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(54) **Title:** COMPOSITION FOR PREPARING A COLOR FILTER

(57) **Abstract:** The invention relates to composition comprising a) A block-copolymer comprising at least three different blocks, b) A colorant, c) A compound having at least one ethylenically unsaturated polymerizable group, and d) An alkali-soluble resin.

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# COMPOSITION FOR PREPARING A COLOR FILTER

The invention relates to a composition comprising a block copolymer, to a process of preparing a color filter, and to a color filter obtainable by the process.

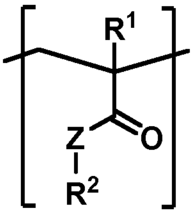
US 6413306 relates to pigment dispersions containing ABC triblock polymer dispersants. The pigment dispersions comprise a non-aqueous carrier liquid. The A segment comprises polymerized monomers of alkyl (meth)acrylates, aryl (meth)acrylates, and cycloalkyl (meth)acrylates. The B segment is of polymerized alkyl amino (meth)acrylate monomers. The polymeric C segment is of polymerized monomers of hydroxy alkyl (meth)acrylate having 1-4 carbon atoms in the alkyl group and monomers selected from the following group: an alkyl (meth)acrylate having 1-12 carbon atoms in the alkyl group, an aryl (meth) acrylate, or a cycloalkyl (meth)acrylate and optionally contains polymerized monomers of glycidyl (meth)acrylate or polyalkylene glycol (meth)acrylate.

US 4755563 relates to block copolymer dispersants. This document describes BAB triblock copolymers, wherein the A block comprises ammonium ions, and wherein the B block is polymerized from alkyl (meth)acrylates or alkyl ether (meth)acrylates.

There is an ongoing need for improved compositions for color filters having a low-viscosity, storage-stability, and good developing properties, for example in the fields of color filters for liquid crystal displays. A low viscosity of the pigment concentrate and of the coating material is needed for the application of the coating material to the substrate. If the pigment dispersions are not storage-stable and agglomerate, the viscosity of the pigmented composition generally increases and the contrast is impaired. Moreover, wetting and dispersing agents should have no negative influence on the developing step as for modern color filters the pigment loading is increased and therewith the amount of wetting and dispersing additive which is used in the formulation, too. For use in color filters, a good balance of developing properties and re-solubility in organic solvent, in particular in 1-Methoxy-2-propyl acetate, is desirable for obtaining a high productivity in industrial processes. The compositions should also be suitable for use with a variety of different pigments.

The invention provides a composition comprising

a) A block-copolymer comprising
    i) at least one block A comprising repeating units 1,



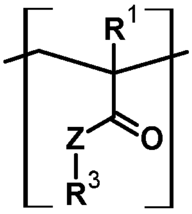
repeating unit 1

wherein Z represents O or NH,

$R^1$ represents H or $CH_3$,

$R^2$ represents a hydrocarbyl group

    ii) at least one block B comprising repeating units 2,



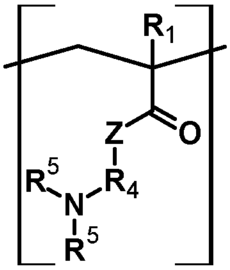
repeating unit 2

wherein Z represents O or NH,

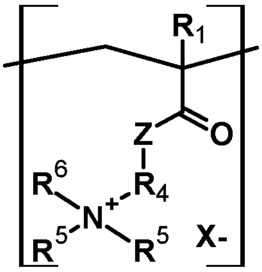
$R^1$ represents H or $CH_3$,

$R^3$ represents a group having at least one non-cyclic ether group,

    iii) at least one block C comprising at least one of repeating units 3 or 4



repeating unit 3



repeating unit 4

wherein

Z represents O or NH,

$R^1$ represents H or $CH_3$,

$R^4$ represents an organic group having 2 to 4 carbon atoms,

$R^5$ independently of each other represents an organic group, wherein two $R^5$ groups are optionally linked to each other to form a cyclic structure,

$R^6$ represents an organic group or hydrogen, and $X^-$ represents a non-polymeric anion,

b) A colorant

c) A compound having at least one ethylenically unsaturated polymerizable group, and

d) An alkali-soluble resin.

The compositions of the invention have a low-viscosity, storage-stability, and can be used in the manufacture of color filters having good developing properties.

The block A of the block co-polymer a) comprises repeating units 1 as described above. According to the invention, the block A comprises one or more different types of repeating units 1. Generally, block A comprises 1 to 12 different types of repeating units 1. The repeating units 1 in the block co-polymer are generally derived by polymerization of suitable ethylenically unsaturated polymerizable monomers.

The ethylenically unsaturated monomers that form the repeating unit 1 in the block co-polymer are generally selected from acrylic esters, methacrylic esters, acrylamides and/or methacrylamides which preferably carry no primary, secondary, tertiary or quaternized amino group. Herein the term "(meth)acryl" refers to both methacryl and acryl. The same applies for the term "(meth)acrylate" which refers to both methacrylate and acrylate, likewise.

Examples for such monomers are:

(i) (meth)acrylic esters of straight-chain, branched or cycloaliphatic alcohols having 1 to 22, preferably 1 to 12, more preferably 1 to 8 and most preferably 1 to 6 carbon atoms, such as methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, tert-butyl (meth)acrylate, n-hexyl (meth)acrylate, isobutyl (meth)acrylate, isopentyl (meth)acrylate, lauryl (meth)acrylate, 2-ethylhexyl (meth)acrylate, stearyl (meth)acrylate, cyclohexyl (meth)acrylate, behenyl (meth)acrylate, isodecyl (meth)acrylate, 2-propylheptyl (meth)acrylate, 3,5,5-trimethyl-1-hexyl (meth)acrylate, nonanyl (meth)acrylate, 2-propylheptyl (meth)acrylate, 2-isopropyl-5-methyl-hexyl (meth)acrylate, tridecyl (meth)acrylate, heptadecyl (meth)acrylate, heneicosanyl (meth)acrylate and isobornyl (meth)acrylate; and (meth)acrylic ester having dicyclopentadienyl functionality, such as dicyclopentenyl oxyethyl acrylate or methacrylate.

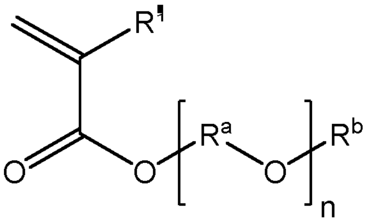
(ii) aryl (meth)acrylic esters whose aryl ring, without possible additional substituents, contains 5 to 12, preferably 6 to 10, carbon atoms, such as phenyl acrylate; and aralkyl (meth)acrylic esters whose aralkyl radical, without possible additional substituents on the aryl radical, contains 6 to 11, preferably 7 to 11, carbon atoms, such as benzyl methacrylate, it being possible for the aryl radicals of the aryl (meth)acrylic esters and of the aralkyl (meth)acrylic esters in each case to be unsubstituted or to be substituted up to four times, such as, for example, 4-methylphenyl methacrylate.

Preferred are esters of methacrylic acid, rather than esters of acrylic acid. More preferably $R^2$ in repeating unit 1 stands for a branched or unbranched alkyl residue with 1 to 12, preferably 1 to 10 carbon atoms, a cycloalkyl residue with 4 to 8, preferably 6 carbon atoms, an araliphatic residue with 7 to 12 carbon atoms, like benzyl.

In a preferred embodiment, more than 50 weight-%, more preferably, more than 70 weight-%, the most preferably, more than 90 weight-% of the repeating units of block A are selected from repeating units 1. In some embodiments, all or essentially all repeating units of block A are selected from repeating units 1.

The block B of the block co-polymer a) comprises repeating units 2 as described above.

Such repeating units are suitably provided by monomers of the following formula (I)



(I)

wherein

$R^1$ represents H or $CH_3$,

$R^a$ represents a linear or branched alkylene group with 2 to 6 carbon atoms,

$R^b$ represents aralkyl, preferably benzyl; or alkyl with 1 to 8 carbon atoms, preferably methyl, ethyl, propyl or butyl; and

n represents an integer from 1 to 150, preferably 1 to 50, more preferably 1 to 25,

and in case at least two different types of residue $R^a$ present the n $[R^aO]$ units, the $[R^aO]_n$ chain may have a random, block or gradient architecture along the chain.

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According to the invention, the block B comprises one or more different types of repeating units 2. Generally, block B comprises 1 to 12 different types of repeating units 2. The repeating units 2 in the block co-polymer are generally derived by polymerization of suitable ethylenically unsaturated polymerizable monomers.

Examples of suitable monomers are (meth)acrylic acid esters of monoether monoalcohols or polyether monoalcohols, such as ethers, polyethylene glycols, polypropylene glycols, polybutylene glycols or mixed polyalkylene glycols having 4 to 80 carbon atoms and a statistical, a block or a gradient distribution of the different monomers along the chain, such as, for example, di(ethylene glycol) methyl ether (meth)acrylate, 2-butoxyethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, allyloxyethyl (meth)acrylate, 1-ethoxybutyl (meth)acrylate, methyltriglycol (meth)acrylate, ethyltriglycol (meth)acrylate, butyldiglycol (meth)acrylate, poly(propylene glycol) methyl ether (meth)acrylate, poly(ethylene glycol) alkyl ether (meth)acrylate and poly(ethylene glycol)-b-poly(propylene glycol) alkyl ether (meth)acrylate, wherein alkyl stands for a straight-chain or branched alkyl residue having 1 to 22, preferably 1 to 15, more preferably 1 to 12, even more preferably 1 to 8 carbon atoms and most preferable 1 to 4 carbon atoms.

In a further embodiment, the block B comprises repeating units derived from monomers selected from ethyl triglycol methacrylate, methyl triglycol methacrylate, butyl diglycol methacrylate, methoxy poly(ethylene glycol) methacrylate and mixtures thereof.

In a further embodiment, repeating units 2 are prepared by a post polymerization modification reaction. Examples of such reactions are ring-opening addition reactions of amine- or hydroxyl functional polyethers with epoxide-functional polymers. Epoxide-functional polymers can be prepared by co-polymerization of epoxide-functional monomers, such as glycidyl (meth)acrylate. Amine-functional polyethers are commercially available under the trade designation Jeffamine® from Huntsman.

In a preferred embodiment, more than 10 weight-%, more preferably, more than 30 weight-%, the most preferably, more than 50 weight-% of the repeating units of block B are selected from repeating units 2. In some embodiments, all or essentially all repeating units of block B are selected from repeating units 2.

The block C of the block co-polymer a) comprises at least one of repeating units 3 or 4 as described above.

Repeating units 3 have a tertiary amino group. Repeating units 3 can be generated by polymerization of acrylic esters, methacrylic esters, acrylamides and methacrylamides which have at least one tertiary amino group. The monomers are preferably selected from the group of tert-aminoalkyl (meth)acrylic esters having 2 to 12, preferably 2 to 8 carbon atoms in the tert-aminoalkyl group, including possible additional substituents, like further additional tert-amino groups in residues $R^4$ and $R^5$. Examples for repeating unit 3 are N,N-dimethylaminoethyl (meth)-acrylate, N,N-diethylaminoethyl (meth)acrylate, N,N-dibutylaminoethyl (meth)acrylate, 2-(2-dimethylaminoethyl(methyl)amino]ethyl (meth)acrylate, 2-(2-dimethylaminoethyloxy)ethyl (meth)acrylate, 2-morpholinoethyl (meth)acrylate, 2-(1-piperidyl)ethyl (meth)acrylate, 2-(N-ethylanilino)ethyl (meth)acrylate, 2-imidazol-1-ylethyl (meth)acrylate, N,N-dimethylaminopropyl (meth)acrylate, and N,N-dimethylaminoethyl (meth)acrylamide. Most preferred is the use of N,N-dimethylaminoethylmethacrylat (DMAEMA).

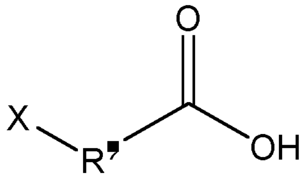
Repeating units 3 containing at least one tertiary amino group can also be produced by reactions after the construction of the polymer chain. By way of example, oxiran-containing ethylenically unsaturated monomers such as glycidyl methacrylate can be (co)polymerized to form a polymeric block having oxirane groups.

They can be reacted with amines after the polymerization. In such case residue $R^3$ will contain a hydroxyl group. If desired, $R^4$ and/or $R^5$ may contain further hydroxyl groups. Suitable for this purpose are primary amines which additionally carry one or more tertiary amino groups or secondary amines, which optionally additionally carry one or more tertiary amino groups. Examples include dimethylaminopropylamine and diethylaminoethylamine; dialkylamines such as diethylamine, dibutylamine and dicyclohexylamine; secondary amines having two different substituents such as, for example, N-(2-hydroxyethyl)aniline; secondary amines which additionally carry one or more tertiary amino groups, such as bis(3-dimethylaminopropyl)amine; dihydroxyalkylamines, such as diethanolamine and diisopropanolamine. Preference is given to secondary amines which, optionally, additionally carry one or more tertiary amino groups.

In a further embodiment, block C further comprises repeating units 4.

Repeating units 4 can be described as reaction product of a quaternization reaction of the tertiary amine group of repeating units 3. In one embodiment, quaternization is carried out after formation of the polymer. Alternatively, quaternization may be carried out on the corresponding unsaturated monomers prior to polymerization.

Thus, repeating units 4 can be introduced by partial quaternization of the amine groups of repeating units 3.
Suitable quaternization agents may be selected from alkyl halides and aralkyl halides, or epoxides, for example glycidyl ethers in the presence of acids. Typically, alkyl halides and aralkyl halides like benzyl chloride, benzyl bromide, 2- or 4-vinylbenzylchloride, methyl chloride or methyl iodide can be used. Moreover, tosylates like methyl tosylate can be used. Examples of suitable glycidyl ethers are alkyl glycidyl ethers like 2-ethylhexyl glycidyl ether and $C_{13}/C_{15}$-alkyl glycidyl ether or aryl glycidyl ethers like cresylglycidyl ether as well as glycidyl methacrylate. Examples for acids used in this quaternization reaction are carboxylic acids like benzoic acid, acetic acid or lactic acid. Further acids are phosphoric acid ester with one or two ester substituents. Preferred are benzyl chloride, 4-vinylbenzyl chloride and glycidyl methacrylate in combination with a carboxylic acid.
In a further embodiment, quaternization is carried out with a quaternization agent of formula (II)



(II)

wherein X is a so-called leaving group, like halide, triflate or tosylate that can undergo a nucleophilic substitution reaction with a tertiary amine group; and $R^7$ is a linear or branched hydrocarbon group with 1 to 8 carbon atoms.
Preferred compounds of general formula (II) are monochloroacetic acid, derivatives of lactic acid, such as tosylated lactic acid, monochloropropionic acid, and higher homologous carboxylic acids substituted with a leaving group.

One or more types of quaternization agents may be used, either simultaneously or subsequently.

The conversion of repeating units 3 via quaternization can be determined by the amine value of the polymer by DIN 16945.
Generally, the block co-polymer has an amine value in the range of 1 to 250 mg KOH/g. In preferred embodiments, the amine value of the block copolymer is in the range of 10 to 180 mg KOH/g, more preferred 30 to 160 mg KOH/g, and most preferred 50 to 160 mg KOH/g.

In a preferred embodiment, more than 50 weight-% of the repeating units of block C are selected from repeating units 3 and/or repeating units 4. In some embodiments, all or essentially all repeating units of block C are selected from repeating units 3 and/or repeating units 4.

A preferred block co-polymer of the invention is a block co-polymer preferably having a number-average molecular weight $M_n$ of 2000 to 20000 g/mol, more preferably of 3000 to 17000 g/mol and most preferably of 4000 to 14000 g/mol. The number-average molecular weight $M_n$ and the weight-average molecular weight $M_w$ are determined in accordance with DIN 55672-1:2007-08 by means of gel permeation chromatography using tetrahydrofuran containing 1 % by volume of dibutylamine as eluent and polystyrene as standard. If the number-average molecular weight is too high, the viscosity may deteriorate.

The block co-polymer of the invention generally has a low polydispersity. Polydispersity is the weight average molecular weight $M_w$ divided by the number average molecular weight $M_n$. Preferably, the polydispersity of the block co-polymer is in the range of 1.03 to 1.80, more preferably 1.05 to 1.40.

In typical embodiments of the block co-polymer, the weight ratio of block A to block B to block C in the copolymer is described as follows;

block A: 5 to 90 % by weight, preferably, 15 to 70 % by weight, more preferably, 20 to 55 % by weight
block B: 5 to 90 % by weight, preferably, 15 to 70 % by weight, more preferably, 20 to 55 % by weight
block C: 2 to 70 % by weight, preferably, 8 to 60 % by weight, more preferably, 13 to 50 % by weight

wherein the % by weight are calculated on the sum of the weight of blocks A, B, and C.

The composition of the invention further comprises a colorant b). Suitable colorants include pigments, and dyes, opaqueness providing fillers, and combinations thereof.

Examples of suitable colorants, for example, pigments and/or dyes, are described in international patent application PCT/EP2018/081346, page 9, line 30 to page 13, line 16, and JP 6248838 B, Page 6, line 32 to page 9, line 33. In addition, Pigment Red-291, Pigment Yellow-231, Pigment Green-62, Pigment Green-63 and carbon black (Raven 5000 Ultra 3, Birla Carbon) may be mentioned as a very suitable colorant.

It is preferable that pigments used as colorant in the composition have an average median particle diameter of 1 µm or less, preferably 0.3 µm or less, further preferably 50 nm or less determined by laser diffraction according ISO 13320:2009.

For black pigments the median primary particle diameter determined by laser diffraction according to ISO 13320:2009 is preferably 0.01 to 0.08 µm and the "nitrogen absorption specific surface area" is preferably 50 to 120 $m^2/g$ for the black pigments determined via ISO 9277:2010.

The relative weight ratio of block-copolymer a) to colorants b) in the compositions of the present invention is preferably 95:5 to 5:95, more preferably 65:35 to 7:93 and in particular preferably 50:50 to 10:90.

The composition of the invention further comprises compound c) having at least one ethylenically unsaturated polymerizable group. Examples of such compounds are described in international patent application PCT/EP2018/081346, page 15, line 23 to page 16, line 33.

The composition of the invention further comprises an alkali soluble resin d). Examples of suitable alkali-soluble resins are described in international patent application PCT/EP2018/081346, page 14, line 20 to page 15, line 21, and JP 6248838 B, Page 11, line 20 to page 13, line 6.

Preferred alkali-soluble resins are:

Co-polymers of ethylenically unsaturated monomers with (meth)acrylic acid and/or maleic anhydride, wherein preferred ethylenically unsaturated co-monomers are selected from the group consisting of styrene, benzyl methacrylate, 2-hydroxyethyl (meth)acrylate, methyl methacrylate, cyclohexyl methacrylate, isobornyl methacrylate, adamantly (meth)acrylate and glycidyl methacrylate. In case a glycidyl group is incorporated in the polymer a post reaction with acids or acid anhydrides to incorporate functional groups like carboxylic acid or (meth)acrylate moieties can be performed.

Reaction products of ethylenically unsaturated monocarboxylic acid or its ester with an epoxy resin and a carboxylic acid anhydride, wherein examples of epoxy resins are monomeric and oligomeric bisphenol A, F, S-type epoxy resins, novolak-type epoxy resin, trigylcidyl isocyanurate, fluorene epoxy resin, so called cardo resin, and wherein examples of acid anhydrides are maleic anhydride, succinic anhydride, itaconic anhydride, phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, pyromellitic anhydride and trimellitic anhydride.

Each of these alkali-soluble resins can be used alone or in combination. In some embodiments, the alkali-soluble resin has an acid value in the range of 80 to 100 mg KOH/g. Alkali-soluble resins having number average molecular weight in the range of 400 to 8000 g/mol are often used.

If so desired, further components may be included in the composition. Examples of further components include film-forming binders, other resins and polymers, reactive diluents and solvents, curing catalysts, as well as further additives.

The solvent is suitably an organic solvent. The content of the organic solvent of the inventive composition is preferably 10 to 99% by weight, more preferably 20 to 97 % by weight of the total weight of the inventive composition.

Examples of such an organic solvent include glycol monoalkyl ethers such as ethylene glycolmonobutyl ether, propylene glycol monomethyl ether; glycol dialkyl ethers such as ethylene glycol diethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether; glycol alkyl ether acetates such as ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol monopropyl ether acetate, methoxybutyl acetate; dialkyl ethers such as diethyl ether; ketones such as acetone, methyl ethyl ketone, cyclohexanone; monohydric or polyhydric alcohols such as ethanol, propanol, butanol, hexanol, cyclohexanol, ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, and glycerin; aliphatic hydrocarbons such as n-hexane; alicyclic hydrocarbons such as cyclohexane; aromatic hydrocarbons such as toluene, xylene, and cumene; linear or cyclic esters such as ethyl acetate, butyl acetate; nitriles such as acetonitrile, and benzonitrile or mixtures thereof. Also suitable are ethoxy ethyl propionate, and solvent blends containing n-butanol, for example blends of n-butanol and dimethyl sulfoxide.

Preferably, the organic solvent is selected from the group consisting of glycol monoalkyl ethers, glycol dialkyl ethers, glycol alkyl ether acetates and mixtures thereof. Glycol alkyl ether acetates are even more preferred. Most preferred is propylene glycol monomethyl ether acetate. Glycol alkyl ether acetates may be used alone or in combination with other solvents.

As mentioned above, the composition of the invention is very suitable for preparing a color filter. Therefore, the invention further relates to a process for preparing a color filter, wherein the process comprises the steps of applying the composition of the invention to a substrate and curing selected areas of the composition by exposure to actinic radiation.

Actinic radiation is radiation capable of triggering chemical reactions. Examples of actinic radiation are UV radiation and electron beam radiation.

In a preferred embodiment, the process further comprises the step of treating the color filter with an alkali-containing solution and removing uncured material.

Preferably, the color filter is included in a device such as a liquid crystal display, a liquid crystal screen, a color resolution device or a sensor.

## Examples

Raw materials:

| | |
|---|---|
| MMA: | Methyl methacrylate (Evonik) |
| BMA: | n-Butyl methacrylate (Evonik) |
| EHMA: | 2-Ethylhexyl methacrylate (Evonik) |
| ETMA: | Ethyltriglycol methacrylate (Evonik) |
| BDGMA: | Butyldiglycol methacrylate (Evonik) |
| MPEG-400MA: | Methoxy polyglycol (average number of ethyleneoxide unit: 9) methacrylate (Shin-Nakamura Chemical) |
| MPEG-1000MA: | Methoxy polyglycol (average number of ethyleneoxide unit: 23) methacrylate (Shin-Nakamura Chemical) |
| DMAEMA: | N,N-Dimethylaminoethyl methacrylate (Evonik) |
| MMTP: | 1-Methoxy-1-(trimethylsiloxy)-2-methylpropene (Sigma-Aldrich) |
| ‘Catalyst’: | Tetrabutylammonium 3-chlorobenzoate, 50% strength in acetonitrile, see US 4,588,795 |
| AMBN: | 2,2'-Azodi(2-methylbutyronitrile) (Akzo Nobel) |
| PMA: | 1-Methoxy-2-propyl acetate (DOW Chemicals) |
| PM: | 1-Methoxy-2-propylalcohol (DOW Chemicals) |
| BzCl: | Benzyl chloride (Sigma-Aldrich) |
| Grilonit RV 1814: | Alkyl (number of carbon: 13 – 15) glycidyl ether (EMS-GRILTECH) |
| CGE: | o-Cresylglycidylether (Sigma-Aldrich) |

1-Methoxy-2-propyl acetate and all monomers were stored over 3 Å molecular sieve for 48 hours before use.

Gel Permeation Chromatography (GPC)

Number-average Mn and weight-average Mw molecular weights and the molecular weight distribution were determined according to DIN 55672-1:2007-08 at 35°C using a high-pressure liquid chromatography pump (WATERS 600 HPLC pump) and a refractive index detector (Waters 410). As separating columns, a combination was used of 3 Styragel columns from WATERS with a size of 300 mm x 7.8 mm ID/column, a particle size of 5 µm, and pore sizes HR4, HR2 and HR1. The eluent used was tetrahydrofuran with 1% by volume of dibutylamine, with an elution rate of 1 mL/min. The conventional calibration was carried out using polystyrene standards.

Measurement of non-volatile content (solids content)

The sample (1.0 ± 0.2 g of the tested substance) was weighed accurately into a previously dried aluminum dish and approximately 2 ml of Ethanol was added. After being homogenized, it is dried for 20 minutes at 150°C in the varnish drying cabinet, cooled in a desiccator and then reweighed. The residue corresponds to the solids content in the sample (ISO 3251).

Measurement of the amine value

1.5 to 3.0 g of a sample was precisely weighed out into a 80 mL beaker and is dissolved with 50 mL of acetic acid. Using an automatic titration device provided with a pH electrode, this solution was neutralization-titrated with a 0.1 mol/L $HClO_4$ acetic acid solution. A flexion point of a titration pH curve was used as a titration endpoint, and an amine value was obtained by the following equation.

Amine value [mg KOH/g] = $(561 \times 0.1 \times f \times V) / (W \times S)$

(wherein f: factor of titration agent, V: titration amount at titration endpoint [mL], W: weighed amount of sample [g], S: solid matter concentration of sample [wt%])

Measurement of the acid value

1.5 to 3.0 g of a sample was precisely weighed out into a 80 mL beaker and is dissolved with 50 mL of ethanol. Using an automatic titration device provided with a pH electrode, this solution was neutralization-titrated with a 0.1 mol/L ethanolic KOH solution. A flexion point of a titration pH curve was used as a titration endpoint, and an amine value was obtained by the following equation.

Acid value [mg KOH/g] = $(561 \times 0.1 \times f \times V) / (W \times S)$

(wherein f: factor of titration agent, V: titration amount at titration endpoint [mL], W: weighed amount of sample [g], S: solid matter concentration of sample [wt%])

Synthesis of diblock copolymer DB-1

42.4 g of 1-methoxy-2-propyl acetate (PMA) were placed into a water-free reaction vessel. 46.2 g of monomer mixtures in block A were added dropwise over 60 minutes. Immediately after the start of the metering, the respective amount of MMTP and 'Catalyst' described above were introduced into the reaction vessel. Throughout the reaction, the reaction temperature was kept at 20°C. After the end of the metering of monomer mixtures in block A, 8.1 g of monomer mixtures in block B were added dropwise over 30 minutes. The subsequent reaction time after the end of the metering of monomer mixtures in block B was 60 minutes. Afterwards 1.6 g of 2-methoxypropanol was added.

Experimental results of diblock copolymer DB-1 are described in Table 1.

Synthesis of diblock copolymer DB-2 – DB-5

Diblock copolymer DB-2 – DB-5 were synthesized using the same procedure as used for block copolymer DB-1, except using different dosages of MMTP, 'Catalyst' described above, monomer mixtures in block A and monomer mixtures in block B (Details are described in Table 1).

Synthesis of random copolymer RC-1

25.0 g of PMA was placed into a reaction vessel and the reactor vessel was heated up to 120°C. Then, 60.0 g of monomer mixtures and 13.5 g of initiator solution (3.5 g of AMBN was dissolved in 10.0 g of PMA) were separately added dropwise to the reaction vessel over 3 hours. After the addition of monomer mixtures and initiator solution was finished, the reactor vessel was kept at 120°C for 1 hour under stirring. After that, 5.5 g of initiator solution (0.5 g of AMBN was dissolved in 5.0 g of PMA) was added into the reactor vessel. The subsequent reaction time after adding the initiator solution was 60 minutes.

Experimental results of random copolymer RC-1 are described in Table 1.

Synthesis of triblock copolymer TB-1 (ACB structure)

36.8 g of PMA were placed into a water-free reaction vessel. 15.8 g of monomer mixtures in block A were added dropwise for 30 minutes. Immediately after the start of the metering, the respective amount of MMTP and 'Catalyst' described above were introduced into the reaction vessel. Throughout the reaction, the reaction temperature was kept at 20°C. After the end of the metering of monomer mixtures in block A, 20.2 g of monomers in block C were added dropwise for 30 minutes. After the end of the metering of monomer mixtures in block C, 24.0 g of monomer mixtures in block B were added dropwise for 30 minutes. The subsequent reaction time after the end of the metering of monomer mixtures in block B was 60 minutes. Afterwards 1.6 g of 2-methoxypropanol was added.

Experimental results of triblock copolymer TB-1 are described in Table 2.

Synthesis of triblock copolymer TB-2 (BAC structure)

36.8 g of PMA were placed into a water-free reaction vessel. 23.9 g of monomer mixtures in block B were added dropwise for 30 minutes. Immediately after the start of the metering, the respective amount of MMTP and 'Catalyst' described above were introduced into the reaction vessel. Throughout the reaction, the reaction temperature was kept at 20°C. After the end of the metering of monomer mixtures in block B, 15.9 g of monomers in block A were added dropwise for 30 minutes. After the end of the metering of monomer mixtures in block A, 20.2 g of monomer mixture in block C were added dropwise for 30 minutes. The subsequent reaction time after the end of the metering of monomer mixture in block C was 60 minutes. Afterwards 1.6 g of 2-methoxypropanol was added.

Experimental results of triblock copolymer TB-2 are described in Table 2.

Synthesis of triblock copolymer TB-3 (ABC structure)

36.8 g of PMA were placed into a water-free reaction vessel. 15.0 g of monomer mixtures in block A were added dropwise for 30 minutes. Immediately after the start of the metering, the respective amount of MMTP and 'Catalyst' described above were introduced into the reaction vessel. Throughout the reaction, the reaction temperature was kept at 20°C. After the end of the metering of monomer mixtures in block A, 18.1 g of monomers in block B were added dropwise for 30 minutes. After the end of the metering of monomer mixtures in block B, 26.9 g of monomer mixture in block C were added dropwise for 30 minutes. The subsequent reaction time after the end of the metering of monomer mixture in block C was 60 minutes. Afterwards 1.6 g of 2-methoxypropanol was added.

Experimental results of triblock copolymer TB-3 are described in Table 2.

Synthesis of triblock copolymer TB-4 (ACB structure)

36.8 g of PMA were placed into a water-free reaction vessel. 24.1 g of monomer mixtures in block A were added dropwise for 30 minutes. Immediately after the start of the metering, the respective amount of MMTP and 'Catalyst' described above were introduced into the reaction vessel. Throughout the reaction, the reaction temperature was kept at 20°C. After the end of the metering of monomer mixtures in block A, 11.8 g of monomer mixture in block C were added dropwise for

30 minutes. After the end of the metering of monomer mixtures in block C, 24.1 g of monomer mixtures in block B were added dropwise for 30 minutes. The subsequent reaction time after the end of the metering of monomer mixture in block B was 60 minutes. Afterwards 1.6 g of 2-methoxypropanol was added.
Experimental results of triblock copolymer TB-4 are described in Table 2.

Synthesis of triblock copolymer TB-5 (BAC structure)

36.8 g of PMA were placed into a water-free reaction vessel. 40.0 g of monomer mixtures in block B were added dropwise for 30 minutes. Immediately after the start of the metering, the respective amount of MMTP and 'Catalyst' described above were introduced into the reaction vessel. Throughout the reaction, the reaction temperature was kept at 20°C. After the end of the metering of monomer mixtures in block B, 28.2 g of monomers in block A were added dropwise for 30 minutes. After the end of the metering of monomer mixtures in block A, 11.8 g of monomer mixture in block C were added dropwise for 30 minutes. The subsequent reaction time after the end of the metering of monomer mixture in block C was 60 minutes. Afterwards 1.6 g of 2-methoxypropanol was added.
Experimental results of triblock copolymer TB-5 are described in Table 2.

Synthesis of triblock copolymer TB-6 (BAC structure)

36.8 g of PMA were placed into a water-free reaction vessel. 25.8 g of monomer mixtures in block B were added dropwise for 30 minutes. Immediately after the start of the metering, the respective amount of MMTP and 'Catalyst' described above were introduced into the reaction vessel. Throughout the reaction, the reaction temperature was kept at 20°C. After the end of the metering of monomer mixtures in block B, 25.8 g of monomers in block A were added dropwise for 30 minutes. After the end of the metering of monomer mixtures in block A, 8.4 g of monomer mixture in block C were added dropwise for 30 minutes. The subsequent reaction time after the end of the metering of monomer mixture in block C was 60 minutes. Afterwards 1.6 g of 2-methoxypropanol was added.
Experimental results of triblock copolymer TB-6 are described in Table 2.

Synthesis of triblock copolymer TB-7 (ACB structure)

36.8 g of PMA were placed into a water-free reaction vessel. 19.9 g of monomer mixtures in block A were added dropwise for 30 minutes. Immediately after the start of the metering, the respective amount of MMTP and 'Catalyst' described above were introduced into the reaction vessel.

Throughout the reaction, the reaction temperature was kept at 20°C. After the end of the metering of monomer mixtures in block A, 20.2 g of monomer mixtures in block C were added dropwise for 30 minutes. After the end of the metering of monomer mixtures in block C, 19.9 g of monomer mixtures in block B were added dropwise for 30 minutes. The subsequent reaction time after the end of the metering of monomer mixture in block B was 60 minutes. Afterwards 1.6 g of 2-methoxypropanol was added.

Experimental results of triblock copolymer TB-7 are described in Table 3.

Synthesis of triblock copolymer TB-8 (BAC structure)

36.8 g of PMA were placed into a water-free reaction vessel. 10.0 g of monomer mixtures in block B were added dropwise for 30 minutes. Immediately after the start of the metering, the respective amount of MMTP and 'Catalyst' described above were introduced into the reaction vessel. Throughout the reaction, the reaction temperature was kept at 20°C. After the end of the metering of monomer mixtures in block B, 23.1 g of monomers in block A were added dropwise for 30 minutes. After the end of the metering of monomer mixtures in block A, 26.9 g of monomer mixture in block C were added dropwise for 30 minutes. The subsequent reaction time after the end of the metering of monomer mixture in block C was 60 minutes. Afterwards 1.6 g of 2-methoxypropanol was added.

Experimental results of triblock copolymer TB-8 are described in Table 3.

Synthesis of triblock copolymer TB-9 (ABC structure)

36.8 g of PMA were placed into a water-free reaction vessel. 24.1 g of monomer mixtures in block A were added dropwise for 30 minutes. Immediately after the start of the metering, the respective amount of MMTP and 'Catalyst' described above were introduced into the reaction vessel. Throughout the reaction, the reaction temperature was kept at 20°C. After the end of the metering of monomer mixtures in block A, 24.1 g of monomers in block B were added dropwise for 30 minutes. After the end of the metering of monomer mixtures in block B, 11.8 g of monomer mixture in block C were added dropwise for 30 minutes. The subsequent reaction time after the end of the metering of monomer mixture in block C was 60 minutes. Afterwards 1.6 g of 2-methoxypropanol was added.

Experimental results of triblock copolymer TB-9 are described in Table 3.

Synthesis of triblock copolymer TB-10 (BAC structure)

36.8 g of PMA were placed into a water-free reaction vessel. 23.9 g of monomer mixtures in block B were added dropwise for 30 minutes. Immediately after the start of the metering, the respective amount of MMTP and 'Catalyst' described above were introduced into the reaction vessel. Throughout the reaction, the reaction temperature was kept at 20°C. After the end of the metering of monomer mixtures in block B, 15.9 g of monomers in block A were added dropwise for 30 minutes. After the end of the metering of monomer mixtures in block A, 20.2 g of monomer mixture in block C were added dropwise for 30 minutes. The subsequent reaction time after the end of the metering of monomer mixture in block C was 60 minutes. Afterwards 1.6 g of 2-methoxypropanol was added.

Experimental results of triblock copolymer TB-10 are described in Table 3.

Synthesis of triblock copolymer TB-11 (BAC structure)

36.8 g of PMA were placed into a water-free reaction vessel. 33.0 g of monomer mixtures in block B were added dropwise for 30 minutes. Immediately after the start of the metering, the respective amount of MMTP and 'Catalyst' described above were introduced into the reaction vessel. Throughout the reaction, the reaction temperature was kept at 20°C. After the end of the metering of monomer mixtures in block B, 22.0 g of monomers in block A were added dropwise for 30 minutes. After the end of the metering of monomer mixtures in block A, 5.0 g of monomer mixture in block C were added dropwise for 30 minutes. The subsequent reaction time after the end of the metering of monomer mixture in block C was 60 minutes. Afterwards 1.6 g of 2-methoxypropanol was added.

Experimental results of triblock copolymer TB-11 are described in Table 3.

Synthesis of triblock copolymer TB-12 (ABC structure)

36.8 g of PMA were placed into a water-free reaction vessel. 27.8 g of monomer mixtures in block A were added dropwise for 30 minutes. Immediately after the start of the metering, the respective amount of MMTP and 'Catalyst' described above were introduced into the reaction vessel. Throughout the reaction, the reaction temperature was kept at 20°C. After the end of the metering of monomer mixtures in block A, 12.0 g of monomers in block B were added dropwise for 30 minutes. After the end of the metering of monomer mixtures in block B, 20.2 g of monomer mixture in block C were added dropwise for 30 minutes. The subsequent reaction time after the end of the metering of monomer mixture in block C was 60 minutes. Afterwards 1.6 g of 2-methoxypropanol was added.

Experimental results of triblock copolymer TB-12 are described in Table 3.

Synthesis of quaternized diblock copolymer QB-1

54.2 g of diblock copolymer DB-2, 37.4 g of PMA, 5.9 g of Grilonit RV 1814 and 2.5 g of benzoic acid were placed into a reaction vessel, and the reactor vessel was heated up to 120°C. The quaternization reaction was carried out at 120°C for 4 hours. Experimental results of quaternized diblock copolymer QB-1 are described in Table 4.

Synthesis of quaternized triblock copolymer QTB-1

58.4 g of triblock copolymer TB-1, 7.6 g of PMA, 29.0 g of PM and 5.0 g of benzyl chloride were placed into a reaction vessel, and the reactor vessel was heated up to 120°C. The quaternization reaction was carried out at 120°C for 4 hours. Experimental results of quatemized triblock copolymer QTB-1 are described in Table 4.

Synthesis of quaternized triblock copolymer QTB-2

Quaternized triblock copolymer QTB-2 was synthesized using the same procedure as used for quaternized triblock copolymer QTB-1, except using different type of intermediate polymer (Details are described in Table 4).

Synthesis of quaternized random copolymer QR-1

Quaternized random copolymer QR-1 was synthesized using the same procedure as used for quaternized triblock copolymer QTB-1, except using different type of intermediate polymer (Details are described in Table 4).

Synthesis of alkali-soluble resin R1:

300 g of PMA was placed into a reaction vessel. 137 g of BzMA, 34 g of methacrylic acid and 1.65 g of AMBN were metered in at a temperature of 120°C over 180 minutes. The subsequent reaction time after the end of the metering was 120 minutes. The solids content was then adjusted to 35 wt.-% with PMA (DIN EN ISO 3251:2008-06 at 150°C for 20min).

Table 1 Recipes of diblock copolymer DB-1 – DB-5 and random copolymer RC-1

| Product name | | DB-1 | DB-2 | DB-3 | DB-4 | DB-5 | RC-1 |
|---|---|---|---|---|---|---|---|
| MMTP/'Catalyst' | | 1.10/0.04 | 1.58/0.06 | 1.58/0.06 | 1.10/0.04 | 1.58/0.06 | 4.00/- |
| | MMA | 16.0 | 25.2 | 4.6 | 17.2 | | 16.0 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Monomer mixtures in block A [weight-%] | BMA | | | 4.6 | 3.4 | | 8.0 |
| | EHMA | | 5.6 | 18.5 | | 25.8 | 8.0 |
| | ETMA | | 9.0 | 10.5 | | | 4.0 |
| | BDGMA | | | 10.4 | | 25.8 | 4.0 |
| | MPEG-400MA | | | | 13.5 | | |
| | MPEG-1000MA | 16.0 | | | | | |
| | DMAEMA | | | | | | 20.0 |
| Monomer mixtures in block B [weight-%] | DMAEMA | 8.0 | 20.2 | 11.4 | 5.3 | 8.4 | |
| | MMA | | | | 0.3 | | |
| | BMA | | | | 0.3 | | |
| block A/block B [weight-%] | | 80/20 | 66/34 | 81/19 | 85/15 | 86/14 | |
| Solid content [weight-%] | | 40 | 60 | 60 | 40 | 60 | 60 |
| Amine value of polymers [mg KOH/g] | | 70 | 120 | 70 | 47 | 50 | 120 |
| Molecular weight | Mn [g/mol] | 8539 | 6505 | 6978 | 7403 | 6430 | 3874 |
| | Mw [g/mol] | 10588 | 7416 | 8094 | 9032 | 7780 | 8213 |
| | Mw/Mn | 1.24 | 1.14 | 1.16 | 1.22 | 1.21 | 2.12 |

Table 2 Recipes of triblock copolymer TB-1 – TB-6

| Product name | | TB-1 | TB-2 | TB-3 | TB-4 | TB-5 | TB-6 |
|---|---|---|---|---|---|---|---|
| MMTP/'Catalyst' | | 1.58/0.06 | 1.58/0.06 | 1.58/0.06 | 1.58/0.06 | 1.58/0.06 | 1.58/0.06 |
| Monomer mixtures in block A [weight-%] | MMA | | | | 10.1 | 8.2 | 20.6 |
| | BMA | 10.0 | 12.9 | | 10.0 | | 5.2 |
| | EHMA | 5.8 | 3.0 | 15.0 | 4.0 | | |
| | MMA | | | | | 20.0 | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Monomer mixtures in block B [weight-%] | BMA | | | 10.0 | | | |
| | ETMA | | | 8.1 | 10.0 | | |
| | BDGMA | 14.0 | 23.9 | | | | 25.8 |
| | MPEG-400MA | 10.0 | | | 14.1 | | |
| | MPEG-1000MA | | | | | 20.0 | |
| Monomer mixtures in block C [weight-%] | DMAEMA | 20.2 | 20.2 | 26.9 | 11.8 | 11.8 | 8.4 |
| Chemical structure of block A (A), block B (B) and block C (C) in triblock copolymer | | ACB | BAC | ABC | ACB | BAC | BAC |
| block A/block B/block C [weight-%] | | 26/40/34 | 26/40/34 | 25/30/45 | 40/40/20 | 13/67/20 | 43/43/14 |
| Solid content [weight-%] | | 60 | 60 | 60 | 60 | 60 | 60 |
| Amine value of polymers [mg KOH/g] | | 120 | 120 | 160 | 70 | 70 | 50 |
| Molecular weight | Mn [g/mol] | 7168 | 6386 | 6076 | 7457 | 9253 | 6815 |
| | Mw [g/mol] | 9032 | 7663 | 7170 | 8948 | 11751 | 7916 |
| | Mw/Mn | 1.26 | 1.20 | 1.18 | 1.20 | 1.27 | 1.16 |

Table 3 Recipes of triblock copolymer TB-7 – TB-12

| Product name | | TB-7 | TB-8 | TB-9 | TB-10 | TB-11 | TB-12 |
|---|---|---|---|---|---|---|---|
| MMTP/'Catalyst' | | 1.58/0.06 | 1.58/0.06 | 1.58/0.06 | 0.97/0.04 | 1.58/0.06 | 2.30/0.09 |
| Monomer mixtures in block A | MMA | | | 19.3 | 12.7 | | 11.1 |
| | BMA | 10.0 | 18.1 | 4.8 | 3.2 | 22.0 | 5.6 |
| | EHMA | | 5.0 | | | | 11.1 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| [weight-%] | ETMA | 9.9 | | | | | |
| Monomer mixtures in block B [weight-%] | MMA | | | | 12.7 | | |
| | BMA | 10.0 | | | 3.2 | | |
| | ETMA | 9.9 | | 12.1 | | | 6.0 |
| | BDGMA | | 10.0 | 12.0 | 12.0 | 13.0 | 6.0 |
| | MPEG-400MA | | | | 11.9 | 20.0 | |
| Monomer mixtures in block C [weight-%] | DMAEMA | 18.2 | 26.9 | 11.8 | 20.2 | 5.0 | 20.2 |
| | MMA | 1.0 | | | | | |
| | BMA | 1.0 | | | | | |
| Chemical structure of block A (A), block B (B) and block C (C) in triblock copolymer | | ACB | BAC | ABC | BAC | BAC | ABC |
| block A/block B/block C [weight-%] | | 33/33/34 | 38/17/45 | 40/40/20 | 26/40/34 | 37/55/8 | 46/20/34 |
| Solid content [weight-%] | | 60 | 60 | 60 | 60 | 60 | 60 |
| Amine value of polymers [mg KOH/g] | | 108 | 160 | 70 | 120 | 30 | 120 |
| Molecular weight | Mn [g/mol] | 6896 | 6258 | 5988 | 8350 | 6691 | 4909 |
| | Mw [g/mol] | 8689 | 7697 | 7305 | 10028 | 7962 | 5792 |
| | Mw/Mn | 1.26 | 1.23 | 1.22 | 1.20 | 1.19 | 1.18 |

Table 4 Recipes of quaternized diblock copolymer QB-1 – QB-2, quaternized triblock copolymer QTB-1 – QTB-2 and quaternized random copolymer QR-1

| Product name | | QB-1 | QTB-1 | QTB-2 | QR-1 |
|---|---|---|---|---|---|
| Intermediate polymer | NAME | DB-2 | TB-001 | TB-010 | RC-1 |
| | Amount [weight-%] | 58.4 | 58.4 | 58.4 | 58.4 |

| | | | | | |
|---|---|---|---|---|---|
| Quaternization agent [weight-%] | BzCl | 5.0 | 5.0 | 5.0 | 5.0 |
| Solvent [weight-%] | PMA | 7.6 | 7.6 | 7.6 | 7.6 |
| | PM | 29.0 | 29.0 | 29.0 | 29.0 |
| Quaternization degree [mol-%] | | 30 | 30 | 30 | 30 |
| Solid content [weight-%] | | 40 | 40 | 40 | 40 |
| Amine value of polymers [mg KOH/g] | | 71 | 72 | 73 | 74 |

Production of red, green and blue dispersions used for color filter application

| | |
|---|---|
| PG-58: | Fastogen Green A110 (DIC) |
| PR-254: | Irgaphor Red BT-CF (BASF) |
| PB-15:6: | Fastogen Blue EP-193 (DIC) |

Procedure for producing dispersion R-1 used for color filter application:

6.4 g of alkali-soluble resin R1 and 5.6 g of the dispersant DB-1, shown in table 5, were placed into a 140 ml glass bottle. After that, 30.5 g of PMA was added to the glass bottle to dissolve the alkali-soluble resin R1 and the dispersant. Then, 7.5 g of PR-254 and 150 g of zirconia beads (diameter: 0.4 – 0.6 mm) were added into the glass bottle. The dispersion process was performed in a LAU-Disperser DAS 200 over a period of 5 hours at 30°C. After 5 hours, the concentrate was filtered into a 50 ml glass bottle to remove the zirconia beads.

General procedure for producing dispersions R-2 – R-5, G-1 – G10 and B-1 – B-4 used for color filter application

Dispersions R-2 – R-5, G-1 – G-10 and B-1 – B-4 were prepared according to the procedure for dispersion R-1 (Details are described in Table 5).

Table 5 Recipes of red, green and blue dispersions used for color filter application

| Dispersion | Pigment | | Dispersant | | | Alkali-soluble resin R1 [weight-%] | Solvent |
|---|---|---|---|---|---|---|---|
| | Name | Amount [weight-%] | Product name | Amount [weight-%] | SOP* (%) | | PMA [weight-%] |
| R-1 | PR-254 | 7.5 | DB-1 | 5.6 | 30 | 6.4 | 30.5 |
| R-2 | PR-254 | 7.5 | TB-3 | 3.8 | 30 | 6.4 | 32.3 |
| R-3 | PR-254 | 7.5 | TB-4 | 3.8 | 30 | 6.4 | 32.3 |
| R-4 | PR-254 | 7.5 | TB-7 | 3.8 | 30 | 6.4 | 32.3 |
| R-5 | PR-254 | 7.5 | TB-8 | 3.8 | 30 | 6.4 | 32.3 |
| G-1 | PG-58 | 7.5 | DB-3 | 3.8 | 30 | 6.4 | 32.3 |
| G-2 | PG-58 | 7.5 | DB-4 | 5.6 | 30 | 6.4 | 30.5 |
| G-3 | PG-58 | 7.5 | DB-5 | 3.8 | 30 | 6.4 | 32.3 |
| G-4 | PG-58 | 7.5 | RC-1 | 3.8 | 30 | 6.4 | 32.3 |
| G-5 | PG-58 | 7.5 | TB-1 | 3.8 | 30 | 6.4 | 32.3 |
| G-6 | PG-58 | 7.5 | TB-2 | 3.8 | 30 | 6.4 | 32.3 |
| G-7 | PG-58 | 7.5 | TB-5 | 3.8 | 30 | 6.4 | 32.3 |
| G-8 | PG-58 | 7.5 | TB-6 | 3.8 | 30 | 6.4 | 32.3 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| G-9 | PG-58 | 7.5 | TB-11 | 3.8 | 30 | 6.4 | 32.3 |
| G-10 | PG-58 | 7.5 | TB-12 | 3.8 | 30 | 6.4 | 32.3 |
| B-1 | PB-15:6 | 7.5 | QB-1 | 5.6 | 30 | 6.4 | 30.5 |
| B-2 | PB-15:6 | 7.5 | QTB-1 | 5.6 | 30 | 6.4 | 30.5 |
| B-3 | PB-15:6 | 7.5 | QTB-2 | 5.6 | 30 | 6.4 | 30.5 |
| B-4 | PB-15:6 | 7.5 | QR-2 | 5.6 | 30 | 6.4 | 30.5 |

* Amount of dispersant (solid-state)/Amount of pigment x 100

Application test results

Viscosity of red, green and blue dispersions

Viscosity of red, green and blue dispersions were measured by using BROOKFIELD VISCOMETER DV-II+ (BROOKFIELD, upper limitation of viscosity: 1000 mPa·s).

Particle size of red, green and blue dispersions:

Particle size (median diameter: D50) of red, green and blue dispersion were measure by using Particle Size Analyzer ELSZ-1000 (Otsuka Electronics).

Production of resist ink

| | |
|---|---|
| BYK-330: | Silicone-typed additive (BYK-Chemie) |
| Aronix M305: | Pentaerythritol triacrylate (TOA GOSEI) |
| Omnirad 369: | Former name: Irgacure 369, 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (IGM Resins B.V.) |

| | |
|---|---|
| Dispersion | 50.0 g |
| 2% of BYK-330 PMA solution | 1.0 g |
| Alkali-soluble resin R-1 | 14.2 g |
| Aronix M305 | 2.0 g |
| Omnirad 369 | 1.0 g |
| PMA | 31.8 g |

| | |
|---|---|
| Total | 100.0 g |

Application test results

Developing property

Red, Green and Blue resist inks were coated to glass plate by using bar coater No.4 (9.16 µm of thickness at wetting-film), and the coating films were dried at 80°C for 3 minutes. The dried coating films were gradually dipped to 0.05% KOH aqueous solution (interval: 10 – 60 seconds). After washing them by water, the coating films were wiped by using KimWipes (Kimberly Clark Corporation product), and marked appearance of coating film described as follows;

1 (Excellent): The coating film was completely eliminated after wiping
2 (Very good): The coating film was partially eliminated after wiping
3 (Good): The coating film was not eliminated, but the surface of the coating film was mostly removed after wiping
4 (Poor): The coating film was not eliminated, but the surface of the coating film was partially removed after wiping
5 (Miserable): The appearance of the coating film didn’t change after wiping

Re-solubility in PMA

Red, Green and Blue resist inks were coated to glass plate by using bar coater No.4 (9.16 µm of thickness at wetting-film), and the coating films were dried at 80°C for 3 minutes. One droplet of PMA was put on the coating film, and wiped immediately by using KimWipes. The appearance of the coating film after wiping was marked as follows;

1 (Excellent): The coating film in the trace of PMA droplet was completely eliminated after wiping
2 (Very good): The coating film in the trace of PMA droplet was partially eliminated after wiping
3 (Good): The coating film in the trace of PMA was not eliminated, but the surface of the coating film was mostly removed after wiping
4 (Poor): The coating film was in the trace of PMA not eliminated, but the surface of the coating film was partially removed after wiping
5 (Miserable): The appearance of the coating film didn’t change after wiping

Example 1-12: Viscosity and particle size of red (R), green (G) and blue (B) dispersions, and developing property and re-solubility in PMA of red (R), green (G) and blue (B) resist inks

Viscosity (mPa·s at 20 ºC, rotation: 60 rpm) and particle size (D50) of red, green and blue dispersions are described in Table 6. Moreover, developing property and re-solubility in PMA of red, green and blue resist inks are also described in Table 6.

Table 6 Viscosity and particle size of red, green and blue dispersions, and developing property and re-solubility in PMA of red, green and blue resist inks

| Examples | Dispersion | Property of dispersion | | | Property of resist ink | |
|---|---|---|---|---|---|---|
| | | Viscosity (mPa·s) of dispersion (60 rpm) | | Particle size (D50) / nm | Developing property | Re-solubility in PMA |
| | | Initial | Storage at 40°C for 5 days | | | |
| 1 | R-2 | 6.9 | 6.8 | 80 | 1 | 1 |
| 2 | R-3 | 6.2 | 6.3 | 72 | 2 | 1 |
| 3 | R-4 | 6.8 | 6.9 | 81 | 2 | 2 |
| 4 | R-5 | 6.0 | 6.1 | 70 | 1 | 1 |
| 5 | G-5 | 3.9 | 4.3 | 57 | 1 | 2 |
| 6 | G-6 | 3.8 | 3.9 | 54 | 2 | 1 |
| 7 | G-7 | 3.8 | 4.0 | 55 | 1 | 1 |
| 8 | G-8 | 4.1 | 4.4 | 60 | 2 | 1 |
| 9 | G-9 | 4.0 | 4.5 | 61 | 2 | 1 |
| 10 | G-10 | 4.0 | 4.2 | 54 | 2 | 2 |
| 11 | B-2 | 5.3 | 5.5 | 64 | 2 | 2 |
| 12 | B-3 | 4.8 | 4.8 | 60 | 1 | 1 |

Comparison example C-1 to C-7: Viscosity and particle size of red (R), green (G) and blue (B) dispersions, and developing property and re-solubility in PMA of red (R), green (G) and blue (B) resist inks

Viscosity (mPa·s at 20 ºC, rotation: 60 rpm) and particle size (D50) of red, green and blue dispersions are described in Table 7. Moreover, developing property and re-solubility in PMA of red, green and blue resist inks are also described in Table 7.

Table 7

Viscosity and particle size of red, green and blue dispersions, and developing property and re-solubility in PMA of red, green and blue resist inks

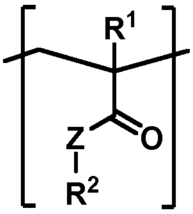
| Comparison examples | Dispersion | Property of dispersion | | | Property of resist ink | |
|---|---|---|---|---|---|---|
| | | Viscosity (mPa·s) of dispersion (60 rpm) | | Particle size (D50) / nm | Developing property | Re-solubility in PMA |
| | | Initial | Storage at 40°C for 5 days | | | |
| C-1 | R-1 | 7.4 | 7.8 | 88 | 1 | 3 |
| C-2 | G-1 | 4.0 | 4.3 | 60 | 2 | 3 |
| C-3 | G-2 | 5.0 | 5.8 | 70 | 4 | 3 |
| C-4 | G-3 | 4.5 | 5.0 | 65 | 3 | 2 |
| C-5 | G-4 | > 100 | Gel | > 100 | | |
| C-6 | B-1 | 6.0 | 6.3 | 68 | 3 | 4 |
| C-7 | B-4 | > 100 | Gel | > 100 | | |

According to the results in Table 6 and 7, red, green and blue dispersions including triblock copolymer showed excellent dispersibility and storage stability. Moreover, red, green and blue resist inks including triblock copolymer also showed excellent balance between developing property and re-solubility in PMA (Example 1 to 12).

On the other hand, green and blue dispersions including random copolymer or quaternized random copolymer showed lower dispersibility and/or storage stability (Comparison example C-5, C-7). Red, green and blue dispersions including diblock copolymer also showed good dispersibility and storage stability. However, red, green and blue resist inks including diblock copolymer showed poor balance between developing property and/or re-solubility in PMA (Comparison examples C-1 to C-4, C-6).

Claims

1. A composition comprising
   a) A block-copolymer comprising
      i) at least one block A comprising repeating units 1,



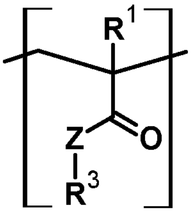
repeating unit 1

wherein Z represents O or NH,

$R^1$ represents H or $CH_3$,

$R^2$ represents a hydrocarbyl group

      ii) at least one block B comprising repeating units 2,



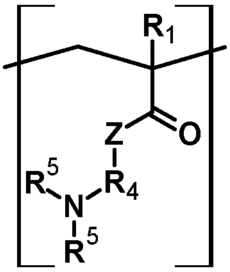
repeating unit 2

wherein Z represents O or NH,

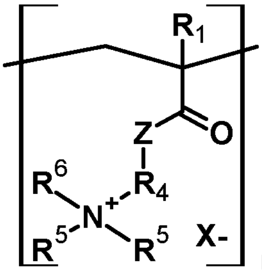
$R^1$ represents H or $CH_3$,

$R^3$ represents a group having at least one non-cyclic ether group,

      iii) at least one block C comprising at least one of repeating units 3 or 4



repeating unit 3



repeating unit 4

wherein

Z represents O or NH,

$R^1$ represents H or $CH_3$,

$R^4$ represents an organic group having 2 to 4 carbon atoms,

$R^5$ independently of each other represents an organic group, wherein two $R^5$ groups are optionally linked to each other to form a cyclic structure,

$R^6$ represents an organic group or hydrogen, and $X^-$ represents a non-polymeric anion,

b) A colorant

c) A compound having at least one ethylenically unsaturated polymerizable group, and

d) An alkali-soluble resin.

2. The composition according to claim 1, wherein in the block-copolymer block A is located between block B and block C.

3. The composition according to claim 1, wherein in the block-copolymer block B is located between block A and block C.

4. The composition according to claim 1, wherein in the block-copolymer block C is located between block A and block B.

5. The composition according to any one of the preceding claims, wherein the block-copolymer consists of blocks A, B, and C.

6. The composition according to any one of the preceding claims, wherein the block-copolymer comprises 5 to 90 % by weight of block A, 5 to 90 % by weight of block B, and

2 to 70 % by weight of block C, wherein the % by weight are calculated on the sum of the weight of blocks A, B, and C.

7. The composition according to any one of the preceding claims, wherein more than 50 weight-% of the repeating units of block A are selected from repeating units 1.

8. The composition according to any one of the preceding claims, wherein more than 10 weight-% of the repeating units of block B are selected from repeating units 2.

9. The composition according to any one of the preceding claims, wherein more than 50 weight-% of the repeating units of block C are selected from repeating units 3 and repeating units 4.

10. The composition according to any one of the preceding claims, wherein the block co-polymer has a number-average molecular weight $M_n$ in the range of 2000 to 20000 g/mol.

11. A process for preparing a color filter, wherein the process comprises the steps of applying the composition according to any one of the preceding claims to a substrate and curing selected areas of the composition by exposure to actinic radiation.

12. The process according to claim 11 comprising the further step of treating the color filter with an alkali-containing solution and removing uncured material.

13. A color filter obtainable by the process according to claim 11 or 12.

14. A device comprising the color filter of claim 13, wherein the device selected from a liquid crystal display, a liquid crystal screen, a color resolution device or a sensor.

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/061246

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D7/40 G02B5/22 G03F7/00 C08L33/02 C09D11/03
C09D11/107 C09D133/02 C09D133/00
ADD.

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)
G03F C09G C09D G02B

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 practicable, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X,P | WO 2019/096893 A1 (BYK CHEMIE GMBH [DE])<br>23 May 2019 (2019-05-23)<br>claims 1, 10, 13-16<br>page 5, line 28 - page 8, line 19<br>page 8, line 23 - line 30<br>page 2, line 1 - line 13<br>----- | 1-14 |
| A | EP 3 147 335 A1 (BYK-CHEMIE GMBH [DE])<br>29 March 2017 (2017-03-29)<br>examples;<br>claims 1, 10, 12, 13<br>----- | 1-14 |
| A | EP 0 556 649 A1 (DU PONT [US])<br>25 August 1993 (1993-08-25)<br>preparation 3, 7;<br>examples 2, 6<br>----- | 1-10 |

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

| | |
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| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Authorized officer<br>Haider, Ursula |

# INTERNATIONAL SEARCH REPORT

**Information on patent family members**

International application No
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