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Elements having hydrophilic layers containing hydrophobes in polymer particles and a method of making same.

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Elements, including radiation-sensitive elements (e.g. color photographic paper products), comprise a support having thereon a substantially crystal- and agglomeration-free hydrophilic layer. This layer comprises a hydrophilic composition comprising a hydrophilic binder and water-insoluble polymer particles dispersed therein. These particles have recurring units derived from one or more ethylenically unsaturated polymerizable monomers, and comprise from 0.5 to 10 percent, based on total monomer weight, of a hydrophobe uniformly distributed throughout the particles. Particularly useful polymer particles are those having recurring units derived from at least one monomer having a crosslinkable moiety. Particularly useful hydrophobes are optical brighteners.

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ELEMENTS HAVING HYDROPHILIC LAYERS CONTAINING
HYDROPHOBES IN POLYMER PARTICLES AND A METHOD
OF MAKING SAME

5 This invention relates to elements,
including radiation-sensitive elements (e.g. color
photographic elements). In particular, it relates to
such elements having a hydrophilic layer which
contains a hydrophobic compound (e.g. optical
10 brightener) uniformly distributed in polymeric
particles. This invention also relates to a method
of making such elements.

Several techniques have been used heretofore
to distribute hydrophobic compounds (hereinafter,
15 "hydrophobe"), particularly non-polymeric compounds
such as color-forming couplers, ultraviolet light
absorbing materials, optical brighteners, etc.,
uniformly throughout layers of gelatin or other
hydrophilic binder materials in the manufacture of
20 radiation-sensitive products. One of the simplest of
these techniques involves mechanically dispersing the
hydrophobe in solid or liquid form in the binder
material by passing a blend of the hydrophobe and
material several times through a high energy mill.
25 This technique, however, generally produces
unsuitable dispersions which are often unstable.

Another technique is described in U. S.
Patent 4,203,716 (issued May 20, 1980 to Chen). The
technique described in this reference involves
30 "loading" polymeric latex particles with the
hydrophobe using an organic solvent. From 20 to 75
weight % of the latex particles consist of
hydrophobe. Generally, "loading" involves (1)
dissolving the hydrophobe in a suitable
35 water-miscible organic solvent; (2) mixing the
resulting solution with polymeric latex particles;
and (3) removing residual solvent as desired,

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particularly if necessary to drive the "loading" process to completion, or to provide material sufficiently "loaded" with the hydrophobe. The solvent is believed to carry the hydrophobe into the polymer particles as the particles are softened by the solvent. The "loaded" latex is then usually dispersed in a hydrophilic binder in preparation for coating.

There are a number of disadvantages encountered with this known procedure. All residual solvent must be removed, otherwise the solvent softens the polymer particles and causes them to stick together or agglomerate. Even if all residual solvent is removed, some of it may migrate out of the polymer particles after the composition has been coated, and agglomeration may result. Further, hydrophobe often migrates out of the latex particles and forms crystals of hydrophobe in the coating. Such crystals deleteriously affect image quality (e.g. reduce sharpness) and, when clumped together, reduce layer smoothness which is important for very thin coatings. The hydrophobe, once out of the polymer particles, can also wander into adjacent layers, causing undesired imaging effects.

It is readily apparent that there is a continuing need in the art for elements comprising hydrophilic compositions which contain hydrophobes in substantially crystal- and agglomeration-free hydrophilic layers.

The object of the present invention is to provide elements, including radiation-sensitive elements, which comprise polymer particles in substantially crystal- and agglomeration-free hydrophilic layers having a hydrophobe uniformly distributed throughout.

Therefore, this invention provides an element comprising a support having thereon a

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hydrophilic layer which comprises a hydrophilic composition comprising a hydrophilic binder and water-insoluble polymer particles dispersed therein,

the polymer particles have recurring units
5 derived from one or more ethylenically unsaturated polymerizable monomers,

the element characterized in that the hydrophilic layer is substantially crystal- and agglomeration-free and the polymer particles comprise
10 from 0.5 to 10 percent, based on total monomer weight, of a hydrophobe uniformly distributed throughout the particles.

In a preferred embodiment, the elements of this invention are radiation-sensitive elements (e.g.
15 color photographic paper products) having one or more radiation-sensitive layers.

This invention also provides a method of making the element described above. The steps of this method comprise:

20 (a) dissolving from 0.5 to 10 percent, based on total monomer weight, of a hydrophobe in solution with one or more ethylenically unsaturated polymerizable monomers;

(b) dispersing and polymerizing the solution
25 formed in step (a) as fine droplets in water under conditions sufficient to promote suspension polymerization of the monomers in the suspended droplets and to form polymeric particles having the hydrophobe uniformly distributed throughout the
30 particles;

(c) dispersing the polymeric particles formed in step (b) in a hydrophilic binder to form a hydrophilic composition; and

(d) applying the hydrophilic composition to
35 a support to form a substantially crystal- and agglomeration-free hydrophilic layer.

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In a preferred embodiment of this invention, a radiation-sensitive composition is applied over the hydrophilic layer formed in step (d).

The present invention avoids the problems
5 encountered with the latex "loading" technique of U.S. Patent 4,203,716 noted above. The polymer particles useful in this invention are made by suspension polymerization, and are distributed in a hydrophilic binder and coated to provide a
10 substantially crystal-free layer, meaning that substantially all (preferably at least 99 percent) of the hydrophobe is distributed within particles of polymer. The hydrophilic layer is also substantially agglomeration-free, meaning very few, if any, of the
15 polymer particles have stuck together or agglomerated. It has also been found that hydrophobes in the elements of this invention are less likely to wander.

The hydrophobe useful in the practice of
20 this invention is a compound which is essentially insoluble in distilled water at 25°C. Preferably, the dissolved concentration of hydrophobe in water under these conditions is less than 0.5 weight percent, based on the weight of the water. Any such
25 hydrophobe can be used in the practice of this invention as long as it can be dissolved or uniformly dispersed in the ethylenically unsaturated polymerizable monomer(s) to be used in making the polymer particles described below. Preferably, the
30 hydrophobe is soluble in the monomers at a concentration of at least 8 weight percent, based on the total monomer weight.

Examples of useful functional classes of hydrophobes include, but are not limited to,
35 photographic dyes; photographic dye-forming couplers; photographic developing agents or other photographic addenda; optical brighteners; ultraviolet light

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absorbing compounds; and others known to one skilled in the photographic art. Specific photographic addenda which can act as hydrophobes include those compounds used to perform coupling, silver halide development, oxidized developer scavenging, absorb light of certain wavelengths, spectral sensitizing or desensitizing, or diffusion transfer dye image-forming. Examples of such hydrophobes are listed in considerable detail in U. S. Patent 4,203,716 (noted above), and in Research Disclosure, publications 15162 (November, 1976) and 17643 (December, 1978), paragraphs III, IV, VI, VII and VIII (Research Disclosure is published by Kenneth Mason Publications Limited, The Old Harbourmaster's, 8 North Street, Emsworth, Hampshire, PO10 7DD, England). Mixtures of hydrophobes can be used if desired.

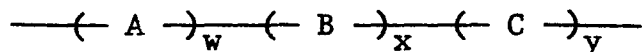
Hydrophobes of particular usefulness in the practice of this invention are optical brighteners. In general, useful optical brighteners include such classes of compounds as: oxazoles; oxadiazoles, including benzoxazoles; imidazoles, including benzimidazoles; pyrazolines; coumarins; stilbenes; triazines; imidazolones; naphthotriazoles; acetylenes; vinylene compounds; and others known to a skilled worker in the art. Specific examples of such optical brighteners are described in Research Disclosure, publication 17643, paragraph V, noted above, U. S. Patent 3,666,680 (issued May 30, 1972 to Briggs) and W. German OLS 2,509,342 (published September 11, 1975).

The amount of hydrophobe in the polymer particles is generally from 0.5 to 10 weight percent, based on total weight of the monomers in which it is dissolved. Preferably, the amount is from 1 to 8 weight percent, based on the total monomer weight.

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The polymer particles useful in the practice of this invention are composed of water-insoluble homopolymers or copolymers having recurring units derived from one or more ethylenically unsaturated polymerizable monomers. These copolymers can have recurring units derived from two or more of such monomers, preferably one of which is a monomer having crosslinkable moieties in the molecule. Such monomers are described in more detail below.

Preferably, the water-insoluble polymeric particles useful in this invention comprise polymers represented by the structure:



- wherein -A- represents randomly recurring units in the polymer chain derived from one or more vinyl aromatics, vinyl esters, olefins and diolefins, or esters of α,β -unsaturated polymerizable carboxylic acids. Examples of useful vinyl aromatics include styrene, α -methylstyrene, *p*-bromostyrene, *o*-chlorostyrene, 2-vinylmesitylene, 1-vinylnaphthalene, *m*- and *p*-vinyltoluene, 3,4-dichlorostyrene and the like. Useful vinyl esters include, for example, vinyl acetate, vinyl propionate, vinyl butyrate and the like. Examples of useful esters of α,β -unsaturated polymerizable carboxylic acids include methyl acrylate, methyl methacrylate, *n*-butyl acrylate, *n*-butyl methacrylate, *t*-butyl methacrylate, benzyl methacrylate, methyl α -bromoacrylate, 4-chlorobutyl acrylate, cyclohexyl acrylate, 2-norbornylmethyl acrylate, 2-ethylhexyl acrylate, lauryl methacrylate, tetrahydrofurfuryl methacrylate, 2-ethoxyethyl methacrylate, 3-chloropropyl acrylate, 2-2-dimethylbutyl acrylate, and the like. Useful olefins and diolefins include, for example, ethylene, propylene, 1,3-butadiene, isoprene, chloroprene, cyclopentadiene, 5-methyl-1,3,6-heptatriene, and the like.

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Preferably -A- represents randomly recurring units derived from one or more vinyl aromatics, e.g. styrene, or esters of α - β -unsaturated polymerizable carboxylic acids, e.g. methyl methacrylate, butyl acrylate and tetrahydrofurfuryl methacrylate.

In the above-identified structure, -B- represents randomly recurring units in the polymer chain derived from one or more ethylenically unsaturated polymerizable monomers having one or more anionic moieties, e.g. sulfo, phosphono or carboxy moieties (including alkali metal or ammonium salts thereof). These recurring units contribute to the dispersibility of the polymer particles in hydrophilic binders. Examples of useful monomers having such anionic moieties include 4-acryloyloxybutane-1-sulfonic acid, sodium salt, 3-acryloyloxy-1-methylpropane-1-sulfonic acid, sodium salt, acrylic and methacrylic acids and alkali metal salts thereof, *m*- and *p*-styrenesulfonic acid and alkali metal salts thereof, 3-methacryloyloxypropane-1-sulfonic acid, sodium salt, lithium methacrylate, N-[3-(N-phenylsulfonyl-N-sodium-sulfamoyl)phenyl]acrylamide, N-[2-(N-methylsulfonyl-N-potassiosulfamoyl)ethyl]methacrylamide, ammonium *p*-styrenesulfonate, 2-acrylamido-2-methylpropanesulfonic acid, sodium salt, and the like.

Preferably, -B- represents randomly recurring units derived from one or more monomers having sulfo or carboxy moieties, such as styrenesulfonic acids or alkali metal salts thereof, acrylic acid, methacrylic acid and 2-acrylamido-2-methylpropanesulfonic acid.

Also, in the above-identified structure, -C- represents randomly recurring units in the polymer chain derived from one or more ethylenically

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unsaturated polymerizable monomers having crosslinkable moieties. Such units contribute to the water-insolubility of the resulting polymer. They also make the polymer less soluble in organic
5 solvents generally used in coating operations and thereby reduce the tendency of the hydrophobe to wander.

These monomers can have two or more ethylenically unsaturated moieties which crosslink
10 during polymerization (e.g. diacrylates, divinylbenzene, etc.). Alternatively, they can have moieties which do not react to provide crosslinking during polymerization, but provide crosslinking because of reaction with a hardener or with another
15 moiety on a different monomer. Such monomers include, for example, 2-acetoacetoxyethyl methacrylate, N-(2-acetoacetoxyethyl)acrylamide, N-(2-acetoacetamidoethyl)acrylamide and 2-aminoethyl methacrylate hydrochloride. Monomers having two or
20 more ethylenically unsaturated sites available for reaction include, for example, diacrylates, dimethacrylates, triacrylates, trimethacrylates, divinyl compounds, and the like. Examples of such monomers include divinylbenzene, ethylene
25 dimethacrylate, 2,2-dimethyl-1,3-propylene diacrylate, propylidene dimethacrylate, 1,6-hexamethylene diacrylate, phenylethylene dimethacrylate, tetramethylene dimethacrylate, 2,2,2-trichloroethylidene dimethacrylate,
30 ethylenebis(oxyethylene) diacrylate, oxydiethylene diacrylate, ethylidyne trimethacrylate, allyl acrylate, vinyl allyloxyacetate, 1-vinyloxy-2-allyloxyethane, 2-crotonoyloxyethyl methacrylate, diallyl phthalate, triallyl cyanurate, 2-(5-phenyl-
35 2,4-pentadienoyloxy)ethyl methacrylate, N,N'-methylenebisacrylamide, N,N'-bis(methacryloyl)urea, and the like.

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Preferably, -C- represents randomly recurring units derived from one or more diacrylates or dimethacrylates, e.g. ethylene diacrylate or ethylene dimethacrylate or both.

5 The polymers useful in the practice of this invention can also comprise minor amounts (less than 5 weight percent) of randomly recurring units in the polymer chain derived from one or more ethylenically unsaturated polymerizable monomers other than those
10 described for -A-, -B- or -C- above. Generally, these units are present in very small amounts in the polymer chain so as not to deleteriously affect polymer water insolubility or other desirable polymer properties. For example, they can be derived from
15 vinyl amides (e.g. acrylamide, methacrylamide, N-isopropylmethacrylamide, N-isopropylacrylamide, N-(3,6-dithiaheptyl)acrylamide, etc.), vinyl nitriles (e.g. acrylonitrile, methacrylonitrile, 3-butenenitrile, etc.), vinyl ketones (e.g. methyl
20 vinyl ketone, diacetone acrylamide, etc.), vinyl halides (e.g. vinyl chloride, vinyl bromide, vinylidene chloride, etc.), vinyl ethers (e.g. allyl methyl ether, allyl phenyl ether, 2-chlorovinyl methyl ether, etc.), N-vinylsuccinamide,
25 N-vinylphthalimide, N-vinylpyrazolidinone, and others known to one skilled in the polymer chemistry art.

Generally, the proportions of the various units of the polymer structure defined herein are as follows:

30 w represents a weight percent of from 75 to 100, and preferably, from 90 to 99 weight percent,
 x represents a weight percent of from 0 to 20, and preferably from 0.5 to 5 weight percent, and
 y represents a weight percent of from 0 to
35 5, preferably from 0.5 to 5 weight percent. All weight percentages are based on total monomer weight.

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In a preferred embodiment of this invention wherein the hydrophobes are optical brighteners, w is generally from 90 to 100 weight percent, x is from 0 to 5 weight percent and y is from 0 to 5 weight percent.

Although the glass transition temperature (T_g) of the polymers useful in the practice of this invention can be varied widely, they generally have a glass transition temperature (T_g) greater than 70°C in order to prevent diffusion of hydrophobe into the coated layers during drying and storage and to improve compatibility with coating addenda. The glass transition temperature can be determined by any convenient method suitable for this purpose. For example, one such method is differential scanning calorimetry as described in Techniques and Methods of Polymer Evaluation, Volume 2, Marcel Dekker, Inc., N.Y., N.Y., 1970.

Examples of polymers useful in the practice of this invention include:

- poly(methyl methacrylate),
- poly(methyl methacrylate-co-styrene) (80:20 weight ratio),
- poly(n-butyl acrylate-co-tetrahydrofurfuryl methacrylate-co-2-acrylamido-2-methylpropanesulfonic acid, sodium salt) (35:60:5 weight ratio),
- poly(methyl methacrylate-co-methacrylic acid) (95:5 weight ratio),
- poly(n-butyl methacrylate-co-methacrylic acid) (80:20 weight ratio),
- poly(methyl methacrylate-co-ethylene dimethacrylate) (98:2 weight ratio),
- poly(methyl methacrylate-co-styrene-co-ethylene dimethacrylate) (49:49:2 weight ratio),
- poly(methyl methacrylate-co-styrene-co-styrene sodium sulfonate-co-ethylene dimethacrylate) (48.5:48.5:1:2 weight ratio),

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poly(methyl methacrylate-co-styrene-co-divinylbenzene) (49:49:2 weight ratio), and

poly(methyl methacrylate-co-styrene-co-sodium styrenesulfonate-co-divinylbenzene)
5 (48.5:48.5:1:2 weight ratio).

The polymer particles useful in the practice of this invention are prepared by addition polymerization of the monomers in an aqueous suspension. This is commonly known as "suspension
10 polymerization." It can be carried out in batch, semi-continuous or continuous operations, as is well known in the art.

Generally, the method of this invention includes dissolving the hydrophobe(s) in solution
15 with the ethylenically unsaturated polymerizable monomers. The monomer solution is then dispersed as fine droplets in water and subjected to conditions sufficient to promote suspension polymerization of the monomers. Although, it is not always required,
20 it is advantageous to use one or more polymerization initiators to initiate polymerization and promote its completion. At least one of the initiators, if used, is oleophilic and is dissolved in the monomers along with the hydrophobe. Useful oleophilic initiators
25 include azo compounds [such as the VAZO™ initiators commercially available from DuPont, Wilmington, Delaware, e.g. VAZO-64™ which is 2,2'-azobis(2-methylpropionitrile), VAZO-52™ which is 2,2'-azobis(2,4-dimethylvaleronitrile), VAZO-33™
30 which is 2,2'-azobis(2,4-dimethyl-4-methoxy-valeronitrile) and VAZO-67™ which is 2,2'-azobis(2-methylbutanenitrile)], peroxides (such as lauroyl peroxide and benzoyl peroxide), and others known to one skilled in the art. Water-soluble
35 polymerization initiators can be used in addition to oleophilic initiators as long as there is sufficient oleophilic initiator to initiate the polymerization

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of the suspended monomer droplets and an insubstantial amount of emulsion polymerization occurs.

One or more surface active agents (i.e. surfactants) are also often employed in suspension polymerization to aid in keeping the dispersed monomer droplets from clumping together in the aqueous medium. At least one of the surfactants, if used, is oleophilic and is incorporated into the reaction mixture by dissolving it in the monomer(s) along with the hydrophobe.

It is often desirable to agitate the monomers in a suitable manner while the hydrophobe, initiator or surfactant is added and dissolved therein. Also, it may be advantageous to heat the monomers prior to and during such addition to facilitate dissolution. Normally, if this is done, the temperature of the monomers is maintained at greater than room temperature (20-25°C), but less than the temperature at which the monomers undergo spontaneous polymerization (this varies with the monomer(s) and initiators used). Generally, the temperature used for mixing is in the range of from 30 to 45°C.

Once the hydrophobe is dissolved within the monomers, the resulting solution is dispersed in water as fine droplets and subjected to pressure and temperature conditions suitable for polymerization of the monomers in the suspended droplets and formation of small, suspended polymer particles. The monomer solution is generally present in droplet form in this dispersion in a range of from 20 to 50 percent, based on total dispersion weight. The pressure employed in the polymerization is generally only that needed to maintain the reaction mixture in liquid form, and is usually atmospheric pressure. The polymerization temperature is subject to wide variation as it

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depends upon several variables including the monomers, initiator and weight percent of monomers in the dispersion. However, generally the temperature is in the range of from 20°C to 120°C. The
5 temperature can vary during the polymerization reaction because of the evolution of heat from the reaction itself.

The monomer solution can be dispersed in the aqueous medium prior to polymerization in any
10 suitable manner which may depend upon the polymerization technique (batch, continuous or semi-continuous) employed. Generally, the solution is dispersed in the aqueous phase by any means which produces high shear sufficient to form very fine
15 droplets containing monomer, hydrophobe and preferably, oleophilic initiator and surfactant. For example, such dispersing can be accomplished by mechanical means such as high-speed stirring or vigorous agitation of some manner, or by pumping a
20 monomer-water mixture through a small orifice or high shear mill into a reactor vessel.

Once polymerization has begun, it is continued until substantially all monomer has reacted. This may take up to 24 hours, depending
25 upon the polymerization conditions employed.

Specific details of polymerization of the monomers having the hydrophobe dissolved therein are illustrated in the examples presented below.

The resulting polymer is in the form of
30 small particles, the size of which can be varied by changing the dispersing conditions or amount of surfactant. The average particle size is generally in the range of from 0.1 to 20 micrometers, with polymer particles in the range of from 0.4 to 1
35 micrometer being particularly useful in the preferred embodiment of this invention utilizing optical brighteners as the hydrophobe.

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The resulting aqueous suspension of polymeric particles can be used directly after polymerization. Water may be removed, if desired, to increase the percent solids of the suspension.

5 The polymeric suspension is then uniformly dispersed in one or more hydrophilic binder materials, or "vehicles" as they are often called in the art, to form a hydrophilic composition. Such binders act as peptizers for the polymeric particles
10 to reduce their tendency to settle. Suitable hydrophilic binders include both naturally-occurring substances, such as proteins (e.g. gelatin, gelatin derivatives, cellulose derivatives), polysaccharides (e.g. dextran), gum arabic, etc., and synthetic
15 polymeric substances such as water-soluble polymers [e.g. poly(vinyl alcohol), acrylamide polymers, poly(vinyl pyrrolidones), etc.], and others known to one skilled in the art, as described, for example, in Research Disclosure, publication 17643, noted above,
20 paragraph IX.

 Generally, the polymeric particles are present within a binder in an amount of at least 15, and preferably from 20 to 70, percent based on total dry weight of hydrophilic composition. This
25 corresponds to a coating coverage of polymeric particles of at least 20 mg/m² of coated surface area. Particles of different polymers containing the same or different hydrophobes can be used in the same hydrophilic composition, if desired.

30 Once the particles are blended in the binder, the resulting hydrophilic composition can be purified, if desired, in any suitable manner to remove any unwanted addenda.

 The described hydrophilic composition can be
35 applied to a suitable substrate, such as a conventional support, using conventional techniques to provide an element having a hydrophilic layer.

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This element can be nonradiation-sensitive, if desired. Additional compositions can be applied simultaneously or subsequently to form additional layers over or under the hydrophilic layer. It is specifically contemplated to apply these compositions to a support using coating hoppers or other coating apparatus conventionally employed in preparing single or multiple layer radiation-sensitive elements. Useful coating and drying techniques and supports (e.g. paper, polymeric films, glass, etc.) are described, for example, in Research Disclosure, publication 17643, noted above, paragraphs XV and XVII.

The hydrophilic layer so formed is substantially crystal- and agglomeration-free. In the context of this application, "substantially crystal-free" and "substantially agglomeration-free" refer to a layer having substantially no crystals of hydrophobe or agglomerations of polymer particles within the layer. In other words, substantially all hydrophobe (preferably at least 99 percent) is in polymer particles rather than external to the particles, and very few polymer particles are stuck together. Generally, in the elements of this invention, less than 5 crystals of hydrophobe can be observed in a 8.9 x 11.4 cm area of the layer containing the hydrophobe as observed at 250x magnification.

The hydrophilic compositions described herein are preferably used in radiation-sensitive elements of various types. Generally, the coating coverage of the hydrophilic composition depends upon its use and the type of element it is incorporated into. Radiation-sensitive elements of this invention include, for example, image transfer materials, lithographic materials, physical development materials, radiographic materials, dry development

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materials, negative- and positive-working color-forming materials (including color films and color photographic papers), black-and-white films and papers, and the like. The details of such materials are well known in the art and are described, for example, in Research Disclosure, publication 17643, noted above.

In a preferred embodiment of this invention, the described hydrophilic compositions are useful in multilayer color photographic paper products having a resin-coated photographic paper support and a plurality of color-forming silver halide emulsion layers coated thereon.

The hydrophilic compositions can be used in any location in the radiation-sensitive elements of this invention, including within the radiation-sensitive layers themselves. Preferably, however, they are coated as individual hydrophilic layers, above, below or in between radiation-sensitive layers. In a preferred embodiment, the hydrophilic composition contains an optical brightener as the hydrophobe and is incorporated between the support and the radiation-sensitive layer(s) to provide an optical brightener layer.

The following examples are provided to illustrate the practice of this invention.

Example 1

A nonradiation-sensitive element of this invention containing an optical brightener hydrophilic layer was prepared in the following manner:

Methyl methacrylate (11.5 kg) monomer was added to a 40 l reactor vessel and warmed to 40°C with gentle stirring. Uvitex OB™ (386 g), an optical brightener commercially-available from Ciba-Geigy (located in Ardsley, New York), was added

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to the stirring monomer until it was completely dissolved. Then, Aerosol OT-100™ (230 g), an oleophilic surfactant commercially available from American Cyanamid (located in Wayne, New Jersey), and
5 2,2'-azobis(2-methylpropionitrile) polymerization initiator (57.5 g) were similarly added to and dissolved in the monomer. Once all of the reagents were dissolved, stirring in the vessel was increased to 200 rpm and distilled water (26.8 kg) heated to
10 50°C was added to the monomer solution.

The resulting dispersion was stirred for an additional 10 minutes and then pumped through a commercially-available high shear Manton-Gaulin mill at 2850 rpm using an orifice clearance of 0.01 cm and
15 a flow rate of 1.5 l/min. into another 40 l reactor vessel where stirring was set at 40 rpm and the temperature controlled at 65°C. The time for pumping through the mill was 26 minutes. This high shear dispersing means provided very fine droplets of
20 monomer in the aqueous phase. Polymerization began immediately and was allowed to proceed for 2 hours at 65°C to give a suspension of polymeric particles of 25% solids.

With the temperature maintained at 65°C,
25 gelatin (1.56 kg) was added to the polymer suspension with agitation. The resulting hydrophilic composition was kept at 65°C and stirred at 40 rpm for 1 hour, filtered through a 30 micron filter at 65°C and chill set at 40°C. The yield of hydrophilic
30 composition was 39 kg.

The hydrophilic composition so prepared was coated on a polyethylene-coated paper support to provide an element of this invention having substantially no crystals or agglomerations.

35 Example 2 Crystal- and Agglomeration-Free Element

This is a comparative example comparing an element of this invention to an element of U.S. Patent 4,203,716 noted above.

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Part A

A "loaded" latex was prepared according to U. S. Patent 4,203,716 as follows.

Distilled water (10.3 kg) was added to a 40
5 l reaction vessel and agitated at 120 rpm while
heating to 85°C. A nitrogen atmosphere was
maintained throughout the preparation. Potassium
persulfate initiator (100 g) was dissolved in
distilled water (2.5 kg) and the resulting solution
10 was added to the reactor vessel along with Triton
770™ surfactant (125 g, 30% solids). In a head
tank, sodium hydroxide (190 g) was added to distilled
water (8.75 kg) while being maintained at 20-25°C.

2-Acrylamido-2-methylpropanesulfonic acid
15 monomer (500 g) was added to the head tank with good
mixing and the pH of the dispersion was adjusted to
3.3 with sodium hydroxide. Also added to the head
tank were potassium persulfate initiator (50 g)
dissolved in distilled water (1.25 kg), Triton 770™
20 surfactant (125 g, 30% solids), butyl acrylate
monomer (3 kg) and tetrahydrofurfuryl methacrylate
monomer (6.5 kg). An air mixer was used to emulsify
the monomer mixture in the head tank.

When the temperature of the contents of the
25 reactor vessel was stabilized at 85°C, a solution of
sodium meta bisulfite initiator (30 g) in distilled
water (500 g) was added to the reaction vessel.
Simultaneously, addition of the monomer mixture to
the reaction vessel from the head tank was begun and
30 continued over 45 minutes. Following total addition
of the monomer mixture, the emulsion polymerization
was allowed to proceed for 3 hours at 85°C. After
this time, the latex was cooled to 25°C and filtered
through a 1 micron Fulflo™ filter (available from
35 Fulflo Corporation located in Lebanon, Indiana).
Further purification was accomplished by diafiltering
the latex (diluted to 10% solids with distilled

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water) for 5 turnovers through a polysulfone membrane, and then concentrating it to 22.5% solids by ultrafiltration.

To a 80 l vessel were added tetrahydrofuran solvent (23.3 kg), Uvitex OB™ optical brightener (408.2) and Biostat PE-878™ biocide (32.6 ml). Biostat PE-878™ is commercially available from Eastman Kodak Company (Rochester, New York). The resulting mixture was agitated with a stirrer at 90 rpm and the temperature was gradually adjusted to 55°C. An antifoam agent SAG-10™ (28.6 g) (commercially available from Union Carbide located in Hackensack, New Jersey) was added to 36.3 kg of the purified latex. When the vessel contents had reached 38-42°C, the latex was added rapidly and vacuum was applied. About 15.1 kg of the solvent was distilled off at 45°C and the vacuum was then released. A sample of the resulting "loaded" latex was removed and evaluated as explained below. Once the temperature had reached 55°C, dry gelatin (1633 g) was sifted into the vessel with good mixing to provide a coating composition of the remaining "loaded" latex. The mixing was continued for 30 minutes after gel addition. The resulting hydrophilic coating composition was then filtered through a 5 micron Fulflo™ filter and chill-set until use.

The sample of "loaded" latex removed prior to gel addition and a sample of the hydrophilic coating composition made with gel were evaluated for crystals and agglomerations by coating the samples on separate glass substrates and drying the coatings to form coated elements. These elements were examined with an optical microscope at 250x magnification using polarized illumination. Table I below lists the elements evaluated and the keeping conditions of each.

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Table I

		Element	Keeping Conditions
5	1	"Loaded" Latex	None-tested immediately after coating and drying
10	2	"Loaded" Latex	Element 1 kept 4 hours at 60°C
15	3	Hydrophilic Composition	None-tested immediately after coating and drying
	4	Hydrophilic Composition	Element 3 kept 4 hours at 60° C

20 In micrographs of the elements, crystals
appeared as bright needle-like spots on the dark
background. Element 1 contained many very fine
crystals immediately after coating. These crystals
became well-formed rectangles and needles after
25 keeping for 4 hours at 60°C as seen in Element 2.
These keeping conditions represent melt-hold
conditions. Elements 3 and 4 contain a "loaded"
latex and a binder. Large numbers of optical
brightener crystals were observed in them. The
30 number of crystals increased under conventional
melt-hold conditions.

The samples of "loaded" latex and
hydrophilic composition were also evaluated for
agglomerations using electron microscopic
35 techniques. The presence of agglomerations was
observed in each sample with the number of
agglomerations greater under conventional melt-hold
conditions (4 hours at 60°C).

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Part B

An element of the present invention was prepared in the following manner.

5 A suspension of polymeric particles was prepared according to the procedure described in Example 1 (Part A) using tetrahydrofurfuryl methacrylate, n-butyl acrylate and 2-acrylamido-2-methylpropanesulfonic acid as monomers and Uvitex OB™ optical brightener as the hydrophobe.

10 The suspension containing polymer particles was taken from the reaction vessel after which the vessel was cleaned. The suspension was returned to the vessel and the pH was adjusted to 7 with 10% sodium hydroxide at 60°C and 200 rpm stirring. A
15 sample of the suspension was taken for evaluation as described below. A 10% gelatin solution in water was added to the reaction vessel and stirring was continued for another 15 minutes.

The resulting hydrophilic composition was
20 filtered through cheesecloth and chill-set. Little or no coagulum was found in the reaction vessel.

A sample of the suspension taken prior to gelatin addition and a sample of the hydrophilic composition containing gelatin were coated and
25 evaluated for crystals and agglomerations as described for the "loaded" latex in Part A above. Table II below lists the corresponding elements evaluated.

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Table II

		Element	Keeping Conditions
5	5	Suspension containing polymer particles	None-tested immediately after coating and drying
10	6	Suspension containing polymer particles	Element 5 kept 4 hours at 60°C
15	7	Hydrophilic Composition	None-tested immediately after coating and drying
	8	Hydrophilic Composition	Element 7 kept 4 hours at 60° C

20 In the micrographs of elements 5-8, as in
Part A, crystals appeared as bright needle-like spots
in the dark background. A few large crystals
appeared in Elements 5 and 6. Elements 7 and 8
containing the hydrophilic composition had only 3
25 crystals in a 8.9 x 11.4 cm coated area viewed at
250x magnification. It is quite clear that Elements
7 and 8, which are prepared according to the practice
of this invention, exhibited significant improvement
over Elements 3 and 4 prepared in Part A according to
30 the prior art.

The suspension of polymer particles and
hydrophilic composition containing same were also
evaluated for agglomerations using electron
microscopic techniques. Substantially no
35 agglomerations were observed in either the suspension
or composition, even after keeping under the
melt-hold conditions.

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Example 3

An element of this invention containing an optical brightener hydrophilic layer was prepared in the following manner. This example differs from
5 Example 1 in that the polymer of this example is a crosslinked polymer.

Methyl methacrylate (1.15 kg), styrene (1.15 kg) and ethylene dimethacrylate (46 g) monomers and Aerosol OT-100™ (23 g) surfactant were stirred in a
10 reactor vessel at 30°C until the surfactant was dissolved. Uvitex OB™ (80 g) brightener and 2,2'-azobis(2-methylpropionitrile) (11.5 g) were similarly added to and dissolved in the monomer solution. Once all of the reagents were dissolved in
15 the monomers, stirring in the vessel was increased to 200 rpm and an aqueous solution of Aerosol A268™ surfactant (46 g in 5.4 l distilled water) was added to the monomer solution.

The resulting dispersion was stirred for an
20 additional 5 minutes and then pumped through a commercially-available high shear Manton-Gaulin mill at 3800 rpm using an orifice clearance of 0.01 cm and a flow rate of 1.5 l/min. into another reactor vessel where stirring was set at 40 rpm and the temperature
25 controlled at 70°C. Polymerization proceeded for 20 hours at 70°C to give a suspension of polymeric particles of 30% solids.

This suspension was mixed with gelatin to provide a hydrophilic composition as described in
30 Example 1 above. The resulting composition was coated on a resin-coated support to provide an element of this invention.

Example 4

A photographic element of this invention was
35 prepared in the following manner.

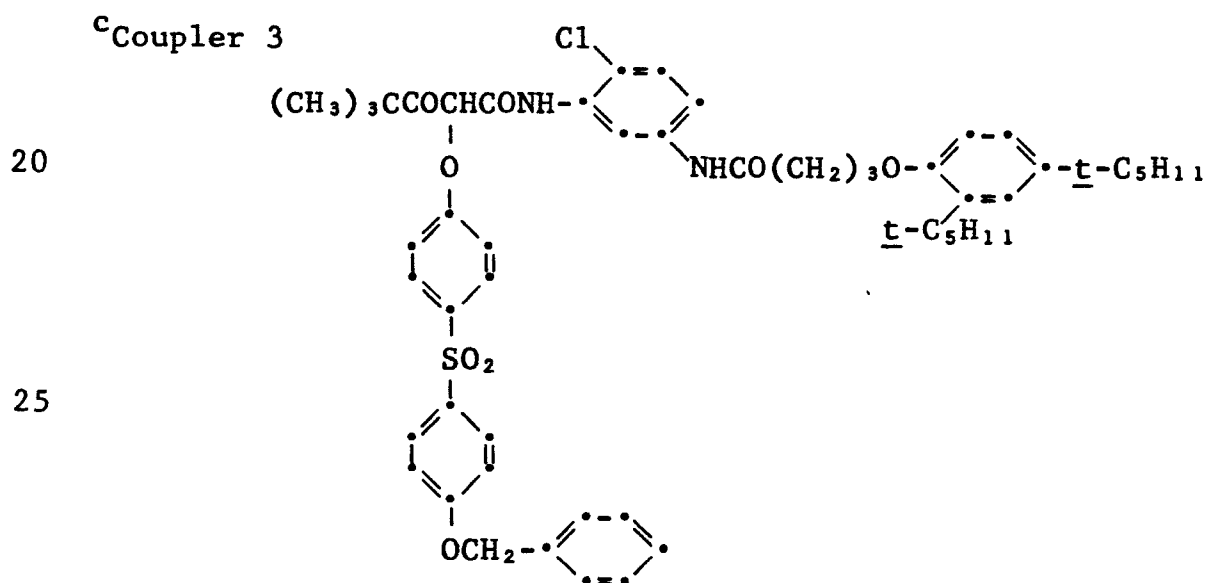
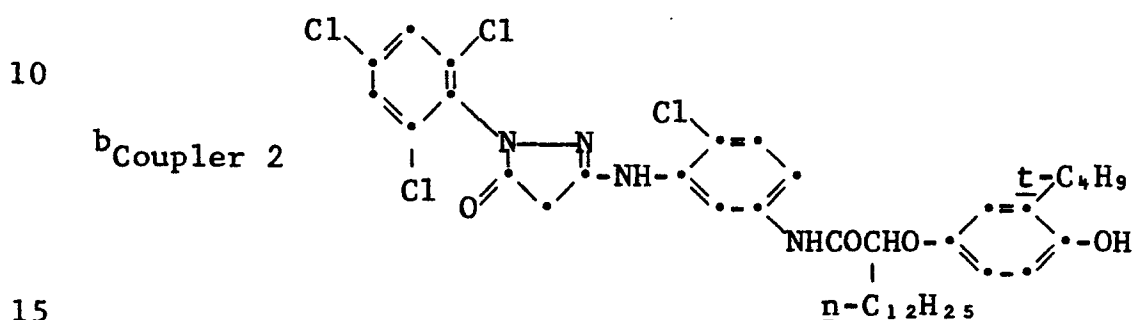
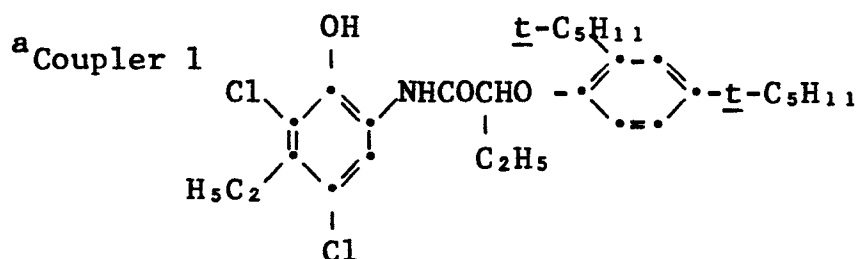
A polymeric suspension of poly(methyl methacrylate-co-styrene-co-p-styrene sodium

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sulfonate-co-ethylene dimethacrylate) (48.5:48.5:1:2 weight ratio) particles containing Uvitex OB[™] optical brightener was prepared as described in Example 3. This suspension was mixed with gelatin and incorporated as a brightener layer in a color photographic paper product having the following format using conventional coating techniques and materials.

10	Overcoat	gelatin	1.1 g/m ²	
	Ultraviolet Light Absorbing Layer	gelatin UV light absorber	0.7 g/m ² 0.4 g/m ²	
		AgClBr (15:85 mole % Cl:Br)	0.25 g/m ²	Ag
15	Cyan Dye Layer	gelatin cyan dye-providing coupler 1 ^a	1.4 g/m ² 0.6 g/m ²	
	Ultraviolet Light Absorbing Layer	gelatin UV light absorber	0.7 g/m ² 0.4 g/m ²	
		AgClBr (15:85 mole % Cl:Br)	0.37 g/m ²	Ag
20	Magenta Dye Layer	gelatin magenta dye-providing coupler 2 ^b	1.6 g/m ² 0.5 g/m ²	
	Interlayer	gelatin	0.75 g/m ²	
		AgClBr (12:88 mole % Cl:Br)	0.3 g/m ²	Ag
25	Yellow Dye Layer	gelatin yellow dye-providing coupler 3 ^c	1.5 g/m ² 1.1 g/m ²	
		Polymer particles	1.8 g/m ²	
		Uvitex OB [™]		
30	Brightener Layer	brightener gelatin	0.054 g/m ² 1.8 g/m ²	
Polyethylene-coated Paper Support				

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Each gelatin-containing layer was hardened with bis(vinylsulfonylmethyl) ether at 1.8% based on the gelatin coverage.

A control paper product was similarly prepared except that the brightener layer was omitted.

Without imagewise exposure, a sample of each element was fixed for 4 minutes at 38°C with a conventional fixing composition, washed 3 minutes at

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38°C and processed with the Kodak Ektaprint™ 2 process (see "Using Kodak Ektaprint 2 Chemicals," 2nd Ed., Eastman Kodak Co. Publication Z-122, 1980). The reflection density ($D_{\min}$) of each sample was then measured using a Wratten 25 filter for the red, Wratten 106 filter for the green and Wratten W48 and 2A filters for the blue. The results are presented in Table I below. 'Kodak' and 'Wratten' are trade marks.

Table I

	Density ($D_{\min}$)		
	Red	Green	Blue
Control	0.116	0.127	0.128
Example 4	0.115	0.124	0.114

It can be seen from these data that while the red and green $D_{\min}$ s are substantially identical for both elements, the blue $D_{\min}$ was significantly decreased in the element containing the brightener layer. These results indicate the effectiveness of the brightener incorporated in the polymer particles. Examples 5 and 6

These examples are similar to Example 4 except that the polymer particles containing an optical brightener was incorporated in the interlayer between the magenta and yellow dye layers instead of a separate brightener layer.

Uvitex OB™ was incorporated in poly(n-butyl acrylate-co-tetrahydrofurfuryl methacrylate-co-2-acrylamido-2-methylpropanesulfonic acid, sodium salt) (30:65:5 weight ratio) particles (Example 5) and poly(methyl methacrylate-co-ethylene dimethacrylate) (98:2 weight ratio) particles (Example 6) according to the procedure described in Example 3.

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The resulting polymer suspensions were incorporated in the interlayer and elements were prepared as described in Example 4. A control element was also prepared like the control element of
 5 Example 4.

A sample of each element was processed and the yellow $D_{\min}$ level of each measured as described in Example 4. The differences in Control $D_{\min}$ and example $D_{\min}$ are shown in Table II below.

10

<u>Table II</u>	
	Change in Yellow ($D_{\min}$)
Example 5	-0.1
Example 6	-0.1

15

These data indicate the brightening effectiveness of the brightener-containing polymeric particles in the interlayers of the elements.

Example 7

20 This example illustrates the incorporation of a cyan dye-forming coupler in polymer particles and the use of such particles in a photographic element.

The coupler was incorporated into
 25 poly(n-butyl methacrylate-co-methacrylic acid) particles in the following manner:

n-Butyl methacrylate (114 g), methacrylic acid (36 g), 2-[α -(2,4-di-t-pentylphenoxy)-butyramido]-4,6-dichloro-5-ethylphenol (90 g) and
 30 Aerosol OT[™] surfactant (7.2 g) were placed in a 1 liter vessel and heated at 50°C under a nitrogen atmosphere until all materials were dissolved. Distilled water (600 g) was placed in a conventional blender, heated to 60°C and the monomer solution was
 35 added thereto and mixed at high speed for 5 minutes. The resulting dispersion was added to a 2 liter reaction vessel and heated to 70°C, after which

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K₂S₂O₈ (1.8 g in 10 ml of water) and Na₂S₂O₅ (0.72 g in 10 ml of water) were added to the vessel. After two hours of reaction, the resulting suspension was filtered to remove a small amount of coagulum and the filtrate was adjusted to pH 5.5.

The polymer particle suspension was then warmed to 50-60°C and a 5% solution of gelatin containing 52 g of dry gelatin was gradually added. The resulting hydrophilic composition was stirred for 30 minutes at 50°C.

This hydrophilic composition was coated in a photosensitive emulsion layer on a polyethylene-coated paper support. The coating coverages were 0.3 g/m² Ag, 2.8 g/m² gelatin and 1.24 g/m² polymer particles. The gelatin was hardened with bis(vinylsulfonylmethyl) ether at 1.75% based on gelatin weight.

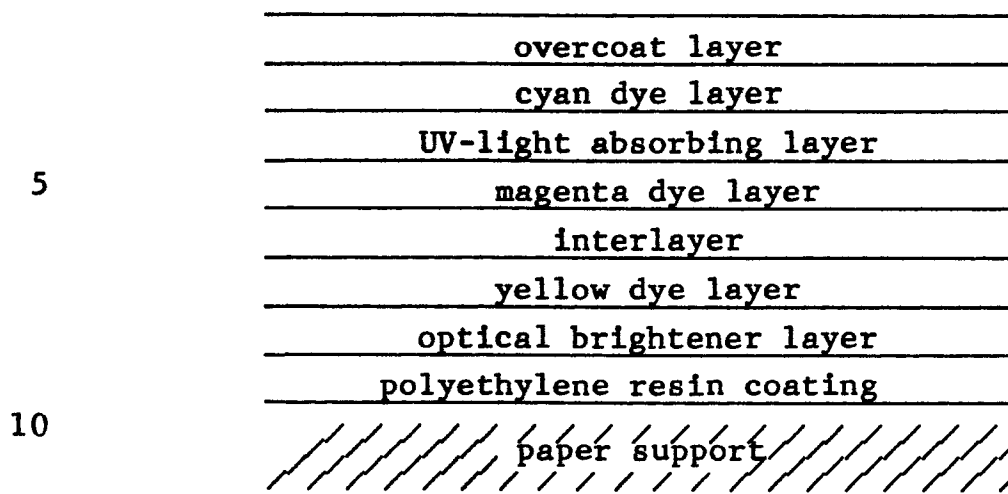
The resulting element was exposed for 0.1 sec. to a 3000°K light source through a Wratten 29 filter and a graduated neutral density tablet, and processed with the Ektaprint™ 2 process described in Example 4. Sensitometric evaluation of the element indicated that it exhibited suitable cyan dye color.

Example 8 Comparison of Optical Brightener
 Wandering in Elements

This is a comparative example showing the reduced tendency of an optical brightener to wander in a multilayer photographic paper product of this invention compared to the wandering tendency of the same optical brightener in a similar paper product prepared according to the prior art, as in Part A of Example 2 above.

The elements of this example had the following general structure:

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The specific ingredients of each layer other than the optical brightener layer are not critical to the purpose of this example, but are conventional in the photographic chemistry art.

The optical brightener layer of the element of this invention contained gelatin as the hydrophilic binder (1.1 g/m^2) and particles of poly(n-butyl acrylate-co-tetrahydrofurfuryl methacrylate-co-2-acrylamido-2-methylpropanesulfonic acid, sodium salt) (49:49:2 weight ratio) (1.8 g/m^2) containing Uvitex OB[™] optical brightener (0.05 g/m^2) uniformly dispersed throughout the particles.

The optical brightener layer of the Control element contained a "loaded" latex (1.8 g/m^2) like that described in Part A of Example 2 of poly(methyl methacrylate-co-styrene-co-ethylene glycol dimethacrylate) (35:60:5 weight ratio) dispersed in gelatin (1.1 g/m^2). The latex was "loaded" with 1 weight percent of Uvitex OB[™] optical brightener although not all of the brightener was in latex particles.

UV-fluorescence microscopy was used to study the optical brightener wandering in each element. A cross-section of each element was subjected to

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fluorescent light at 1000x using an ultraviolet light
filter. Considerable wandering of the optical
brightener occurred in the Control element. However,
little wandering occurred in the element of this
5 invention.

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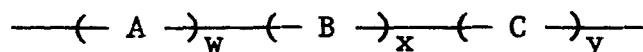
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CLAIMS:

1. An element comprising a support having thereon a hydrophilic layer which comprises a hydrophilic composition comprising a hydrophilic binder and water-insoluble polymer particles dispersed therein, the polymer particles having recurring units derived from one or more ethylenically unsaturated polymerizable monomers, the element characterized in that the hydrophilic layer is substantially crystal- and agglomeration-free and the polymer particles comprise from 0.5 to 10 percent, based on total monomer weight, of a hydrophobe uniformly distributed throughout the particles.
2. The element as claimed in claim 1 comprising a radiation-sensitive layer.
3. The element as claimed in claim 2 which is a multilayer color photographic element comprising a paper support having thereon a plurality of photographic color-forming silver halide emulsion layers.
4. The element as claimed in any of claims 1 to 3 wherein the hydrophobe is a photographic dye, photographic dye-forming coupler, photographic developing agent, optical brightener, or ultraviolet light absorbing compound.
5. The element as claimed in any of claims 1 to 4 wherein the hydrophobe is an optical brightener.
6. The element as claimed in any of claims 1 to 5 wherein the polymer particles have recurring units derived from two or more ethylenically unsaturated polymerizable monomers, at least one of the monomers having a crosslinkable moiety.
7. The element as claimed in any of claims 1 to 6 wherein the polymer particles are composed of polymers represented by the structure:

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wherein -A- represents randomly recurring units derived from one or more vinyl aromatics, olefins and diolefins, vinyl esters or esters of

5 α,β -unsaturated polymerizable carboxylic acids;

-B- represents randomly recurring units derived from one or more ethylenically unsaturated polymerizable monomers having one or more anionic moieties; -C-

10 represents randomly recurring units derived from one or more ethylenically unsaturated polymerizable monomers having a crosslinkable moiety; w represents

a weight percent from 75 to 100; x represents a weight percent of from 0 to 20; and y represents a

15 weight percent of from 0 to 5, all based on total monomer weight.

8. The element as claimed in any of claims 2 to 7 wherein the hydrophilic layer containing the polymer particles is interposed between the support and the radiation-sensitive layer(s).

20 9. The element as claimed in any of claims 1 to 8 wherein the hydrophobe is 2,5-bis(6-butyl-2-benzoxazolyl)thiophene optical brightener and the polymer particles are composed of poly(methyl methacrylate-co-styrene-co-ethylene glycol dimethacrylate).

10. A method of making the element as claimed in claim 1 comprising the steps of:

30 (a) dissolving from 0.5 to 10 percent, based on total monomer weight, of a hydrophobe in solution with one or more ethylenically unsaturated polymerizable monomers;

35 (b) dispersing and polymerizing the solution formed in step (a) in water as fine droplets under conditions sufficient to promote suspension polymerization of the monomers in the droplets and to form polymeric particles having the hydrophobe uniformly distributed throughout the particles;

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(c) dispersing the polymeric particles formed in step (b) in a hydrophilic binder to form a hydrophilic composition; and

(d) applying the hydrophilic
5 composition to a support to form a substantially crystal- and agglomeration-free hydrophilic layer.

11. The method as claimed in claim 10 wherein a radiation-sensitive composition is applied over the hydrophilic layer.

10 12. The method as claimed in any of claims 10 or 11 wherein the hydrophobe is an optical brightener.

13. The method as claimed in any of claims 10 to 12 wherein step (a) is carried out at a
15 temperature greater than room temperature but less than the temperature at which spontaneous polymerization of the monomers occurs.

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