Aug. 27, 1974 H. G. ROGERS ET AL 3,832,183

POLYMER ENCAPSULATED SILVER HALIDE GRAINS

Original Filed Feb. 17, 1971 2 Sheets-Sheet 1

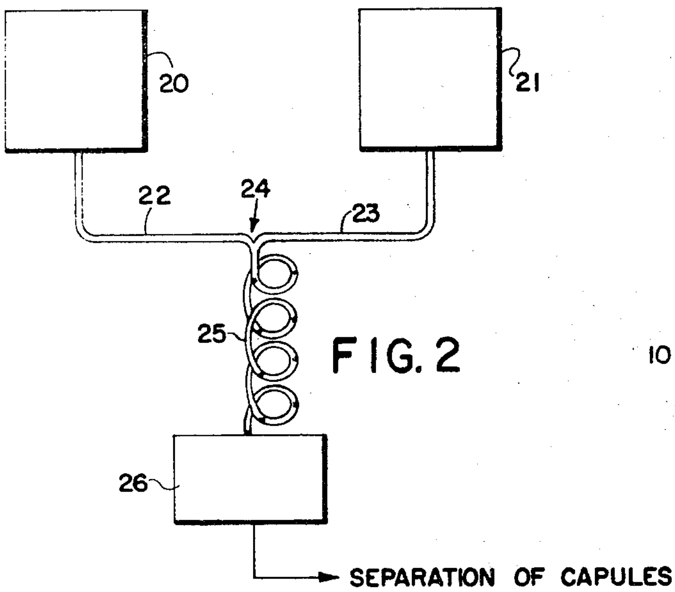

FIG. 2

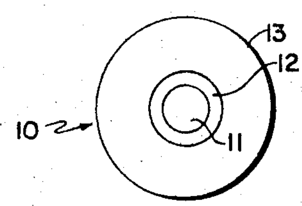

FIG. 1

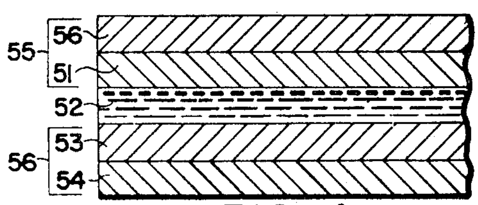

FIG. 4

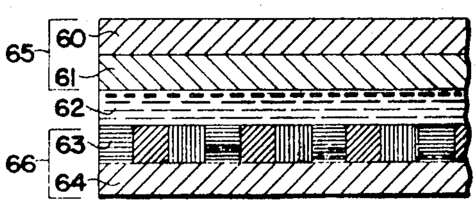

FIG. 5

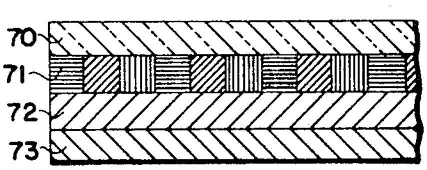

FIG. 6

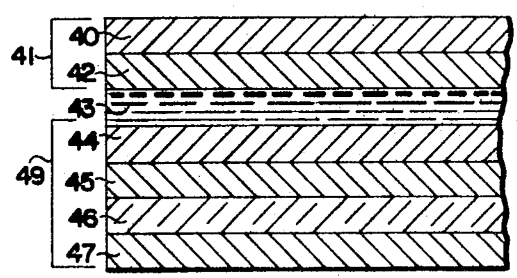

FIG. 3

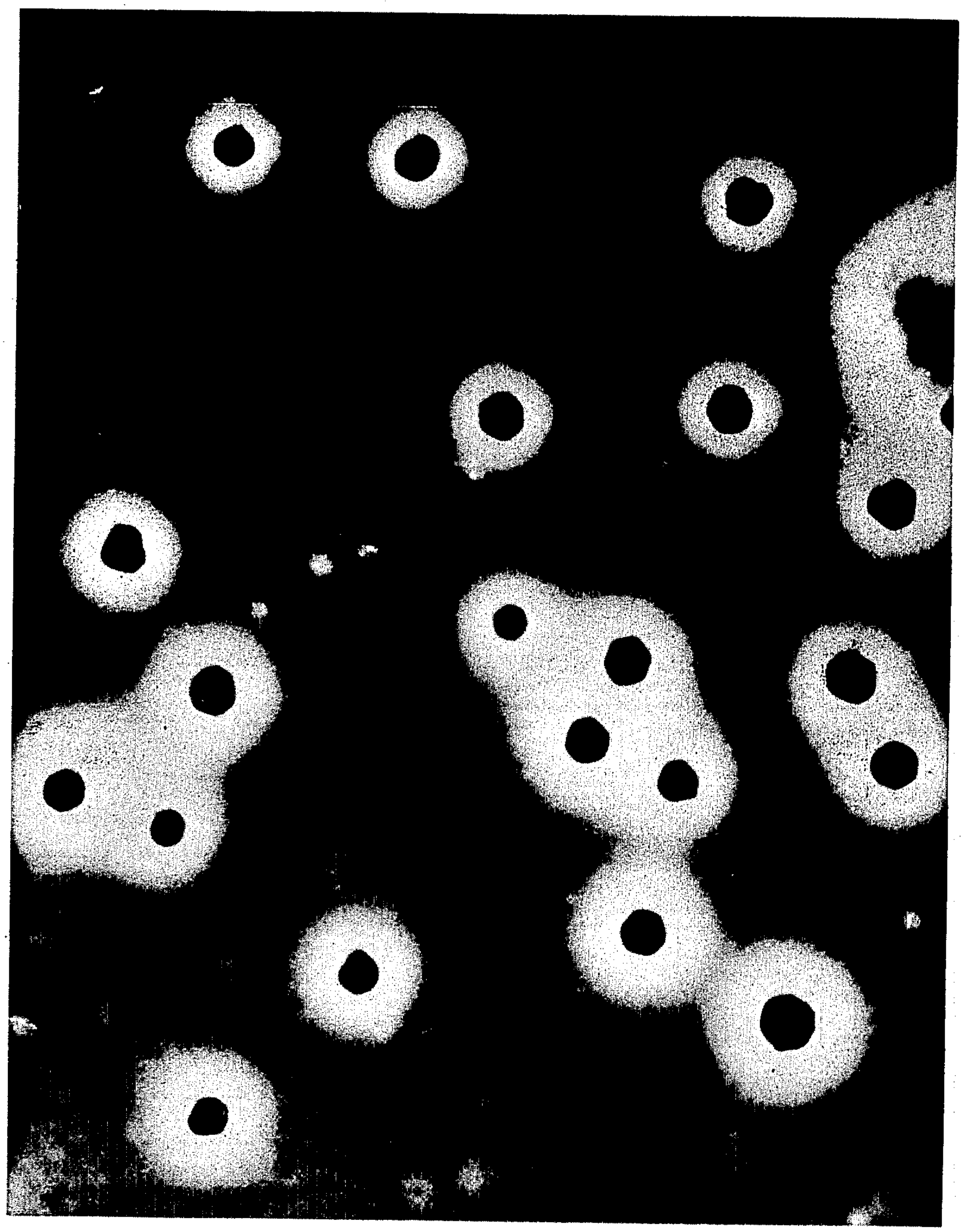

FIG. 7

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POLYMER ENCAPSULATED SILVER HALIDE GRAINS

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Int. Cl. G03c *1/40, 1/02, 1/10, 1/72, 1/28*

U.S. Cl. 96—77 16 Claims

ABSTRACT OF THE DISCLOSURE

This invention is directed to microscopic capsules comprising a continuous synthetic polymeric layer surrounding a nucleus composed of photosensitive silver halide grains wherein the polymeric layer is of sufficient thickness to substantially overcome the attractive forces of said silver halide grains for adjacent silver halide grains. Thus, the present invention contemplates individual grains of photosensitive silver halide which are spatially separated from adjacent grains by means of a polymeric layer encasing the grains. The present invention is also directed to methods for providing such encapsulated products and to photographic products employing said capsules.

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a division of U.S. Patent Application Ser. No. 115,985 filed Feb. 17, 1971, now U.S. Pat. No. 3,697,279.

BACKGROUND OF THE INVENTION

The formation in a variety of sizes and shapes of capsules consisting of a nucleus comprising, for example, a liquid around which is deposited a dense shell-like coating of a film-forming organic polymeric material, is well known to the art. A great number of materials in solid or liquid forms may be encapsulated. Of particular interest is the encapsulation of materials useful for photographic employment, such as the encapsulation of color-providing substances or materials such as dye developers, which may be released at the appropriate time during photographic employment by, for example, rupturing or breaking the capsule, dissolving or melting the capsule wall, or by a process modification of the capsule wall to permit the diffusion of the encapsulated material contained therein.

As an example of such encapsulated materials and photographic products employing such materials, mention may be made of U.S. Pat. No. 3,468,662, wherein minute capsules are formed of film-forming polymeric materials of a hydrphilic nature, such as gelatin, or of film-forming polymeric materials of a hydrophobic nature, such as polyvinyl chloride wherein each capsule consists of a nucleus composed of a solid or liquid material, preferably a color providing substance, around which has been deposited a dense shell-like coating of the above-mentioned polymeric material. In a particularly preferred embodiment, the polymeric layer enclosing the nucleus is itself overcoated by a substantially continuous layer which comprises silver halide, which silver halide may be optically sensitized to provide a product suitable for photographic employment.

Further disclosure of the photographic employment of such capsules may also be found in U.S. Pats. Nos. 3,276,-869 and 3,427,160.

One widely used method of forming capsules employs a deposition of a complex colloid material around microscopic droplets of a water-immiscible medium by the process of causing coacervation by dilution or adjustment of the pH to occur in a mixture of two different colloid salts in which the water-immiscible material is dispersed as droplets, and then gelling the colloid material. As examples of such procedures and products produced therefrom, mention may be made of U.S. Pats. Nos. 3,507,661; 3,328,357; 3,190,837; 3,369,900; and 3,396,026.

While such products are particularly suitable for some phases of photographic employment, they also suffer from a number of deficiencies. A principle disadvantage to the photographic employment of microscopic capsules involves the natural attractive forces of silver halide which results in clumping of a plurality of individual grains of the silver halide. Because of such tendency of silver halide grains to clump or agglomerate, silver halide emulsions generally comprise a dispersion of the silver halide grains in a relatively large body of polymeric binder material, generally gelatin, which will serve to isolate to some degree the silver halide particles spatially throughout the relatively large volume of binder material. However, the employment of such large quantities of binder material in relation to the silver halide grains also introduced disadvantages such as relatively thick photosensitive layers in photographic products with attendant light-scattering problems and efficiency of contact of the silver halide grains with the appropriate processing composition.

A novel microscopic capsule suitable for photographic employment has now been found which is not susceptible to the deficiencies of the prior art.

SUMMARY OF THE INVENTION

The present invention is directed to microscopic capsules comprising silver halide completely surrounded by a continuous synthetic polymeric layer of sufficient thickness to substantially insulate the individual silver halide grains from each other. Preferably, the silver halide employed is optically sensitized. More preferably, photographic reagents such as color providing substances, such as a dye developer, is disposed in the encapsulating polymeric layer.

The present invention is also directed to the method of forming such capsules wherein an ethylenically unsaturated monomer is polymerized on the surface of said silver halide grain.

The present invention is also directed to photographic products and processes employing such capsules.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an enlarged fragmentary cross-sectional view of a capsule within the scope of the present invention, the thickness of the components thereof being exaggerated;

FIG. 2 is a flow of a diagram illustrating a process for the preparation of capsules within the scope of the present invention;

FIGS. 3–5 are diagrammatic cross-sectional views of various embodiments of the present invention for use in obtaining multicolor images during processing and comprising an integral multilayer photosensitive element; an image-receiving element and a processing fluid;

FIG. 6 is a diagrammatic cross-sectional view of another embodiment of the present invention for use in obtaining multicolor images by means of additive color photography employing a multicolor additive color screen; and

FIG. 7 is a photomicrograph showing novel capsules of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a capsule comprising a grain of silver halide which is completely surrounded or encapsulated with a continuous synthetic polymeric layer wherein said polymeric layer is of sufficient thickness to separate the capsules to prevent clumping or agglomeration of a plurality of silver halide grains. Thus, employing the capsules of the present invention, relatively thin layers or even monolayers of photosensitive silver halide grains may be deposited on a surface to provide superior photographic products. Thus, the problems generally encountered with conventional coatings, that is, a random deposition of silver halide, principally the problems of resolution, are avoided employing the novel capsules of the present invention. The uniformity of the coating and the rigidity of the coating provide spatial separation, substantially eliminating the problems of agglomeration, and permits the desired degree of packing or arrangement of the capsules on a support for photographic employment. The novel capsules of the present invention are preferably photosensitized by conventional methods. Such sensitization may be achieved prior to or subsequent to the formation of the capsules, that is, the deposition of a polymeric layer may be achieved on either an unsensitized or a chromatically or panchromatically sensitized silver halide grain.

In a particularly preferred embodiment, the polymeric layer, i.e., the wall of the capsules, contains disposed therein a color-providing substance, i.e., a dye image providing material; diffusion of said color-providing material being a function of exposure of the associated encapsulated silver halide.

The thickness of the polymeric layer is not critical; it is only necessary that the polymeric layer be sufficiently encapsulated silver halide grains from each other to prevent clumping and to permit a uniform distribution of the silver halide in forming a photographic product. Thus, the thickness of the polymeric layer may vary over a relatively wide range. For example, for a silver halide grain 1 micron in diameter, a skin thickness ranging from 0.01 micron to 50 microns and preferably 0.5 micron may be employed.

The term "polymer" employed herein with reference to the polymeric layer encapsulating the silver halide is intended to include polymers prepared from single monomers or copolymers prepared from two or more monomers. It should be further understood that the entire thickness of the polymeric layer may be composed of more than a single polymeric entity; thus, the polymeric layer may be built up to a certain thickness of a single polymer and then continued polymerization to provide the remainder of the polymeric layer being achieved by a second monomer.

The silver halides which are particularly useful in the present invention comprise silver chloride, silver chlorobromide, silver bromide, silver iodobromide, silver iodochlorobromide, and combinations thereof which are conventionally employed in photosensitive elements. The silver halides employed in forming the capsules of the present invention may be obtained in the form of conventional photographic silver halide emulsions, or they may be composed of silver halides in the form of aqueous suspensions obtained by precipitating the silver halides in the absence of a conventional binder material. Thus, in short, silver halide grains from any suitable source may be employed from any conventional method of preparing silver halide photographic emulsions, and in any size or shape.

The encapsulated silver halide crystals of the present invention are prepared by polymerizing on the surface of said crystal a monomer to provide a polymeric layer of sufficient thickness and rigidity to provide the above-described spatial separation properties. In the novel processes of the present invention, the silver halide grain itself provides the necessary sites for the polymerization of an olefinically unsaturated monomer. Thus, polymerization is associated with the surface of the grain, with the wall of the grain forming outwardly from the surface of said grain.

Preferential polymerization of the monomer on the silver halide crystal to the substantial exclusion of free polymer is achieved by providing in the absence of the silver halide grains, sub-threshold concentrations and/or conditions for bulk polymerization. In other words, concentration of reactants, temperature, pH, pressure, energy input, e.g., radiant energy and the like, are selected to provide a system under which polymerization will not occur in a relatively short period of time in the absence of the polymerization sites provided by the silver halide grains. In one embodiment, a relatively dilute concentration of monomer to the silver halide is employed. Thus, in the novel process of the present invention, the presence of free polymer, that is, a polymer other than that associated with the silver halide crystals, is substantially eliminated. It has been found that polymerization, i.e., wall formation, occurs from the silver halide grain outwardly and that formation of the wall forces individual grains apart, thus providing and maintaining the desired spatial relationship between particles. Where incident radiation is one of the polymerizing conditions, some fogging of the silver halide grain may occur. In such a situation it may be desirable to contact the capsules with an oxidizing agent to oxidize the reduced silver back to silver halide.

The wall growth has been found to be proportional to the size of the silver halide grain.

In one embodiment of the present invention, a dilute solution of the monomer is fed to a reaction zone, preferably a constricted zone, more preferably a pipe line reactor, simultaneously with a dispersion of silver halide crystals and a suitable free radical initiator such as ceric ammonium nitrate. The polymerization reaction forms polymer on the surface of the silver halide crystal, which functions as the site for the polymerization. Because of the above-described dilute conditions which are employed in the polymerization process, the process results in a relatively large quantity of fluid medium which constituted the solvent for the monomer and the dispersing medium for the silver halide grains. The capsules thus produced may be separated from such fluid media such as excess monomer, salts, thickeners and the like, by techniques known to the art, for example, by settling, by centrifuging, or by membrane separation techniques. The thus-produced capsules may then be treated further, for example, by being contacted with other conventional photographic adjuvants such as stabilizers, sensitizers, and the like, or may be used directly in photographic products as a component of a photosensitive element.

If desired, various photographic or processing reagents may be incorporated into the capsule by disposing the given reagents in the monomer solution prior to polymerization. Upon formation of the polymer wall around the silver halide crystal, the reagents will be disposed with the wall. As examples of reagents which may be disposed therein, mention may be made of light filtering dyes, dye precursors, such as color couplers, dye developers, developing agents, mordanting groups, silver halide precipitating agents, antifoggants, and the like. In addition to entrained dyes, polymeric dyes may also be employed, e.g., dyes containing a vinyl substituent may be copolymerized into the wall.

As stated above, the silver halide employed in the present invention may be prepared directly in the form of aqueous suspension obtained in the preparation of silver halides or may be obtained in the form of conventional photographic silver halide emulsions, such as gelatin emulsions. If desired, the bulk of the binder material may be removed. It should be understood, therefore, that in such case an intermediate relatively thin coating of gelatin may surround the silver halide grain over which polymerization occurs. It has been found that substantially no significant effect on the polymerization is noted by virtue of the presence of the aforementioned binder.

The silver halide may be treated with conventional sensitizing agents known to the art prior to the polymerization step, or subsequent to the formation of the capsule.

One particular capability of the capsule of the present invention is in certain products or assemblages useful in photographic transfer reversal processes capable of producing a color print. In processes for forming color images by transfer techniques, an imagewise distribution of one or more color-providing substances is formed in unexposed parts of the negative photosensitive element having one or more light sensitive portions having silver halide therein, and transferred to an image-receiving element. The imagewise distribution of each color-providing substance so transferred and deposited on the image-receiving element arranged in superposed relation to the negative photosensitive element colors the image-receiving element a predetermined color to provide therein monochromatic or multichromatic image comprising one or more positive images of negative latent color images formed by the exposure of said photosensitive element. Among the techniques for carrying out a transfer process in color, mention may be made of (a) the processes disclosed and claimed in U.S. Pat. No. 2,983,606, wherein dye developers, i.e., compounds which contain in the same melocule both the chromophoric system of a dye and also a silver halide developing function, or the color providing substances are color forming components; (b) the processes disclosed in U.S. Pats. Nos. 2,774,668; 3,345,163; and 3,087,817 wherein complete dyes of suitable colors and of a nature having a coupling group or function and which are able to couple with silver halide developers in oxidized conditions are the color providing substances; (c) the processes disclosed and claimed in U.S. Pats. Nos. 2,647,049; 2,661,293; 2,698,244; 2,698,798; 2,802,735; 3,148,062; 3,227,550; 3,277,551; 3,227,552; 3,227,554; 3,243,294; 3,330,655; 3,347,671; 3,352,672; 3,364,022; 3,443,939; 3,44,940; 3,443,941; 3,443,943; etc., wherein color coupling techniques are utilized which comprise at least in part reacting one or more developing agents and one or more color formers to provide a positive color image in a superposed image-receiving layer; and (d) the processes disclosed in U.S. Pat. No. 3,185,567 wherein the color-providing substances employed are initially immobile and nondiffusible but which are rendered diffusible in the unexposed areas of the photosensitive layer by reaction with unreacted or unexhausted silver halide developing agent.

As stated above, it has now been found that such color-providing substances can be incorporated into the novel capsules of the present invention by disposing said color-providing substance in the monomer solution prior to the polymerization. As a result of such initial disposition of the color-providing substance, the thus formed capsule walls have disposed therein the indicated color-providing substance; thus providing a capsule composed of a nucleus of photosensitive silver halide enveloped in a polymeric layer having distributed therein a color-providing substance.

Turning to the drawing, FIG. 1 illustrates an enlarged cross-sectional view of a capsule **10** of the present invention which, in the embodiment shown, is composed of a nucleus of photosensitive silver halide **11**, a thin inner coating of said silver halide grain composed of an emulsion binder **12**, e.g., gelatin, and an outer polymeric layer **13** relatively thick with respect to gelatin layer **12**. The illustrated capsule denotes a product formed from a silver halide obtained from a conventional gelatin emulsion which would retain the thin gelatin coating around said silver halide subsequent to the removal of the bulk of the binder. As stated above, polymeric layer **13** may have optionally disposed therein a color-providing material or other photographic reagent.

A flow diagram is illustrated in FIG. 2 for the preparation of the novel capsules of the present invention. A reservoir **20** contains ethylenically unsaturated monomer disposed in a suitable solvent. A reservoir **21** contains silver halide and a suitable free radical initiator. Lines **22** and **23** carry the monomer and silver halide, respectively, to point **24** where they are intermixed, preferably by means of jetting the respective components into a reaction zone shown as a pipe line ractor **25**. The residence time of the components is determined by the velocity of the components through line **25** and the length of line **25**. A reservoir **26** receives the thus-formed capsules, reaction materials, solvents and dispersing medium. The contents of reservoir **26** can be withdrawn and capsules separated by suitable means described above. As stated above, the color-providing material such as the dye developer may be optionally disposed in reservoir **20** with the monomer to provide a capsule having said color-providing material disposed in the wall thereof.

The capsules of the present invention may be employed in a variety of photographic applications. For example, the capsules may be coated on a suitable support in a relatively thin or even a monolayer and with suitable sensitization be employed as a conventional photographic negative. The application of such capsules on a suitable support may be carried out by techniques well known to the art, for example, by rollers, sprayers, brushes, or by any of the commonly used methods. The capsules may be retained on the supports by their own adhesive forces or an additional supplementary adhesive or coating may be employed to secure them thereto.

The novel capsules of the present invention are particularly suitable for obtaining multicolor images using dye developers in diffusion transfer reversal processes. For example, one process for obtaining multicolor transfer images utilizing dye developers employs an integral multicolor photosensitive element wherein at least two selectively sensitized photosensitive layers are superposed on a single support in a process simultaneously and without separation with a single common image-receiving layer. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide layer, a green-sensitive silver halide layer and a blue-sensitive silver halide layer, said layers having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer.

A multilayer photosensitive element of the type described is illustrated in FIG. 3 and is depicted during processing. An exposed multilayer photosensitive element **49** comprises support **47**; a photosensitive layer **46** comprising in substantial contiguity a profusion of capsules comprising a red-sensitized silver halide wherein the walls of said capsules contain cyan dye developer; a photosensitive layer **45** comprising in substantial contiguity a profusion of capsules comprising green-sensitized silver halide wherein the walls of said capsules contain a magenta dye developer; and a photosensitive layer **44** comprising in substantial contiguity a profusion of capsules comprising blue-sensitized silver halide crystals wherein the walls of said capsules contain a yellow dye developer. Each photosensitive layer may be separated from each other by suitable interlayers (not shown), for example, by a layer of gelatin and/or polyvinyl alcohol. In certain instances, it may be desirable to incorporate a yellow filter in front of the green-sensitive and red-sensitive layers, and such yellow filter may be incorporated in an interlayer or disposed within the capsule walls.

Multilayer photosensitive element **49** is shown in processing relationship with image-receiving element **41** and a layer **43** of processing composition. The image-receiving element **41** comprises a support **40** and an image-receiving layer **42**.

The liquid processing composition **43** is effective to initiate development of the latent image in the respective exposed photosensitive layers. After suitable imbibition period, during which at least a portion of the dye developer associated with unexpected areas of each of the photosensitive layers, is transferred to the superposed image-receiving element **41**, the latter element may be separated to reveal a positive multicolor image, or optionally the film unit described may comprise an integral unit wherein support **40** is transparent and photosensitive element **49** and image-receiving element **41** remain in superposed relationship subsequent to development.

The expression "integral multilayer photosensitive element" as used herein is intended to include photosensitive elements comprising at least two separate superposed layers of photosensitive material, each layer being selectively sensitized to an appropriate portion of the spectrum, at least the inner layer or layers having associated therewith appropriate color-providing substances. The integral multilayer photosensitive element is intended to be processed without separation of the layers. The imagewise distribution of diffusible color forming substances present in each layer as a result of the development of latent images therein is transferred to a single common image-receiving element to provide the desired multicolor image.

An alternative process for obtaining multicolor transfer images utilizing dye developers contemplates the use of a single photosensitive layer comprising a profused random dispersion of at least two sets of selectively sensitized capsules, wherein the walls of said capsules contain therein suitable dye developers. FIG. 4 depicts an exposed photosensitive element **56** comprising support **54** and a photosensitive layer **53** comprising in substantial contiguity a profusion of randomly dispersed capsules of red-sensitized silver halide containing a cyan dye developer and a yellow filter dye in the walls thereof, capsules comprising green-sensitive silver halide containing a magenta dye developer and a yellow filter dye in the walls thereof, and capsules comprising blue-sensitized silver halide containing a yellow dye developer and a yellow filter dye in the walls thereof. Said photosensitive element **56** is in processing relationship with image-receiving element **55** and layer **52** of processing composition. The image-receiving element **55** comprises support **50** and image-receiving layer **51**. The processing of the exposed photosensitive element **56** is as described above.

Still another alternative embodiment contemplates the use of layer comprising at least two sets of capsules containing silver halide selectively sensitized and arranged in the form of a photosensitive screen. In such an embodiment, each of said silver halide capsules contains within the walls thereof a suitable dye developer. Thus, FIG. 5 illustrates a film unit wherein photosensitive element **66** comprises a support **64** and a photosensitive color screen **63** which comprises selectively exposable portions, that is, portions which comprise, respectively, capsules of red, green and blue sensitized silver halide containing within the walls thereof, respectively, cyan, magenta and yellow dye developers preferably substantially uniformly distributed over the support such that a contiguous layer arrangement of individually selectively exposed portions have their respective exposure portions arranged in a side-by-side pattern relationship, and forming the exposure surface of a photosensitive element **66**. As shown, photosensitive element **66** is in processing relationship with image-receiving element **65** and processing composition **62**. Image-receiving element **65** comprises support **60** and image-receiving layer **61**. The processing of exposed photosensitive element **66** is as described above.

The novel silver halide capsules of the present invention are also suitably employed in additive color systems wherein said encapsulated silver halide is panchromatically sensitized. A film unit suitable for such employment is depicted in FIG. 6 and comprises a flexible transparent film base or support **70** carrying on one surface, in order, an additive color screen **71**, comprising a geometrically repetitive plurality of actinic radiation filtering colored elements including a set of group of primary red color filter elements, a set of primary blue color filter elements and a set of primary green color filter elements, arranged in a repetitive distribution in side-by-side relationship in a substantially single plane; a substantially photoinsensitive layer **72** comprising silver precipitating nuclei; and a photosensitive layer **73** comprising a profusion of capsules comprising panchromatically sensitized silver halide.

In describing the foregoing film units embodying the capsules containing silver halide, the layer of capsules has generally been described as comprising a profusion of capsules. It should be understood that the novel capsules of the present invention may be employed as a single or monolayer of capsules, or as a plurality of layers of capsules, that is, wherein said photosensitive layer comprises a plurality of separate layers of capsules. However, because of the advantageous characteristics of the present invention, particularly with regard to the spatial separating effects provided by the polymeric walls of the capsules, such capsules are particularly suitable for use as monolayers. Thus, employing such capsules the desired density in effect can be selected depending upon the ratio of silver coverage desired. In employing a monolayer, it is particularly preferred that the silver halide comprise less than 50% of the area covered.

The novel capsules of the present invention are particularly suitable for use in integral film units, that is, where the photosensitive layer and the layer in which the image is formed, is not separated. It has been unexpectedly found that the development of the silver is more globular and less filamentous which results in less covering power in the negative, which effectively provides a greater speed.

The following nonlimiting example illustrates the preparation of the novel capsules of the present invention.

EXAMPLE

A first reservoir is charged with 500 ml. of water, 1 ml. of 30% hydrogen peroxide and 1 g. of diacetone acrylamide at a pH of 4.8. A second reservoir is charged with 500 ml. of water, gelatin-silver halide emulsion containing 0.20 g. of silver bromide and 0.46 g. ferrous nitrate at a temperature of 38° C. and pH of 4.7. Streams from the two reservoirs were combined at an equal ratio and maintained in a reaction zone 1/32 in. diameter tubing for 1 min. after which the reaction mix was discharged into a collection reservoir. The capsules were separated by settling and decantation.

FIG. 7 is a dark field electron photomicrograph of the capsules prepared according to the procedure of the Example at a magnification of 8000×. The dark areas are the silver halide grains surrounded by uniform areas of polymer which completely surround and constitute the walls of said capsules. The photomicrograph illustrates the uniform coverage and lack of agglomeration of the particles and absence of free polymer.

Any suitable monomer capable of polymerization catalyzed by silver halide may be employed in the present invention. Thus, ethylenically unsaturated monomers capable of forming polymers which are permeable to processing composition are suitable for the forming of the walls of the capsules of the present invention. As examples of suitable monomers, mention may be made of diacetone acrylamide, p-styrene sulfonamide, 1-vinyl imidazole, 2-

methyl-vinyl imidazole, sodium methacrylate, vinyl chloride, acrylonitrile, styrene, dienes such as butadiene, ethylene and propylene. In an optional embodiment, porosity enhancing materials such as silica and diatomaceous earth may be incorporated into the polymeric layer to provide greater permeability to the capsule wall.

As stated above, the novel capsules of the present invention are particularly suitable for use in additive color photography. In general, color photographic reproduction may be provided by exposing a photoresponsive material such as, for example, a photosensitive silver halide emulsion, to selected subject matter through an optical screen element possessing filter media or screen elements of selected radiation modulating characteristics such as filter media selectivity transmitting predetermined portions of the electromagnetic radiation spectrum's visible segment. The color information thus recorded is read out by viewing resultant image conformation in the photoresponsive material through the same or a similar screen element in appropriate registration with the image. For the reproduction of subject matter in color and in accordance with the principles of additive color photography, the individual filter media or screen elements constituting the optical screen will be constructed to effect selective filtration of predetermined portions of the visible electromagnetic spectrum substantially corresponding to its red, blue and green regions and color information recordation is accomplished by point-to-point incidence of radiation actinic to the selected photoresponsive material as modulated by such screen element. Visual reproduction of the information content recorded by the photoresponsive material is accomplished by read out of the impressed image as modulated by the original or a substantially identical screen element in accurate registration with the image record.

Additive color photographic reproduction thus may be provided by exposing a photoresponsive material, preferably a photosensitive silver halide emulsion, through an additive color screen having a plurality of filter media or screen element sets each of an individual additive color such as red, blue or green, and by viewing the resultant photographic image, preferably a silver image, subsequent to development of such image, through the same or a substantially identical screen element suitably registered.

In general, silver precipitating nuclei comprise a specific class of adjuncts well known in the art as adapted to effect catalytic reduction of solubilized silver halide specifically including heavy metals and heavy metal compounds such as the metals of Groups IB, IIB, IVA, VIA, and VIII and the reaction products of Groups IB, IIB, IVA, and VIII metals with elements of Group VIA, and may be effectively employed in the conventional concentrations traditionally employed in the art, preferably in a relatively low concentration in the order of about $1\text{–}25\times 10^{-6}$ moles/ft.^{2}.

Especially suitable as silver precipitating agents are those disclosed in U.S. Pat. No. 2,698,237 and specifically the metallic sulfides and selenides, there detailed, these terms being understood to include the selenosulfides, the polysulfides, and the polyselenides. Preferred in this group are the so-called "heavy metal sulfides." For best results it is preferred to employ sulfides whose solubility in an aqueous medium at approximately 20° C. vary between 10^{-23} and 10^{-30}, and especially the salts of zinc, copper, cadium and lead. Also particularly suitable as precipitating agents are heavy metals such as silver, gold, platinum and palladium and in this category the noble metals illustrated are preferred and are generally provided in the matrix as colloidal particles.

The supports or film bases may comprise any of the various types of transparent rigid or flexible supports, for example, glass, polymeric films of both the synthetic type and those derived from naturally occurring products, etc. Especially suitable materials, however, comprise flexible transparent synthetic polymers such as polymethacrylic acid, methyl and ethyl esters; vinyl chloride polymers; polyvinyl acetals; polyamides such as nylon; polyesters such as the polymeric films derived from ethylene glycol terephthalic acid; polymeric cellulose derivatives such as cellulose acetate, triacetate, nitrate, propionate, butyrate, acetate-butyrate, or acetate propionate; polycarbonates; polystyrenes; and the like.

In the preferred embodiment of the present invention, the processing composition will include an alkaline material, for example, sodium hydroxide, potassium hydroxide or sodium carbonate, or the like, and most preferably in a concentration providing a pH to the processing composition in excess of about 12. The processing composition may, where desired, contain the sole silver halide developing agent or agents employed, or a silver halide developing agent in addition to that disposed within the film unit.

It will be apparent that the relative proportions of the agents comprising the developing composition set forth herein may be altered to suit the requirements of the operator. Thus, it is within the scope of this invention to modify the herein described developing compositions by the situation of preservatives, alkalis, silver halide solvents, etc., other than those specifically mentioned. When desirable, it is also contemplated to include, in the developing composition, components such as restrainers, accelerators, etc. The concentration of such agents may be varied over a relatively wide range commensurate with the art.

Where desired conventional silver toning agent or agents may be disposed within the emulsion composition in a concentration effective to provide a positive image toned in accordance with the desires of the operator.

In addition to the described essential layers, it will be recognized that the film unit may also contain one or more subcoats or layers, which, in turn, may contain one or more additives such as plasticizers, intermediate essential layers for the purpose, for example, of enhancing adhesion, and that one or more of the described layers may comprise a composite of two or more strata which may be contiguous or separated from each other.

What is claimed is:

1. A microcapsule comprising a substantially uniform synthetic polymeric layer surrounding a silver halide grain, said polymeric layer having sufficient thickness to substantially prevent agglomeration of said grains.

2. A product as defined in claim **1** which includes a layer of gelatin intermediate said silver halide grain and said polymeric layer.

3. A product as defined in claim **1** wherein said silver halide is optically sensitized.

4. A product as defined in claim **1** wherein said silver halide is chemically sensitized.

5. A product as defined in claim **1** wherein said silver halide is panchromatically sensitized.

6. A product as defined in claim **1** wherein a color-providing substance is disposed in said polymeric layer.

7. A product as defined in claim **1** wherein said color providing substance is a dye developer.

8. A product as defined in claim **1** wherein said polymeric layer is prepared from an ethylenically unsaturated monomer.

9. A product as defined in claim **8** wherein said monomer is diacetone acrylamide.

10. A product as defined in claim **8** wherein said monomer is para-styrene sulfonamide.

11. A product as defined in claim **8** wherein said monomer is 1-vinylimidazole.

12. A product as defined in claim **8** wherein said monomer is sodium methacrylate.

13. A product as defined in claim **1** wherein said silver halide grain is 0.1 to 10 microns in diameter.

14. A product as defined in claim **13** wherein said silver halide is 1 micron in diameter.

15. A product as defined in claim 1 wherein said polymeric layer has a thickness ranging from 0.01 micron to 50 microns.

16. A product as defined in claim 15 wherein said polymeric layer has a thickness of about 0.5 micron.

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