R_9$ are each independently of the other hydrogen, phenylamino or N-phenyl-N-methylaminosulfonyl;

wherein

the phenyl ring $B_1$ may be substituted by at least one substituent selected from the group halogen, $C_1$-$C_4$alkyl and sulfo, and
$R_9$ is $\alpha$-bromoacryloylamino;

![Chemical structure](image)

wherein

$R_9$ has the meanings given above,

$R_{10}$ is $C_1$-$C_6$alkyl, and

$R_{11}$ is halogen; and

![Chemical structure](image)

1:2 metal complex dyes, such as 1:2 chromium complex dyes of azo and azomethine dyes of formulae

![Chemical structure](image)

wherein

$R_{12}$ is hydrogen, sulfo or phenylazo,

$R_{13}$ is hydrogen or nitro, and
the phenyl ring \( B_3 \) may be substituted by at least one substituent selected from the group halogen, \( C_1-C_4 \) alkyl and sulfo;

1:2 metal complex dyes, such as asymmetric (mixed) or symmetric 1:2 chromium complex dyes, preferably symmetric 1:2 chromium complex dyes, of azo dyes of formulae

\[
\text{formula (8)}
\]

wherein

the phenyl ring \( B_3 \) may be substituted by at least one substituent selected from the group halogen, \( C_1-C_4 \) alkyl and sulfo, and

\( R_{14} \) and \( R_{15} \) are each independently of the other hydrogen, nitro, sulfo, halogen, \( C_1-C_4 \) alkylsulfonyl, \( C_1-C_4 \) alkylaminosulfonyl or \(-\text{SO}_2\text{NH}_2\); and

\[
\text{formula (9) or (10)}
\]

wherein

\( R_{16} \) is hydrogen, \( C_1-C_4 \) alkoxy carbonylamino, benzyolamino, \( C_1-C_4 \) alkylsulfonylamino, phenylsulfonylamino, methylphenylsulfonylamino or halogen,

\( R_{17} \) is hydrogen or halogen, and

\( R_{16} \) is \( C_1-C_4 \) alkylsulfonyl, \( C_1-C_4 \) alkylaminosulfonyl, phenylazo, sulfo or \(-\text{SO}_2\text{NH}_2\),

the hydroxy group in the benzo ring \( D_1 \) being bound in the \( \alpha \)-position relative to the azo group on the benzo ring \( D_1 \);
symmetric 1:2 cobalt complexes of the azo dyes of formulae

\[
\text{HO} \quad \text{N=N} \quad \text{R}_{19} \quad \text{R}_{21} \\
\text{R}_{20} \quad \text{N=N} \quad \text{aryl} \\
\]

\text{(11)},

wherein

\( R_{19} \) is an -OH or -NH₂ group,
\( R_{20} \) is hydrogen or \( C_1-C_4 \)alkylaminosulfonyl, and
\( R_{21} \) is nitro or \( C_1-C_4 \)alkoxy-\( C_1-C_4 \)alkyleneaminosulfonyl, and

\[
\text{OH} \quad \text{NH-SO}_2 \quad \text{O} \quad \text{N=N} \quad \text{CH-CH-CO-N} \\
\text{R}_{22} \quad \text{aryl} \quad \text{aryl} \quad \text{aryl} \\
\]

\text{(12)},

wherein

\( R_{22} \) is carboxy or sulfo, and
\( R_{23} \) is halogen;

asymmetric 1:2 chromium complex dyes of the azo dyes of formulae

\[
\text{OH} \quad \text{HO} \\
\text{NO}_2 \quad \text{aryl} \quad \text{aryl} \quad \text{aryl} \\
\]

\text{(13)} + \text{OH} \quad \text{HO} \\
\text{NO}_2 \quad \text{aryl} \quad \text{aryl} \quad \text{aryl} \\
\]

\text{(14)},

wherein
one substituent $R_{24}$ is hydrogen and the other is sulfo;

wherein

$R_{25}$ is hydrogen or nitro, the phenyl rings $B_4$ and $B_6$ each independently of the other may be substituted by at least one substituent selected from the group halogen, $C_1$-$C_4$ alkyl and sulfo, and

$R_{26}$ is hydrogen or halogen; and

wherein
the phenyl rings B_6, B_7 and B_8 each independently of the other may in each case be substituted by at least one substituent selected from the group halogen, C_1-C_4 alkyl and sulfo, R_{26} is hydrogen or nitro, R_{27} is hydrogen, methoxycarbonylamino or acetylamino, and R_{28} is C_1-C_4 alkylsulfonyl, C_1-C_4 alkylamino-sulfonyl, phenylazo, sulfo or -SO_2NH_2;

![Chemical Structure](image)

(22),

wherein the benzo rings D_2 are substituted by sulfo or sulfonamido;

anthraquinone dyes of formulae

![Chemical Structure](image)

(23),

wherein R_{29} is α-bromoacryloylamino, the substituents R_{30} are each independently of the others hydrogen or C_1-C_4 alkyl, and R_{31} is hydrogen or sulfo;
wherein

the substituents $R_{32}$ are each independently of the other cyclohexyl or a diphenyl ether radical that may be substituted by sulfo or by the radical $-\text{CH}_2\text{-NH-}R_{29}$ in which $R_{29}$ has the meanings given above; and

wherein

$R_{29}$ is $\alpha$-bromoacryloylamino,

$R_{30}$ has the meanings given for formula (23), and

$R_{33}$ is $C_4$-$C_8$alkyl;

(24),

(25)

(26) and
wherein

(R_{34})_{1-4} denotes from 1 to 5 identical or different substituents selected from the group C_{1}-C_{4}-alkyl unsubstituted or substituted by C_{2}-C_{4}alkanoylamino (which may in turn be substituted in the alkyl group by halogen) or by benzoyleamino; C_{1}-C_{4}alkoxy; C_{2}-C_{4}alkanoylamino and C_{2}-C_{4}hydroxyalkylsulfamoyl;

R_{35} is C_{1}-C_{4}alkyl, C_{6}-C_{7}cycloalkyl unsubstituted or substituted by C_{1}-C_{4}alkyl, or phenyl unsubstituted or substituted by phenoxo, C_{1}-C_{4}alkyl or by sulfo, the phenoxy group in turn being unsubstituted or substituted in the phenyl ring by C_{1}-C_{4}alkyl, C_{1}-C_{4}alkoxy, halogen or by sulfo, especially by C_{1}-C_{4}alkyl or by sulfo;

R_{36} and R_{37} are each independently of the other sulfo, C_{1}-C_{4}alkyl unsubstituted or substituted by C_{2}-C_{4}alkanoylamino (which may in turn be substituted in the alkyl group by halogen) or phenoxy unsubstituted or substituted in the phenyl ring by C_{1}-C_{4}alkyl, C_{1}-C_{4}alkoxy, halogen or by sulfo, especially by C_{1}-C_{4}alkyl or by sulfo; and

wherein

R_{36} is halogen, phenylsulfonyl, trifluoromethyl or \(-\text{SO}_{2}\text{N}^{\text{R}_{41}}_{\text{R}_{42}}\) in which R_{41} is cyclohexyl

and R_{42} is C_{1}-C_{4}alkyl, or the radicals R_{41} and R_{42}, together with the nitrogen atom linking them, form an azepinyl ring;
$R_{39}$ is hydrogen or halogen,
and $R_{40}$ is hydrogen or is phenoxy unsubstituted or substituted in the phenyl ring by halogen;

wherein

$R_{43}$ is hydrogen, halogen or sulfo;
$R_{44}$ is hydrogen; halogen; phenoxy or phenoxy sulfanyl unsubstituted or substituted in the phenyl ring by $C_1$-$C_6$alkyl, $C_1$-$C_6$alkoxy or by halogen; a radical of formula

$$\begin{array}{c}
\text{in which } R_{48} \text{ is phenyl unsubstituted or substituted by } C_1$-$C_6$alkyl, $C_1$-$C_6$alkoxy, halogen or by sulfo, $R_{49}$ is hydrogen or $C_1$-$C_6$alkyl and $R_{50}$ is halogen; or a radical

of formula

$$\begin{array}{c}
in which $R_{50}$ is as defined above;

$R_{46}$ is hydroxy or amino; and
$R_{46}$ and $R_{47}$ are each independently of the other hydrogen, $C_1$-$C_6$alkyl or halogen;

$$\begin{array}{c}
\text{wherein}
\end{array}$$
$R_{51}$ and $R_{52}$ are each independently of the other hydrogen, C$_{1-4}$alkyl, C$_{1-2}$alkoxy, halogen or C$_{2-4}$alkanoylamino, preferably hydrogen or C$_{1-4}$alkyl,

$R_{53}$ is phenyl unsubstituted or substituted by C$_{1-4}$alkyl, C$_{1-2}$alkoxy, halogen or by C$_{2-4}$-alkanoylamino, preferably unsubstituted phenyl or phenyl substituted by C$_{1-4}$alkyl;

\[
\begin{array}{c}
\text{HO}_3\text{S-} \\
\text{N-} \\
\text{N-} \\
\text{R}_{54} \\
\text{R}_{55}
\end{array}
\]

(31),

wherein

$R_{54}$ is hydrogen or C$_{1-4}$alkyl,

$R_{55}$ is hydrogen or phenylsulfonyl unsubstituted or substituted in the phenyl ring by C$_{1-4}$alkyl, C$_{1-4}$alkoxy, halogen or by C$_{2-4}$alkanoylamino, preferably unsubstituted phenylsulfonyl;

\[
\begin{array}{c}
\text{(R}_{56}\text{)}_{0-2} \\
\text{N-} \\
\text{N-} \\
\text{HO}_3\text{S-} \\
\text{SO}_3\text{H}
\end{array}
\]

(32),

wherein

$(R_{56})_{0-2}$ denotes from 0 to 2 identical or different substituents selected from the group C$_{1-4}$alkyl, C$_{1-4}$alkoxy, halogen and phenoxy unsubstituted or substituted in the phenyl ring by C$_{1-4}$alkyl, C$_{1-4}$alkoxy, sulfo, halogen or by C$_{2-4}$alkanoylamino, preferably unsubstituted phenoxy or phenoxy substituted by C$_{1-4}$alkyl or by halogen, and

$R_{57}$ is benzoyl unsubstituted or substituted in the phenyl ring by C$_{1-4}$alkyl, C$_{1-4}$alkoxy, sulfo or by halogen, preferably unsubstituted benzoyl, C$_{2-4}$alkanoyl unsubstituted or substituted in the alkyl group by hydroxy or by C$_{1-4}$alkoxy, preferably unsubstituted C$_{2-4}$alkanoyl, e.g. acetyl, phenylsulfonyl or methylphenylsulfonyl; and
wherein

$R_{58}$ is hydrogen, C$_1$-C$_4$ alkyl, C$_1$-C$_4$ alkoxy, halogen or C$_2$-C$_4$ alkanoylamino unsubstituted or substituted in the alkyl group by hydroxy, C$_1$-C$_4$ alkoxy or by halogen;

$R_{59}$ is phenyl unsubstituted or substituted by C$_1$-C$_4$ alkyl, C$_1$-C$_4$ alkoxy, sulfo or by halogen, preferably unsubstituted phenyl, and

$R_{60}$ is hydrogen or C$_1$-C$_4$ alkyl; and

$\text{HO}_3S_{1-3}$

(34),

wherein

$R_{61}$ is a radical of formula

in which $R_{48}$, $R_{49}$ and $R_{50}$ each

independently of the others, has the meaning given for formula (29) above;

(35),

wherein
R_{62} and R_{63} are radicals of formula

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{N} = \text{N} \\
\text{R}_{45} \\
\text{N} = \text{N} \\
\text{R}_{46} \\
\text{SO}_3\text{H}
\end{array}
\]

wherein

R_{45}, R_{46} and R_{47}, each independently of the others, has the meaning given for formula (29) above;

\[
\begin{array}{c}
\text{NH} - \text{O}_2\text{S} \\
\text{N} = \text{N} \\
\text{R}_{45} \\
\text{N} = \text{N} \\
\text{R}_{46} \\
\text{HO}
\end{array}
\] \quad \text{(36)};

\[
\begin{array}{c}
\text{N} = \text{N} \\
\text{R}_{45} \\
\text{N} = \text{N} \\
\text{R}_{46} \\
\text{HO}
\end{array}
\] \quad \text{(37)};

and

\[
\begin{array}{c}
\text{HO}_3\text{S} \\
\text{N} = \text{N} \\
\text{R}_{64} \\
\text{N} = \text{N} \\
\text{R}_{65} \\
\text{R}_{66}
\end{array}
\] \quad \text{(38)},

wherein
\( (R_{64})_{3-2} \) denotes from 0 to 2 identical or different substituents selected from the group C1-C4-alkyl and C1-C4-alkoxy,
\( (R_{86})_{3-2} \) denotes from 0 to 2 identical or different substituents selected from the group sulfo, C1-C4-alkyl, C1-C4-alkoxy, ureido, C2-C4-alkanoylamino and ureido, and
\( (R_{86})_{1-2} \) denotes from 0 to 2 identical or different substituents selected from the group sulfo, C1-C4-alkyl and C1-C4-alkoxy.

As C1-C4-alkyl radicals there come into consideration, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl and isobutyl, preferably methyl and ethyl.

As C1-C8-alkyl or C1-C8-alkyl radicals there come into consideration, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, isobutyl, n-pentyl, sec-pentyl, isopentyl, n-hexyl, n-heptyl and n-octyl.

As C1-C4-alkoxy radicals there come into consideration, for example, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, tert-butoxy and isobutoxy, preferably methoxy and ethoxy, and especially methoxy.

As halogen there come into consideration, for example, fluorine, chlorine, bromine and iodine, preferably chlorine and bromine, and especially chlorine.

As C2-C4-alkanoylamino radicals there come into consideration, for example, acetylamino and propionylamino, especially acetylamino.

As C1-C8-alkylsulfonyl radicals there come into consideration, for example, methylsulfonyl, ethylsulfonyl, n-propylsulfonyl, isopropylsulfonyl and n-butylsulfonyl, preferably methylsulfonyl and ethylsulfonyl.

As C1-C4-alkylaminosulfonyl radicals there come into consideration, for example, methylaminosulfonyl, ethylaminosulfonyl, n-propylaminosulfonyl, isopropylaminosulfonyl and n-butylaminosulfonyl, preferably methylaminosulfonyl and ethylaminosulfonyl.
As C₁-C₄ alkoxy carbonylamino radicals there come into consideration, for example, methoxycarbonylamino, ethoxycarbonylamino, n-propoxycarbonylamino, isopropoxycarbonylamino and n-butoxycarbonylamino, preferably methoxycarbonylamino and ethoxycarbonylamino.

As C₁-C₄ alkylsulfonylamino radicals there come into consideration, for example, methylsulfonylamino, ethylsulfonylamino, n-propylsulfonylamino, isopropylsulfonylamino and n-butylsulfonylamino, preferably methylsulfonylamino and ethylsulfonylamino.

As C₁-C₄ alkoxy-C₁-C₄ alkenylaminosulfonyl radicals there come into consideration, for example, methoxy-methyleneaminosulfonyl, methoxy-ethyleneaminosulfonyl, ethoxy-methyleneaminosulfonyl and ethoxy-ethyleneaminosulfonyl, preferably methoxyethylenaminosulfonyl.

As C₂-C₄ hydroxyalkylsulfamoyl radicals there come into consideration, for example, β-hydroxyethylsulfamoyl.

As C₅-C₇ cycloalkyl radicals there come into consideration, for example, cyclopentyl and cyclohexyl, preferably cyclohexyl.

As C₂-C₄ alkanoyl radicals there come into consideration, for example, acetyl and propionyl, preferably acetyl.

In a dedicated embodiment of the present invention the inks comprise dyes of formulae (5), (9), (22), (26), (34) and (35).

Suitable dyes are, for example, the dyes of formulae
The dyes used in accordance with the present invention may be used as single compounds or as a mixture of two or more dyes.

Preferred are the dyes of formulae (5.1), (5.2), (9.1), (22.1), (26.2), (26.3), (26.4), (26.5), (26.6), (26.7), (26.8), (27.4), (28.2), (28.4), (29.3), (30.1), (31.1), (32.1), (32.2), (32.3), (32.4),
(34.1), (35.1), (37.1), (38.1) and (38.2), in particular the dyes of formulae (5.2), (9.1), (22.1), (26.6), (26.7), (34.1) and (35.1).

The dyes of formulae (1) to (38) are known or can be obtained analogously to known compounds, e.g. by customary diazotisation, coupling, addition and condensation reactions.

As the fiber reactive dyes there come into consideration, for example, dyes of the formula

$$A_1 (Z_1)_{1-3}$$  \hspace{1cm} (39),

wherein

$A_1$ is the radical of a monoazo, disazo, polyazo, metal-complexed azo, anthraquinone, phthalocyanine, formazan or dioxazine chromophore having at least one sulfo group, and

$(Z_1)_{1-3}$ is 1 to 3 identical or different fiber reactive radicals, or
dyes of the formula

$$\begin{array}{c}
\begin{array}{c}
Q_1 \\
N
\end{array}
\begin{array}{c}
A_2 \\
N
\end{array}
\begin{array}{c}
N
\end{array}
\begin{array}{c}
G_1 \\
N
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
Q_2 \\
N
\end{array}
\begin{array}{c}
B \\
N
\end{array}
\begin{array}{c}
N
\end{array}
\begin{array}{c}
G_2 \\
N
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
Q_3 \\
N
\end{array}
\begin{array}{c}
A_3 \\
N
\end{array}
\begin{array}{c}
(Z_3)_{0-1}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
Q_4 \\
N
\end{array}
\end{array}
\end{array}$$  \hspace{1cm} (40),

wherein

$Q_1$, $Q_2$, $Q_3$ and $Q_4$ are each independently of the others hydrogen or unsubstituted or substituted $C_1$-$C_4$ alkyl,

$G_1$ und $G_2$ are halogen,

$B$ is an organic bridge member,

$A_2$ and $A_3$ are each independently of the other as defined for $A_1$, or one of $A_2$ and $A_3$ is hydrogen or unsubstituted or substituted $C_1$-$C_4$ alkyl, phenyl or naphthyl and the other one of $A_2$ and $A_3$ is as defined for $A_1$. 

\( (Z_2)_{b_1} \) and \( (Z_3)_{b_1} \) are each independently of the other 0 or 1 identical or different fiber reactive radicals, and

\( b \) is the number 0 or 1.

The radicals \( Q_1, Q_2, Q_3 \) and \( Q_4 \) in the reactive dye of formula (1) as alkyl radicals are straight-chain or branched. The alkyl radicals may be further substituted, for example by hydroxy, sulfo, sulfato, cyano or by carboxy. The following radicals may be mentioned by way of example: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl and tert-butyl, and also the corresponding hydroxy-, sulfo-, sulfato-, cyano- or carboxy-substituted radicals. Preferred as substituents are hydroxy, sulfo and sulfato, especially hydroxy and sulfato, and preferably hydroxy.

\( Q_1 \) and \( Q_4 \) are preferably hydrogen or \( C_1^-C_4 \)alkyl, especially hydrogen.

\( Q_2 \) and \( Q_3 \) are preferably each independently of the other hydrogen or unsubstituted or hydroxy-, sulfo-, sulfato-, cyano- or carboxy-substituted \( C_1^-C_4 \)alkyl. According to an embodiment of interest, one of the radicals \( Q_2 \) and \( Q_3 \) is hydroxy-, sulfo-, sulfato-, cyano- or carboxy-substituted \( C_1^-C_4 \)alkyl, and the other of the radicals \( Q_2 \) and \( Q_3 \) is hydrogen or \( C_1^-C_4 \)alkyl, especially hydrogen.

\( Q_2 \) and \( Q_3 \) are especially preferably each independently of the other hydrogen or \( C_1^-C_4 \)alkyl, especially hydrogen.

\( G_1 \) and \( G_2 \) are preferably each independently of the other chlorine or fluorine, especially fluorine.

The following come into consideration as organic bridge members \( B \), for example: \( C_2^-C_{12} \)alkylene radicals, especially \( C_2^-C_6 \)alkylene radicals, which may be interrupted by 1, 2 or 3 members from the group -NH-, -N(CH_3)- and -O-, especially -O-, and are unsubstituted or substituted by hydroxy, sulfo, sulfato, cyano or by carboxy, preferred substituents of the alkyene radicals mentioned for \( B \) being hydroxy, sulfo and sulfato, especially hydroxy;
C₆-C₉ cycloalkylene radicals, such as especially cyclohexylene radicals, that are unsubstituted or substituted by C₁-C₄ alkyl, C₁-C₄ alkoxy, C₂-C₄ alkanoylamino, sulfo, halogen or by carboxy, especially by C₁-C₄ alkyl;
methylene-cyclohexylene-methylene radicals that are unsubstituted or substituted in the cyclohexylene ring by C₁-C₄ alkyl;
C₁-C₉ alkylenephenylenes, or preferably phenylene, that is unsubstituted or substituted by C₁-C₄ alkyl, C₁-C₄ alkoxy, C₂-C₄ alkanoylamino, sulfo, halogen or by carboxy.

Also suitable as a radical of formula -N(Q₂)-B-N(Q₃)- is a radical of the formula

\[ \text{\textbullet} \text{N} \text{\textbullet} \text{N} \text{\textbullet} \]

Preferably B is a C₂-C₁₂ alkylene radical which may be interrupted by 1, 2 or 3 members from the group -NH-, -N(CH₃)- and -O- and is unsubstituted or substituted by hydroxy, sulfo, sulfato, cyano or by carboxy; or
a phenylene radical that is unsubstituted or substituted by C₁-C₄ alkyl, C₁-C₄ alkoxy, C₂-C₄ alkanoylamino, sulfo, halogen or by carboxy.

B is especially a C₂-C₁₂ alkylene radical which may be interrupted by 1, 2 or 3 members from the group -NH-, -N(CH₃)- and -O-, especially -O-, and is unsubstituted or substituted by hydroxy, sulfo, sulfato, cyano or by carboxy. The alkylene radical is preferably unsubstituted or substituted by hydroxy, sulfo or by sulfato, especially by hydroxy.

B is more especially a C₂-C₁₂ alkylene radical, especially a C₂-C₆ alkylene radical, which may be interrupted by 1, 2 or 3 -O- members and is unsubstituted or substituted by hydroxy.

Bridge members B of special interest are C₂-C₆ alkylene radicals.

Fibre-reactive radicals are to be understood as meaning those which are capable of reacting with the hydroxyl groups of cellulose, the amino, carboxyl, hydroxyl and thiol groups in wool and silk, or with the amino and possibly carboxyl groups of synthetic polyamides, to form covalent chemical bonds. The fibre-reactive radicals are as a rule bonded to the dye radical.
directly or via a bridge member. Suitable fibre-reactive radicals are, for example, those which contain at least one substituent which can be split off on an aliphatic, aromatic or heterocyclic radical, or in which the radicals mentioned contain a radical which is capable of reaction with the fibre material, for example a vinyl radical.

Preferably fiber reactive radicals $Z_1$, $Z_2$ and $Z_3$ independently of the other have the formula

$$-\text{SO}_2-Y$$

(41a),

$$-\text{NH-CO-(CH}_2)_n\text{-SO}_2-Y$$

(41b),

$$-\text{CONR}_{70}(\text{CH}_2)_m\text{-SO}_2-Y$$

(41c),

$$-\text{NH-CO-CH(Hal)-CH}_2\text{-Hal}$$

(41d),

$$-\text{NH-CO-C(Hal)=CH}_2$$

(41e),

\[
\begin{array}{c}
\text{NR}_{88} \\
N \hspace{1cm} N \\
\text{X}_1 \\
\text{NR}_{87} \\
N \hspace{1cm} T_1 \\
\text{X}_1
\end{array}
\] (41f) or

\[
\begin{array}{c}
\text{NR}_{88} \\
N \hspace{1cm} N \\
\text{T}_2 \\
\text{X}_2 \\
\text{NR}_{87} \\
N \hspace{1cm} \text{X}_3
\end{array}
\] (41g),

in which

Hal is chlorine or bromine;

$X_1$ is halogen, 3-carboxypyridin-1-yl or 3-carbamoylpyridin-1-yl;

$T_1$ independently has the meaning of $X_1$, or is a substituent which is not fiber reactive or a fiber reactive radical of the formula

$$\begin{array}{c}
\text{R}_{71} \\
\text{N} \hspace{1cm} \text{alk} \hspace{1cm} \text{SO}_2-Y \\
\text{R}_{70}
\end{array}$$

(42a),
\[ \begin{align*}
\text{N} & \quad \text{alk} \quad \text{Q} \quad \text{alk}_1 \quad \text{SO}_2 \quad \text{Y} \\
R_{69} & \\
\text{N} & \quad \text{arylene} \quad \text{SO}_2 \quad \text{Y} \\
R_{69} & \\
\text{N} & \quad \text{arylene} \quad (\text{alk})_n \quad W \quad \text{alk}_1 \quad \text{SO}_2 \quad \text{Y} \\
R_{69} & \\
\text{N} & \quad \text{alk} \quad \text{SO}_2 \quad \text{Y} \\
R_{69} & \\
\text{N} & \quad \text{arylene} \quad \text{NH} \quad \text{CO} \quad \text{Y}_1 \\
R_{69} & \\
\end{align*} \]

(42b), (42c), (42d), (42e), (42f)

in which

- \( R_{67}, R_{68} \) and \( R_{69} \) independently of one another are each hydrogen or \( \text{C}_1-\text{C}_4 \) alkyl,
- \( R_{70} \) is hydrogen, \( \text{C}_1-\text{C}_4 \) alkyl which is unsubstituted or substituted by hydroxyl, sulfo, sulfato, carboxyl or cyano or a radical \( R_{71} \)
- \( \text{alk} \) and \( \text{alk}_1 \) independently of one another are linear or branched \( \text{C}_1-\text{C}_6 \) alkylene,
- arylenel is a phenylene or naphthylene radical which is unsubstituted or substituted by sulfo, carboxyl, \( \text{C}_1-\text{C}_4 \) alkyl, \( \text{C}_1-\text{C}_4 \) alkoxy or halogen,
- \( Q \) is a radical -\( \text{O}^- \) or -NR\(_{69}^- \), in which \( R_{69} \) is as defined above,
- \( W \) is a group -SO\(_2^-\)NR\(_{70}^-\), -CONR\(_{70}^-\) or -NR\(_{70}^-\)CO\(_-\), in which \( R_{70} \) is as defined above,
- \( Y \) is vinyl or a radical -CH\(_2\)-CH\(_2\)-U and \( U \) is a group which can be split off under alkaline conditions,
- \( Y_1 \) is a group -CH(Hal)-CH\(_2\)-Hal or -C(Hal)=CH\(_2\) and Hal is chlorine or bromine and
- \( l \) and \( m \) independently of one another are an integer from 1 to 6 and \( n \) is the number 0 or 1; and
$X_2$ is halogen or $C_1-C_4$ alkylsulfonyl;
$X_3$ is halogen or $C_1-C_4$ alkyl and
$T_2$ is hydrogen, cyano or halogen.

A group $U$ which can be split off under alkaline conditions is, for example, -Cl, -Br, -F, -
$\text{OSO}_3\text{H}$, -SSO$_3$H, -OCO-CH$_3$, -OPO$_3$H$_2$, -OCO-C$_6$H$_5$, -OSO$_2$-C$_1$-C$_4$alkyl or -OSO$_2$-N(C$_1$-
C$_4$alkyl)$_2$. $U$ is preferably a group of the formula -Cl, -OSO$_3$H, -SSO$_3$H, -OCO-CH$_3$, -OCO-
C$_6$H$_5$ or -OPO$_3$H$_2$, in particular -Cl or -OSO$_3$H, and particularly preferably -OSO$_3$H.

Examples of suitable radicals $Y$ are accordingly vinyl, $\beta$-bromo- or $\beta$-chloroethyl,
$\beta$-acetoxyethyl, $\beta$-benzozoxyethyl, $\beta$-phosphatoethyl, $\beta$-sulfatoethyl and $\beta$-thiosulfatoethyl. $Y$
is preferably vinyl, $\beta$-chloroethyl or $\beta$-sulfatoethyl, and in particular vinyl or $\beta$-sulfatoethyl.

$R_{67}$, $R_{68}$ and $R_{69}$ independently of one another are each preferably hydrogen, methyl or ethyl,
and particularly preferably hydrogen.

$R_{70}$ is preferably hydrogen or $C_1-C_4$ alkyl, such as methyl, ethyl, propyl, isopropyl, butyl,
isobutyl, sec-butyl or tert-butyl, and particularly preferably hydrogen, methyl or ethyl. $R_{70}$ is
particularly preferably hydrogen.

$R_{71}$ is preferably hydrogen.

$I$ and $m$ independently of one another are preferably the number 2, 3 or 4, and particularly
preferably the number 2 or 3.

Especially preferably, $I$ is the number 3 and $m$ is the number 2.

Substituents $T_1$ which are not fiber reactive are, for example, the following radicals:
hydroxyl;
$C_1-C_4$alkoxy, for example methoxy, ethoxy, n- or isopropoxy or n-, sec-, iso- or tert-butoxy, in
particular methoxy or ethoxy; the radicals mentioned are unsubstituted or substituted in the
alkyl moiety, for example by $C_1-C_4$alkoxy, hydroxyl, sulfo or carboxyl;
C_{1-4} alkylthio, for example methylthio, ethylthio, n- or isopropylthio or n-butylthio; the radicals mentioned are unsubstituted or substituted in the alkyl moiety, for example by C_{1-4} alkoxy, hydroxyl, sulfo or carboxyl;
amino;
N-mono- or N,N-di-C_{1-6} alkylamino, preferably N-mono- or N,N-di-C_{1-6} alkylamino; the radicals mentioned are unsubstituted, uninterrupted or interrupted in the alkyl moiety by oxygen or substituted in the alkyl moiety, for example by C_{2-6} alkanoylamino, C_{1-4} alkoxy, hydroxyl, sulfo, sulfato, carboxyl, cyano, carbamoyl or sulfamoyl; examples are N-methylamino, N-ethylamino, N-propylamino, N,N-di-methylamino or N,N-di-ethylamino, N-β-hydroxyethylamino, N,N-di-β-hydroxyethylamino, N-2-(β-hydroxyethoxy)ethylamino, N-2-[2-(β-hydroxyethoxy)ethoxy]ethylamino, N-β-sulfatoethylamino, N-β-sulfoethylamino, N-carboxymethylamino, N-β-carboxyethylamino, N-α,β-dicarboxyethylamino, N-α,γ-dicarboxypropylamino, N-ethyl-N-β-hydroxyethylamino or N-methyl-N-β-hydroxyethylamino; C_{6-10} cycloalkylamino, for example cyclohexylamino, which includes both the unsubstituted radicals and the radicals substituted in the cycloalkyl ring, for example by C_{1-4} alkyl, in particular methyl, or carboxyl;
phenylamino or N-C_{1-4} alkyl-N-phenylamino, which includes both the unsubstituted radicals and the radicals substituted in the phenyl ring, for example by C_{1-4} alkyl, C_{1-4} alkoxy, C_{2-6} alkanoylamino, carboxyl, carbamoyl, sulfo or halogen, for example 2-, 3- or 4-chlorophenylamino, 2-, 3- or 4-methylphenylamino, 2-, 3- or 4-methoxyphenylamino, 2-, 3- or 4-sulfophenylamino, disulfophenylamino or 2-, 3- or 4-carboxyphenylamino; naphthylamino which is unsubstituted or substituted in the naphthyl ring, for example by sulfo, preferably the radicals substituted by 1 to 3 sulfo groups, for example 1- or 2-naphthyaminosulfo, 1-sulfo-2-naphthylamino, 1,5-disulfo-2-naphthylamino or 4,8-disulfo-2-naphthylamino; or benzylamino which is unsubstituted or substituted in the phenyl moiety, for example by C_{1-4} alkyl, C_{1-4} alkoxy, carboxyl, sulfo or halogen.

A radical T_{1} which is not fiber reactive is preferably C_{1-4} alkoxy, C_{1-4} alkylthio, hydroxyl, amino, N-mono- or N,N-di-C_{1-6} alkylamino which are optionally substituted in the alkyl moiety by hydroxyl, sulfato or sulfo, morpholino, phenylamino or N-C_{1-4} alkyl-N-phenylamino which are unsubstituted or substituted in the phenyl ring by sulfo, carboxyl, acetylamino,
chlorine, methyl or methoxy and in which the alkyl is unsubstituted or substituted by hydroxyl, sulfato or sulfonato, or naphthylamino which is unsubstituted or substituted by 1 to 3 sulfato groups.

Particularly preferred radicals $T_1$ which are not fiber reactive are amino, N-methylamino, N-ethylamino, N-$\beta$-hydroxyethylamino, N-methyl-N-$\beta$-hydroxyethylamino, N-ethyl-N-$\beta$-hydroxyethylamino, N,N-di-$\beta$-hydroxyethylamino, N-$\beta$-sulfatoethylamino, N-$\beta$-sulfoethylamino, morpholino, 2-, 3- or 4-carboxyphenylamino, 2-, 3- or 4-sulfophenylamino or N-C$_1$-C$_4$-alkyl-N-phenylamino.

$X_1$ is preferably halogen, for example fluorine, chlorine or bromine, and particularly preferably chlorine or fluorine.

Halogen $T_2$, $X_2$ and $X_3$ are, for example, fluorine, chlorine or bromine, in particular chlorine or fluorine.

C$_1$-C$_4$ alkylsulfonyl $X_2$ is, for example, ethylsulfonyl or methylsulfonyl, and in particular methylsulfonyl.

C$_1$-C$_4$ alkyl $X_3$ is, for example, methyl, ethyl, n- or iso-propyl or n-, iso or tert-butyl, and in particular methyl.

$X_2$ and $X_3$ independently of one another are preferably chlorine or fluorine.

$T_2$ is preferably cyano or chlorine.

Hal is preferably bromine.

alk and alk$_1$, independently of one another are, for example, a methylene, ethylene, 1,3-propylene, 1,4-butylene, 1,5-pentylene or 1,6-hexylene radical or branched isomers thereof.

alk and alk$_1$, independently of one another are preferably each a C$_1$-C$_4$ alkylene radical, and particularly preferably an ethylene radical or propylene radical.
arylene is preferably a 1,3- or 1,4-phenylene radical which is unsubstituted or substituted, for example by sulfo, methyl, methoxy or carboxyl, and particularly preferably an unsubstituted 1,3- or 1,4-phenylene radical.

Q is preferably -NH- or -O-, and particularly preferably -O-.

W is preferably a group of the formula -CONH- or -NHCO-, in particular a group of the formula -CONH-.

n is preferably the number 0.

The reactive radicals of the formulae (4a) to (4f) are preferably those in which W is a group of the formula -CONH-, R_{89}, R_{70} and R_{71} are each hydrogen, Q is the radical -O- or -NH-, alk and alk_{1} independently of one another are each ethylene or propylene, arylene is phenylene which is unsubstituted or substituted by methyl, methoxy, carboxyl or sulfo, Y is vinyl or β-sulfatoethyl, Y_{1} is -CHBr-CH_{2}Br or -CBr=CH_{2} and n is the number 0.

A fibre-reactive radical Z_{1}, Z_{2} and Z_{3} is particularly preferably a radical of the formula (3a), (3c), (3d), (3e) or (3f), in which Y is vinyl, β-chloroethyl or β-sulfatoethyl, Hal is bromine, R_{67} and R_{70} are hydrogen, m is the number 2 or 3, X_{1} is halogen, T_{1} is C_{1}-C_{4}alkoxy, C_{1}-C_{4}alkylthio, hydroxyl, amino, N-mono- or N,N-di-C_{1}-C_{4}alkylamino which are unsubstituted or substituted in the alkyl moiety by hydroxyl, sulfato or sulfo, morpholino, phenylamino or N-C_{1}-C_{4}alkyl-N-phenylamino which are unsubstituted or substituted in the phenyl ring by sulfo, carboxyl, acetylamino, chlorine, methyl or methoxy and in which the alkyl is unsubstituted or substituted by hydroxyl, sulfo or sulfato, or naphthylamino which is unsubstituted or substituted by 1 to 3 sulfo groups, or a fibre-reactive radical of the formula

-NH-(CH_{2})_{2,3}-SO_{2}Y \quad \text{(42a')},

-NH-(CH_{2})_{2,3}-O-(CH_{2})_{2,3}-SO_{2}Y \quad \text{(42b')},
in particular (42b'), (42c') or (42d'), in which
Y is as defined above and
Y₁ is a group -CH(Br)-CH₂-Br or -C(Br)=CH₂.

Preferred are dyes of the formula (1) which contain 1 or 2, in particular 2, fiber reactive radicals Z₁.

Preferred are dyes of the formula (2) which do not contain fiber reactive radicals Z₂ and Z₃.

When one of A₂ and A₃ is unsubstituted or substituted C₁-C₄ alkyl, phenyl or naphthyl, it may be, for example, C₁-C₄ alkyl that is unsubstituted or substituted by sulfo, sulfato, hydroxy, carboxy or by phenyl; or phenyl or naphthyl each of which is unsubstituted or substituted by C₁-C₄ alkyl, C₁-C₄ alkoxy, carboxy, sulfo or by halogen. Preference is given to phenyl that is unsubstituted or substituted by C₁-C₄ alkyl, C₁-C₄ alkoxy, carboxy, sulfo or by halogen.

Preferably A₂ and A₃ are each independently of the other the radical of a monoazo, polyazo, metal-complexed azo, anthraquinone, phthalocyanine, formazan or dioxazine chromophore having at least one sulfo group.
A radical $A_1$, $A_2$ or $A_3$ as the radical of a monoazo, polyazo, metal-complexed azo, anthraquinone, phthalocyanine, formazan or dioxazine chromophore may have the substituents customary in organic dyes bonded to its base structure.

The following may be mentioned as examples of substituents in the radicals $A_1$, $A_2$ and $A_3$: alkyl groups having from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl or butyl, it being possible for the alkyl radicals to be further substituted e.g. by hydroxy, sulfo or by sulfato; alkoxy groups having from 1 to 4 carbon atoms, such as methoxy, ethoxy, propoxy, isopropoxy or butoxy, it being possible for the alkyl radicals to be further substituted e.g. by hydroxy, sulfo or by sulfato; phenyl that is unsubstituted or substituted by $C_1$-$C_4$alkyl, $C_1$-$C_2$alkoxy, halogen, carboxy or by sulfo; acylamino groups having from 1 to 8 carbon atoms, especially such alkanoylamino groups, e.g. acetylamino or propionylamino; benzoylamino that is unsubstituted or substituted in the phenyl ring by $C_1$-$C_4$alkyl, $C_1$-$C_2$alkoxy, halogen or by sulfo; phenylamino that is unsubstituted or substituted in the phenyl ring by $C_1$-$C_2$alkyl, $C_1$-$C_2$alkoxy, halogen or by sulfo; $N,N$-di-$\beta$-hydroxyethylamino; $N,N$-di-$\beta$-sulfatoethylamino; sulfobenzylamino; $N,N$-disulfobenzylamino; alkoxy carbonyl having from 1 to 4 carbon atoms in the alkoxy radical, such as methoxy carbonyl or ethoxy carbonyl; alkysulfonyl having from 1 to 4 carbon atoms, such as methylsulfonyl or ethylsulfonyl; trifluoromethyl; nitro; amino; cyano; halogen, such as fluorine, chlorine or bromine; carbamoyl; $N$-alkylcarbamoyl having from 1 to 4 carbon atoms in the alkyl radical, such as $N$-methylcarbamoyl or $N$-ethylcarbamoyl; sulfamoyl; $N$-mono- or $N,N$-di-alkylsulfamoyl each having from 1 to 4 carbon atoms, such as $N$-methylsulfamoyl, $N$-ethylsulfamoyl, $N$-propylsulfamoyl, $N$-isopropylsulfamoyl or $N$-butylsulfamoyl, it being possible for the alkyl radicals to be further substituted e.g. by hydroxy or by sulfo; $N$-($\beta$-hydroxyethyl)-sulfamoyl; $N,N$-di($\beta$-hydroxyethyl)-sulfamoyl; $N$-phenylsulfamoyl that is unsubstituted or substituted by $C_1$-$C_4$alkyl, $C_1$-$C_2$alkoxy, halogen, carboxy or by sulfo; ureido; hydroxy; carboxy; sulfonyl or sulfo.

When $A_1$, $A_2$ and $A_3$ are the radical of a monoazo, polyazo or metal-complexed azo chromophore, the following radicals, especially, come into consideration:

Chromophore radicals of a mono- or dis-azo dye of formula

\[
\text{D-N=N-}(\text{M-N=N})_{n-K}\]  

(43)
wherein \( D \) and \( D^* \) independently of the other are the radicals of a diazo component of the benzene or naphthalene series, \( M \) is the radical of a middle component of the benzene or naphthalene series, \( K \) is the radical of a coupling component of the benzene, naphthalene, pyrazolone, 6-hydroxypyridone-(2) or acetoacetic acid arylamide series and \( u \) is the number 0 or 1, it being possible in the case of azo dyes for \( D, D^*, M \) and \( K \) to carry customary substituents, e.g. \( C_1-C_4 \) alkyl or \( C_1-C_4 \) alkoxy each of which is unsubstituted or may be further substituted by hydroxy, sulfo or by sulfato; halogen; carboxy; sulfo; nitro; cyano; trifluoromethyl; sulfamoyl; carbamoyl; amino; ureido; hydroxy; carboxy; sulfomethyl; \( C_2- C_4 \) alkanoylamino; benzoylamino that is unsubstituted or substituted in the phenyl ring by \( C_1-C_4 \) alkyl, \( C_1-C_4 \) alkoxy, halogen or by sulfo; phenyl that is unsubstituted or substituted by \( C_1-C_4 \) alkyl, \( C_1-C_4 \) alkoxy, halogen, carboxy or by sulfo. Also suitable are the metal complexes derived from the above dye radicals of formulae (43), (44) and (45), especially dye radicals of a 1:1 copper-complexed azo dye of the benzene or naphthalene series wherein the copper atom is bonded to a group capable of mettallation, e.g. a hydroxy group, on each side in the ortho-position to the azo bridge.

The radicals of formulae (43), (44) and (45) are preferably those of formula

\[
\begin{align*}
\text{(46a),}
\end{align*}
\]

wherein

\( (R_{72})_{0-3} \) denotes from 0 to 3 identical or different substituents from the group \( C_1-C_4 \) alkyl, \( C_1-C_4 \) alkoxy, \( C_2-C_4 \) alkanoylamino, ureido, sulfamoyl, carbamoyl, sulfomethyl, halogen, nitro, cyano, trifluoromethyl, amino, hydroxy, carboxy and sulfo,
(R_{73})_{0-2} denotes from 0 to 2 identical or different substituents from the group hydroxy, amino, N-mono-C_{1-4}alkylamino, N,N-di-C_{1-4}alkylamino, C_{2-4}alkanoylamino and benzoylamino;

\[
\begin{array}{c}
\begin{array}{c}
\text{(SO}_3\text{H)}_{1-3}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{(R}_{73}\text{)}_{0-2}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{(SO}_3\text{H)}_{1-3}
\end{array}
\end{array}
\text{(46b),}
\]

wherein

(R_{73})_{0-2} is as defined above;

\[
\begin{array}{c}
\begin{array}{c}
\text{OH, NH}_2
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{N}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{N}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{CH}_3\text{COOH}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{(R}_{74}\text{)}_{0-3}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{(R}_{75}\text{)}_{0-3}
\end{array}
\end{array}
\text{(46c),}
\]

wherein

(R_{74})_{0-3} und (R_{75})_{0-3} independently of the other denotes from 0 to 3 identical or different substituents from the group C_{1-4}alkyl, C_{1-4}alkoxy, halogen, carboxy and sulfo;

\[
\begin{array}{c}
\begin{array}{c}
\text{(SO}_3\text{H)}_{0-2}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{N=N}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{O}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{OH}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{N}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{R}_{76}
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{R}_{77}
\end{array}
\end{array}
\text{(46d),}
\]

wherein

R_{76} und R_{78} are each independently of the other hydrogen, C_{1-4}alkyl or phenyl, and
$R_{77}$ hydrogen, cyano, carbamoyl or sulfomethyl;

\[
\begin{array}{c}
\begin{array}{c}
\text{(46e)}
\end{array}
\end{array}
\]

wherein

$(R_{80})_{0-3}$ denotes from 0 to 3 identical or different substituents from the group $C_1$-$C_4$alkyl, $C_1$-$C_4$alkoxy, halogen, amino, carboxy and sulfo, and

$(R_{78})_{0-3}$ and $(R_{81})_{0-3}$ independently of the other are as defined for $(R_{72})_{0-3}$;

\[
\begin{array}{c}
\begin{array}{c}
\text{(46f)}
\end{array}
\end{array}
\]

wherein

$(R_{79})_{0-3}$ and $(R_{81})_{0-3}$ independently of the other are as defined above

$(R_{82})_{0-2}$ denotes from 0 to 2 identical or different substituents from the group $C_1$-$C_4$alkyl, $C_1$-$C_4$alkoxy, halogen, carboxy, sulfo, hydroxy, amino, N-mono-$C_1$-$C_4$alkylamino, N,N-di-$C_1$-$C_4$alkylamino, C$_2$-$C_4$alkanoylamino and benzoylamino.

When $A_1$, $A_2$ and $A_3$ are the radical of a formazan dye the following radicals, especially, come into consideration:
wherein

the benzene nuclei do not contain any further substituents or are further substituted by
C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4alkylsulfonyl, halogen or by carboxy.

When A_1, A_2 and A_3 are the radical of a phthalocyanine dye the following radicals, especially,
come into consideration:

\[
\begin{align*}
\text{Pc}^\ast & \quad \text{SO}_2 \cdot N - A - \\
\text{SO}_2 & \quad \text{W}^\dagger \\
\end{align*}
\]

wherein

Pc is the radical of a metal phthalocyanine, especially the radical of a copper or nickel
phthalocyanine,
W is -OH and/or -NR_94R_94, and R_94 and R_94' are each independently of the other hydrogen
or C_1-C_4alkyl that is unsubstituted or substituted by hydroxy or by sulfo,
R_93 is hydrogen or C_1-C_4alkyl,
A is a phenylene radical that is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy,
halogen, carboxy or by sulfo or is a C_2-C_8alkylene radical and
k is from 1 to 3.
When $A_1$, $A_2$ and $A_3$ are the radical of a dioxazine dye the following radicals, especially, come into consideration:

\[
\begin{array}{c}
\text{HO}_3\text{S} \\
\text{Cl} \\
\text{Cl} \\
\text{N} \\
\text{H} \quad \text{A'}_v \quad \text{A'}_v \\
\text{HN} \\
\end{array}
\]

\[\text{(49)},\]

wherein

$\text{A'}$ is a phenylene radical that is unsubstituted or substituted by $C_1$-$C_4$alkyl, $C_1$-$C_4$alkoxy, halogen, carboxy or by sulfo or is a $C_2$-$C_6$alkylene radical,

$r$ independently is the number 0, 1 or 2, preferably 0 or 1, and

$v$ and $v'$ are each independently of the other the number 0 or 1.

When $A_1$, $A_2$ and $A_3$ are the radical of a anthrachinon dye the following radicals, especially, come into consideration:

\[
\begin{array}{c}
\text{NH}_2 \\
\text{SO}_3\text{H} \\
\text{NH} \quad \text{G} \\
\text{O} \\
\end{array}
\]

\[\text{(50)},\]

wherein

G is a phenylene radical that is unsubstituted or substituted by $C_1$-$C_4$alkyl, $C_1$-$C_4$alkoxy, halogen, carboxy or by sulfo or is a cyclohexylene, phenylenemethylene or $C_2$-$C_6$alkylene radical.

Preferably $b$ in the dye of formula (40) is the number 1.
Special interest is accorded to reactive dyes of formulae

(39.1),

(39.2),

(39.3),

(39.4),
(39.5),

(39.6),

(39.7),

(39.8),

(39.9),
(39.14),

(39.15),

(39.16),

(39.17),
(39.22),

(39.23),

(39.24),

(39.25),

(39.26),

(39.27),
(39.28),

(39.29),

(39.30),

(39.31),

(39.32),
CuPhC = Cu-Phthalocyanin

(39.39),

CuPhC = Cu-Phthalocyanin

(39.40),

(39.41),

(39.42),

(39.43),
(39.44),

(39.45),

(39.46),

(39.47),

(39.48),
(40.3),

(40.4),

(40.5),

(40.6),
In a particular preferred embodiment of the present invention the dyes of formulae (39.1), (39.4), (39.9), (39.12), (39.14), (39.15), (39.19), (39.23), (39.25), (39.27), (39.29), (39.33), (39.35), (39.39), (39.40), (39.44), (39.45), (39.46) to (39.49), (40.4), (40.10), (40.14), (40.15), (40.17) and (40.19) are used.

The reactive dyes of formulae (39) and (40) are known or can be obtained analogously to known compounds, e.g. by customary diazotisation, coupling and condensation reactions.

Suitable disperse dyes for the process of the invention are carboxyl- and/or sulfo-free nitro, amino, amino ketone, ketone imine, methine, polymethine, diphenylamine, quinoline, benzimidazole, xanthene, oxazine or coumarin dyes, and especially anthraquinone dyes and azo dyes, such as monoazo or disazo dyes.

As the disperse dyes there come into consideration, for example, dyes of the formula

\[
\begin{array}{c}
R_{96} \quad N=N \\
R_{97} \quad N R_{90} R_{91}
\end{array}
\]

(51),

in which

- \(R_{96}\) is halogen, nitro or cyano,
- \(R_{96}\) is hydrogen, halogen, nitro or cyano,
- \(R_{97}\) is hydrogen, halogen or cyano,
- \(R_{98}\) is hydrogen, halogen, \(C_1-C_4\)alkyl or \(C_1-C_4\)alkoxy,
- \(R_{99}\) is hydrogen, halogen or \(C_2-C_3\)alkanoylamino, and
R_{90} and R_{91} independently of one another are hydrogen, allyl, C_{1-6}alkyl which is unsubstituted or substituted by hydroxy, cyano, C_{1-6}alkoxy, C_{1-6}alkoxy-C_{1-6}alkoxy, C_{2-6}alkanoyloxy, C_{1-4}alkoxycarbonyl, phenyl or phenoxy,

\[ (52), \]

in which
R_{92} is hydrogen, C_{1-6}alkyl, phenyl or phenylsulfonyl, the benzene ring in phenyl and phenylsulfonyl being unsubstituted or substituted by C_{1-6}alkyl, sulfo or C_{1-6}alkyl-sulfonyloxy,
R_{93} is hydroxy, amino, N-mono- or N,N-di-C_{1-6}alkylamino, phenylamino, the benzene ring in phenyl being unsubstituted or substituted by C_{1-6}alkyl, C_{1-6}alkoxy, C_{2-6}alkanoylamino or halogen,
R_{94} is hydrogen, C_{1-6}alkoxy or cyano,
R_{95} is hydrogen, C_{1-6}alkoxy, phenoxy or the radical -O-C_{6}H_{5}-SO_{2}-NH-(CH_{2})_{3}-O-C_{2}H_{5},
R_{96} is hydrogen, hydroxy or nitro, and
R_{97} is hydrogen, hydroxy or nitro,

\[ (53), \]

in which
R_{98} is C_{1-6}alkyl which is unsubstituted or substituted by hydroxy,
R_{99} is C_{1-6}alkyl,
R_{100} is cyano,
R_{101} is the radical of the formula -(CH_{2})_{3}-O-(CH_{2})_{2}-O-C_{6}H_{5},
R_{102} is halogen, nitro or cyano, and
$R_{103}$ is hydrogen, halogen, nitro or cyano,

\[
\begin{array}{c}
\text{HO} \\
\text{N=N} \\
\text{R}_{104} \text{CN} \\
\text{R}_{107} \\
\text{R}_{106}
\end{array}
\]  

(54),

in which

$R_{104}$ is $C_1$-$C_4$-alkyl,

$R_{106}$ is $C_1$-$C_4$-alkyl which is unsubstituted or substituted by $C_1$-$C_4$-alkoxy and $R_{106}$ is the radical $-\text{COOCH}_2\text{CH}_2\text{OC}_6\text{H}_5$ und $R_{107}$ is hydrogen or $R_{106}$ is hydrogen and $R_{107}$ is the radical $-\text{N}=\text{N}=\text{C}_6\text{H}_5$,

\[
\begin{array}{c}
\text{NO}_2 \\
\text{S}=\text{O} \\
\text{N} \\
\text{A} \\
\text{B}
\end{array}
\]  

(55),

where the rings A and B are unsubstituted or substituted one or more times by halogen,

\[
\begin{array}{c}
\text{NH}_2 \\
\text{N} \\
\text{R}_{108} \\
\text{O} \\
\text{NH}_2
\end{array}
\]  

(56),

in which

$R_{108}$ is $C_1$-$C_4$-alkyl, which is unsubstituted or substituted by hydroxy, $C_1$-$C_4$-alkoxy, $C_1$-$C_4$-alkoxy-$C_1$-$C_4$-alkoxy, $C_2$-$C_4$-alkanoyloxy or $C_1$-$C_4$-alkoxycarbonyl,
in which

$R_{109}$ is C$_1$-C$_4$alkyl,

$R_{110}$ is C$_1$-C$_4$alkyl, which is unsubstituted or substituted by C$_1$-C$_4$alkoxy,

$R_{111}$ is hydrogen, C$_1$-C$_4$alkoxy or halogen, and

$R_{112}$ is hydrogen, nitro, halogen or phenylsulfonyloxy,

in which

$R_{113}$, $R_{114}$, $R_{115}$ and $R_{116}$ independently of one another are hydrogen or halogen,

$R_{117}$ is hydrogen, halogen, C$_1$-C$_4$alkyl or C$_1$-C$_4$alkoxy,

$R_{118}$ is hydrogen, halogen or C$_2$-C$_5$alkanoylaminio, and

$R_{119}$ and $R_{120}$ independently of one another are hydrogen, C$_1$-C$_4$alkyl, which is unsubstituted or substituted by hydroxy, cyano, acetooxy or phenoxy,
in which

\( R_{121} \) is hydrogen or halogen,

\[ \text{(60),} \]

\[ \text{(61),} \]

in which

\( R_{122} \) is hydrogen, \( C_1-C_4 \)-alkyl, tetrahydrofuran-2-yl or \( C_1-C_4 \)-alkoxycarbonyl, which is unsubstituted or substituted in the alkyl by \( C_1-C_4 \)-alkoxy,

\[ \text{(62),} \]

in which

\( R_{123} \) is hydrogen or thiophenyl, which is unsubstituted or substituted in the phenyl by \( C_1-C_4 \)-alkyl or \( C_1-C_4 \)-alkoxy,

\( R_{124} \) is hydrogen, hydroxy or amino,
$R_{126}$ is hydrogen, halogen, cyano or thiophenyl, which is unsubstituted or substituted in the phenyl by $C_1$-$C_4$alkyl or $C_1$-$C_4$-alkoxy, phenoxy or phenyl, and

$R_{126}$ is phenyl, which is unsubstituted or substituted by halogen, $C_1$-$C_4$alkyl or $C_1$-$C_4$-alkoxy,

\[(63),\]

in which

$R_{127}$ is hydrogen or $C_1$-$C_4$alkyl,

$R_{128}$ and $R_{129}$ independently of one another are hydrogen, halogen, nitro or cyano,

$R_{130}$ is hydrogen, halogen, $C_1$-$C_4$alkyl or $C_1$-$C_4$-alkoxy,

$R_{131}$ is hydrogen, halogen or $C_2$-$C_4$-alkanoylamino, and

$R_{132}$ and $R_{133}$ independently of one another are hydrogen or $C_1$-$C_4$alkyl, which is unsubstituted or substituted by hydroxy, cyano, $C_1$-$C_4$alkoxy, $C_1$-$C_4$alkoxy-$C_1$-$C_4$alkoxy, $C_2$-$C_4$alkanoyloxy, $C_1$-$C_4$alkoxycarbonyl, phenyl or phenoxy.

As $C_1$-$C_4$alkyl radicals there come into consideration, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl and isobutyl, preferably methyl and ethyl.

As $C_1$-$C_4$alkoxy radicals there come into consideration, for example, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, tert-butoxy and isobutoxy, preferably methoxy and ethoxy, and especially methoxy.

As halogen there come into consideration, for example, fluorine, chlorine, bromine and iodine, preferably chlorine and bromine, and especially chlorine.

As $C_2$-$C_4$alkanoylamino radicals there come into consideration, for example, acetylamino and propionylamino, especially acetylamino.

As $C_1$-$C_4$alkoxy-$C_1$-$C_4$alkoxy radicals there come into consideration, for example, methoxy-methoxy, methoxy-ethoxy, ethoxy-methoxy, ethoxy-ethoxy, ethoxy-ethoxy, ethoxy-n-propoxy, n-propoxy-
methoxy, n-propoxy-ethoxy, ethoxy-n-butoxy and ethoxy-isopropoxy, preferably ethoxy-methoxy and ethoxy-ethoxy.

As N-mono- or N,N-di-C_{1-4}alkylamino radicals there come into consideration, for example, N-methylamino, N-ethylamino, N-propylamino, N-isopropylamino, N-butylamino, N-sec-butylamino, N-isobutylamino, N,N-dimethylamino and N,N-diethylamino, preferably N-isopropylamino.

As C_{2-4}alkanoyloxy radicals there come into consideration, for example, acetyloxy and propionyloxy, preferably acetyloxy.

As C_{1-4}alkoxycarbonyl radicals there come into consideration, for example, methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl, isopropoxycarbonyl and n-butoxycarbonyl, preferably methoxycarbonyl and ethoxycarbonyl.

As C_{1-4}alkylsulfonyloxy radicals there come into consideration, for example, methylsulfonyloxy, ethylsulfonyloxy, n-propylsulfonyloxy, isopropylsulfonyloxy and n-butylsulfonyloxy, preferably methylsulfonyloxy and ethylsulfonyloxy.

In the process of the invention, preference is given to using the dyes of the formulae

\[ \text{(51.1)} \]

\[ \text{(51.2)} \]

\[ \text{(51.3)} \]
(51.4),

(51.5),

(51.6),

(51.7),

(51.8),

(51.9),

(51.10),
(52.5),

(52.6),

(52.7),

(52.8),

(52.9),
(52.10),

(52.11),

(52.12),

(53.1),

(54.1),
(61.2),

(61.3) und

(62.1),

(63.1),

(63.2),
The disperse dyes used in accordance with the present invention may be used as single compounds or as a mixture of two or more dyes.

Preferred are the disperse dyes of formulae (51.3), (51.4), (51.5), (51.6), (51.7), (51.8), (51.9), (51.10), (51.11), (52.6), (52.7), (52.8), (52.9), (52.10), (52.11), (52.12), (54.1), (56.2), (58.1), (58.2), (58.3), (58.4), (60.1), (61.2), (63.1), (63.2), (63.3), (63.4), (63.5) and (63.6), in particular the dyes of formulae (51.3), (52.6), (52.7), (52.8), (52.9), (52.10), (52.11), (52.12), (58.1) and (60.1).

The disperse dyes of formulae (51) to (63) are known or can be obtained analogously to known compounds, e.g. by customary diazotisation, coupling, addition and condensation reactions.
Suitable pigments for the process according to the invention include both inorganic pigments, e.g. carbon black, titanium dioxide and iron oxides, and organic pigments, especially those of the phthalocyanine, anthraquinone, perinone, indigoid, thioindigoid, dioxazine, diketopyrrolopyrrole, isoindolinone, perylene, azo, quinacridone and metal complex series, for example metal complexes of azo, azomethine or methine dyes, and also classic azo dyes of the β-oxynaphthoic acid and acetoacetarylide series or metal salts of azo dyes. It is also possible to use mixtures of different organic pigments or mixtures of one or more inorganic pigments with one or more organic pigments. Pigments of the monoazo, disazo, phthalocyanine and anthraquinone series and also inorganic pigments, such as carbon black and iron oxides, are of special interest.

As pigments there come into consideration, for example, pigments of the formula

\[ \text{(64)} \]

wherein

- \( R_{134} \) is hydrogen, halogen, \( C_1-C_4 \)alkyl, \( C_1-C_4 \)alkoxy, nitro or cyano,
- \( R_{135} \) is hydrogen, halogen, nitro or cyano,
- \( R_{136} \) is hydrogen, halogen or phenylaminocarbonyl,
- \( R_{137} \) is hydrogen or hydroxy, and
- \( R_{138} \) is hydrogen or a radical of formula \( -\text{CONHR}_{140} \), wherein

- \( R_{139} \) is hydrogen, \( C_1-C_4 \)alkyl or \( C_1-C_4 \)alkoxy,
- \( R_{140} \) is hydrogen, \( C_1-C_4 \)alkoxy or halogen, and
- \( R_{141} \) is hydrogen, \( C_1-C_4 \)alkyl, \( C_1-C_4 \)alkoxy or halogen,
wherein

$R_{142}$ and $R_{143}$ are each independently of the other $C_1$-$C_6$alkyl and $R_{144}$ and $R_{145}$ are halogen,

wherein the rings A, B, D and E are unsubstituted or mono- or poly-substituted by halogen,

wherein

$R_{146}$ is $C_1$-$C_6$alkyl,

$R_{147}$ is hydrogen, halogen, $C_1$-$C_6$alkyl, $C_1$-$C_6$alkoxy, nitro or cyano,

$R_{148}$ is hydrogen, halogen, nitro or cyano,

$R_{149}$ is hydrogen, halogen, $C_1$-$C_6$alkyl, $C_1$-$C_6$alkoxy, nitro or cyano,
wherein the rings A' and B' are unsubstituted or mono- or poly-substituted by halogen and the ring C' is unsubstituted or mono- or poly-substituted by halogen, C<sub>1</sub>-C<sub>4</sub>alkyl or C<sub>1</sub>-C<sub>4</sub>alkoxy,

\[ K_1 - N = N - \begin{array}{c} \text{(R}_{150}\text{o-2)} \\ \text{(R}_{151}\text{o-2)} \end{array} - N = N - K_2 \]  

wherein 
(R<sub>150</sub>)<sub>0-2</sub> and (R<sub>151</sub>)<sub>0-2</sub> each independently of the other denote from 0 to 2 substituents selected from the group halogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy, nitro and cyano, and 
K<sub>1</sub> and K<sub>2</sub> are each independently of the other a radical of formula

\[
\begin{array}{c}
\text{HO} \\
\text{C} \hspace{0.01cm} \text{CH}_3 \\
\text{C} \hspace{0.01cm} \text{C} \hspace{0.01cm} \text{NH} \hspace{0.01cm} \begin{array}{c} \text{(R}_{152}\text{o-3)} \end{array} \\
\text{O}
\end{array}
\quad \text{or} \quad
\begin{array}{c}
\text{HO} \\
\text{C} \hspace{0.01cm} \text{C} \hspace{0.01cm} \text{N} \hspace{0.01cm} \text{O} \\
\text{C} \hspace{0.01cm} \text{CH}_3 \\
\text{(R}_{153}\text{o-3)}
\end{array}
\]

wherein 
(R<sub>152</sub>)<sub>0-3</sub> and (R<sub>153</sub>)<sub>0-3</sub> each independently of the other denote from 0 to 3 substituents selected from the group halogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy, nitro and cyano, especially halogen, C<sub>1</sub>-C<sub>4</sub>alkyl and C<sub>1</sub>-C<sub>4</sub>alkoxy, and
wherein

$(R_{154})_0$ and $(R_{155})_{0-2}$ each independently of the other denote from 0 to 3 substituents

selected from the group halogen, phenyl, C$_1$-C$_4$alkyl, C$_1$-C$_4$alkoxy, nitro and cyano, especially halogen nd phenyl.

Inorganic pigments, such as carbon black and iron oxides, are also of interest.

Of special interest are pigments of formulae

$(64.1)$,

$(64.2)$,

$(64.3)$,
(68.2),

(69.2),

(69.1),

(69.2),

(70.1),

(70.2) and
Further interesting pigments are C.I. Pigment Black 7, C.I. Pigment Red 101, C.I. and Pigment Yellow 34.

In the process according to the invention it is especially preferred to use as pigments those of formulae (64.1) to (70.2) and C.I. Pigment Black 7.

The mentioned pigments are known or can be obtained analogously to known preparation procedures, such as diazotisation, coupling, addition and condensation reactions.

Advantageously, the aqueous compositions or the inks applied in accordance with the claimed process comprise disperse dyes or pigments, such as the dyes of formulae (51) to (63) or the pigments of formulae (64) to (70) and (71.1), in a finely dispersed form. For this purpose the disperse dyes or pigments are milled or kneaded to an average particle size of between 0.1 and 10 microns, preferably between 0.1 and 1 microns. Milling can be carried out in the presence of dispersants. For example, the dried disperse dye or pigment is milled with a dispersant or kneaded in paste form with a dispersant and, if desired, is dried under reduced pressure or by spraying. The resulting preparations can be used to prepare the inks of the invention by addition of water and, if desired, of further auxiliaries.

Suitable dispersants for disperse dyes are, for example, anionic dispersants from the group (aa) acidic esters or their salts of alkylene oxide adducts of the formula
in which
$R_{156}$ is C$_{1}$-C$_{12}$alkyl, aryl or aralkyl, "alkylen" is the ethylene radical or propylene radical,
$R_{157}$ is the acid radical of an inorganic, oxygen-containing acid, such as sulfuric or,
preferably, phosphoric acid, or else the radical of an organic acid, and
k is from 1 to 4 and t is from 4 to 50,
(ab) polystyrenesulfonates,
(ac) fatty acid taurides,
(ad) alkylated diphenyl oxide mono- or disulfonates,
(ae) sulfonates of polycarboxylic esters,
#af) an adduct of from 1 to 60, preferably from 2 to 30, mol of ethylene oxide and/or
propylene oxide with fatty amines, fatty amides, fatty acids or fatty alcohols each having 8 to
22 carbon atoms or with trihydric to hexahydric alkanols having 3 to 6 carbon atoms, the said
adduct being converted into an acidic ester with an organic dicarboxylic acid or with an
inorganic polybasic acid,
(ag) ligninsulfonates,
(ah) naphthalenesulfonates, and
(a) formaldehyde condensates.

As ligninsulfonates (ag) use is made primarily of those ligninsulfonates, or their alkali metal
salts, whose content of sulfo groups does not exceed 25% by weight. Preferred
ligninsulfonates are those having a content of from 5 to 15% by weight of sulfo groups.

Examples of suitable formaldehyde condensates (aj) are condensates of ligninsulfonates
and/or phenol and formaldehyde, condensates of formaldehyde with aromatic sulfonic acids,
such as condensates of ditolyl ether sulfonates and formaldehyde, condensates of
naphthalenesulfonic acid with formaldehyde and/or of naphthol- or naphthylaminsulfonic
acids with formaldehyde, condensates of phenolsulfonic acids and/or sulfonated
dihydroxydiphenyl sulfone and phenols or cresols with formaldehyde and/or urea, and condensates of diphenyl oxide disulfonic acid derivatives with formaldehyde.

Preferred products (ai) are
- condensates of ditolyl ether sulfonates and formaldehyde, as described for example in US Patent No. 4,386,037,
- condensates of phenol and formaldehyde with ligninsulfonates, as described for example in US Patent No. 3,931,072,
- condensates of 2-naphthol-6-sulfonic acid, cresol, sodium bisulfite and formaldehyde [cf. FIAT Report 1013 (1946)], and
- condensates of diphenyl derivatives and formaldehyde, as described for example in US Patent No. 4,202,838.

A particularly preferred compound (aj) is the compound of the formula

\[
\begin{array}{c}
\text{(73),} \\
\end{array}
\]

in which
- \( R_{158} \) is a direct bond or oxygen,
- \( R_{159} \) is the radical of an aromatic compound and is attached to the methylene group by a ring carbon atom,
- \( M \) is hydrogen or a salt-forming cation, such as an alkali metal, alkaline earth metal or ammonium, and
- \( d \) and \( g \) independently of one another are a number from 1 to 4.
A very particularly preferred compound (a) is a compound based on the sulfonated condensate of a chloromethylbiphenyl isomer mixture and naphthalene, of the formula

![Chemical structure](image)

\[(\text{SO}_3\text{Na})_{1,4-1,6}\] (74),

in which \((\text{SO}_3\text{Na})_{1,4-1,6}\) denotes an average degree of sulfonation of from 1.4 to 1.6.

The above dispersants are known or can be prepared in analogy to known compounds by widely known processes.

Advantageously, the aqueous dye compositions or the inks comprising disperse dyes may contain anionic copolymers, in particular, those based on acrylic, methacrylic or maleic acid. Among these, preference is given to those obtainable by polymerization of acrylic and/or methacrylic acid and one or more copolymerizable monomers selected from the group consisting of maleic acid, N-vinylformamide, N-vinylacetamide, allylamine and diallylamine derivatives, N-vinylpyrrolidone, N-vinyl-N-methylformamide, N-vinyl-N-methylacetamide, N-vinyl-N-ethylacetamide, vinyl acetate, vinyl propionate, acrylonitrile, styrene, methacrylonitrile, acrylamide, methacrylamide and N-mono/N,N-di-C_1-C_10 alkyl(meth)acrylamide.

Particularly preferred anionic copolymers are those obtainable by copolymerization of acrylic or methacrylic acid and styrene.

Very particular preference is given to acrylic and methacrylic acid-styrene copolymers having a molecular weight of from 3000 to 16 000, in particular from 3000 to 10 000.
Suitable non-ionic dispersants for pigments are, for example, compounds selected from the group of

(ba) alkylene oxide adducts of formula

\[ \begin{align*}
R_{160} & \quad (\text{alkylene} - O)_{p} - \text{H} \\
(\text{alkylene}) & \quad (\text{alkylene} - O)_{p} - \text{H}
\end{align*} \]

wherein \( R_{160} \) is \( C_{1}-C_{12} \)-alkyl, aryl or aralkyl,
"alkylene" is the ethylene radical or propylene radical and
q is from 1 to 4 and p is from 4 to 50,

(bb) alkylene oxide adducts with

(bba) saturated or unsaturated mono- to hexa-hydric aliphatic alcohols,

(bbb) fatty acids,

(bbc) fatty amines,

(bbd) fatty amides,

(bbe) diamines,

(bbf) sorbitan esters,

(bc) alkylene oxide condensation products (block polymerisates),

(bd) polymerisates of vinylpyrrolidone, vinyl acetate or vinyl alcohol and

(be) co- or ter-polymers of vinylpyrrolidone with vinyl acetate and/or vinyl alcohol.

Suitable components (ba) are polyadducts of from 4 to 40 mol of ethylene oxide with 1 mol of a phenol that contains at least one \( C_{4}-C_{12} \)-alkyl group, a phenyl group, a tolyl group, an \( \alpha \)-tolylethyl group, a benzyl group, an \( \alpha \)-methylbenzyl group or an \( \alpha,\alpha \)-dimethylbenzyl group, e.g. butylphenol, tributylphenol, octylphenol, nonylphenol, dinonylphenol, \( \alpha \)-phenylphenol, benzylphenol, dibenzylphenol, \( \alpha \)-tolylethylenphenol, dibenzyl(nonyl)phenol, \( \alpha \)-methylbenzylphenol, bis(\( \alpha \)-methylbenzyl)phenol or tris(\( \alpha \)-methylbenzyl)phenol, such adducts being used on their own or in admixture.
Of special interest as component (ba) are adducts of from 6 to 30 mol of ethylene oxide with 1 mol of 4-nonylphenol, with 1 mol of dinonylphenol or especially with 1 mol of compounds prepared by addition of from 1 to 3 mol of styrenes to 1 mol of phenols.

The preparation of the styrene addition products is carried out in known manner, preferably in the presence of catalysts, such as sulfuric acid, p-toluenesulfonic acid or especially zinc chloride. As styrenes there come into consideration advantageously styrene, α-methylstyrene and vinyltoluene (4-methylstyrene). Examples of the phenols are phenol, cresols and xylenols.

Very especially preferred are ethylene oxide adducts of formula

\[
\begin{array}{c}
\text{[H]}
\end{array}
\begin{array}{c}
\text{[CH}_3\text{]}_f
\end{array}
\begin{array}{c}
\text{[H]}
\end{array}
\begin{array}{c}
\text{[O-(CH}_2\text{-CH}_2\text{-O)}_s\text{]}_f
\end{array}
\]

(76),

wherein \( f \) is from 1 to 3 and \( s \) is from 8 to 30.

Also preferred are ethylene oxide adducts of formula

\[
\begin{array}{c}
\text{[H]}
\end{array}
\begin{array}{c}
\text{[R}_{161}\text{]}_y
\end{array}
\begin{array}{c}
\text{[O-(CH}_2\text{-CH}_2\text{-O)}_w\text{]}_f
\end{array}
\]

(77),

wherein \( R_{161} \) is \( C_4\text{-C}_{12}\text{alkyl, phenyl, tolyl, tolyl-C}_1\text{-C}_9\text{alkyl or phenyl-C}_1\text{-C}_9\text{alkyl, e.g. } \alpha\text{-methyl-}
\]
or \( \alpha,\alpha\text{-dimethyl-benzyl, and } y \) is from 1 to 3 and \( w \) is from 4 to 40.

The non-ionic component (bb) is advantageously
- an alkylene oxide addition product of from 1 to 100 mol of alkylene oxide, e.g. ethylene oxide and/or propylene oxide, with 1 mol of an aliphatic monoalcohol having at least 4 carbon atoms, of a tri- to hexa-hydrich aliphatic alcohol or of a phenol unsubstituted or substituted by alkyl, phenyl, \( \alpha\text{-tolylethyl, benzyl, } \alpha\text{-methylbenzyl or by } \alpha,\alpha\text{-dimethylbenzyl (bba);} \)
- an alkylene oxide addition product of from 1 to 100 mol, preferably from 2 to 80 mol, of ethylene oxide (wherein individual ethylene oxide units may have been replaced by substituted epoxides, such as styrene oxide and/or propylene oxide) with higher unsaturated or saturated monoalcohols (bba), fatty acids (bbb), fatty amines (bbc) or fatty amides (bbd) having from 8 to 22 carbon atoms;
- an alkylene oxide addition product, preferably an ethylene oxide/propylene oxide adduct with ethylenediamine (bbe);
- an ethoxylated sorbitan ester having long-chain ester groups, e.g. polyoxyethylene sorbitan monolaurate having from 4 to 20 ethylene oxide units or polyoxyethylene sorbitan trioleate having from 4 to 20 ethylene oxide units (bbf).

Preferred components (bc) are ethylene oxide adducts with polypropylene oxide (so-called EO-PO block polymers) and propylene oxide adducts with polyethylene oxide (so-called reverse EO-PO block polymers).

Special preference is given to ethylene oxide/propylene oxide block polymers wherein the molecular weight of the polypropylene oxide base is from 1700 to 4000 and the ethylene oxide content in the total molecule is from 30 to 80 %, especially from 60 to 80 %.

Also of interest are dispersants based on naphthalenesulfonates.

Aqueous pigment compositions or pigment inks further comprise a water-dispersible or water-soluble pigment dye binder in order to bind the pigment to the textile fiber material.

Examples of binders that come into consideration include pigment dye binders based on the polymerisation product of at least one of the components acrylic acid; other acrylic monomers, e.g. acrylic acid esters; and urethane. Preference is given to pigment dye binders based on the polymerisation product of at least one of the components acrylic acid and urethane. Of special importance are pigment dye binders based on the polymerisation product of acrylic acid; or urethane; or urethane and acrylic acid. Of special interest are mixtures of pigment dye binders wherein one component of the mixture is based on the polymerisation product of acrylic acid and another component of the mixture is based on the polymerisation product of acrylic acid and urethane. The pigment dye binders are water-
dispersible or, preferably, water-soluble. Examples that may be mentioned include Carboset® 531 and Sancure® AU-4010 from BFGoodrich.

In a very special embodiment of the process according to the invention, the polymerisates that come into consideration as binders do not contain sulfo or sulfato groups.

The pigment dye binder is present in the ink preferably in an amount of from 2 to 30 % by weight, especially in an amount of from 5 to 20 % by weight.

When ultraviolet radiation is used for fixation, the presence of a photoinitiator is generally necessary. The photoinitiator absorbs the radiation in order to produce free radicals that initiate the polymerisation. Examples of photoinitiators and photoinitiators used according to the invention include carbonyl compounds, such as 2,3-hexanedione, diacetylacetophenone, benzoin and benzoin ethers, such as dimethyl, ethyl and butyl derivatives, e.g. 2,2-diethoxyacetophenone and 2,2-dimethoxyacetophenone, benzophenone or a benzophenone salt, and phenyl-(1-hydroxycyclohexyl)-ketone or a ketone of formula

\[
\text{HO} - \text{CH}_2 - \text{CH}_2 - O
\]

benzophenone in combination with a catalyst such as triethylamine, N,N'-dibenzylamine and dimethylaminoethanol and benzophenone plus Michler's ketone; acylphosphine oxides; nitrogen-containing compounds, such as diazomethane, azo-bis-isobutyroneitrile, hydrazine, phenylhydrazine and trimethylbenzylammonium chloride; and sulfur-containing compounds, such as benzenesulfonate, diphenyl disulfide and also tetramethylthiuram disulfide, as well as phosphorus-containing compounds, e.g. phosphine oxides. Such photoinitiators are used on their own or in combination with one another.

The proportion of photoinitiators in the applied dye components, immediately before irradiation, is from 0.01 to 20 %, preferably from 0.1 to 5 %, based on the total amount of colourless polymerisable compounds used.
Both water-soluble and water-insoluble photoinitiators are suitable. In addition, copolymerisable photoinitiators, such as those mentioned, for example, in "Polymers Paint Colour Journal", 180, page 42f (1990), are especially advantageous.

Also suitable are cationic photoinitiators, such as triarylsulfonium salts, diaryldiodonium salts, diaryl-iron complexes or generally structures such as those described in "Chemistry & Technology of UV & EB Formulation for Coatings, Inks & Paints" Vol. 3, published by SITA Technology Ltd., Gardiner House, Broomhill Road, London, 1991.

Fibrous textile materials that come into consideration for the dyeing or printing with aqueous compositions comprising acid dyes are nitrogen-containing or hydroxyl-group-containing fibrous materials. As nitrogen-containing fibrous materials there come into consideration natural or synthetic polyamide materials, e.g. fibrous textile materials of silk, wool or synthetic polyamides. Synthetic fibrous polyamide materials are, for example, fibrous polyamide-6 and polyamide-66 materials.

Aqueous compositions comprising acid dyes may be used especially for dyeing and printing of silk or silk-containing mixed fibrous material. As silk there come into consideration not only natural silk and cultured silk (mulberry silk, Bombyx mori) but also the various wild silks, especially tussah silk, and also eria and fagar silks, slab silk, Senegal silk, muga silk, and also mussel silk and spider silk. Silk-containing fibrous materials are especially blends of silk with polyester fibres, acrylic fibres, cellulose fibres, polyamide fibres or with wool. The said textile material can be in a wide variety of processing forms, e.g. in the form of woven or knitted fabrics.

For printing silk or silk-containing fibrous material, the fibrous material is preferably subjected to a pretreatment. To that end the fibrous material is pretreated with an aqueous liquor comprising a thickener and, where appropriate, a hydrotropic agent. The thickeners preferably employed are alginate thickeners, such as commercially available sodium alginate thickeners, which are used, for example, in an amount of from 50 to 200 g/l of liquor, preferably from 100 to 200 g/l of liquor. The hydrotropic agent preferably employed is urea, which is used, for example, in an amount of from 25 to 200 g/l of liquor, preferably from 25 to 75 g/l of liquor. The
liquor may in addition comprise further ingredients, e.g. ammonium tartrate. The liquor is preferably applied to the fibrous material according to the pad-dyeing method, especially with a liquor pick-up of from 70 to 100%. Preferably, the fibrous material is dried after the above pretreatment.

Aqueous compositions comprising reactive dyes are used for dyeing and printing of hydroxy-group-containing fibre materials. Preference is given to cellulosic fibre materials that consist wholly or partly of cellulose. Examples are natural fibre materials, such as cotton, linen and hemp, and regenerated fibre materials, for example viscose and lyocell. Special preference is given to viscose and cotton, especially cotton. The said fibre materials are preferably in the form of textile woven fabrics, knitted fabrics or webs.

As already indicated above, the fibre material may be subjected to a pretreatment with an aqueous alkaline liquor and the treated fibre material is optionally dried.

The aqueous alkaline liquor comprises at least one of the customary bases used for fixing the reactive dyes in conventional reactive printing processes. The base is used, for example, in an amount of from 10 to 100 g/l of liquor, preferably from 10 to 50 g/l of liquor. Suitable bases are, for example, sodium carbonate, sodium hydroxide, disodium phosphate, trisodium phosphate, sodium acetate, sodium propionate, sodium hydrogen carbonate, aqueous ammonia or sources of alkali, such as sodium chloroacetate or sodium fomate. It is preferable to use sodium hydrogen carbonate, sodium carbonate or a mixture of water glass and sodium carbonate. The pH value of the alkaline liquor is generally from 7.5 to 13.5, preferably from 8.5 to 12.5. In addition to the bases, the aqueous alkaline liquor may also comprise further additives, e.g. hydrotrropic agents. The hydrotrropic agent preferably used is urea, which is used, for example, in an amount of from 25 to 200 g/l of liquor, preferably from 50 to 150 g/l of liquor. In addition the liquor for pretreating the fibre material may contain the sodium salt of nitrobenzene sulfonic acid in an amount of 1 to 100 g/l of liquor and a copolymer of acrylamide basis in an amount of 50 to 500 g/l of liquor as well as a silicon based softener, for example a Megasoft® product in an amount of 0.1 to 100 g/l of liquor.

An excellent colour performance is obtained with the following pretreatment of the fibre material, whereby the fabric is pretreated, for example by printing, padding, jet or spray
application, preferably pad-dyed with the liquor comprising a pad dyeing auxiliary comprising acrylic acid amide / acrylic acid copolymer from acrylic acid amide and acrylic acid monomer in an amount of 0.5 to 5 g/l of liquor, urea in an amount of 50 to 150 g/l of liquor, a base, preferably soda ash, in an amount of 20 to 80 g/l of liquor, sodium salt of nitrobenzene sulfonic acid in an amount of 5 to 50 g/l of liquor, a softener based on a amino functional siloxane in an amount of 10 to 100g/l of liquor and optionally a salt, preferably sodium chloride, in an amount of 50 to 200 g/l of liquor.

Preferably the fibre material is dried after the above pretreatment.

Aqueous compositions comprising reactive dyes or acid dyes may also be used for dyeing and printing of synthetic polyamide fibre materials, for example, polyamide-6 (poly-ε-caprolactam), polyamide-6,6 (polyhexamethyleneadipamide), polyamide-7, polyamide-6,12 (polyhexamethyleneundecanamide), polyamide-11 and polyamide-12, copolyamides with polyamide-6,6 or with polyamide-6, e.g. polymers of hexamethylenediamine, ε-caprolactam and adipic acid and polymers of adipic acid, hexamethylenediamine and isophthalic acid or of adipic acid, hexamethylenediamine and 2-methylpentamethylenediamine or 2-ethyltetramethylenediamine, and also blend fabrics or mixed yarns of synthetic polyamide and wool.

Aqueous compositions comprising acid dyes or, in particular, reactive dyes may also be used for dyeing and printing of microfibres of synthetic polyamides. Microfibres are understood to mean fibre materials constructed from threads having an individual thread fineness of 1 denier (1.1 dTex). Such microfibres are known and are usually produced by melt-spinning.

Aqueous compositions comprising disperse dyes may be used for dyeing and printing of a variety of types of fibre material, such as wool, silk, cellulose, polyvinyl, polyacrylonitrile, polyamide, aramid, polypropylene, polyester or polyurethane.

Preference is given to polyester-containing fibre materials. Suitable polyester-containing fibre materials are those consisting wholly or partly of polyester. Examples are cellulose ester fibres, such as secondary cellulose acetate and cellulose triacetate fibres, and especially linear polyester fibres with or without acid modification, which are obtained, for example, by
condensation of terephthalic acid with ethylene glycol or of isophthalic acid or terephthalic acid with 1,4-bis(hydroxymethyl)cyclohexane, and also fibres made from copolymers of terephthalic and isophthalic acid with ethylene glycol. Suitability extends to polyester-containing mixed-fibre materials; in other words, to blends of polyester with other fibres.

Dyeing or printing of blends of polyester with other fibres, for example cotton, may be advantageously carried out by supplying at least one dispensing device, such as one, two, three or four dispensing devices, of the printing or dyeing apparatus with the selected dyes suitable for the polyester part of the blend, e.g. disperse dyes, and by supplying at least one dispensing device, such as one, two, three or four dispensing devices, of the printing or dyeing apparatus with the selected dyes suitable for the cotton part of the blend, e.g. fiber reactive dyes, it being possible to adjust the ratio of the disperse and the fiber reactive dyes applied to the fabric to the composition of the blend.

After printing, the fibre material is advantageously dried, preferably at temperatures of up to 150°C, especially from 80 to 120°C, and then subjected to a heat treatment process in order to complete the print, that is to say to fix the dye, where required.

The subsequent fixing of the fibre material takes place in general by means of dry heat (thermofixing) or by means of superheated steam under atmospheric pressure (HT fixing). Fixing is carried out under the following conditions:
- Thermofixing: from 1 to 2 minutes at from 190 to 230°C;
- HT fixing: from 4 to 9 minutes at from 170 to 190°C.

The heat treatment can be carried out, for example, by means of a hot batch process, a thermosol process or, preferably, by means of a steaming process.

In the case of the steaming process the printed fibre material is subjected, for example, to treatment in a steamer with steam which is optionally superheated, advantageously at a temperature of from 95 to 180°C, more especially in saturated steam.

Subsequently the printed fibre material is generally washed off with water in customary manner in order to remove unfixed dye.
Aqueous compositions comprising pigments may be used for dyeing and printing of any of the fiber materials indicated above. Fibrous textile materials that come into consideration are especially hydroxyl-group-containing fibrous materials. Preference is given to fibrous cellulosic materials that consist wholly or partly of cellulose. Examples are natural fibrous materials, such as cotton, linen and hemp, and regenerated fibrous materials, for example viscose and lyocell. Special preference is given to viscose and especially cotton. Further fibrous materials include wool, silk, polyvinyl, polyacrylonitrile, polyamide, aramide, polypropylene and polyurethane.

After printing, the fibrous material is advantageously dried, preferably at temperatures of up to 150°C, especially from 80 to 120°C, and then the print is fixed.

The print can be fixed, for example, by means of a heat treatment, which is preferably carried out at a temperature of from 120 to 190°C, the fixing preferably taking from 1 to 8 minutes.

The fixing can, however, also be carried out using irradiation with UV light.

The printed or dyed fibrous material is advantageously irradiated and fixed at elevated temperature, e.g. from 40 to 120°C, especially from 60 to 100°C. The irradiation can take place immediately after the drying operation or alternatively the cold printed fibrous material can be heated to the desired temperature, e.g. in an infra-red heating apparatus, prior to the irradiation.

The following examples serve to illustrate the invention. Temperatures are stated in degrees Celsius, parts are parts by weight and the percentage data are based on percentages by weight, unless noted otherwise. Parts by weight bear the same relation to parts by volume as the kilogram to the litre.

**Example 1:**
To dye polyamide, there are selected the acid dyes that, in the form of the free acid, correspond to the formulae indicated hereinafter:
as yellow component, the dyes of formulae (29.3), (31.1),
as red component, the dye of formula (28.4),
as blue component, a mixture of 75 % by weight of the dye of formula (26.5)
and 25 % by weight of the dye of formula (26.8)
and the dye of formula (27.4).

First the calibration data of the dyes are ascertained for the dyeing for which the colour
catalogue is being produced. For that purpose, in each case a polyamide-6.6 fiber material
(Helanka tricot) is dyed with a jet- or spray-dyeing apparatus using aqueous compositions of
different concentrations of the acid dyes specified above. The jet- or spray-dyeing apparatus
may be equipped with a dispensing device as described above. The dyeings are measured by
spectral photometry and the CIE Lab colour coordinates are determined. The depths of shade
for the individual dyeings are ascertained in known manner.
The depths of shade and the associated a* and b* data yield the colour position of the above-
mentioned dyes in the FTA*b* colour space.
The colour space is then segmented within a depth of shade plane. Such segmentation is
shown for a pale shade within a depth of shade plane in Fig. 1, where P1 corresponds to the
colour position of the yellow dye of formula (29.3) for that dyeing; P2 corresponds to the colour
position of the yellow dye of formula (31.1); P3 corresponds to the colour position of the red
dye of formula (28.4); P4 corresponds to the colour position of the blue dye mixture of the dyes
of formulae (26.5) and (26.8); and P5 corresponds to the colour position of the blue dye of
formula (27.4).

For the trichromy consisting of the dyes of formulae (28.4), (31.1) and the dye mixture of the
dyes of formulae (26.5) and (26.8), the triangular area in that depth of shade plane is divided
arithmetically into a grid. The triangular area corresponds to the area having the corner points
P2, P3 and P4. The gridded triangular area is shown in Fig. 3. Colour positions P2, P3 and P4
of the selected dyes in that depth of shade plane correspond to 0.13 % by weight of the yellow
dye of formula (31.1) for P2, 0.173 % by weight of the red dye of formula (28.4) for P3 and
0.194 % by weight of the blue dye mixture of the dyes of formulae (26.5) and (26.8) for P4.
The individual grid points on the connecting lines and within the triangular area correspond to
specific concentration ratios between the dyes of formulae (28.4), (31.1), (26.5) and (26.8),
that is to say to a specific dye recipe, from which the corresponding reflectance curves are
 calculated. The reflectance curves are stored in a data base and formatted in such a manner
that they can be imported into a commercially available colour communication system. The stored data are rendered visible as colours using a calibrated colour screen. A user is looking for a pale violet shade which he can use to dye polyamide-6.6 fibre material. He decides upon the shade denoted by Px in Fig. 3, which he locates quickly on the screen. The dye recipe for the colour is recalculated by way of the corresponding reflectance curve. The recipe is as follows:

0.0247 % by weight of the yellow dye of formula (31.1),
0.0739 % by weight of the red dye of formula (28.4) and
0.0747 % by weight of the blue dye mixture of the dyes of formulae (26.5) and (26.8).

The digital recipe data are communicated to the jet- or spray-dyeing apparatus to control e.g. an automatic dosing system indicated above, either directly as communicated or after being submitted to an arithmetic operation to yield a format which may be processed by the jet- or spray-dyeing apparatus, thereby dyeing polyamide-6.6 fiber material. The fabric is dried on line with an integrated hot air dryer at 100°C, fixed in saturated steam at 102°C and is then washed off. A dyeing having good fastness properties is obtained. The colour of the dyed fabric is identical in terms of shade, colour saturation and depth of shade to the shade Px from the catalogue that was determined arithmetically.

**Example 2:**

To dye cotton, there are selected the reactive dyes that, in the form of the free acid, correspond to the formulae indicated hereinbelow:

as yellow component, the dyes of formulae (39.44), (40.17) and (40.19),
as orange component, a mixture of the dyes of formulae (40.4), (40.14) and (40.15)
and a dye of formula (39.25),
as red component, the dyes of formulae (39.33) and (40.10),
as blue component, the dyes of formulae (39.4) and (39.12),
and a mixture of 32 % by weight of the dye of formula (39.4) and 68 % by weight of the dye of formula (39.1).

First the calibration data of the dyes are ascertained for the dyeing for which the colour catalogue is being produced. For that purpose, in each case mercerised cotton satin fabric is dyed with a jet- or spray-dyeing apparatus using aqueous compositions of different
concentrations of the reactive dyes specified above. Prior to be dyed the cotton satin fabric is
padded in a pre-treatment operation with a liquor comprising 2 g/l of a pad dyeing auxiliary
comprising acrylic acid amide / acrylic acid copolymer from acrylic acid amide and acrylic acid
monomer, 100 g/l of urea, 40 g/l soda ash, 100 g/l of sodium chloride, 20 g/l of sodium salt of
nitrobenzene sulfonic acid and 30 g/l of a softener based on a amino functional siloxane (liquor
pick-up 70%) and dried. The jet- or spray-dyeing apparatus may be equipped with a
dispensing device as described above. The dyeings are measured by spectral photometry and
the CIE Lab colour coordinates are determined. The depths of shade for the individual dyeings
are ascertained in known manner.

The depths of shade and the associated a* and b* data yield the colour position of the dyes
specified above in the FTA*b* colour space.

The colour space is then segmented within a depth of shade plane. Such segmentation is
shown for a medium shade within a depth of shade plane in Fig. 2, where P1 corresponds to
the colour position of the yellow dye of formula (39.44) for that dyeing; P2 corresponds to the
colour position of the yellow dye of formula (40.19); P3 corresponds to the colour position of
the orange dye mixture of the dyes of formulae (40.4), (40.14) and (40.15); P4 corresponds to
the colour position of the orange dye of formula (39.25); P5 corresponds to the colour position
of the red dye of formula (39.33); P6 corresponds to the colour position of the red dye of
formula (40.10); P7 corresponds to the colour position of the blue dye of formula (39.12); P8
 corresponds to the colour position of the blue dye of formula (39.4); and P9 corresponds to the
colour position of the blue dye mixture of the dyes of formulae (39.1) and (39.4).
For a trichromy consisting of the dyes of formulae (40.17), (39.33) and (39.4), the triangular
area in that depth of shade plane is divided arithmetically into a grid. The triangular area
corresponds to the area having the corner points P10, P5 and P8. The colour position P10 for
the yellow dye of formula (40.17) is not shown in Fig. 2. The gridded triangular area is shown
in Fig. 4. The colour positions P10, P5 and P8 of the selected dyes in that depth of shade
plane correspond to 1.51 % by weight of the yellow dye of formula (40.17) for P10, 3.43 % by
weight of the red dye of formula (39.33) for P5 and 2.84 % by weight of the blue dye of formula
(39.4) for P8.

The individual grid points on the connecting lines and within the triangular area correspond to
specific concentration ratios between the dyes of formulae (40.17), (39.33) and (39.4), that is
to say to a specific dye recipe, from which the corresponding reflectance curves are
calculated. The reflectance curves are stored in a data base and formatted in such a manner
that they can be imported into a commercially available colour communication system. The stored data are rendered visible as colours using a calibrated colour screen. A user is looking for a dull orange shade which he can use to dye cotton tricot. He decides upon the shade denoted by Px in Fig. 4, which he locates quickly on the screen. The dye recipe for the colour is recalculated by way of the corresponding reflectance curve. The recipe is as follows:

1.17 % by weight of the yellow dye of formula (40.17),
0.707 % by weight of the red dye of formula (39.33) and
0.0465 % by weight of the blue dye of formula (39.4).

The digital recipe data are communicated to the jet- or spray-dyeing apparatus to control e.g. an automatic dosing system indicated above, either directly as communicated or after being submitted to an arithmetic operation to yield a format which may be processed by the jet- or spray-dyeing apparatus, thereby dyeing the mercerised cotton satin fabric pretreated as given above.

The fabric is dried on line with an integrated hot air dryer at 100°C. A dyeing having very good fastness to washing is obtained.

The colour of the dyed fabric is identical in terms of shade, colour saturation and depth of shade to the shade Px from the catalogue that was determined arithmetically.
Description of the Figures:

Fig. 1 is a diagram showing a depth of shade plane in the F\text{Ta}^*b^* colour space, being segmented into 3 triangular areas, points P1 to P5 being corner points of the triangular areas.

Fig. 2 is a diagram showing a depth of shade plane in the F\text{Ta}^*b^* colour space, being segmented into 12 triangular areas, points P1 to P9 being the corner points of the triangular areas.

Fig. 3 shows the gridded segment having the corner points P2, P3 and P4 of Fig. 1.

Fig. 4 shows the gridded segment having the corner points P10, P5 and P8, wherein P5 and P8 correspond to the corresponding data of Fig. 2.

Fig. 5 shows the segment of Fig. 4 with a smaller number of grid points.
What is claimed is:

1. A method for dyeing or printing a textile fiber material, which comprises the steps of
   (i) providing a printing or dyeing apparatus capable of processing digital data;
   (ii) providing a digital data processing device organizing reflectance curve data which
        are associated with the corresponding dye recipes, wherein the reflectance curve
        data are generated by
        (a) drawing up a requirement profile for the desired dyeing,
        (b) selecting a group of dyes that meet the requirement profile that has been drawn
            up,
        (c) determining within the colour space the colour position of the said dyes for the
            desired dyeing,
        (d) segmenting the colour space of the dyes within a depth of shade plane into
            triangular areas according to shade, wherein the corner points of the triangular
            areas correspond to the colour position of the dyes in question, and the said dyes
            define a range of shades delimited by the triangular areas,
        (e) dividing the triangular areas within a depth of shade plane arithmetically into a grid
            in such a manner that the points of intersection of the grid are distributed evenly
            over the triangular areas, where the points of intersection of the grid correspond to
            a colour position and a reflectance curve calculated on the basis of a dye recipe is
            associated with each of those colour positions;
    (iii) providing a device enabling the colour corresponding to the reflectance curve data
          to be rendered visible; wherein
          the colour of the desired dyeing is defined by browsing the reflectance curve data
          organized by the digital data processing device (ii) using device (iii), communicating the
          data corresponding to the colour defined from the digital data processing device (ii) to the
          printing or dyeing apparatus (i), in which the communicated data are used to control the
          printing or dyeing apparatus (i), thereby dyeing or printing a textile fiber material in the
          defined colour.

2. A method according to claim 1, wherein the printing or dyeing apparatus capable of
   processing digital data is a jet- or spray-dyeing apparatus or an ink-jet printing apparatus.
3. A method according to claim 1 or 2, wherein printing or dyeing is carried out by unwinding a web from a support and passing it through a dyeing or printing unit, wherein the textile fiber is impregnated with at least one aqueous dyeing composition containing the selected dyestuff, before it is rewinded onto another support.

4. A method according to claim 3, wherein the dyed or printed web is subjected to a drying or fixing operation in a drying and fixing unit after having passed the dyeing or printing unit and before being rewinded.

5. A method according to claim 3, wherein the dyeing or printing unit comprises at least one dispensing device, which allows the web to be uniformly impregnated with an aqueous dyeing composition over its entire width.

6. A method according to any one of claims 1 to 5, wherein the printing or dyeing apparatus according to claim 1 comprises a reservoir for each of the dyes selected for segmentation of the color space from the group of dyes that meet the requirement profile according to step (b) of claim 1.

7. A method according to any one of claims 1 to 6, wherein mixing of the dyes is accomplished by means of an automatic dosing system, which receives the required commands from the digital data processing device according to claim 1 and, in accordance with the commands received, doses or injects the liquid compositions of the selected dyes into a mixing chamber.

8. A method according to claim 1, wherein the digital data processing device is a personal computer.

9. A method according to claim 1, wherein the FTA*b* colour space is used as colour space.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 D06P/30 G01J3/46

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D06P G01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO—Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
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<tbody>
<tr>
<td>X</td>
<td>US 5 255 350 A (DEFAISO RAYMOND ET AL) 19 October 1993 (1993-10-19) examples</td>
<td>1-9</td>
</tr>
<tr>
<td>X</td>
<td>EP 0 527 108 A (CIBA GEIGY AG) 10 February 1993 (1993-02-10) examples page 7, line 1 - line 6 page 10, line 58 - page 11, line 8</td>
<td>1-9</td>
</tr>
<tr>
<td>X,P</td>
<td>WO 2004/046670 A (MAEGI-SCHMITZ INGRID; CIBA SC HOLDING AG (CH); KLUMB HARALD (DE)) 3 June 2004 (2004-06-03) examples</td>
<td>1-9</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of box C.

**X** Patent family members are listed in annex.

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed
- *X* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *A* document member of the same patent family

**Date of the actual completion of the International search**

30 June 2005

**Date of mailing of the international search report**

07/07/2005

**Name and mailing address of the ISA**

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**Authorized officer**

Fiocco, M
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<thead>
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