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(54) Photographic production of images

(57) In the photographic production of multi-colour images on a substrate, a first pigmented photosensitive layer is applied to the substrate, imagewise exposed and developed with water to wash out the non-exposed material from the exposed first pigmented layer, the layer is then dried and a second pigmented photosensitive layer of a different colour is applied. This second layer is then imagewise exposed, developed and dried as before. According to the present invention, when either the pigment of the first or second pigmented layer is a pigment which bleeds, there is used a blocking layer comprising an immobilising agent for the dye of the pigment which prevents movement of the dye from one layer to contaminate the other.

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PHOTOGRAPHIC PRODUCTION OF IMAGES

This invention relates to the photographic production of multi-colour images.

It is known to produce multi-colour images on a substrate by applying a first pigmented photosensitive layer to the substrate, imagewise exposing and developing with water to wash out the non-exposed material from the exposed first pigmented layer. The layer is then dried and a second pigmented photosensitive layer of a different colour is applied. This second layer is then imagewise exposed, developed and dried as before. The process can be repeated with further differently coloured pigmented photosensitive layers to build up the final multi-colour image.

Variations within this general process are known. For example, although it is generally more convenient to provide the pigmented photosensitive layers in a single layer, it is also known to use two sub layers, one, which may or may not be photosensitive, containing the pigmented material and the other an unpigmented photosensitive material. It is also known to provide adhesive within each, or at least the top, photosensitive layer so that the final multi-coloured image is transferable from its substrate to a receptor surface as required. Alternatively adhesive may be applied as a separate overlayer to render the image transferable. Additionally

our European Patent Application No: 86308448.9 describes the use of a separate opacifying layer comprising a water-soluble polymer, water-insoluble polymer and a, preferably white, pigment in photographically produced colour images. The use of this opacifying layer behind the photographically produced coloured layer serves to increase the colour intensity of the image.

It has been found that, when there is used a pigment, which bleeds in water, in at least one of the photosensitive layers, there is a tendency for the pigment colour to bleed out of its layer into other layers of the image product. The bleeding of the pigments in this way causes considerable problems in the production of multi-coloured images. Thus the colour from one layer bleeds through into another layer causing colour contamination and resulting in poor colour matches and poor colour consistency.

According to the present invention there is provided a method of producing an image which method comprises

imagewise exposing photosensitive material, the photosensitive material comprising a carrier sheet which has thereon a first water-removable photosensitive layer containing a first pigment of a first colour, which first photosensitive layer material is rendered non-water-removable on exposure to radiation, and, optionally, over the first water-removable photosensitive layer, a blocking layer,

developing the image thereby obtained with water to remove the first photosensitive layer material and any overlying blocking layer material in the non-image areas and drying the product thereby obtained,

if the photosensitive material does not comprise a blocking layer, applying over the imaged material at least in the image area or areas a blocking layer,

applying over the composite obtained a second water-removable photosensitive layer containing a second

pigment of a second colour, which second photosensitive layer material is rendered non-water-removable on exposure to radiation,

imagewise exposing the second photosensitive layer,

developing the image thereby obtained with water to remove the second photosensitive layer material in the non-image areas and drying the product thereby obtained;

at least one of the first and second pigments being a pigment which bleeds in water and the blocking layer comprising an immobilising agent which prevents passage through the layer of dye from the pigment, which bleeds in water, or at least one of the pigments, which bleed in water.

It has been found that the use of an immobilising agent in a blocking layer separate from that containing the pigment, which bleeds in water, effectively prevents movement of the colour from the pigment and the colour does not pass through the blocking layer. Thus the provision of a blocking layer between the bleeding pigment-containing layer and a subsequent (or preceding) coloured layer prevents the colour of the subsequent (or preceding) layer being contaminated due to bleeding through of colour from the pigment layer. It should be appreciated in the multi-coloured images method according to the invention there may be used both layers which contain pigments which bleed in water and layers which contain pigments which do not bleed in water. In this case the number and positioning of the blocking agents used should be such that for each layer used containing a pigment, which bleeds in water, there is provided an associated blocking layer, to prevent the dye moving to the adjacent pigment layer. If succeeding pigment layers both contain pigments, which bleed, there is provided between them an immobilising agent preventing movement of the colour of both pigments. If one immobilising agent acts for both pigments, then of course a single blocking

layer between the pigment layers will prevent each being contaminated by the other. If different immobilising agents are required then these can be in the same blocking layer or in different ones.

The immobilising agent may be provided as a continuous layer over the entire imaged product surface. Alternatively, and preferably, the immobilising agent-containing blocking layer may be provided only over the image areas. Most preferably the blocking agent layer is a water washout layer; that is a layer which, when applied as a continuous layer, may be subjected to water washout to leave blocking agent layer material in register with the image areas and to remove the blocking agent material from the non-image areas.

The immobilising agent may be included with any layer of the imaged product other than that containing the pigment to provide the blocking layer. For example it may be included in an opacifying layer as described in European Patent Application No: 86308448.9.

According to a preferred embodiment of the invention, there is provided a method of producing a multi-coloured image which method comprises

imagewise exposing photosensitive material, the photosensitive material comprising a carrier sheet having a release surface which has thereon the first water-removable photosensitive layer containing the first pigment,

developing the image thereby obtained with water to remove the first photosensitive layer material in the non-image areas and drying the product thereby obtained,

applying over the image material obtained an opacifying layer comprising a water-soluble polymer, a water-insoluble polymer and a, preferably white, pigment

applying over the opacifying layer a blocking layer,

treating the product obtained with water and drying,

applying over the composite obtained the second

water-removable photosensitive layer containing the second pigment,

imagewise exposing the second photosensitive layer,

developing the image thereby obtained with water;

at least one of the first and second pigments being a pigment which bleeds in water and the blocking layer comprising an immobilising agent which prevents passage through the layer of dye from the pigment which bleeds in water, or from at least one of the pigments, which bleed in water.

The presence of the immobilising agent-containing blocking layer prevents bleeding through of the colour of the first layer to contaminate the second layer (or vice versa).

According to this preferred embodiment there is applied over the first image layer an opacifying layer and subsequently an immobilising agent-containing blocking layer. When this material is contacted with water, that in the non-image areas, i.e. in contact with the release surface of the carrier sheet, is removed. However in the image areas, the opacifying layer (and immobilising agent-containing overlayer) is retained on the image layer.

The immobilising agent used in the blocking layer according to the invention may precipitate, absorb, adsorb or otherwise prevent the passage of the dye through the layer to prevent contamination of the adjacent pigment-containing layer. The immobilising agent may be organic or inorganic, molecular or polymeric, water-insoluble or water-soluble. Of course when a water-soluble agent is used it is necessary for it to be used in combination with a water-insoluble binder to prevent it being leach out during water development.

A particularly convenient class of immobilising agents for use according to the invention are laking agents. The term "laking agent" is one which is well

known but used slightly differently in different industries. Generally speaking they are agents used to provide water-insoluble pigments of enhanced perceived colour. For example The Printing Ink Manual (3rd Edn Northwood Books, London 1979 pages 137 and 304) refers to the reduction of water-solubility of alcohol based inks using laking agents. Laking agents take different forms and act in different ways. They may be water-soluble or water-insoluble. The most commonly used laking agents are water-soluble laking agents which react with dyes to form water-insoluble, dye-containing precipitate and water-insoluble laking agents which adsorb water-soluble dye from solution.

It has been found that use of the laking agent in the same layer as a pigment, which bleeds in water, does not overcome the problem with which the present application is concerned. That is it does not prevent the migration of colour from that layer to contaminate adjacent colour layers. Surprisingly however when the laking agent is placed in a separate layer, it does act to prevent colour migration. The reason why laking agent should be ineffective in restricting colour mobility when placed in the pigment-containing layer while being effective when in a separate layer, is not fully understood. It may perhaps be due to the pigment maintaining an equilibrium between a dye solution in the water and the pigment or derived dye adsorbed by the laking agent. This equilibrium may then require an impractically high level of laking agent effectively to shift the equilibrium and stop the colour migration.

The laking agent used as immobilising agent according to the invention may be organic or inorganic, monomer or polymeric, water-insoluble or water-soluble.

Most suitable according to the present invention as laking agent is phenol formaldehyde resin. Other suitable laking agents include silicates, barium and manganese

salts. Also tannic acid may be used though it is not preferred because of its toxic qualities. Also there may be used shellac, phenol-sulphur condensates, dimethyl salicylic acid and tartar emetic.

According to the present invention, there is used, for at least one of the colour pigments a pigment which bleeds in water. Amongst such pigments are pigments derived from water-soluble dyes, e.g. water-soluble basic dyestuffs. Particularly troublesome are toned pigments obtained from the precipitation of basic dyestuffs with acid. For example benefits are obtained using toners derived from precipitation with phosphotungstomolybdic acid (PTMA). Pigments, which bleed in water, can also be obtained when acidic dyes and their derived toners are used.

Other pigments which bleed in water include laked pigments in which the laking agent used insufficiently insolubilises the dye component of the pigment. In this case the laking agent used as immobilising agent in the blocking layer may be the same as that used in the pigment. Alternatively it may be different. Indeed the laking agent of the blocking layer need not necessarily be a recognised laking agent for the particular water-soluble dye involved.

If it is desired that the multi-coloured image is transferable from the carrier sheet, the image is preferably provided with an adhesive at least in or over its top layer. Thus for example a pressure-sensitive adhesive may be included in the second photosensitive layer. Alternatively a pressure-sensitive adhesive layer may be provided over that second layer after development and drying.

The invention is further illustrated by way of Example in the following Example. In this Example parts and percentages are by weight unless otherwise indicated.

EXAMPLE

A silicone release coating composition was prepared according to the following formulation

	Parts
Silicone polymer containing catalyst (Syl-off 7046 ex Dow Corning)	20.5
Crosslinker (Syl-off 7048 ex Dow Corning)	0.102
Adhesion modifier (Syl-off Q2-7089 ex Dow Corning)	0.92
Hydrocarbon solvent (Exsol 145/160 ex Esso)	14.24
Methyl ethyl ketone	14.24

This composition was coated onto polyethylene terephthalate (542 Melinex ex I.C.I.) using a no. 72 Meyer bar, and cured at 120°C for 5 minutes.

There were prepared the following starting mixtures:

A 33% polyvinyl alcohol solution in water was prepared using Gohsenol GL03 (ex Nippon Gohsei).

A dispersion of 30% silica (Neosyl GP ex Crossfield Limited) in a 10% solution of polyvinyl alcohol (Gelvatol 4020 ex Monsanto Limited) was prepared by the simple addition of the silica to the solution with mixing.

A mixture of surface active agents was made by adding Tween 80 (62%) to Span 80 (38%) (both ex Honeywell and Stein) and mixing the two solutions to homogeneity.

A solution of the initiator isopropyl thioxanthone (Quantacure ITX ex Ward Blenkinsop) in the amine 2-(dimethyl amino) ethyl benzoate (Quantacure DMB ex Ward Blenkinsop) in the ratio 1:2 was made by mixing the initiator into the amine heated to about 50°C.

A 10% solution of the surface active agent Aerosol OT (ex Hopkin and Williams) was made in water.

A dispersion of titanium dioxide (Tiona 472 ex Laport) in a 10% solution of polyvinyl alcohol (Gelvatol

4020) was manufactured by ball milling in 60 parts pigment in 40 parts solution for 24 hours.

A dispersion of Monastral Blue BG in 10% polyvinyl alcohol solution (Gelvatol 4020) was made by adding 30 parts of the pigment to 70 parts of the solution and ball milling for 48 hours.

A clear precoat composition was prepared using the following formulation; the ingredients of which were mixed in an even dispersion using high shear stirring.

	Parts
Polyvinyl alcohol solution (33% Gohsenol in water)	12.0
Acrylate monomer (AM 548 ex Synthese BV)	19.2
Silicone acrylate monomer (Ebecryl 350 ex UCB BV)	4.1
Polyvinyl acetate copolymer emulsion (Vinnapas MV70H ex Wacker Chemie)	16.0
Polyvinyl acetate copolymer emulsion (Vinnapas EP 11 ex Wacker Chemie)	8.8
Polyvinyl acetate homopolymer (Mowilith DHL ex Harco)	28.7
10% solution of Aerosol OT	21.2
Surface active agent mixture	1.1
Initiator mixture	1.25

This clear "pre coat" composition was coated on the silicone release coating using a no. 8 Meyer bar.

The following ink formulation was mixed to give an even dispersion using high shear stirring

	Parts
Polyvinyl alcohol solution (33% Gohensol in water)	8.21
Acrylate monomer (Setalin AM 548 ex UCB)	14.75

	Parts
Silicone acrylate monomer (Ebecryl 350)	0.75
Polyvinyl acetate copolymer emulsion (Vinnapas MV70H)	20.0
Polyvinyl acetate copolymer emulsion (Vinnapas EP 11)	6.05
Polyvinyl acetate homopolymer (Mowilith DHL)	11.1
10% Aerosol OT solution	9.2
Surface active agent mixture	1.93
Silicone surface active agent (L77 ex Union Carbide)	0.3
Silica dispersion	4.13
Polyvinyl acetate copolymer dispersion (Emultex AC43 ex Harco)	15.02
10% polyvinyl alcohol solution in water (Gelvatol 4020)	12.0
Initiator mixture	2.8
Monastral Blue BG dispersion	4.2
Titanium dioxide dispersion	17.7

This formulation was coated onto the precoated carrier using a no. 20 Meyer bar.

After drying, the sheet was exposed to ultraviolet light and developed by water wash-out.

An opaquing formulation was prepared as follows:

	Parts
Polyvinyl alcohol solution (3[illegible]% solution of Gohsenol GL03)	193
Acrylate (AM548)	15
Silicone acrylate monomer (Ebecryl 350)	4.7
Silica dispersion	15
Surface active agent mixture	7
Polyvinyl acetate copolymer dispersion (Emultex AC43)	87

	Parts
Polyvinyl acetate copolymer dispersion (Vinnapas MV70H)	82
10% Aerosol OT solution	170
Surface active agent (Silwett 7001 ex Union Carbide)	14.6
Titanium dioxide dispersion	223

This opaquing dispersion was applied over the blue image with a no. 20 Meyer bar and dried.

A laking agent-containing composition was prepared by reducing a phenol formaldehyde resin (Printan G ex Ciba-Geigy) on a coffee grinder and then dispersing in 15% polyvinyl pyrrolidone (Luviscol K 30 ex BASF) in water. This dispersion was applied over the opaquing composition with a no. 20 Meyer bar and again dried.

The whole sheet was then washed out with water to remove the opaquing composition and subsequent coating in the non-image areas.

A second precoat composition as described above was applied over the imaged sheet. There was then applied a second ink formulation of the same composition as above except that in place of the 4.2 parts of Monastrol Blue BG dispersion there were used 11.0 parts of a dispersion of Irgalite magenta TCB in water made by milling 40% of the pigment in 60% of a 10% solution of polyvinyl alcohol solution (Gelvatol 4020) in water.

The sheet was then imaged to a negative carrying the magenta image and developed with water.

There was obtained a final product containing clear blue and magenta transferable images.

A similar sheet made without the Printan G dispersion coating showed the blue images stained purple from the magenta ink having bled in.

CLAIMS

1. A method of producing an image which method comprises

imagewise exposing photosensitive material, the photosensitive material comprising a carrier sheet which has thereon a first water-removable photosensitive layer containing a first pigment of a first colour, which first photosensitive layer material is rendered non-water-removable on exposure to radiation, and, optionally, over the first water-removable photosensitive layer, a blocking layer,

developing the image thereby obtained with water to remove the first photosensitive layer material and any overlying blocking layer material in the non-image areas and drying the product thereby obtained,

if the photosensitive material does not comprise a blocking layer, applying over the imaged material at least in the image area or areas a blocking layer,

applying over the composite obtained a second water-removable photosensitive layer containing a second pigment of a second colour, which second photosensitive layer material is rendered non-water-removable on exposure to radiation,

imagewise exposing the second photosensitive layer,

developing the image thereby obtained with water to remove the second photosensitive layer material in the non-image areas and drying the product thereby obtained;

at least one of the first and second pigments being a pigment, which bleeds in water, and the blocking layer comprising an immobilising agent which prevents passage through the layer of dye from the pigment, which bleeds in water, or at least one of the pigments, which bleed in water.

2. A method of producing a multi-coloured image which method comprises

imagewise exposing photosensitive material, the photosensitive material comprising a carrier sheet having a release surface which has thereon the first water-removable photosensitive layer containing the first pigment,

developing the image thereby obtained with water to remove the first photosensitive layer material in the non-image areas and drying the product thereby obtained,

applying over the image material obtained an opacifying layer comprising a water-soluble polymer, a water-insoluble polymer and a pigment

applying over the opacifying layer a blocking layer,

treating the product obtained with water and drying,

applying over the composite obtained the second water-removable photosensitive layer containing the second pigment,

imagewise exposing the second photosensitive layer,

developing the image thereby obtained with water;

at least one of the first and second pigments being a pigment which bleeds in water and the blocking layer comprising an immobilising agent which prevents passage through the layer of dye from the pigment which bleeds in water, or from at least one of the pigments, which bleed in water.

3. A method according to claim 1 or 2 wherein the immobilising agent used is a laking agent.

4. A method according to claim 1 substantially as described in the Example.

5. An image produced by the method claimed in any one of claims 1 to 4.

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