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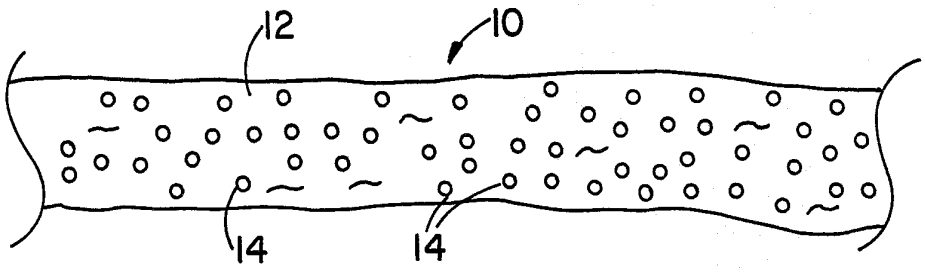

(57) Abstract

Light sensitive recording media such as a silver halide photographic emulsion (10) or an optical recording disk or plate (50a or 50b). The photographic emulsion comprises a colloid or gel (12), and a multitude of silver halide particles (14) dispersed in that colloid. Each of these particles (16) includes at least a core (16a) surrounded by a shell (16b), one of the core and shell includes a silver halide (20c), and the other of the core and shell includes a dielectric (20a). The optical recording disk or plate comprises a solid, light reflecting or light transmitting substrate (52), a colloid (56) applied onto the substrate, and a multitude of particles (54), dispersed in that colloid. Each of these particles includes a core surrounded by a shell, and at least one of the core and shell consists essentially of a metal (20b).

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LIGHT-SENSITIVE RECORDING MEDIA

BACKGROUND OF THE INVENTION

This invention generally relates to light sensitive recording media such as a light-sensitive silver-halide emulsion.

Light sensitive recording media are used in many different applications; and, for example, light sensitive silver halide emulsions are often used as photographic emulsions. The requirements for a commercially successful photographic silver halide emulsion are quite severe. Among other needs, such emulsions must be highly sensitive, have fine grain, sharpness and abundant latitude, and have sufficiently high optical density and sufficiently low fog density. In addition, the emulsions must be highly processable, easy to develop and to wash, but at the same time, the emulsions must be able to hold or fix an image and be highly resistant to various chemical agents. Further, it is important that the photographic and processing properties of the emulsions be stable over lengthy periods of time prior to use, that the quality of the emulsions be highly dependable and reproducible, and that the cost of producing the emulsions be low.

Numerous specific light sensitive emulsions are known that, to one degree or another, satisfy these requirements; and several known emulsions contain particles of silver halide dispersed as a colloid or in gel, with either the construction or properties of the particles being designed to improve or enhance the quality of the emulsions.

For instance, U.S. Patent 4,484,877 discloses a light sensitive silver halide emulsion which comprises silver

halide grains composed of a core and a shell. The core consists essentially of silver halide containing silver iodide, and the shell covers the core and consists essentially of silver bromide, silver chloride or silver chlorobromide. The shells have thicknesses from 0.01 to 0.1 micrometers.

U.S. Patent 4,728,602 discloses a light sensitive silver iodobromide emulsion containing silver iodobromide grains composed of a core and a shell. The core substantially comprises silver iodobromide containing at least about 5 mol percent of silver iodide; and the shell substantially comprises iodobromide having a lower silver iodide content than the silver iodobromide content of the core, or the shell substantially comprises silver bromide. The relative standard deviation of the silver iodide content of the individual grains of the emulsion is lower than about 20 percent.

U.S. Patent 4,639,410 discloses a silver halide color photographic light sensitive material including a core-shell type silver halide emulsion. The shells in the emulsion consist substantially of silver bromide, but they may contain silver iodide, silver chloride or silver iodochloride; and the core of each sphere is preferably silver iodobromide, although it may contain a silver halide other than silver iodobromide, such as silver chloride.

All of these emulsions, as well as most or even all other conventional silver halide photographic emulsions, contain relatively large amounts of silver and color films contain relatively large amounts of dyes and/or precursors of dyes. Because of the high cost of silver, it is very desirable to provide a silver halide photographic emulsion

containing less silver and less dyes and dye precursors than these conventional emulsions.

Light sensitive recording media are also used as optical disks or plates to record data. In such applications, a first light beam, referred to as a write beam, is passed over the recording medium in a given pattern to alter the morphology of the recording medium over a path or selected areas, which thereby represents stored data. After this change in morphology, the portions of the recording medium that were exposed to the write beam are very much less able to absorb light than are the portions of the recording medium that were not exposed to the write beam.

Another light beam, referred to as a read beam, of an intensity low enough so that it does not change the morphology of the recording medium, can then be passed over that medium. The read beam is reflected or transmitted when it strikes a portion of the recording medium previously exposed to the write beam, while the read beam is absorbed when it strikes a portion of the recording medium not previously exposed to the write beam. In this way, the read beam can be used to determine, or read, the data stored in the recording medium.

Heretofore, optical recording media were not made in a manner that takes advantage of the plasmon resonance effect, which is an effect that increases the intensity of certain electromagnetic fields. In accordance with the present invention, it has been determined that optical recording media can be made that effectively employ the plasmon resonance effect to significantly improve the sensitivity of the recording media to light and other electromagnetic radiation in the optical spectrum.

The plasmon resonance effect is shown by certain small particles and this effect includes the enhancement of electromagnetic fields at certain frequencies inside and near the particle, and the enhancement of the scattering, absorption and extinction of certain frequencies of light. The extinction is defined as the sum of the absorption and scattering. The extent to which a particle exhibits the plasmon resonance effect depends on a number of factors, including the size and shape of the particle, the material or materials from which the particle is made, and, in a particle made of a plurality of materials, the order, number, shape and dimensions of the materials from which the particle is made. For example, the plasmon resonance effect may be enhanced in particles that have sizes on the order of magnitude of tens of nanometers, and thus are commonly referred to as nanoparticles. Because of the above considerations, nanoparticles that consist of a number of materials are of special interest because they can be made to exhibit an enhanced plasmon resonance effect in a selected electromagnetic frequency range. One consequence of the frequency dependence of the plasmon resonance effect, and hence the frequency dependence of absorption and scattering, is that the particles are colored and consequently can be useful in color photography, color printing, color copying, etc. Any frequency at which a particle exhibits the plasmon resonance effect is referred to as a resonance frequency or a plasmon resonance frequency of the particle.

It has been recognized for many years that the plasmon resonance effect in small metal particles can be responsible for absorption and scattering phenomena of electromagnetic radiation.

Recently Kerker et al. in Phy. Rev. B, 26, 052-4062 (1982), have recognized that by designing composite nano particles comprised of metal and dielectric layers, the plasmon resonance can be greatly enhanced. This now makes it possible to use the effect in many processes from nonlinear optics to photochemical catalysis.

Consider, for example, a spherically shaped nano particle suspended in a medium, and consisting of a spherical core made of a dielectric material surrounded by a shell made of a metal. When electromagnetic radiation of a wavelength much longer than the size of the particle is incident on that particle, the radiation scattering coefficient, a_1, of the particle, including the effect thereon of the plasmon resonance effect, is given by the equation:

$$a_1 \cong 2/3\ i\alpha \left[\frac{(\varepsilon_2-\varepsilon_1)(\varepsilon_1-2\varepsilon_2) + q^3(2\varepsilon_2+\varepsilon_3)(\varepsilon_1-\varepsilon_2)}{(\varepsilon_2+2\varepsilon_3)(\varepsilon_1+2\varepsilon_2) - q^3(2\varepsilon_2-2\varepsilon_3)(\varepsilon_1-\varepsilon_2)} \right]$$

where, $q = a/b$

$$\alpha = 2\pi b/\lambda$$

i is the imaginary number, $\sqrt{-1}$,
a is the radius of the core of the particle,
b is the radius of the particle,
λ is the wavelength of the incident electromagnetic radiation,

ε_1 is the dielectric constant of the core,
ε_2 is the dielectric constant of the shell, and
ε_3 is the dielectric constant of the surrounding medium.

In the computations for this patent application, all the coefficients of any significant magnitude were included. As mentioned above, optical recording media have not previously been made so as to utilize fully the plasmon resonance effect. Pursuant to the present invention, by providing an optical recording medium with selected nano particles, the plasmon resonance effect can be effectively employed to enhance dramatically the photoprocesses that occur in the media.

In the present invention, particles are designed and made which use various features of the plasmon resonance effect to improve and enhance photographic emulsions and the photographic process. First, particles which enhance the fields are used to increase the intensity in the silver halide layer of the particles and hence to enhance the sensitivity of the silver halide to a given intensity of light incident upon the emulsion. Second, coated particles, which enhance the absorption and scattering of light with a much smaller amount of silver than required with solid silver particles, are used to decrease the amount of silver needed in photographic emulsions, prints and films made with silver. Third, coated particles, which enhance the frequency-dependent absorption and scattering, and hence are colored, are used to decrease the amount of dyes needed in photographic prints and films.

SUMMARY OF THE INVENTION

An object of this invention is to provide enhanced optical responses in light sensitive media.

Another object of this invention is to reduce the amount of silver needed in a light sensitive silver halide emulsion.

Another object of this invention is to reduce the amount of dyes and dye precursors needed in a light sensitive emulsion.

Another object of the present invention is to use silver halide coated dielectric particles in a light sensitive recording medium.

A further object of this invention is to use particles comprising silver halide coated dielectric cores in a light sensitive silver halide emulsion, where those particles also include a metal shell to enhance the sensitivity of the silver halide to light.

Still another object of the present invention is to utilize the plasmon resonance effect to enhance the sensitivity of an optical recording medium.

Another object of this invention is to provide an optical recording medium with a multitude of nanoparticles, each of which is made to exhibit the plasmon resonance effect, to enhance the photo processes that occur in the recording medium.

These and other objectives are attained with light sensitive recording media constructed according to the present invention. With a first embodiment, the medium is a light sensitive silver halide photographic emulsion, comprising a colloid or gel, and a multitude of silver halide particles dispersed in that colloid. Each of these particles includes at least a core surrounded by a shell, one of the core and shell includes silver halide, and the other of the core and shell includes a dielectric. Preferably, one of the

core and shell consists essentially of silver halide, the other of the core and shell consists essentially of the dielectric material, and this dielectric material is substantially free of silver.

With a second embodiment, the recording medium is a light sensitive optical recording disk or plate, comprising a solid, light reflecting or light transmitting substrate, a colloid applied onto the substrate, and a multitude of particles dispersed in that colloid. Each of these particles includes a core surrounded by a shell, and at least one of the core and shell consists essentially of a metal. Preferably, the other of the core and shell consists essentially of a dielectric; and more specifically, the core of each of these preferred particles consists essentially of a dielectric material, and the shell of each of these particles consists of a metal.

Further benefits and advantages of the invention will become apparent from a consideration of the following detailed description given with reference to the accompanying drawings, which specify and show preferred embodiments of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 diagrammatically illustrates a photographic emulsion according to the present invention.

Figures 2-5 and 5A, which are not drawn to scale, show particles that may be used in the emulsion of Figure 1.

Figures 6-11 show the light absorption efficiency of solid silver spheres and silver coated silica spheres at wavelengths of 355nm, 382nm, 414nm, 497nm, 621nm and 828nm respectively.

Figures 11a-11f show similar wavelength dependent spectra observed in the scattering and extinction spectra.

Figures 12 and 13 show optical recording media also according to the present invention.

Figures 14-27, which are not drawn to scale, show various particles that may be used in the optical recording media of Figures 12 and 13.

Figures 28-36 outline several processes that may be used to form the particles shown in Figures 2-5 and 14-27.

Figure 37 is a transmission electron micrograph of silver-coated silver bromide nanoparticles.

Figure 38 is a transmission electron micrograph of silver coated silver bromide nanoparticle treated with ammonia.

Figure 39 shows various optical extinction spectra of silver coated silver bromide nanoparticles. (a) to (d) are spectra of illuminated solutions of Ag, Br, and EDTA with specific concentrations. In going from a to d the illumination time increases. (e) typical spectrum observed after the addition of ammonia to any of the above solutions either untreated or treated with ammonia, which were measured shortly after light exposure at different illumination times.

Figure 40 shows computed extinction efficiencies for silver coated silver bromide nanoparticles. The diameter of the core particle is 20 nm and the thickness of the silver coats are indicated in nm. The spectrum marked solid is that of a homogeneous 20 nm diameter silver sphere.

Figure 41 is an optical extinction spectra of a measured silver coated silver bromide nanoparticle and two computed spectra. The measured spectrum lies between the two computed spectra. In the upper curve all of the silver is assumed to come from the reduction of AgBr at the particle surface.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Figure 1 illustrates a first light sensitive recording medium 10 according to the present invention. This medium is a light sensitive silver halide photographic emulsion, comprising a colloid or gel 12, and a multitude of silver halide particles 14 dispersed in that colloid. Figures 2-5 show four types of particles, referenced at 16, 20 and 22, and 24, respectively, that may be used in emulsion 10. Each of these particles includes at least a core surrounded by a shell; and in each of these particles, one of the core and shell includes silver halide, and the other of the core and shell includes a dielectric material. Preferably, the one of the core and shell consists essentially of silver halide, the other of the core and shell consists essentially of a dielectric material, and moreover, this dielectric material is substantially free of silver. For example, particle 16 consists of core 16a and shell 16b, the core consists essentially of a dielectric material.

The term "dielectric" material or core as used herein, refers to a material which is a non-conductor or a semi conductor. The conductivity of the material may range from 0, but preferably as low as 10^{-40} to 10^{6} mhos. In a preferred embodiment, the conductivity ranges from 10^{-40} to 10^{5} mhos. In a most preferred embodiment, the conductivity ranges from 10^{-30} to 10^{4} mhos. Examples of dielectric material includes glass, silica, cadmium sulfide, gallium arsenide, polydiacetylene, lead sulfide, titanium dioxide, polymethylacrylate (PMMA), silver bromide, carbon fibers, copper sulfide, silver sulfide, and the like.

The shell consists essentially of silver halide. Further, with this particle, shell 16b is disposed immediately over and substantially completely covers core 16a.

In particle 20, a metal coating such as silver, copper, aluminum, gold or palladium is disposed between the dielectric core and the silver halide shell to increase the sensitivity of the silver halide to light. This increased sensitivity is caused by the plasmon resonance effect produced by the metal coating. More specifically, particle 20 consists of dielectric core 20a, metal coating 20b disposed immediately over and covering that core, and a layer of silver halide 20c disposed immediately over and covering layer 20b.

If it is desired to use a layer of metal between the dielectric core and the silver halide shell, it may be preferred, as is done in particle 22, to separate or space the metal from the silver halide to prevent interference in the development of the latent image. In particular, particle 22 consists of dielectric core 22a, a layer of silver 22b disposed immediately over and covering core 22a, a layer of dielectric material 22c such as a polymer, disposed immediately over and substantially covering the silver layer, and shell 22d formed of silver halide disposed immediately over and substantially completely covering layer 22c.

It is not necessary to the present invention in its broadest sense that the dielectric material and the silver halide of the particles used in emulsion 10 form the core and shell of the particle, respectively, and Figure 5 shows a fourth particle 24 that may be used in emulsion 10 and which comprises core 24a comprised of silver halide and shell 24b

comprised of a dielectric material. With the particle 24 shown in Figure 5, it is also desirable for some emulsions to provide the particle with a layer of metal (not shown) to enhance the sensitivity of the silver halide of the particle; and if this is done, to further provide the particle with a still further coating of a dielectric material (also not shown) between that metal layer and the silver halide core of the particle to prevent interference in the development of the latent image.

Coated nanoparticles can be designed and made which use features of the plasmon resonance effect to improve photographic emulsions. Plasmon resonances of nanoparticles can be used to improve both the recording (writing) of an image and the regeneration (reading) of the image. In the next two paragraphs the ways in which plasmon resonant particles can be used in photography are explained briefly. A more detailed discussion follows.

When light from a scene illuminates a typical silver halide photographic emulsion it generates very small silver particles in the silver halide grains. The pattern of small silver particles form a latent image. It is often desirable to increase the sensitivity of an emulsion to light, i.e, to make an emulsion in which a latent image can be formed with less light. By replacing the solid silver halide particles in an emulsion with coated nanoparticles where there is a silver layer underneath the silver halide layer, the sensitivity of the silver halide to light can be enhanced. A layered particle having the appropriate thicknesses of dielectric, silver, polymer, and silver halide can have a plasmon resonant enhancement of the light in the silver halide layer. The enhanced optical intensity induces

the formation of more latent image centers in a plasmon resonant particle than in solid silver halide particles illuminated with the same light intensity. Hence, the plasmon resonance effect can be used to increase the sensitivity of a given amount of silver halide to light, and can improve the recording of an image.

After a typical silver halide emulsion is exposed, the small clusters of silver in the latent image act as nucleation centers for the reduction of the rest of the silver in the grain and/or silver from solution. In black and white photography, the absorption and scattering by the reduced silver is responsible for the image observed when illuminated with light. In color photography, the reduction of the silver is coupled to the generation of dyes. When illuminated with white light, the dyes in the emulsion absorb certain wavelengths and consequently the film transmits and/or reflects the complementary wavelengths. The solid silver particles generated after development in black and white photographs can be replaced with silver coated nanoparticles that use less silver to absorb and scatter more light. The same volume of silver can be much more absorbing when it is coated at the right thickness onto the surface of a dielectric nanoparticle. So it is possible to reduce the amount of silver required in the photograph. Also, the dyes generated during development in a color photograph can be replaced with plasmon resonant silver coated nanoparticles that, when illuminated with white light, reflect and transmit colored light. By replacing expensive dyes with coated nanoparticles, the cost of film can be reduced. So, plasmon resonant coated nanoparticles can be used to reduce the cost of both color and black and white photographs.

Particles must be designed to enhance those aspects of plasmon resonance required for each particular purpose. The next five paragraphs state in more detail the aspects of plasmon resonance used in the coated nanoparticles, how these aspects are used in light recording devices, and the advantages of using particles having such resonances. Improvements in recording the image are discussed in (1). Improvements in reading or regenerating the image are discussed in (2)-(4). Improved particles to absorb stray light are discussed in (5). Emulsions combining some of the particles are discussed in (6).

(1) Coated nanoparticles having a plasmon resonant enhancement of the light in the silver halide layer of an emulsion can be used to increase the sensitivity of a given amount of silver halide to a given incident intensity of light. Such coated particles can be of use in recording an image in either color or black and white photography. One type of appropriate nanoparticle has a dielectric core, a first coat of silver, a second coat of a polymer, and a third coat of a silver halide. The thicknesses of the core and coats must be chosen to enhance the light intensity at the appropriate wavelength range in the silver halide layer. An advantage of using these particles is an increased sensitivity of the emulsion and a decreased requirement for silver.

(2) Coated particles having a plasmon resonant enhancement of the absorption of light can be used as the absorbing regions in black and white films. Prior to development, the coat of a particle is a layer of silver halide. During development, the silver halide is reduced to a coat of silver that has the correct thickness for a plasmon

resonance. Such nanoparticles require a relatively small amount of silver to scatter and absorb light as efficiently as do solid silver particles. These particles can be used to decrease the amount of silver needed in photographic emulsions, prints and films. For black and white photography, a group of particles having plasmon resonances at different frequencies should be combined in the emulsion. An advantage of using such particles is that less silver is required. Also, since a smaller particle can have a significant absorption and a thinner layer of particles is required, there can be some increase in the resolution of the film.

(3) Coated particles, which enhance the frequency-dependent scattering and absorption (i.e. the extinction), and hence transmit light that is colored, can be used to decrease the amount of dyes needed in photographic films and slides. For applications where the light is transmitted through the emulsion, colored light can be generated using either scattering or absorption or any combination. The particles in a color photographic film or slide that go into the layer whose transmitted light is to appear red (for example), are particles that, when developed, absorb and scatter blue and yellow light, while transmitting the red. The particles, before development, have a layer of silver halide that has a thickness such that, when developed, the resulting thickness of the silver coat and the thickness of the other layers result in a particle that absorbs and scatters as desired. The advantage of using such particles is that they will replace dyes which are expensive.

(4) Coated nanoparticles having a plasmon resonant light scattering spectrum can be used to decrease the amount

of dyes needed in color prints since the light reflected from these particles is colored. These particles should have a relatively large plasmon enhancement of the frequency dependent scattering and a relatively smaller enhancement of the frequency dependent absorption. Relatively large nanoparticles, typically having diameters in the range of 60 to 200 nanometers, should be used since their ratio of scattering to absorption is larger. The particles, before development, have a layer of silver halide that has a thickness such that, when developed, the resulting thickness of the silver coat and the thicknesses of the other layers result in a particle that scatters as desired. The particles in a photographic print placed in the layer of the emulsion that is to appear red (for example), are particles that, when developed scatter red light. Such particles can also be used for color copiers and colored inks.

(5) Coated nanoparticles having a plasmon resonant enhancement of the absorption of light can be used to decrease the amount of silver needed in the absorbing layers of photographic emulsions, prints and films. These particles should have a more enhanced absorption than scattering and hence are particularly small, in the range 5 to 60 nanometers. Such particles can be used to replace the Cary-Lea sols now used to absorb stray light in both black and white and in color films. They can also be used as the absorbing regions in black and white films. An advantage of using such particles is that less silver is required.

(6) Emulsions in which combinations of the above particles and effects, and particles in which the above advantages and effects are combined are also useful. An example of a particle in which (1) and (2) is employed is a

particle having a dielectric core, a silver coat, a polymer coat and then a silver halide coat. The plasmon resonance enhances the fields in the silver halide layer. When the silver halide is developed to silver, the plasmon resonances in the scattering and absorption by the particle provide the advantages described in (2) above. The particles described in (5) can also be used in the same emulsion.

To achieve the advantages described in (2), (3) and (4) above, it is preferable that the silver halide coat is reduced to a relatively smooth silver coat. With reference to Figure 5A, one way to force the reduced silver to form a smooth coat on the dielectric is to precoat the original particles 16 with a polymer 16C that is porous enough to allow ions to pass. For example, the coat 16C can prevent Ag+ ions from migrating to sites on the surface next to the polymer. The polymer 16C encourages the Ag+ to go to the positions where growth is desired. Such a polymer coat can be made in a manner similar to that specified herein.

Also, independently of the photographic process, this is another way to make silver coated particles.

Figures 2-5 are only representative of nanoparticles that may be used in the practice of the present invention, and in particular, only illustrate the general relationship between the cores and the shells of the shown particles. In any nanoparticle used in this invention, the particle and the core thereof may have any suitable shapes, and specifically, the particles and the cores may have shapes other than spherical. For instance, the particles and the cores may be cylindrical or ellipsoidal, have a thread-like shape, or be crystalline shaped. The actual crystal form of

the core may be any suitable form; and, for example, these cores may be:

Tetragonal crystal forms,
Orthorhombic crystal forms,
Monoclinic crystal forms,
Triclinic crystal forms,
Isometric crystal forms,
Hexagonal crystal forms.

Furthermore, the emulsion 10 may include a mixture of particles of different sizes and shapes, and the emulsion may include silver halide particles of the type conventionally used in photographic emulsions. Still further, any suitable dielectric material may be used in the particles employed in this invention; and, in particular, the dielectric material may be linear or non-linear. In addition, as the term is used herein, "metal" includes any material having a negative dielectric constant, and so can include superconductors, conducting polymers, and materials with an anomalous dispersion of carrier electrons, and heavily doped semiconductors where free carrier motion dominates the dielectric function.

The development of emulsion 10 is based, in part, on the fact that at various wavelengths of light, silver coated dielectric spheres may be made that absorb and scatter light at a much higher efficiency than do solid silver spheres of the same size, and this fact is demonstrated in Figures 6-11.

Figures 6-11 show the light absorption efficiency of solid silver spheres and silver coated silica spheres at various wavelengths of light; and in particular, at wavelengths of 355nm, 382nm, 414nm, 497nm, 621nm and 828nm

respectively. The efficiencies were computed using a procedure described by Toon and Ackerman, Applied Optics, 1981. The light absorption efficiency, Q, of the particles is plotted along the vertical axis of each Figure; and a size parameter, x, equal to $2\pi r/\lambda$, where r is the radius of the particle and λ is the wavelength of interest for the respective Figure, is plotted along the horizontal axis of each Figure. Curves 32a, 34a, 36a, 40a, 42a, and 44a of Figures 6-11 indicate the light absorption efficiencies of solid silver spheres. Curves 32b-d, 34b-f, 36b-e, 40b-g, 42b-f and 44b-e indicate the light absorption efficiencies of silver coated silica spheres; and in particular, each of these curves represent a constant value (shown in parenthesis) for the ratio of the diameter of the internal silica core to the diameter of the whole coated sphere.

Thus, for instance, the values determined from curve 32b of Figure 6 are for silver coated silica spheres comprising an internal silica core having a diameter that is half the diameter of the whole coated sphere, and the absorption values determined from curve 36d of Figure 8 are for silver coated silica spheres comprising an internal silica core having a diameter that is 0.6 times the diameter of the whole coated sphere.

For example, Figure 6 shows that at a wavelength of 355nm, for a coated sphere having an outside diameter of about 113nm (x=1.0) and including an internal silica core having a diameter half that of the whole coated sphere, the absorption efficiency of that coated sphere is about 0.93. Similarly, Figure 9 shows that at a wavelength of 497nm, for a coated sphere having an outside diameter of about 79nm (x=0.5) and including an internal silica core having a

diameter that is 0.7 times the diameter of the outside diameter of the whole coated sphere, the absorption efficiency of that coated sphere is about 5.2.

Figures 10 and 11 show that, for spheres having outside diameters between 1 and 100 nanometers and for light in the wavelength range of 621 to 828 nanometers, spherical particles comprised of silica cores coated with an appropriate thickness of silver absorb many times more light than do solid silver spheres of the same diameter. For example, Figure 10 shows that at a wavelength of 621nm, first, the absorption efficiency of a solid silver sphere having an outside diameter of about 198 nanometers (x= 1.0) is about 0.3, and second, a coated sphere having the same outside diameter and an internal silica core having a diameter 0.9 times the diameter of the whole coated sphere, has an absorption efficiency of about 2.0, which is more than six times the absorption efficiency of the solid silver sphere of the same size. Figure 11 shows that at a wavelength of 828nm, first, the absorption efficiency of a solid silver sphere having an outside diameter of about 132 nanometers (x= 0.5) is about 0.2, and second, a coated sphere having the same outside diameter and an internal silica core having a diameter 0.9 times the diameter of the whole coated sphere, has an absorption efficiency of about 5.8, which is about twenty-nine times the absorption efficiency of the solid silver sphere of the same size.

Figures 6 and 7 show that, in the near ultraviolet wavelengths (at wavelengths of 355 and 382 nanometers), the solid silver spheres absorb more light than do the silver coated silica cores, at least with spheres between 1 and 100 nanometers in diameter. However, with some of the larger

spheres, some of the silver coated particles absorb as much or more light in the ultraviolet wavelengths than do the solid silver spheres. Also, with some of the larger sizes of the spheres, the silver coated particles and the solid silver spheres have similar absorption efficiencies. The absorption cross section of a sphere is the absorption efficiency of that sphere multiplied by πr^2, where r is the radius of the sphere.

Similar wavelength dependent spectra are also observed in the scattering and extinction spectra. With smaller sized spheres, say 10 nm, the absorption is greater than the scattering and with larger sized coated spheres, say 200 nm, the scattering can be greater than the absorption when there is an appropriate thickness of core to coat. Figures 11a and 11b show: (1) λ dependent spectra, and (2) $Q_s \ll Q_a$ when the particles are small. Figure 11c shows $Q_s \sim Q_a$ when diameter $\sim$ 100nm. Figures 11d and 11e show C_{abs}/Vol for coated sphere $\gg$ than for the solid sphere especially when $\lambda > 500$ nm.

Because the light absorption profile of each coated particle is a function of the diameter of the internal silica core, the thickness of the coating on that core, and the wavelength of the light incident on the particle, a desired light absorption profile can be obtained for a film emulsion by combining appropriate amounts of different sizes of coated particles, which in certain instances might be in combination with uncoated particles. To avoid repeating the phrase "absorption, scattering or extinction profile" too many times, in the following description of the synthesis of a profile we refer to it only as an absorption profile although

the method works just as well for scattering or extinction spectra.

One way to synthesize an absorption profile is to take a multitude of coated particles that absorb light over a wavelength range of interest, to separate that multitude of particles into groups according to the sizes or coating thicknesses of the particles, and then to form a mixture of particles from these groups, with the amount or proportion of particles taken from each group weighted so that the resulting mixture has the desired absorption profile.

For instance, assume that a particular absorption profile, $D(\lambda)$, is desired over the wavelength range of visible light, and that the initial multitude of coated particles absorbs light over this wavelength range, with these particles being dispersed in water and with the dielectric cores of the coated particles having uniform diameters of approximately 30nm. The coated particles can be grouped according to their coating thicknesses; and, for example, the particles can be separated into 14 groups having coating thicknesses of 1.5nm, 1.75nm, 2.0nm, 2.25nm, 2.5nm, 3.0nm, 3.5nm, 4.0nm, 4.5nm, 5.0nm, 6.0nm, 7.0nm, 9.0nm, and 12.0nm respectively. The light absorption of each group of particles can be expressed as a function of the wavelength of light incident on the particles; and, more generally, the absorption of the ith group of particles can be expressed as $A_i(\lambda)$, where λ is the wavelength of the light incident on the particles.

The actual absorption profile, $T(\lambda)$, of a mixture containing N groups of particles can be expressed as follows:

$$T(\lambda) = \sum_{i=1}^{N} a_i A_i(\lambda)$$

where a_i is the proportion of the ith group of particles in the mixture. To achieve the desired absorption profile, the a_i (that is a_1, $a_2 \cdots a_N$) are chosen so that $T(\lambda)$ is equal to or closely approximates $D(\lambda)$. Any suitable procedure may be used to determine or to estimate the a_i. According to one very well known technique, the a_i can be estimated to minimize the sum, or the integral, C, of the squares of the difference between $D(\lambda)$ and $T(\lambda)$. According to this technique,

$$C = \int (D(\lambda) - T(\lambda))^2 d\lambda$$

The set of a_i that minimizes this difference can be found or suitably estimated by many known methods such as by a gradient search procedure (for example, as disclosed in "Practical Methods of Optimization," by Fletcher (1981)). Numerous computer programs are also known and may be used to estimate or determine the set of a_i that minimizes the difference between $D(\lambda)$ and $T(\lambda)$.

The mixture of coated particles needed to achieve the desired absorption profile is then made by combining the N groups of particles, each weighted by the associated a_i.

Another way to obtain a film emulsion with a desired light absorption profile is to form the film emulsion from a series of layers, with the layers containing different particle sizes or types.

Figures 12 and 13 illustrate two embodiments of a second type of light sensitive recording medium, generally referenced at 50a and 50b respectively, and also according to the present invention. This medium is a light sensitive optical recording disk or plate, comprising a solid, light reflecting or light transmitting substrate 52 and a multitude

of particles 54 carried by that substrate. The particles 54 may be carried directly by substrate 52, as shown in Figure 12; or, as illustrated in Figure 13, the particles 54 may be dispersed in a colloid or gel 56 that is applied onto the substrate. Each of the particles 54 includes a core surrounded by a shell, and at least one of the core and shell consists essentially of a metal. Preferably, the other of the core and shell consists essentially of a dielectric material; and more specifically, preferably the core of each of these particles consists essentially of a dielectric material, and the shell of each particle consists of a metal.

To record data in medium 50a or 50b, a light beam, referred to as a write beam, of sufficient intensity to change the morphology of the coated particles 54, such as by melting the silver coating or the dielectric core, is passed over the recording medium in a given pattern to change the morphology of the particles over a path or selected areas, to thereby represent stored data. Because of this change in morphology, the portions of the medium that were exposed to the write beam are very much less able to absorb light than are the portions of the medium that were not exposed to the write beam.

Another light beam, referred to as a read beam, of an intensity low enough so that it does not change the morphology of the particles 54, can then be passed over the recording medium. The read beam is reflected or transmitted when it strikes a portion of the recording medium previously exposed to the write beam, while the read beam is absorbed when it strikes a portion of the recording medium not previously exposed to the write beam. In this way, the read

beam can be used to determine, or read, the data stored in the recording medium.

As will be appreciated by those of ordinary skill in the art, in any nanoparticle used in this invention, the particle and the core thereof may have any suitable shapes, and specifically, the particles and the cores may be cylindrical or ellipsoidal, have a thread-like shape, or be crystalline shaped. Also, the write beam may be used to change these particles in various specific ways to produce the desired results. Moreover, with the particles 54 that include dielectric material, any suitable dielectric material may be used, and in particular, that dielectric may be a linear or a non-linear material. In addition, as the term is used herein, "metal" includes any material having a negative dielectric constant, and so can include superconductors, conducting polymers, materials with an anomalous dispersion of carrier electrons, and heavily doped semiconductors where free motion dominates the dielectric function.

The following considerations are helpful in forming and selecting suitable or preferred particles for use in the recording media illustrated in Figures 12 and 13.

i) at light wavelengths at which the plasmon resonance effect shown by certain particles is significant (referred to as resonance frequencies), the electromagnetic fields around the particles are enhanced,

ii) the electromagnetic fields, or the heat caused by the absorption of those fields, in and around certain particles can cause those particles to change so that they absorb or scatter less light,

iii) the plasmon resonance effect exhibited by small metal-dielectric layered particles is dependent on the

size and dielectric constants of those layers, and particles can be made so that only a comparatively small change in the physical structures of the particles results in significant changes in the way in which, or the extent to which, the particles absorb or scatter light, and

iv) magnetic materials become non magnetic when heated to or above the Curie points of the materials.

Based on the above facts, particles 54 for recording media 50a and 50b can be made so that, on the one hand, a write beam can be used to change significantly the ability of the particles to absorb or scatter light, but on the other hand, the ability of the particles to absorb or scatter light will not change significantly in the absence of the write beam.

For example, with a first general class of particles, the particle may comprise a core and first and second layers of materials over that core, with each of these layers comprised of a material different than the material of the other layer, and the write beam may cause these two materials to react with each other to form a third material having a dielectric constant different than the dielectric constants of the original materials of the particles. Figure 14 shows a particle 60 comprising core 60a, first layer 60b and second layer 60c, and one of these layers 60b and 60c is a dielectric, such as an oxide, and the other of these layers 60b and 60c is a metal, such as silver. The energy of the write beam may cause layers 60b and 60c to react with each other to form a dielectric, silver oxide. The altered particle is shown at 62 in Figure 15, and this particle consists of core 62a and the formed dielectric layer 62b. Because the formed particle 62 does not have a layer of

metal, that particle does not exhibit the plasmon resonance effect; and, consequently, the light absorption and reflection characteristics of particle 62 are significantly different than the light absorption and reflection characteristics, respectively, of particle 60.

As another example, Figure 16 shows a particle 64 comprised of a core 64a and first and second layers 64b and 64c, and each of these latter two layers is comprised of a respective one type of dielectric material. The write beam may cause these dielectric materials to react with each other to form a third dielectric material having a dielectric constant different than the dielectric constants of the materials used to form layers 64b and 64c. This altered particle is shown at 66 in Figure 17, and the particle consists of core 66a and the formed dielectric material 66b.

With a second general class of particles, represented by particle 70 of Figure 18, the particle includes a core 70a and one or more outside layers 70b and 70c, with one of these layers being comprised of a monomer. The write beam causes the monomer layer to polymerize, changing that layer to a solid that has a dielectric constant different than the dielectric constant of the monomer. The formed particle is shown at 72 in Figure 19; and the particle comprises core 72a, first layer 72b and polymer layer 72c. To make particle 70 itself, it may be preferred to form or apply the layer of monomer 70c onto the core 70a of the particle at low temperatures.

With a third general class of particles, the write beam is used to change the shape of the particle and thereby change its light absorption or reflection characteristics. For example, Figure 20 shows a non-spherical particle 74

comprised of a core 74a and first and second shells 74b and 74c. The energy from the write beam that is absorbed by the particle 74 causes shell 74c to melt, and then the surface tension between the remaining shell 74b and the medium in which the particle is suspended, causes the shell and the core to become spherical. The formed particle is shown at 76 in Figure 21, and the particle comprises core 76a and shell 76b. The plasmon resonance effect exhibited by particle 76 is different than the plasmon resonance effect exhibited by particle 74, and thus the light absorption and light reflection characteristics of the former particle are different than those of the latter particle.

With a fourth general class of particles, the write beam is used to melt the outside layer of the particle, and this melted material then mixes with and changes the dielectric constant of the medium surrounding the particle or of the substrate on which the particle is carried. For instance, Figure 22 shows particle 80 comprising core 80a and shells 80b and 80c, dispersed in a medium 82. In use, the write beam melts shell 80c, and the material from the shell mixes with medium 82. The result of this process is illustrated in Figure 23, which shows particle 84, comprising core 84a and shell 84b, dispersed in a medium 86. The plasmon resonance effect exhibited by particle 84 in medium 86 is different than the plasmon resonance effect shown by particle 80 in medium 82. As a result, the light absorption and reflection characteristics of particle 84 in medium 86 are different, respectively, than the light absorption and reflection characteristics of particle 80 in medium 82.

With a fifth class of particles, the write beam is used to melt the outside layer of the particle and to change

the structure of an inner layer of the particle, for example, from amorphous to crystalline or from crystalline to amorphous. Figure 24 shows a particle 90 of this type, and comprising core 90a and shells 90b and 90c. The write beam melts outside shell 90c and changes the structure of inside shell 90b, producing a particle shown at 92 in Figure 25, comprising core 92a and shell 92b. The plasmon resonance effect produced by particle 92 is different than that shown by particle 90, and consequently, the light absorption and reflection characteristics of these two particles differ.

A sixth class of particles includes a layer of a magnetized material, and the energy of the write beam is used to raise the temperature of this material above the curie point of that material, where it is no longer magnetic. For example, Figure 26 shows a particle 94 of this general type, and including core 94a comprised of a magnetic material, and shell 94b comprised of a metal. In operation, the write beam raises the temperature of particle 94 to a level above the curie point of core 94a, so that the core is no longer magnetic. As another example, Figure 27 shows a particle 96 that includes core 96a and two shells 96b and 96c. Core 96a consists of a dielectric material, shell 96b is a metal, and shell 96c is a magnetic material. In recording media 50a or 50b, a write beam is used to raise the temperature of shell 96c to a point above its curie point so that the shell ceases to be magnetic.

As will be understood by those of ordinary skill in the art, reversible procedures may be used to alter the particles of recording media 50a and 50b, producing a write-many read-many system. For example, the coated spheres could be used to enhance the fields only to increase the

temperature to the curie point (as low as 150°C for some magnetic materials used in optical discs) and a magnetic field can be used to set the orientation of the magnetic domains. This procedure could be reversible.

The above-discussed changes, and other similar changes, produced by a write beam will alter the extent to which light is absorbed by or transmitted through a recording medium. The particles in recording media 50a or 50b may be either located on a surface, such as in an optical disk, or dispersed throughout a volume. When the particles are dispersed throughout a volume, it may be preferred to provide that volume with a low density of such particles. In addition, layered particles in which a metal is reacted with a dielectric to form another dielectric, such as particle 60, may be particularly useful for forming volume phase holograms. Particles in which the polymerization of a monomer is initiated by the write beam may also be particularly useful for forming volume phase holograms.

Sensitizers used with conventional photographic emulsions may be used with the coated spheres employed in the photographic emulsion of the present invention, either on the outside of or on the inside of the silver halide layer.

Also, the silver-halide emulsion of this invention may be treated by many known chemical sensitization methods. For example, the emulsion may be treated by a sulfur sensitization method using a sulfur-containing compound capable of reacting with active gelatin and silver (e.g., a thiosulfate, a thiourea, a mercapto compound or a rhodamine); a reduction sensitization method using a reducing material (e.g., a stannous salt, an amine, a hydrazine derivative, formamidinesulfinic acid or a silane compound); or a noble

metal sensitization method using a noble metal compound (e.g. a gold complex salt, complex salts of metals belonging to group VIII of the periodic table, such as Pt, Ir or Pd).

As a protective colloid for use in the preparation of the silver halide emulsions of this invention, gelatin may be used but other hydrophilic colloids may be used, such as, for example, gelatin derivatives; graft polymers of gelatin and other polymers; proteins such as albumin and casein; cellulose derivatives such as hydroxyethyl cellulose, carboxymethyl cellulose and cellulose sulfuric acid esters; sugar derivatives such as sodium alginate and starch derivatives; and various synthetic hydrophilic polymers or copolymers such as polyvinyl alcohol, partial acetal of polyvinyl alcohol, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinyl imidazole and polyvinyl pyrazole.

As gelatin, lime-processed gelatin as well as acid-processed gelatin, and enzyme-processed gelatin may be used, as well as the hydrolyzed products and enzyme-decomposition products of gelatin.

Various compounds can be added to the silver halide photographic emulsions of this invention for stabilizing the photographic properties of the emulsions and for preventing the formation of fog during the production, storage, or processing of the photographic materials containing the silver halide emulsions. Examples of antifoggants and stabilizers include benzothiazolium salts; nitroimidazoles; nitrobenzimidazoles; cholorbenzimidazoles; bromobenzimidazoles, mercaptothiazoles; mercaptothiadiazoles; aminotraizoles; benzotraizoles; nitrobenzotriazoles; mercaptotetrazoles; mercaptopyrimidines; mercaptotriazines;

thioketo compounds such as oxazolinethione; azaindenes such as triazaindenes, tetraazaindenes, pentaazaindens; benzenethio-sulfonic acid; benzenesulfinic acid; and benzenesulfonic acid amide.

The silver halide photographic emulsions of this invention may further contain polyalkylene oxides or the derivatives thereof, such as the ethers, esters, amines, thioether compounds; thiomorpholines; quaternary ammonium salt compounds; urethane derivatives; urea derivatives; imidazole derivatives; and 3-phyrazolidone derivatives for increasing sensitivity and contrast or for accelerating the development of the photographic materials containing the silver halide emulsions.

The silver halide photographic emulsions of this invention may be spectrally sensitized by methine dyes, including cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyannine dyes, styrl dyes, and hemioxonol dyes. Particularly useful dyes are cyanine dyes, merocyanine dyes, and complex merocyanine dyes. For these dyes, conventional cyanine dye nuclei such as basic heterocyclic nuclei can be used, including a pyrroline nucleus, an oxazoline nucleus, a thiazoline nucleus, a pyrrole nucleus, an oxazole nucleus, a tetrazole nucleus and a pyridine nucleus. The foregoing nuclei may be fused to aromatic hydrocarbon rings, such as an indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxazole nucleus, a napththoxazole nucleus, a benzoselenazole nucleus, a benzimidazole nucleus and a quinoline nucleus.

A 5- or 6-membered heterocyclic nucleus having a ketomethylene structure such as a pyrazoline-5-one nucleus, a

thiohydantoin nucleus, a 2-thioxazolidine-2,4-dione nucleus, a thiazolidine-2,4-dione nucleus, rhodanine nucleus or thiobarbituric acid nucleus can be used as a nucleus for the merocyanine dyes or complex merocyanine dyes.

These sensitizing dyes may be used alone or in combination, and a combination of sensitizing dyes is frequently used for supersensitization.

The silver halide photographic emulsions of this invention may further contain dyes having a spectral sensitizing action or materials which do not substantially absorb visible light but which exhibit a supersensitizing effect when used together with the foregoing sensitizing dyes.

The photographic materials using the silver halide emulsions of this invention may contain water-soluble dyes as filter dyes or for various purposes such as irradiation prevention. Examples of such dyes are oxonal dyes, hemioxonol dyes, styryl dyes, merocyanine dyes, cyanine dyes, and azo dyes. Among these dyes, oxonol dyes, hemioxonol dyes and merocyanine dyes are useful.

The photographic materials containing the silver halide emulsions of this invention may contain stilbene series, triazine series, oxazole series, or cumarine series whitening agents in the silver halide emulsion layers and other hydrophilic colloid layers. These materials may be water soluble or water insoluble and in the latter case, they may be used as dispersions.

Known fading preventing agents may be used along with color image stabilizers in this invention, alone or in combination. The photographic materials using the silver halide emulsions of this invention may further contain

hydroquinone derivatives, aminophenol derivatives, gallic acid derivatives and ascorbic acid derivatives, as color fogging preventing agents.

The silver halide photographic emulsions of this invention can be used for both black and white photographic materials and multilayer multicolor photographic materials. A multilayer natural color photographic material ordinarily has at least one red-sensitive layer, at least one green-sensitive layer and at least one blue-sensitive silver halide emulsion layer on a support. The red-sensitive layer usually contains a cyan dye-forming coupler, the green-sensitive layer contains a magenta dye-forming coupler, and the blue-sensitive layer contains a yellow dye-forming coupler, but if desired, other combinations may be employed.

As the yellow coloring couplers, known closed chain ketomethylenic couplers can be used, including benzoylacetoanilide series compound and pivaloylacetoanilide series compounds. As magenta coloring couplers, pyrazolone series compounds, indazolone series compounds and cyanoacetyl compounds can be used and pyrazolone series compounds are particularly useful. As cyan coloring couplers, phenolic compounds and naphtholic compounds and couplers having a ureido group can be used. DIR couplers (development inhibitor releasing couplers) can also be used in this invention.

The photographic materials using the silver halide emulsions of this invention may contain compounds capable of releasing development inhibitors (apart from DIR couplers) with the progress of the development. Also, couplers capable of releasing development accelerators or fogging agents with the process of development can be used in this invention.

The photographic materials containing the silver halide emulsions of this invention may contain ultraviolet absorbents in the hydrophilic colloid layers, such as aryl group-substituted benzotriazole compounds. 4-thiazolidone compounds; benzophenone compounds, cinnamic acid ester compounds, butadiene compounds and benzoxydol compounds. In addition, ultraviolet absorbents can be used in this invention. Still further, ultraviolet absorbing couplers (e.g., a-naphtholic cyan dye-forming couplers) and ultraviolet absorbing polymers may be used in this invention. These ultraviolet absorbents may be mordanted in specific layers of the photographic materials.

For processing the photographic materials containing the silver halide emulsions of this invention, known processes and known processing solutions can be used. The processing temperatures are usually in the range of about 18°C. to 50°C. but may be lower than 18° C. or higher than 50°C. According to the purposes, a development processing forming silver image (black and white development process) or color photographic process composed of development process for forming dye images can be used for developing the photographic materials.

The color developer which is used for developing the photographic materials of this invention is generally composed of an alkaline aqueous solution containing a color developing agent. Color developing agents include aromatic primary amino color developing agents such as phenylenendiamines (e.g., 4-amino-N,N-diethylaniline, 3-methyl-4-amino-N,N-diethylaniline, 4-amino-N-ethyl-N-B-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-B-hydroxyethylaniline,

3-methyl-4-amino-N-ethyl-N-B-methanesulfoamide-ethylaniline and 4-amino-3-methyl-N-ethyl-N-B-methoxyethlaniline).

The photographic emulsion layers are usually bleached after color development. The bleach process may be performed simultaneously with or separately from the fix process. Bleaching agents include compounds of multivalent metals such as iron(III), cobalt(III), chromium(VI) and copper(II); peracids; quinones and nitroso compounds such as ferricyanides; dichromates; organic complex salts of iron(III) or cobalt(III); aminopolycarboxylic acids such as ethylenediaminetetraacetic acid, nitrotriacetic acid and 1,3-diamino-2-propanoltetraacetic acid; complex salts of organic acids such as citric acid, tartaric acid and malic acid; persulfates; permanganates and nitrosophenol. Among these materials, potassium ferricyanide, ethylenediaminetetraacetic acid iron(III) sodium salt and ethylenediaminetetraacetic acid iron(III) ammonium salt are particularly useful. The ethylenediaminetetraacetic acid iron(III) complex salts are useful for a bleach solution and for a fix solution.

Any suitable procedure may be used to prepare the coated particles used in the recording media of the present invention. For example, with reference to Figure 28, silver halide coated dielectric particles, such as particle 16 of Figure 2, may be made by a process generally comprising the steps of providing an aqueous solution including negatively charged colloidal dielectric particles, positively charged silver ions, and a halide, and reacting the halogen of the halide with the silver ions to bond, or grow, coatings of silver halide completely covering individual dielectric particles. Preferably, the concentrations of dielectric

may be dispersed in the solution, then the silver ions may be added, and then the halide may be added.

With a preferred process, after the dielectric particles are added to the solution, the pH of that solution is adjusted to and thereafter maintained at a level slightly above 2, and even more preferably, between about 3 and 5. With this procedure, the dielectric particles do not have to be negatively charged when they are added to the solution, and, instead, the acidity of the aqueous solution causes the dielectric particles to become negatively charged once the particles are in the solution. Further, with the preferred process, the initial concentration of the silver ions in the solution is relatively low, less than 10^{-4}M; the initial concentration of the halide in the solution is slightly greater than, such as about 10% greater than, the concentration of the silver ions in the solution; and also, the solution is constantly stirred while the halide is being added to it.

The silver ions may be added to the solution in any suitable form, and for instance, these ions may be added in the form of a soluble salt, e.g., silver nitrate. Likewise, the halide that is added to the solution may be any suitable halide, such as an alkali halide, e.g., sodium bromide, sodium chloride, potassium bromide, potassium bromide and the like. In addition, any suitable dielectric may be used in the above-discussed process, and the dielectric may be linear or non-linear and may have any suitable shape and size. For example, the dielectric particles may be spherically shaped silica particles. When, first, the dielectric particles are these silica particles, second, the silver ions are added to the solution in the form of silver nitrate, and third, the

halide is sodium bromide, then the silver from the silver nitrate reacts with the bromide from the sodium bromide to form silver bromide, which bonds to and forms layers over the silica particles.

Figure 29 generally outlines a process for making a metal coating on a dielectric particle, such as coating 20b of particle 20, or coating 22b of particle 22. This process generally comprises the steps of providing an aqueous solution including negatively charged colloidal dielectric particles, metal ions, a secondary alcohol containing 3-7 carbon atoms, and an alkyl ketone containing 3-7 carbon atoms; removing oxygen from the solution; and exposing the solution to ultraviolet light to cause the metal ions to attach to the dielectric particles and form metal coatings completely covering individual dielectric particles. Preferably, the concentrations of the dielectric particles, the metal ions, the isopropanol and the acetone, and the length of time the solution is exposed to the ultraviolet light are selected so that coatings of a uniform, preselected thickness are formed on the dielectric particles.

As used herein, the term lower alkyl, when used alone or in combination, contain 1-7 carbon atoms. These alkyl groups may be staight chained or branched and include such groups as methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, isobutyl, t-butyl, pentyl, amyl, hexyl, heptyl, and the like. As used herein, a secondary alkanol refers to a lower alkyl alcohol in which the hydroxy group is attached to a secondary carbon. Such groups include isopropanol, sec-butanol and the like.

The preferred alkyl ketone is acetone.

In the above-discussed procedure, without wishing to be bound, it is believed that the ketone (acetone) absorbs energy from the ultraviolet light and then reacts with the secondary alcohol (isopropanol) to form alkyl secondary (isopropyl) radicals. These radicals are powerful reducing agents and cause metal ions that have become attached to the dielectric particles to form metal molecules. The particular order in which the dielectric particles, the metal ions, the secondary alcohol and the ketone are added to the aqueous solution is not critical; and, for instance, the secondary alcohol and ketone may be added to the solution, the dielectric particles may then be dispersed in the solution, and then the metal ions may be added.

With a preferred process, as with the process outlined in Figure 28, after the dielectric particles are added to the solution, the pH of the solution is adjusted to and thereafter maintained at a level slightly above 2, and even more preferably, between about 3 and 5. In this way, the dielectric particles do not have to be negatively charged when they are added to the solution and the acidity of the aqueous solution causes the dielectric particles to become negatively charged. In addition, the initial concentration of the metal ions in the solution is relatively low, such as 2×10^{-4}M; and the initial concentration of the acetone and isopropanol in the solution are about equal to each other and much greater than, such as about 400 times greater than, the initial concentration of the metal ion in the solution. In addition, preferably the solution is stirred while exposed to the ultraviolet light.

Numerous specific types of metal coatings may be made using a procedure as described above. The types of

metals that can be used include transition metals, the lanthanides and the Group IIIA metals. The especially preferred metals include the Group VIII and IB metals, especially copper, silver, gold, iron, nickel, palladium, platinum, cobalt, rhodium, iridium, ruthenium, aluminum and the like. Especially preferred metals include copper, silver, gold, nickel, palladium, platinum and nickel.

It is most preferred that the process may be used to form silver coated dielectric particles, gold coated particles or palladium coated particles. In addition, the metal ions may be provided in the solution in any suitable manner; and, for example, these ions may be provided by adding a water soluble metal salt such as silver nitrate, to the solution.

Moreover, any suitable dielectric may be used in the above-discussed process, and the dielectric may be linear or non-linear and may have any suitable shape and size. For instance, the dielectric particles may be spherically shaped silica particles. When such dielectric particles are used, and the metal ions are added to the solution in the form of silver nitrate, then the ultraviolet light, in combination with the acetone and the isopropanol, causes the silver ions to bond to and form metal silver coatings over the silica particles.

EXAMPLE 1

The following example illustrates this process for forming metal coated dielectric particles.

An aqueous solution is prepared by mixing the following solutions in a 50 ml beaker:

(1) 0.5 ml of 0.01 M $AgNO_3$,

(2) 0.5 ml of 0.50 M of low porosity SiO_2 particles.

The particle diameter is chosen to be between 5 to 20 nanometers, although other sizes can be readily substituted,

(3) 1.5 ml of pure isopropanol,

(4) 1.5 ml of pure acetone.

All chemicals used are of reagent grade quality, unless otherwise specified. The above mixture is diluted with 16 ml of distilled water, and the pH adjusted to be between 4 to 5 by dropwise addition of a 0.01 M nitric acid solution. In this pH range, the silica particles are negatively charged, causing the positively charged silver ions to be bound to the surface. After thorough mixing by stirring for one minute using a magnetic stirrer, the sample is transferred to a UV photolysis vessel, equipped with a quartz window and provision for careful deoxygenation by bubbling nitrogen gas for one hour. It is important that no oxygen be present in the solution. The sample is irradiated by a 450 Watt Hg-Xe lamp for one hour, with gentle stirring continued by means of a magnetic stirrer. The solution color, and consequently the thickness of the coat, can be controlled by adjusting the period of illumination by UV

light. This forms the basis for the preparation of the silver coated silica particles in the present example.

Silver coated dielectric particles may also be made by a process employing photoreduction of silver halide, and one such process is outlined in Figure 30. In this process, silver halide coated dielectric particles are made, for example, by the process discussed above in connection with Figure 28, and then the coated particles are exposed to light to change the silver halide coatings over the individual particles to metal silver coatings.

Preferably, though, a more integrated process, generally outlined in Figure 31, is used to form silver coated dielectric particles. In accordance with this process, dielectric particles are dispersed in a solution including silver ions, a halide and an electron hole scavanger, and the silver ions react with the halogen of the halide to form silver halide coatings completely covering the dielectric particles. The solution is then exposed to ultraviolet light, and this light changes the silver halide coatings to silver coatings. Preferably, the concentrations of the dielectric particles, the silver ions, the halide and the electron hole scavanger in the solution, and the length of time the solution is exposed to the ultraviolet light are selected so that coatings of a uniform, preselected thickness are formed on the dielectric particles.

Preferably, with this process, the initial concentration of silver ions in the solution is greater than the initial concentration of the halide in the solution; and for instance, the former concentration may be about 5 times the latter concentration. The silver ions may be in the solution in any suitable form, and for instance, these ions

may be added to the solution in the form of a salt that is soluble in aqueous solution, e.g., silver nitrate. Similarly, the halide that is added to the solution may be any suitable halide such as an alkali halide, e.g., sodium bromide, sodium chloride, potassium bromide, potassium chloride, and the like. Further, any suitable dielectric may be used in this process, and the dielectric may be linear or non-linear and have any suitable shape and size. For example, the dielectric particles may be spherically shaped silica particles. When (i) the dielectric particles are the silica particles, (ii) the silver ions are added to the solution in the form of silver nitrate, and (iii) the halide is sodium bromide, then the silver from the silver nitrate reacts with the bromide from the sodium bromide to form silver bromide; and the ultraviolet light, in the presence of EDTA, then reduces the silver bromide coatings to metallic silver.

In the above procedure, it is preferred that the light source used contain ultraviolet light. It is preferred that the light source contain wavelength ranging from 150-550 nm. The preferred wavelengths range from 200-400 nm.

Furthermore, it is preferred that the intensity of light used ranges from 50 watts to 1.5 kilowatts, with the preferred intensity ranging from 250-1000 watts. Especially preferred intensity ranges from 350-550 watts, with an intensity of about 450 watts being the most preferred.

EXAMPLE 2

Metallic silver on SiO_2 particles can be obtained by photoreduction of silver halides, which are typically prepared in the presence of excess Ag^+ ions. A hole (h^+) scavanger, EDTA, is added to the solution. One ml of a 0.002 M NaBr solution is added to 19 ml of a solution which is prepared in a 50 ml beaker by mixing the following:

(1) 1 ml of 0.01 M $AgNo_3$,

(2) 0.5 ml of 0.50 M of low porosity SiO_2 particles. The particle diameter was 12 nanometers, although other sizes can be readily substituted,

(3) 1 ml of 0.02 M EDTA,

(4) 16 ml of distilled water.

After thorough mixing, the solution is transferred to a 1 cm UV quartz cuvette and exposed to a 375 Watt tungsten halogen light source. Under these conditions, very little light is actually absorbed since the colloidal AgBr has a very low absorbance above 350 nm. A possible mechanism for the reduction process is given by:

$$AgBr \longrightarrow AgBr(e^- + h^+)$$

$$AgBr + e^- \longrightarrow Ag^o + Br^-$$

$$EDTA + h^+ \longrightarrow \text{product}$$

$$Br^- + Ag^+(\text{excess}) \longrightarrow AgBr$$

The duration of illumination, which is in the order of minutes, determines the color of the silver coated silica particles. This color is a result of the thickness of the silver layer, and can range from yellow to a purplish gray.

Once the silver coated silica spheres are prepared, they are purified by dialysis and then placed in a sodium dodecyl sulfate micellar solution, or a microemulsion.

A variation of the process described above may be employed to form metal coatings other than silver on nano particles, and this variation utilizes the fact that metallic silver on the dielectric particles will act as a catalyst to help grow metal coatings on those particles from other metal ions in the solution. In accordance with this variation, which is outlined in Figure 32, a solution is provided including dielectric particles, silver halide is formed on those particles, the solution is exposed to light to change at least a portion of the silver halide to metallic silver, and ions of a metal are added to the solution to form coatings of that metal completely covering individual dielectric particles, with the metallic silver on those particles acting as a catalyst to accelerate the formation of the metal coatings. These metal ions may be added to the solution in any suitable manner, and for instance, conventional photographic developing solutions may be added to the solution to reduce the metal ions.

Only minute amounts of metallic silver are needed on the dielectric particles to help grow the metal coatings thereon; and hence, in the above-described process, it is only necessary to form minute amounts of silver halide on the dielectric particles. Alternatively, complete coatings of silver halide may be formed on the dielectric particles, with only minute amounts of the silver halide on individual

particles being changed to metallic silver. With another variation, silver halide coatings may be made completely covering dielectric particles, only minute amounts of the silver halide may be changed to metallic silver on individual particles, and then these minute amounts of metallic silver may be used to help form metal coatings completely covering the silver halide that remains on the dielectric particles. The resulting product comprises a dielectric core, a first coating of silver that substantially completely covers the dielectric core, and a second coating of a metal that completely covers the layer of silver halide.

The following example illustrates the coating of silver on a dielectric core of silver bromide. The silver bromide nanoparticles exposed briefly to intense UV light in the presence of EDTA have optical extinction spectra similar to those computed for distribution of silver-coated silver bromide nanoparticles. By intense, it is meant that the intensity of the light ranges from 50 watts to 1.5 kilowatts, with the preferred range being 250-550 watts, and the most preferred having a range of 350-550 watts.

As clearly shown by the following discussion, with shorter exposure time, the plasmon resonance maximum is shifted to longer wavelengths, a result consistent with theory so long as the coat thickness increases with exposure to light. The resonance maximum of the distributions of coated particles can be controllably shifted to 600 to 700 nm.

EXAMPLE 3

Silver bromide colloids were prepared by rapidly mixing equal volumes of $AgNO_3$ and NaBr solutions. A growth stabilizer (SDS) and an electron doner (EDTA) were added immediately after precipitation. Typically the final concentrations were 1×10^{-4} M Br^-, 4×10^{-4} mAg^+, 5×10^{-4} M (SDS). and 5×10^{-4} M EDTA. The concentration of SDS was far below the critical micellization concentration (10^{-2} M). Freshly prepared solutions were exposed to light from a 450 Watt Hg-Xe lamp for a few seconds. With the shortest exposures the spectra appeared blue. With longer exposures the solution appeared orange. When ammonia, which dissolves AgBr by forming complexes with Ag^+ was added to any of the illuminated solutions the color changed to a yellow color characteristic of small metallic silver colloids.

The particle size distributions were characterized with transmission electron microscopy (JEOL 1200EX). A typical micrograph is shown in (Fig. 19a). A size distribution consistent with the limited micrograph data is the log normal distribution.

$$N(r)=N_o\exp(-((\ln(r)-\ln(r_m))/\ln(s))^2), \qquad (1)$$

with r_m equal to 1 nm or less and s in the range of 4 to 4.5 nm. The size distributions as determined by TEM did not appear to change markedly with exposure to light.

After the addition of ammonia to any of the illuminated samples only small particles having diameters 5 nm or less were observed in the TEM (Fig 19b). The most likely interpretation is that only part of the AgBr was

reduced to Ag during the illumination and that the larger particles are AgBr/Ag composites.

Example optical extinction spectra measured shortly after exposure are shown in Figs 20a) to d). The exposure time and/or EDTA concentration and hence the reduction of Ag^+, increases in going from a) to d). The peak extinction shifts to shorter wavelengths as the illumination time is increased. This result is consistent with theory so long as the coat thickness increases with exposure. A spectrum of the ammonia treated solution shown in Fig 20e), is typical of homogeneous silver nanoparticles. The general shapes of the above spectra are readily reproducible. At comparable illumination times, in the absence of Br^-, the appearance of color in a given sample is negligible.

Theoretical optical extinction spectra of individual silver coated spheres are shown in Fig. 21. The peak of the theoretical extinction shifts from red to blue as the ratio of coat thickness to core radius increases. This data is consistent with the measured spectra where the absorption maxima shift toward the blue as the time of exposure increases since the coat thickness should increase with exposure time. The compound spectra are very sensitive to the coat thickness. The measured spectra are much more broad than the spectra shown in Fig. 21 because of the distributions of core diameters and coat thicknesses.

The magnitudes of the extinction spectra are also characteristic of silver coated particles. For example, at a wavelength of 700 nm the extinction cross section per unit volume of silver is 100's of times larger in a silver coated nanoparticle having the appropriate ratio of core radius to coat thickness than it is in a solid silver sphere. The fact

that the theoretical extinction is so large can be used to help verify that the particles are coated with silver. However, since there is a broad distribution of sizes care must be taken in making the comparison.

Here we started with the size disbribution of core particles described by the above equation, then used trial and error to determine the distributions of coat thicknesses required to match the measured spectra, and then found that the magnitudes of the spectra were within the range of values expected from the initial concentrations of Ag^+ and Br^-.

The assumptions made in computing the spectra are as follows:

1. The reduced silver is in the form of a smooth coat on the surface of a spherical AgBr particle. The extinction efficiencies were computed using the separation of variables solution for concentric spheres based on algorithms.

2. The size distribution of the core particles is described by the log-normal distribution of the above equation. The values of N_o were determined by setting the total volume of all the particles prior to illumination in the distribution equal to the volume of AgBr. The initial total volume of AgBr was determined by solving the ionic equilibria equations including the Ag^+ - EDTA complex.

3. The size distribution of the coat thicknesses is a Gaussian, typically with a standard deviation of 2 to 8 nm.

4. The silver coat may be formed either from the reduction of the silver halide of the initial particle, or from the reduction of Ag^+ from solution. Computations have been done for each of the two limiting cases.

5. The total extinction is computed by numerically integrating over distributions of core radii and coat thicknesses.

$$b_e(\lambda) = \int N_n(r_c)N_g(t)Q(r_c,t,m_c,m_t,\lambda)\pi r^2 dr_c dt \quad (2)$$

where N_n is the size distribution of the cores, N_g is the size distribution of the coats. Q is the extinction efficiency, m_c is the refractive index of the core, and m_t is the refractive index of the coat. Typically the integrations over cores were from r = 2 to r = 18.

6. The refractive index fo the silver was computed from the data of Hagemann et al. in J. OP. Soc. Am., 65, 742-744 (1975) and Kerker, in J. OP. Soc. Am. B., 1327-1329 (1985), either by itself, or combined with a Drude model in which the increased electron scattering at the surfaces of the very thin coat was taken into account. The refractive index data of Johnson and Christy in Phy Rev. B, 6, 4370-4379 (1972) was also used for some computations not shown. Linear interpolation was used to obtain the values of refractive index at points not in the data.

7. The refactive index of AgBr was obtained by combining the data from White, J. opt. Soc. Am., 62, 212 (1972), and James, "Theory of the Photographic Process", MaMillan (1977) p. 216.

Fig. 41 shows a measured spectrum and two computed spectra. In the topmost curve the Ag in the coat is assumed to come only from the solution. i.e., the AgBr cores are not reduced in size as the coat grows. In the bottom curve the Ag in the coat is assumed to come only from the reduction of AgBr at the surface of the particle and so the core shrinks

as the coat grows. Since the measured curve lies between the two computed spectra, the magnitudes of the plasmon enhanced extinction is in the range of values computed.

The main parameters that can be adjusted in fitting the distributions to the spectra are: 1) the thickness and standard deviation of the coats and the limits of the numerical integration for the coats. 2) the size distribution and limits of integration for the cores. 3) the data for the refractive index of silver, the fraction of the reduced silver that came from solution. The computed spectra are very sensitive to the distributions of cores and coats chosen and to the limits of integration, which also define the size distributions. The computed spectra depend on the refractive index of silver used. However, by varying the size distributions, similar spectra can be obtained with the different models for silver. The effect of the different assumptions about the source of the Ag for the coat can be seen in Fig. 40. In a preliminary experiment without excess silver a spectrum similar to that shown in Fig. 39d was generated.

Without wishing to be bound, it is believed that the silver coat is formed by the coalescing of many small silver particles. The coat may also contain some AgBr or voids, but it is homogeneous enough to have a refractive index similar to that of bulk silver. The bonds between the particles may be relatively weak because the coat breaks into many small particles when the solution is treated with ammonia.

It might have been thought that the spectra could be accounted for by nonsherical silver particles. The fact that ammonia, which dissolves AgBr but not Ag, reduces the

spectrum to that of small solid particles, and the fact that the particles in the TEM do not have large eccentricities, argue against this hypotheses. Also, the particle shapes do not seem to be related to the colors of the solutions.

In summary, the predicted tunability of the surface-plasmon resonance frequency and enhanced extinction at longer wavelengths was experimentaly confirmed with Ag-AgBr colloidal composites. The particles scatter as if the Ag is smoothly coated on the AgBr.

Silver coated dielectric particles may also be formed by a process utilizing chemical reduction of silver ions by hydroquinone at elevated temperatures. The following example, generally outlined in Figure 33, illustrates this process.

EXAMPLE 4

100 ml of a silica solution (particle diameter 7 nm) which had been purified by overnight dialysis was transferred to a 250 ml beaker, and the pH adjusted to 4.0 by dropwise addition of 0.01 M $AgNO_3$ solution added dropwise under gentle stirring to achieve the final concentration shown in the table below. After about 2 minutes, sufficient quantity of 0.01 M hydroquinone was added in a similar manner. The reduction to metallic silver takes place gradually over a time period of about five minutes, accompanied by a color change from pale yellow to dark brown. The rate of silver deposition by this method can be controlled by varying the temperature between 85 to 95°C. A transparent solution is obtained in every case, and is allowed to cool and then purified by dialysis.

EXAMPLE 5

The following table summarizes the experimental conditions, including final concentrations (in molar), which were used in four different sets:

	I	II	III	IV
SiO_2	1%	1%	1%	1%
$AgNO_3$	$5.0x10^{-4}$	$1.0x10^{-3}$	$1.5x10^{-3}$	$2.0x10^{-3}$
Hydro-quinone	$5.0x10^{-5}$	$1.0x10^{-4}$	$1.5x10^{-4}$	$2.0x10^{-4}$

The amount of silver deposited increases from I to IV, and is evident from the color of the solutions (light yellow to dark brown). Electron microscopy also provided evidential support. The optical absorption specra show the presence of a single peak maximum at about 400 nm.

ELECTRON MICROSCOPIC RESULTS:

Solution I consists of particles which are smaller and better defined, appear darker, and were in the size range of 10 to 30 nm. In solution II, III, and IV, the particle size range was found to be between 40 to 100 nm, the particles were similarly dark, but contained elongated as well as spherical shapes. The final size distribution may be due in part to the non uniform size of the silica core particles, found to be between 7 to 11 nm by electron microscopy.

With all of the processes described above, after the coated particles are prepared, they may be removed from the solution in which they were prepared by dialysis, and then placed in a sodium dodecyl sulfate micellar solution or a micro emulsion. Additional coatings of either silver halide, a metal or a polymer, may then be added until the desired final configuration is reached. Polymer coating of any of these particles may be readily achieved in a solution by the well known emulsion polymerization method, in which a suitable amount of monomer and initiator have been added.

For instance, the following process, outlined in Figure 34, shows how a polymer coating may be made on a silver coated particle.

The following aqueous stock solutions were prepared:

(I) 0.1 M KH_2PO_4,
(II) 0.1 M NaOH,
(III) 2 % solution of sodium salt of styrene sulfonic acid, NaSS (co-monomar),
(IV) 3 % solution of $K_2S_2O_8$

All solutions were prepared in doubly distilled water, and all chemicals were reagent grade.

131.6 ml of a 1% solution of the silver coated silica particles were transferred to a three necked flask. 8 ml of solution IV, followed by 6.4 ml of solution II, were added with constant stirring using a magnetic stirrer. The flask was equipped with a condenser, and a platinum thermometer, which, in combination with a thermoregulator and a heating mantle, allowed regulation of the temperature of the flask to 65 ± 1 °C. At this temperature, nitrogen gas was bubbled through the mixture continuously, and 30 ml of styrene was added. After 15 minutes, 10 ml of solution III were added, and after another 20 minutes 4 ml of the initiator, solution IV, were added. Depending upon the thickness of the polymer film desired, the reaction can be terminated by addition of 25 ml of a 1 % solution of hydroquinone, and cooling the reaction mixture to room temperature. The particles are filtered, washed several times with doubly distilled water, resuspended in water, and further purified by dialysis.

EXAMPLE 6

Coating of carbon fibres with copper was carried out by photochemical reduction of Cu^{++} using highly reductive short lived 1-hydroxy-1-methylethyl radicals. These radicals were produced in situ by illuminating a mixture of 1 M acetone and 1 M propanol-2 with an UV source of Hg-Xe lamp operated at 450 watt. The reaction can be presented by

$$(CH_3)_2CO \rightarrow (CH_3)_2CO^*$$

$$(CH_3)_2CO^* + (CH_3)_2CHOH \rightarrow 2(CH_3)_2COH$$

$$2(CH_3)_2COH + Cu^{+2} \rightarrow 2(CH_3)_2CO + Cu + 2H^+$$

$$nCu \longrightarrow Cu_n$$

Two different solutions of Cu^{++} (1×10^{-2} M and 1×10^{-3} M) were used to achieve two different coating thicknesses. Both solutions contained 1 M acetone, 1 M propanol-2, and carbon fibers. The illumination time was two hours.

These coated fibres, washed with distilled water and observed under an optical microscope, show a very fine and smooth coating and visibly exhibit a metallic lustre of copper. The amount of copper on these fibres was detected using atomic absorption spectroscopy after removing the coat with 1 M nitric acid. The presence of copper on these fibres was also confirmed using Energy Dispersive Spectroscopy (EDS), which shows a peak for copper. The thickness of the coat can be controlled by the copper concentration in

solution and the duration of illumination. It can be readily varied in the range of tens of nanometers to microns.

The processes discussed above may be used in various combinations to form particles of a desired configuration. For example, Figure 35 generally outlines a procedure to make particle 20 of Figure 3. First, metal coating 20b is formed over dielectric core 20a, for example using the method illustrated in Figure 31; and then silver halide coating 20c is made over metal layer 20b, for instance by generally following the method shown in Figure 28. Similarly, Figure 36 generally illustrates a procedure to make particle 22 of Figure 4. In this procedure, first, metal coating 22b is formed over dielectric core 22a, for example by the process described above in connection with Figure 29, then polymer coating 22c is applied over coating 22b, and then silver halide layer 22d is formed over coating 22c, for example by generally following the procedure discussed above in connection with Figure 28.

While it is apparent that the invention herein disclosed is well calculated to fulfill the objects previously stated, it will be appreciated that numerous modifications and embodiments may be devised by those skilled in the art, and it is intended that the appended claims cover all such modifications and embodiments as fall within the true spirit and scope of the present invention.

CLAIMS

1. A light sensitive silver halide photographic emulsion, comprising:

a colloid; and

a multitude of silver halide particles dispersed in said colloid, each of said particles including a core surrounded by a shell, one of said core and shell consisting essentially of silver halide, and the other of the core and shell consisting essentially of a dielectric material.

2. A photographic emulsion according to claim 1, wherein said dielectric material is substantially free of silver atoms.

3. A photographic emulsion according to claim 1, wherein each of the particles further includes a layer of a metal disposed between the core and the shell of the particle.

4. A photographic emulsion according to claim 3, wherein each of the particles further includes a layer of polymeric material disposed between the layer of the metal and said one of the core and shell of the particle.

5. A photographic emulsion according to claim 1, wherein:

the core of each particle consists essentially of dielectric material; and

the shell of each particle consists essentially of silver halide.

6. A photographic emulsion according to claim 5, wherein each of the particles further includes a layer of a metal disposed between the core and the shell of the particle.

7. A photographic emulsion according to claim 6, wherein each of the particles further includes a layer of polymeric material disposed between the layer of metal and the shell of the particle.

8. A photographic emulsion according to claim 7, wherein:

the layer of metal of each particle substantially completely covers the core of the particle; and

the layer of polymeric material of each particle substantially completely covers the layer of metal of the particle.

9. A photographic emulsion according to claim 1, wherein each of the particles further includes a polymer coating extending around the shell of the particle.

10. A photographic emulsion according to claim 2, wherein each of the particles further includes a polymer coating extending around the shell of the particle.

11. A photographic emulsion according to claim 5, wherein each of the particles further includes a polymer coating extending around the shell of the particle.

12. A light sensitive silver halide photographic emulsion, comprising:

a colloid; and

a multitude of silver halide particles, each of said particles consisting of

i) a core consisting essentially of a dielectric material,

ii) a first shell consisting essentially of a metal, and disposed immediately over and substantially completely covering the core of the particle,

iii) a second shell consisting essentially of a polymeric material, and disposed immediately over and substantially completely covering the first shell of the particle, and

iv) a third shell consisting essentially of a silver halide, and disposed immediately over and substantially completely covering the second shell of the particle.

13. A photographic emulsion according to claim 12, wherein the dielectric material of the core is substantially free of silver.

14. A photographic emulsion according to claim 13, wherein the first shell of each particle consists essentially of silver.

15. A photographic emulsion according to claim 9, wherein the core of each particle consists of silica.

16. The use of the enhanced plasmon resonance effect to increase absorption and scattering processes.

17. A light-sensitive recording medium, comprising:

a solid, light reflecting or light transmitting substrate;

a colloid applied onto the substrate; and

a multitude of particles dispersed in said colloid, each of the particles including a core surrounded by a shell, at least one of the core and shell consisting essentially of a metal.

18. A recording medium according to claim 17, wherein the other of the core and shell consists essentially of a dielectric material.

19. A recording medium according to claim 18, wherein:

the core of each particle consists essentially of the dielectric material;

the shell of each particle consists essentially of the metal; and

each of the particles further includes a layer of polymeric material disposed over and substantially completely covering the shell of the particle.

20. A light sensitive optical recording medium, comprising:

a support medium;

a multitude of particles supported by the support medium, each of the particles including a core and a shell, one of the core and shell consisting essentially of a metal.

21. A recording medium according to claim 20, wherein the other of the core and shell consists essentially of a dielectric material.

22. A recording medium according to claim 21, wherein each of the particles further includes another shell consisting essentially of silver halide.

23. A light sensitive recording medium, comprising:

a solid, light reflecting or light transmitting substrate;

a colloid applied onto the substrate; and

a multitude of particles dispersed in the colloid, each of the particles consisting of

i) a core consisting essentially of a dielectric material,

ii) a shell disposed immediately over and substantially covering the core, and consisting of a metal, and

iii) a coating disposed immediately over and substantially covering the shell, and consisting essentially of a polymeric material.

24. A recording medium according to claim 23, wherein the shell of each particle consists of silver.

25. A method of storing and reading data in an optical recording medium of the type having a solid, light reflecting or light transmitting substrate and a multitude of particles carried by the substrate, the method comprising the steps of:

passing a write beam over the recording medium in a given pattern to change the morphology of said particles over a selected area of the recording medium to represent stored data therein; and

passing a read beam over the recording medium to read data stored therein;

wherein said particles are nanoparticles, each nanoparticle including a plurality of layers, the plurality of layers including a core surrounded by a shell, one of said core and said shell consisting essentially of a metal.

26. A method according to Claim 25, wherein:

one layer of each nanoparticle comprises a first material having a first dielectric constant, and another layer of each nanoparticle comprises a second material having a second dielectric constant; and

the step of passing the write beam over the recording medium includes the step of using the write beam to react the first and second materials, of each of a multitude

of nanoparticles, with each other to form a third material having a third dielectric constant different than the first and second dielectric constants.

27. A method according to Claim 25, wherein:

one layer of each nanoparticle is a monomer; and

the step of passing the write beam over the recording medium includes the step of using the write beam to polymerize the monomer layer of each of a multitude of nanoparticles over the selected area.

28. A method according to Claim 25, wherein the step of passing the write beam over the recording medium includes the step of using the write beam to change the shape of each of a multitude of nanoparticles over the selected area.

29. A method according to Claim 25, wherein:

the nanoparticles are suspended in a medium having a dielectric constant; and

the step of passing the write beam over the recording medium includes the step of using the change in morphology in said particles to change the dielectric constant of the medium over the selected area.

30. A method according to Claim 25, wherein the step of passing the write beam over the recording medium includes the step of using the write beam to melt one layer and to change the shape of another layer of each of a multitude of nanoparticles over the selected area.

31. A method according to Claim 25, wherein the step of passi g the write beam over the recording medium includes the step of using the write beam to melt one layer and to change the structure of another layer of each of a multitude of nanoparticles over the selected area.

32. A method according to Claim 25, wherein:

a layer of each of the nanoparticles is comprised of a magnetized material; and

the step of passing the write beam over the recording medium includes the step of using the write beam to de-magnetize the magnetized material of a multitude of nanoparticles over the selected area.

33. A method according to claim 25, wherein:

a layer of each of the nanoparticles is comprised of a magnetized material; and

the step of passing the write beam over the recording medium includes the step of using the write beam to heat the magnetic region either of the particle, or surrounding the particle, to its curie temperature while that region of the medium is subjected to an externally applied magnetic field so that the magnetic domains become oriented along the direction of the field.

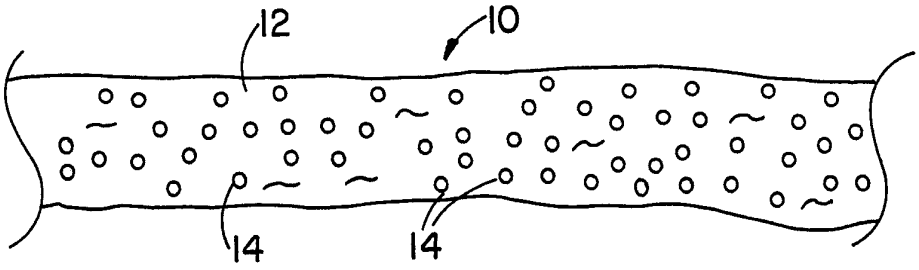

FIG. 1

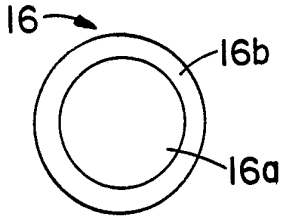

FIG. 2

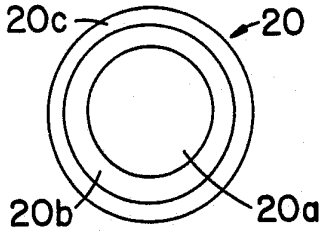

FIG. 3

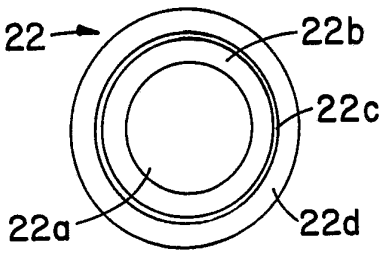

FIG. 4

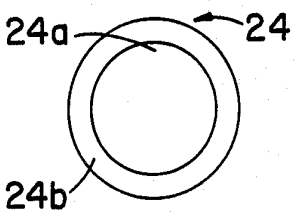

FIG. 5

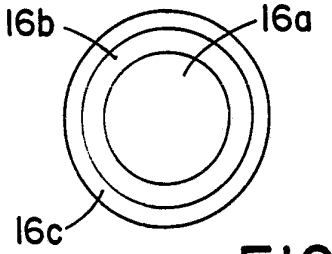

FIG. 5a

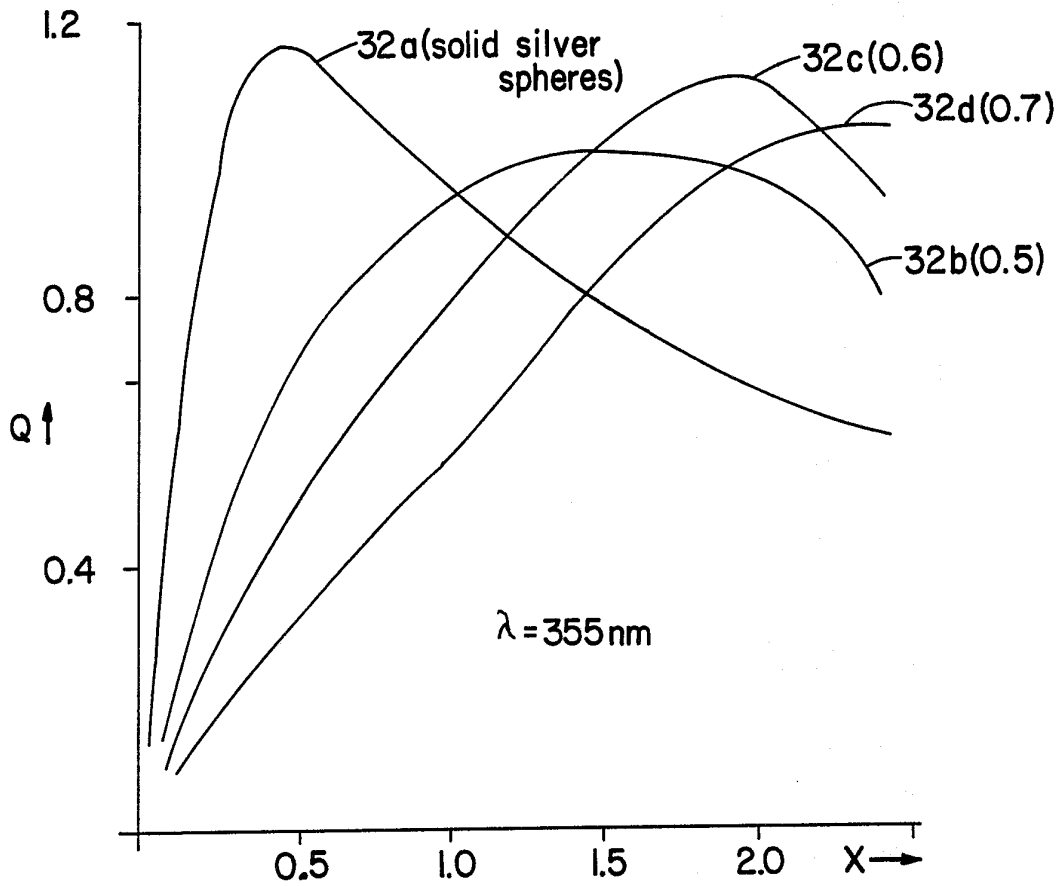
1.2
0.8
0.4
Q
32a(solid silver spheres)
32c(0.6)
32d(0.7)
32b(0.5)
λ=355nm
0.5
1.0
1.5
2.0
X

FIG.6

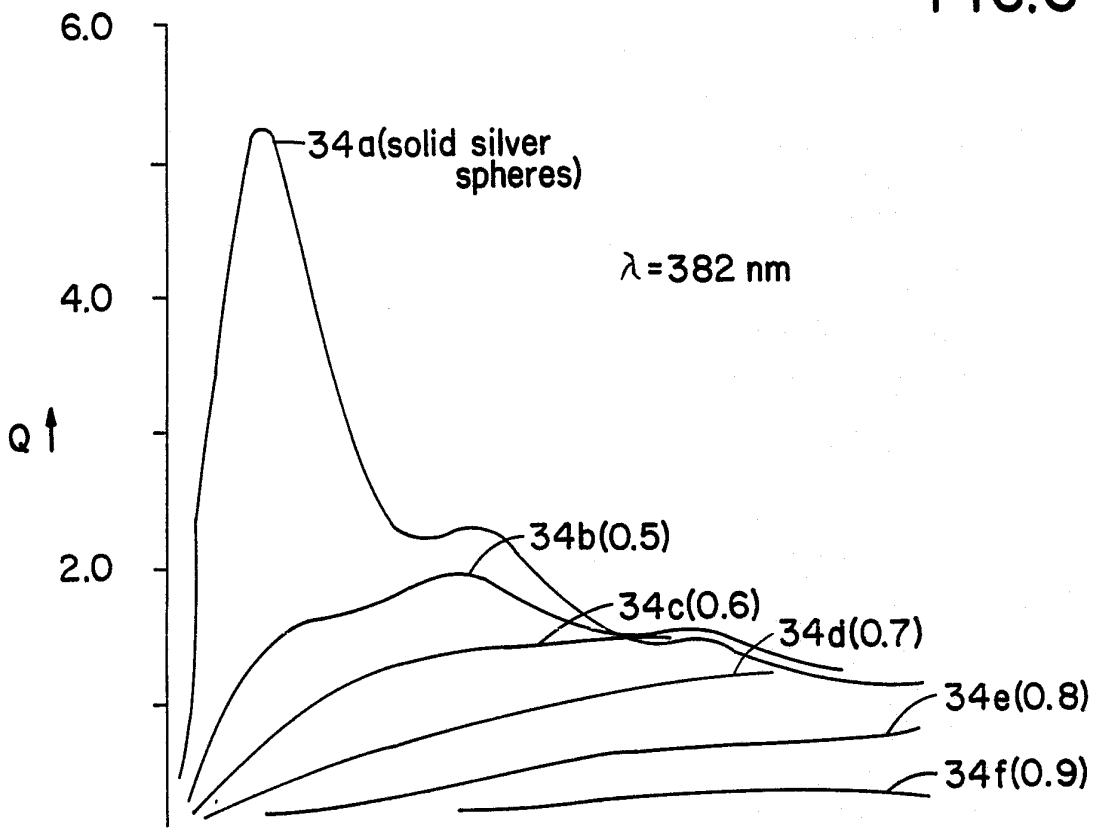
6.0
4.0
2.0
Q
34a(solid silver spheres)
λ=382 nm
34b(0.5)
34c(0.6)
34d(0.7)
34e(0.8)
34f(0.9)

FIG.7

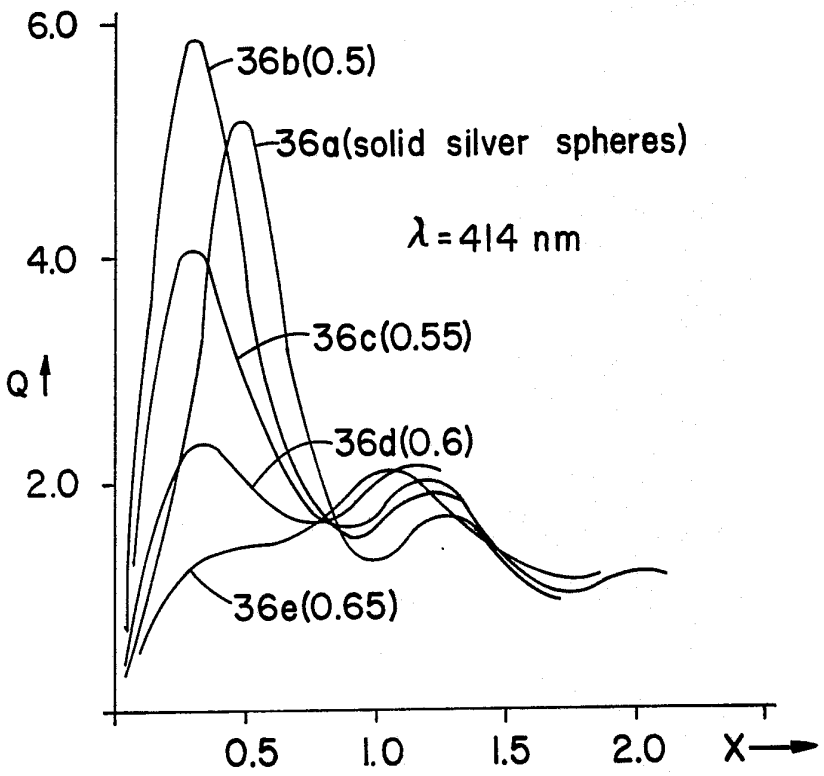
6.0
4.0
2.0
Q
36b(0.5)
36a(solid silver spheres)
λ = 414 nm
36c(0.55)
36d(0.6)
36e(0.65)
0.5
1.0
1.5
2.0
X

FIG. 8

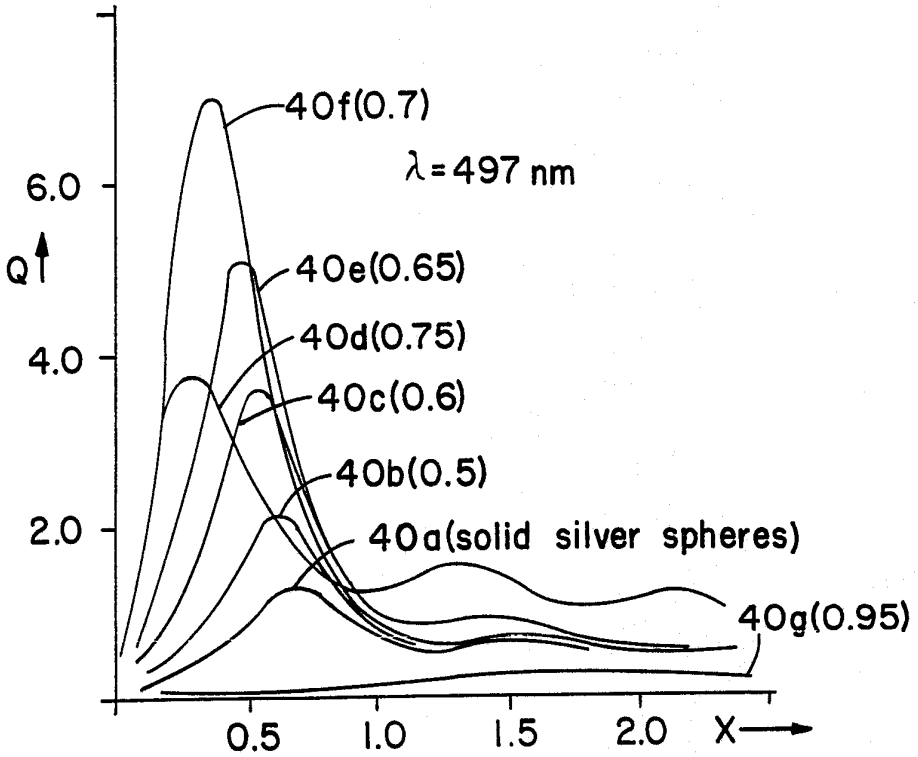
6.0
4.0
2.0
Q
40f(0.7)
λ = 497 nm
40e(0.65)
40d(0.75)
40c(0.6)
40b(0.5)
40a(solid silver spheres)
40g(0.95)
0.5
1.0
1.5
2.0
X

FIG. 9

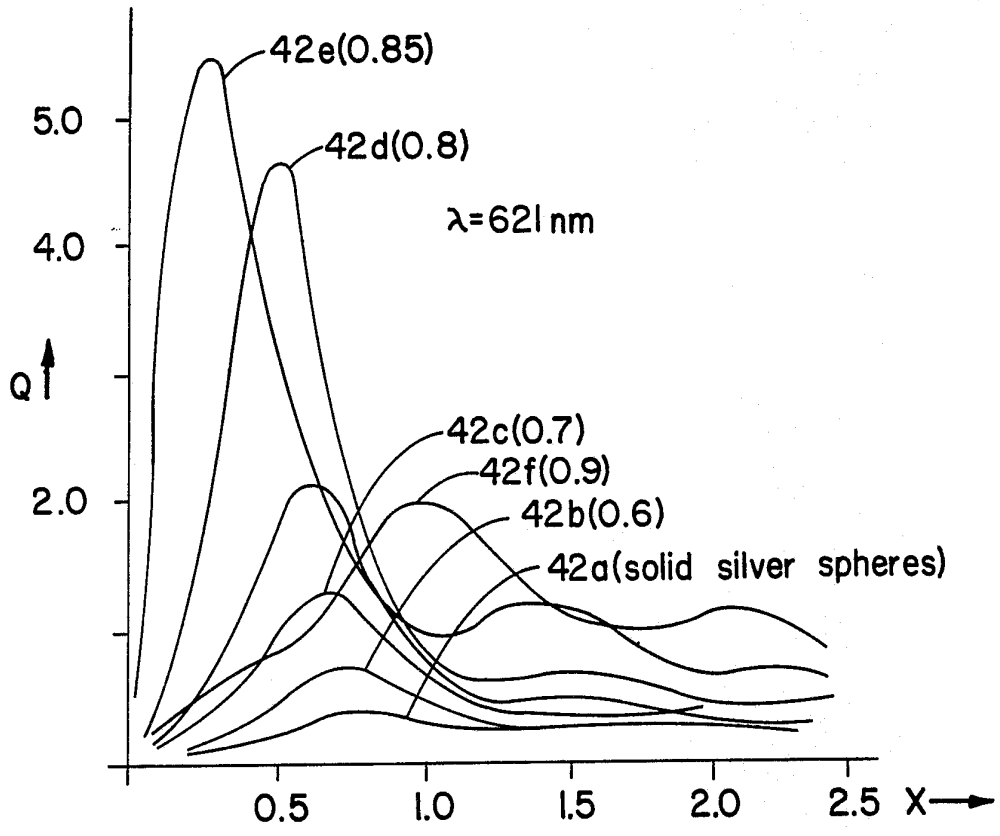
42e(0.85)
42d(0.8)
λ=621 nm
42c(0.7)
42f(0.9)
42b(0.6)
42a(solid silver spheres)
5.0
4.0
2.0
Q
0.5
1.0
1.5
2.0
2.5
X

FIG.10

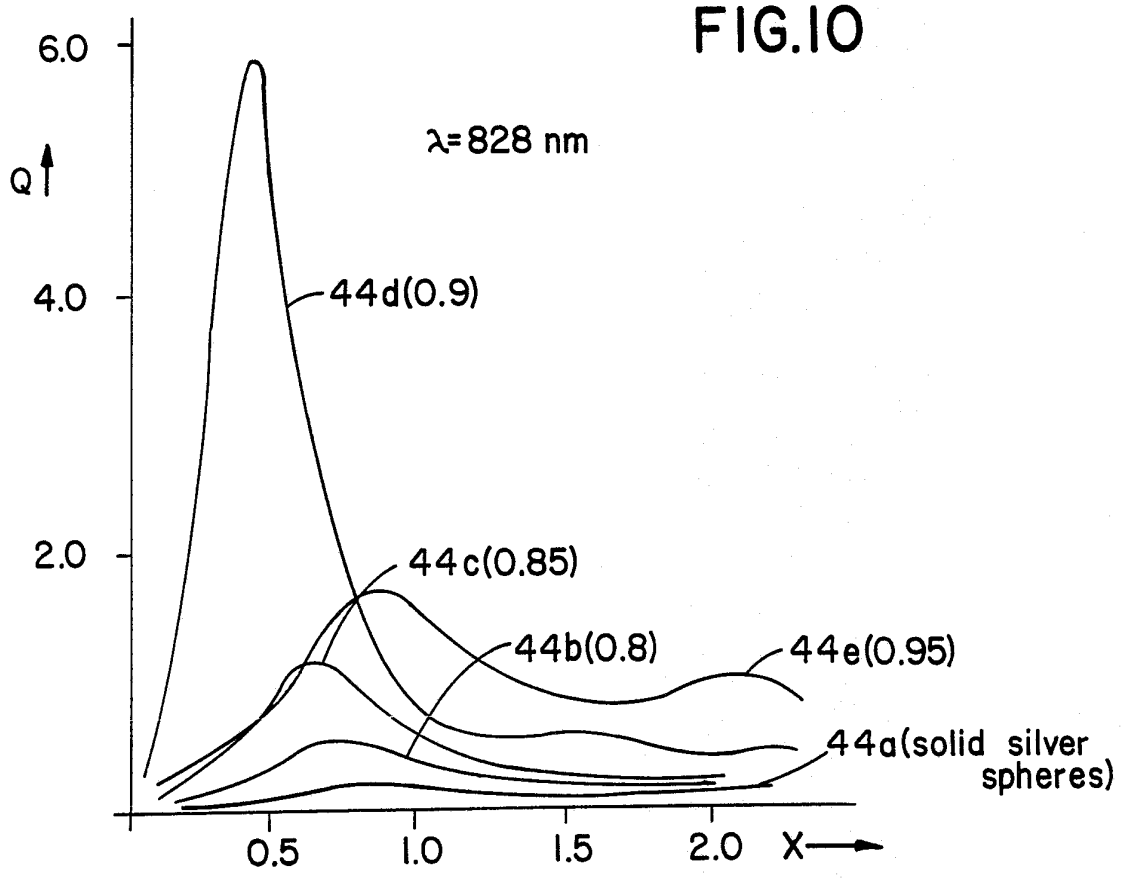
λ=828 nm
44d(0.9)
44c(0.85)
44b(0.8)
44e(0.95)
44a(solid silver spheres)
6.0
4.0
2.0
Q
0.5
1.0
1.5
2.0
X

FIG.11

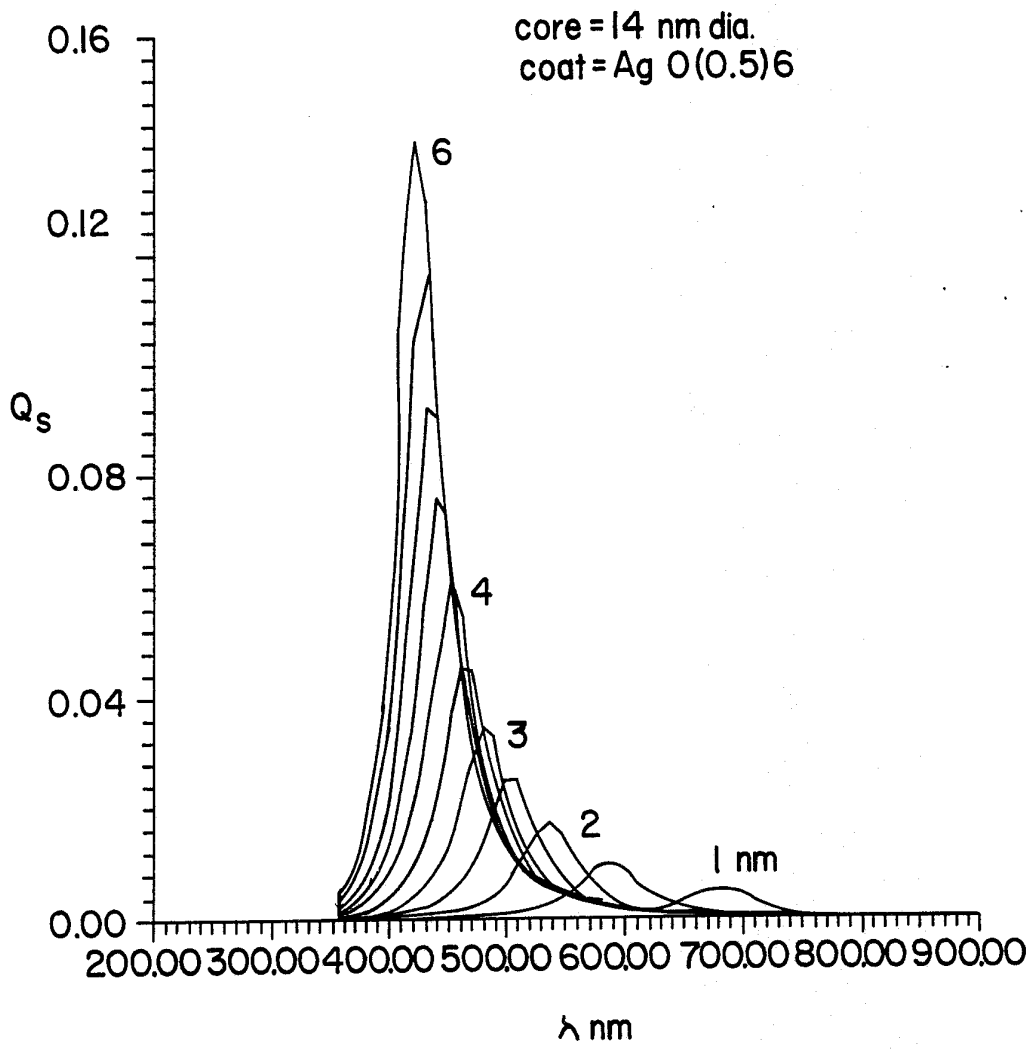
core = 14 nm dia.
coat = Ag 0(0.5)6
0.16
0.12
0.08
0.04
0.00
Q_s
6
4
3
2
1 nm
200.00 300.00 400.00 500.00 600.00 700.00 800.00 900.00
λ nm

FIG. IIa

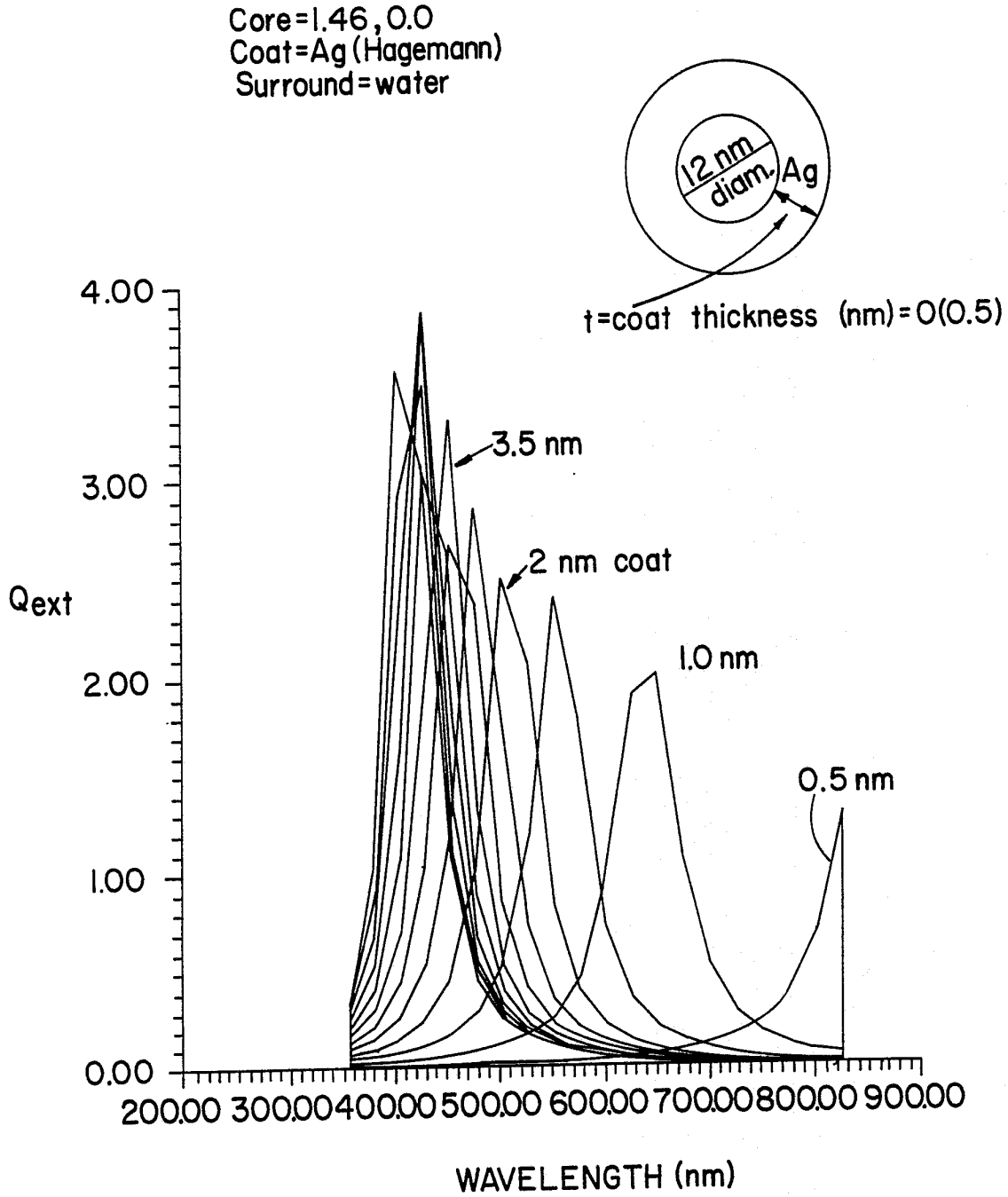
Core=1.46,0.0
Coat=Ag (Hagemann)
Surround=water
12 nm diam.
Ag
t=coat thickness (nm)=0(0.5)
4.00
3.00
2.00
1.00
0.00
Qext
3.5 nm
2 nm coat
1.0 nm
0.5 nm
200.00 300.00 400.00 500.00 600.00 700.00 800.00 900.00
WAVELENGTH (nm)

FIG. 11b

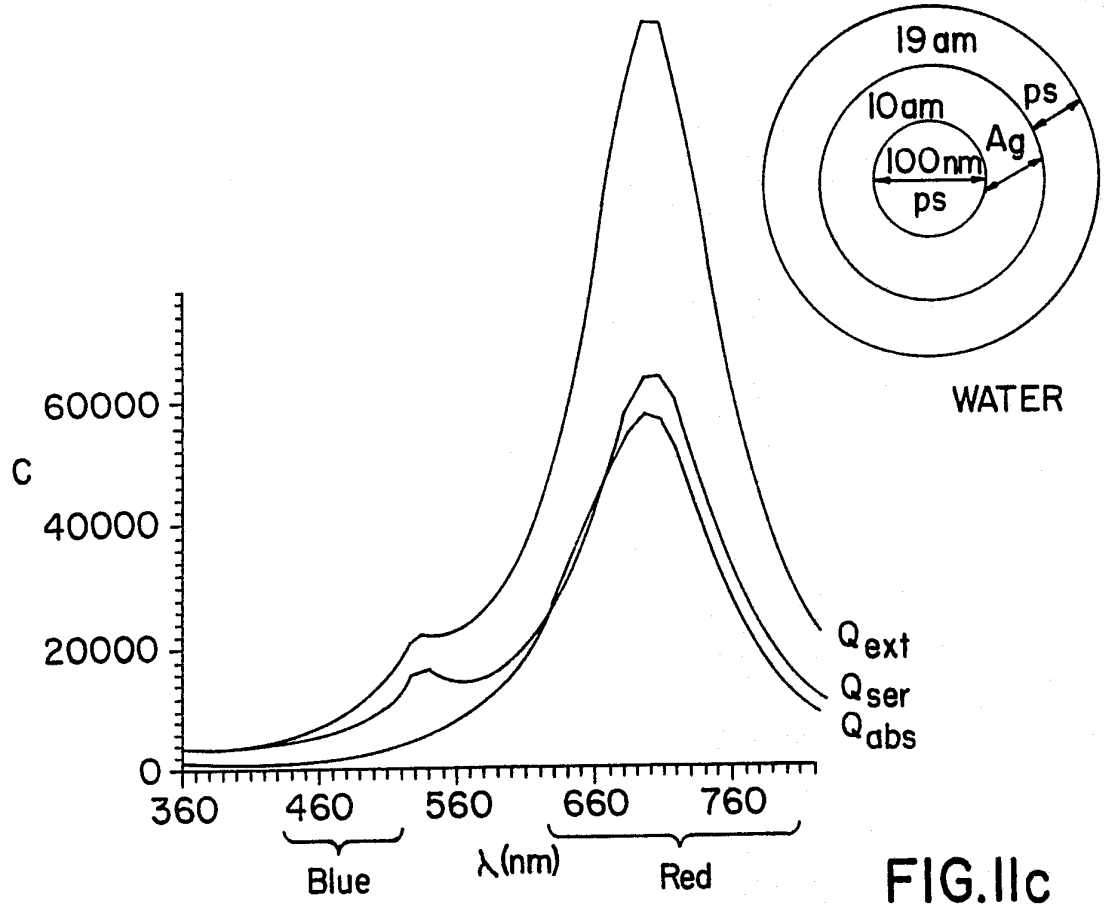

FIG.IIc

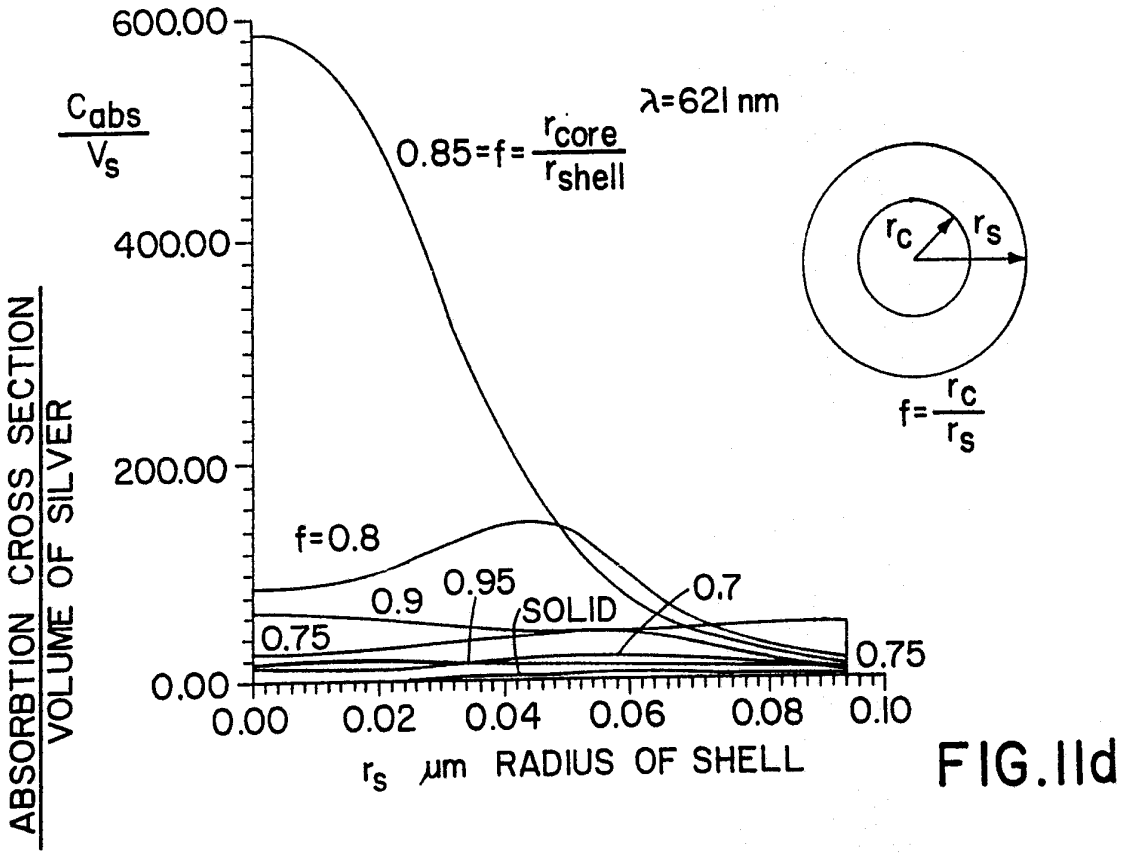

FIG.IId

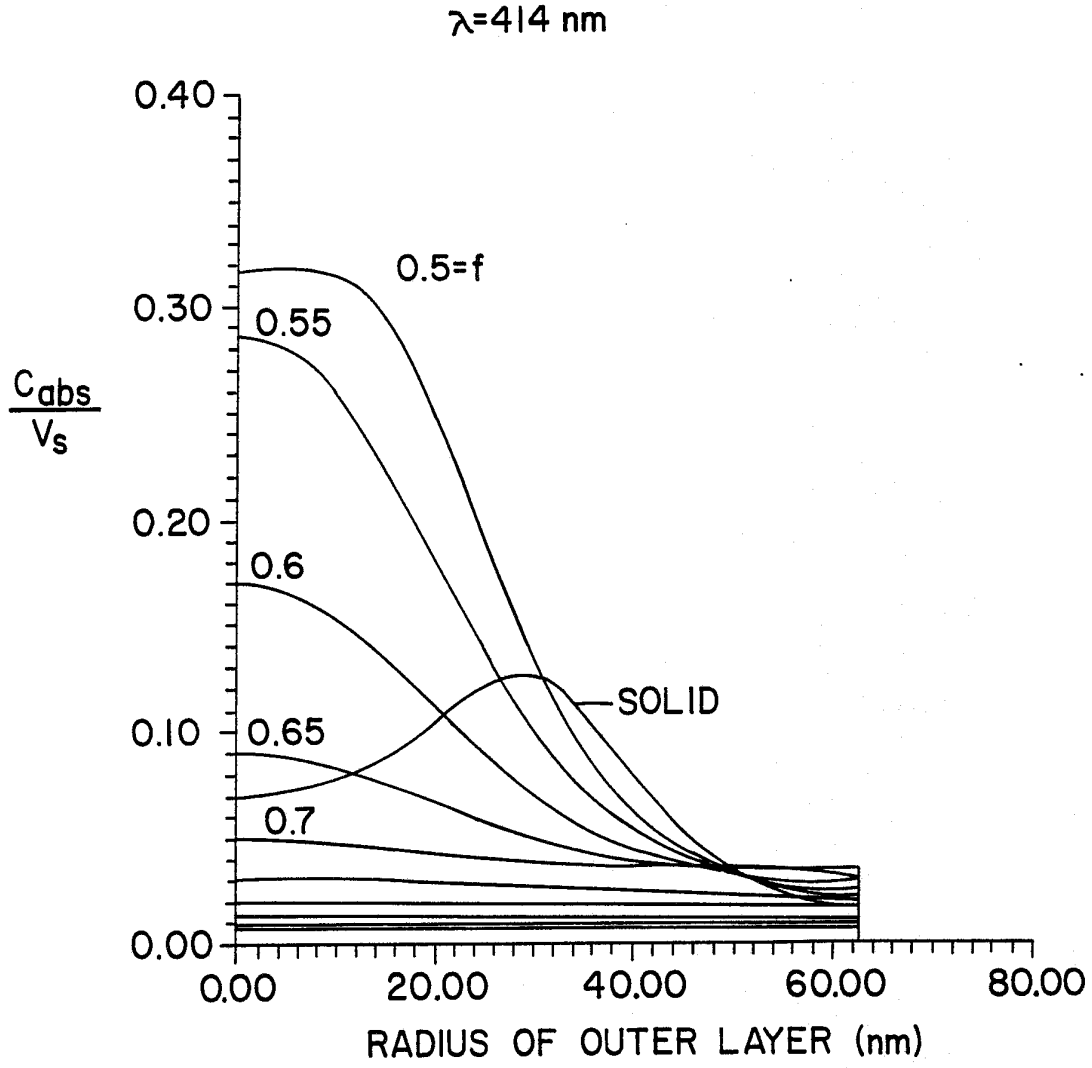
λ=414 nm
0.40
0.30
0.20
0.10
0.00
$\frac{C_{abs}}{V_s}$
0.5=f
0.55
0.6
0.65
0.7
SOLID
0.00
20.00
40.00
60.00
80.00
RADIUS OF OUTER LAYER (nm)

FIG. IIe

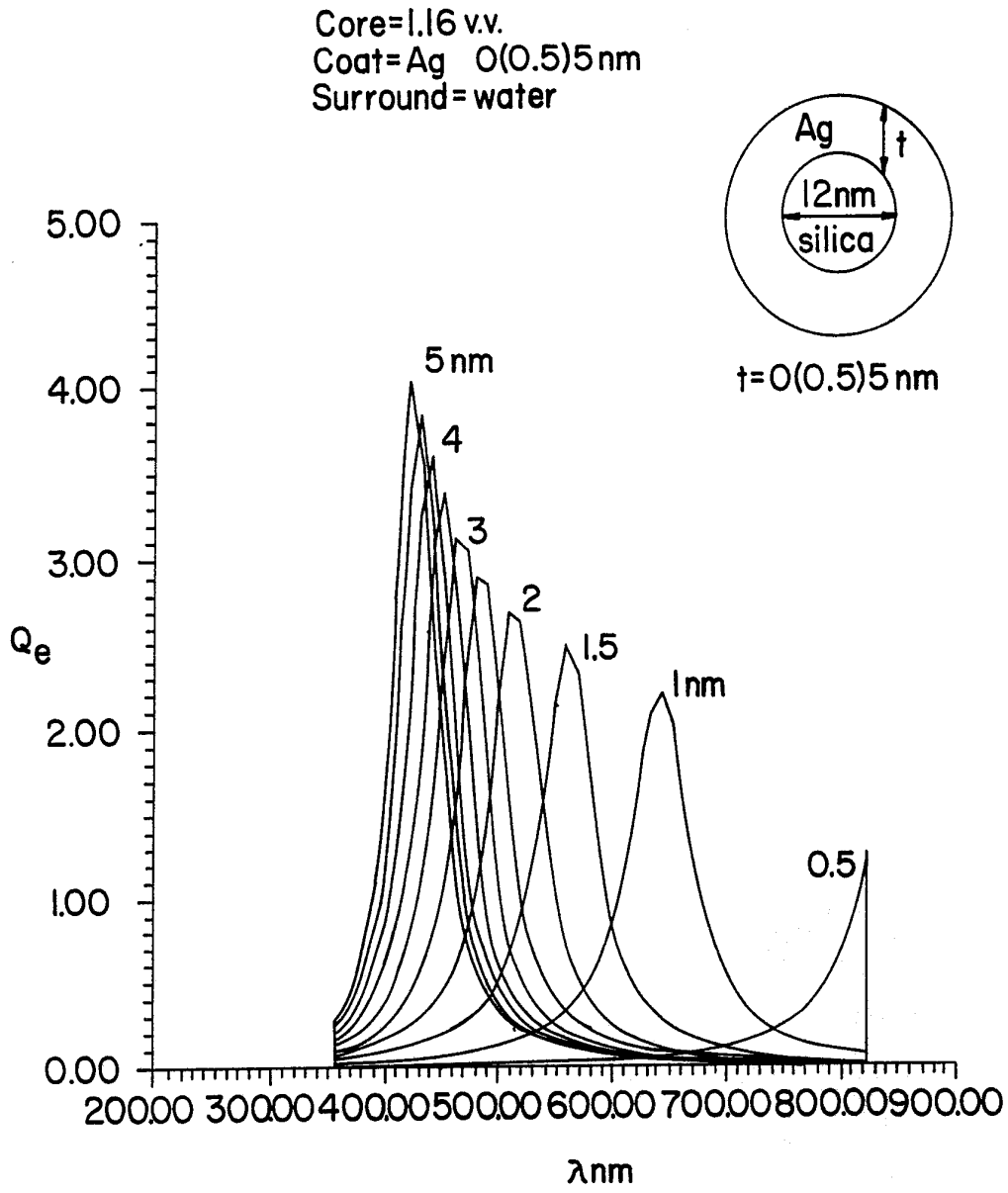
Core=1.16 v.v.
Coat=Ag 0(0.5)5nm
Surround=water
Ag
t
12nm
silica
t=0(0.5)5 nm
5.00
4.00
3.00
2.00
1.00
0.00
Qe
5nm
4
3
2
1.5
1nm
0.5
200.00 300.00 400.00 500.00 600.00 700.00 800.00 900.00
λnm

FIG.11f

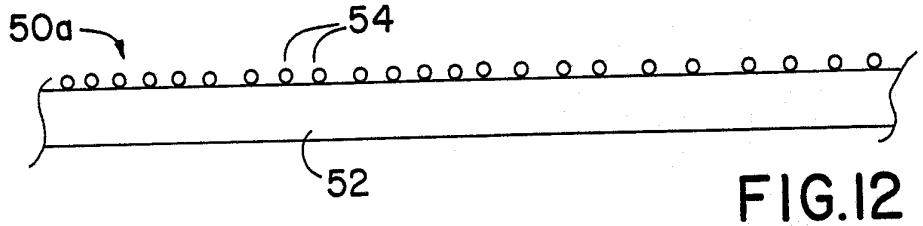

FIG.12

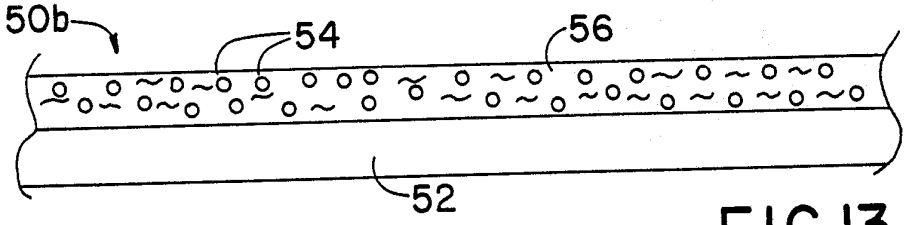

FIG.13

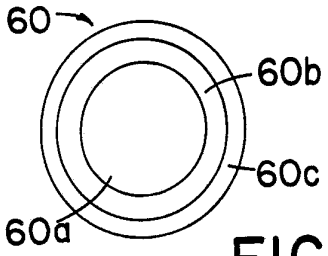

FIG.14

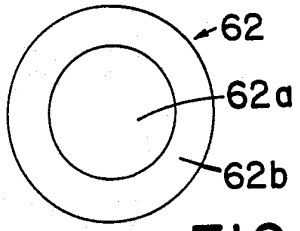

FIG.15

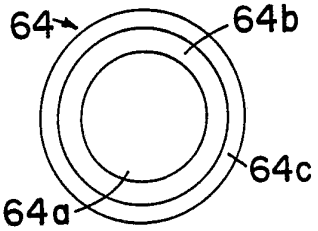

FIG.16

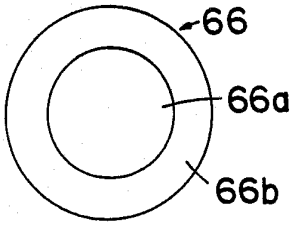

FIG.17

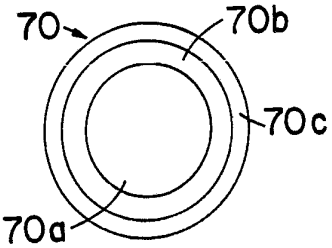

FIG.18

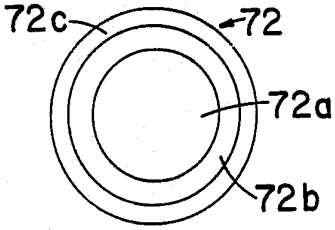

FIG.19

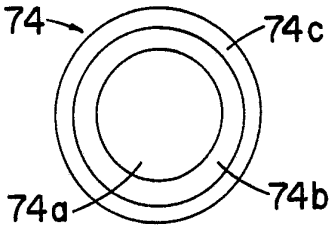

FIG.20

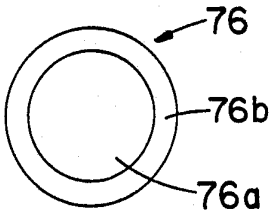

FIG.21

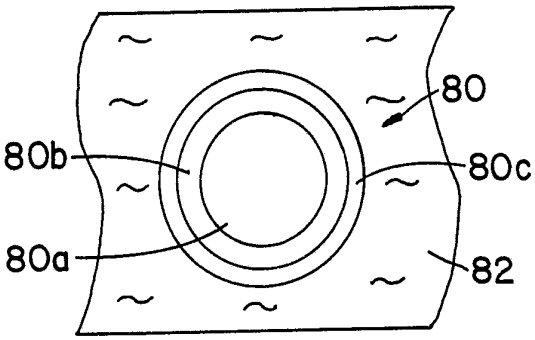

FIG.22

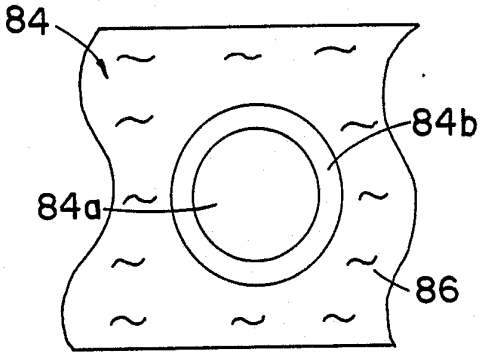

FIG.23

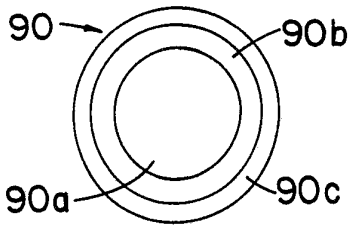

FIG.24

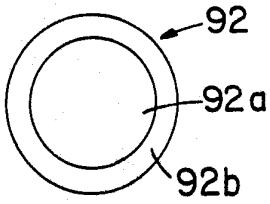

FIG.25

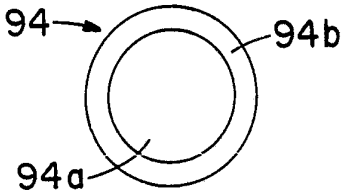

FIG.26

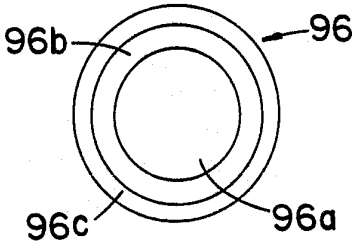

FIG.27

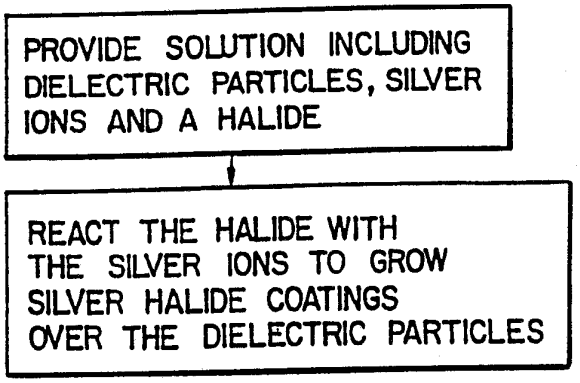

FIG. 28

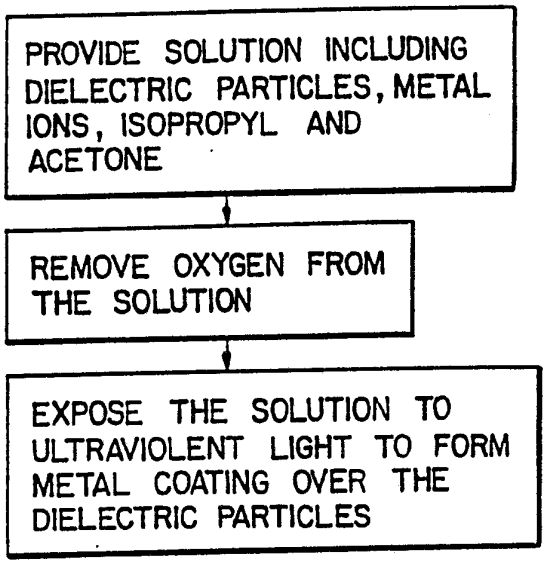

FIG. 29

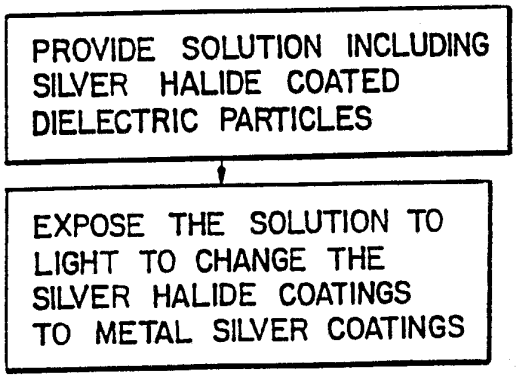

FIG. 30

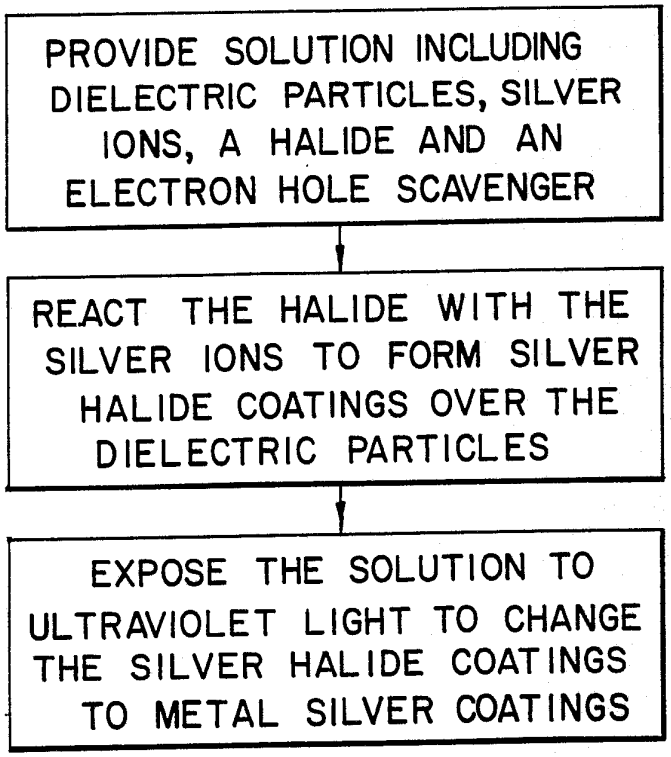
PROVIDE SOLUTION INCLUDING DIELECTRIC PARTICLES, SILVER IONS, A HALIDE AND AN ELECTRON HOLE SCAVENGER
REACT THE HALIDE WITH THE SILVER IONS TO FORM SILVER HALIDE COATINGS OVER THE DIELECTRIC PARTICLES
EXPOSE THE SOLUTION TO ULTRAVIOLET LIGHT TO CHANGE THE SILVER HALIDE COATINGS TO METAL SILVER COATINGS

FIG.31

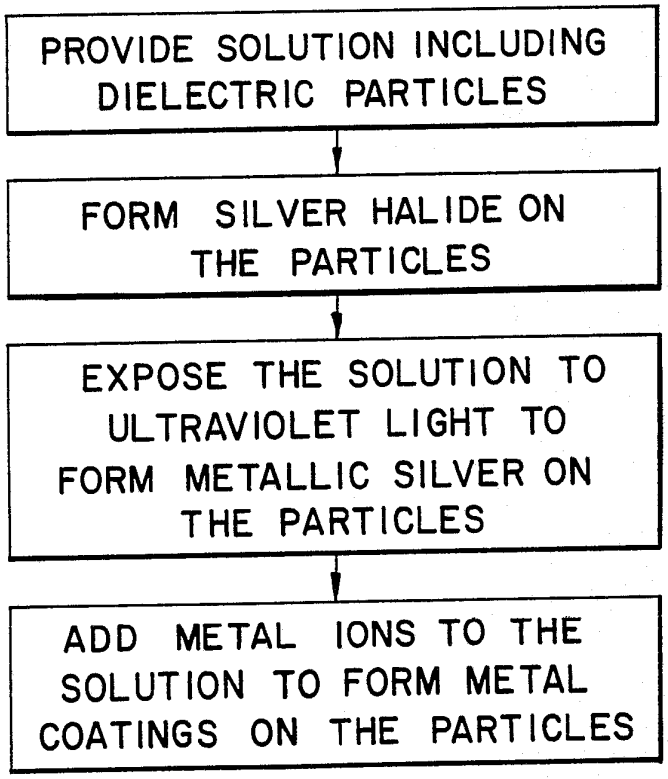
PROVIDE SOLUTION INCLUDING DIELECTRIC PARTICLES
FORM SILVER HALIDE ON THE PARTICLES
EXPOSE THE SOLUTION TO ULTRAVIOLET LIGHT TO FORM METALLIC SILVER ON THE PARTICLES
ADD METAL IONS TO THE SOLUTION TO FORM METAL COATINGS ON THE PARTICLES

FIG.32

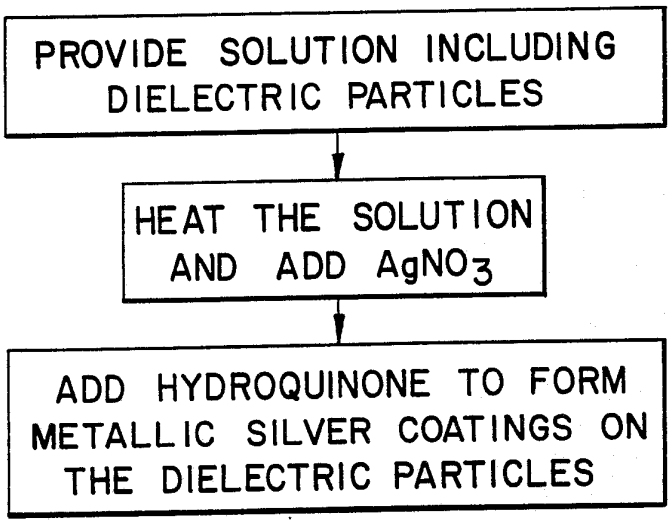
PROVIDE SOLUTION INCLUDING DIELECTRIC PARTICLES
HEAT THE SOLUTION AND ADD $AgNO_3$
ADD HYDROQUINONE TO FORM METALLIC SILVER COATINGS ON THE DIELECTRIC PARTICLES

FIG.33

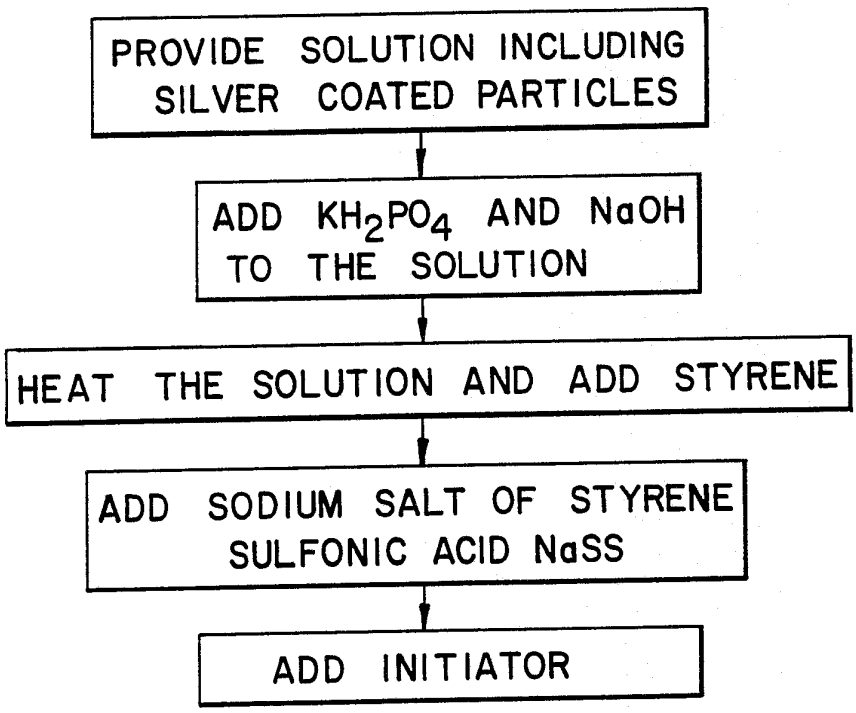
PROVIDE SOLUTION INCLUDING SILVER COATED PARTICLES
ADD KH_2PO_4 AND NaOH TO THE SOLUTION
HEAT THE SOLUTION AND ADD STYRENE
ADD SODIUM SALT OF STYRENE SULFONIC ACID NaSS
ADD INITIATOR

FIG.34

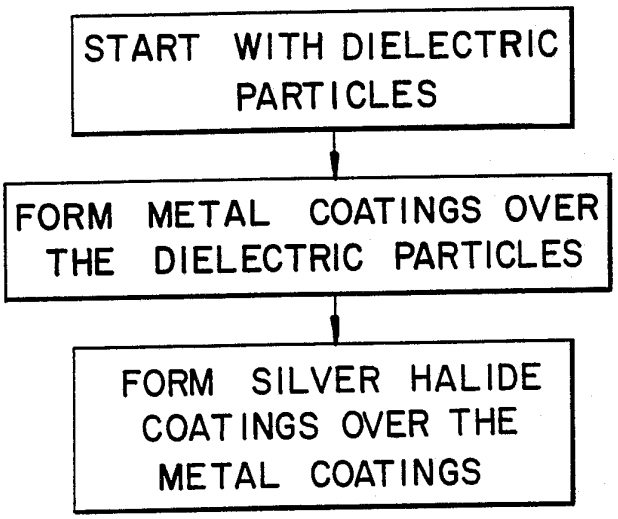
START WITH DIELECTRIC PARTICLES
FORM METAL COATINGS OVER THE DIELECTRIC PARTICLES
FORM SILVER HALIDE COATINGS OVER THE METAL COATINGS

FIG.35

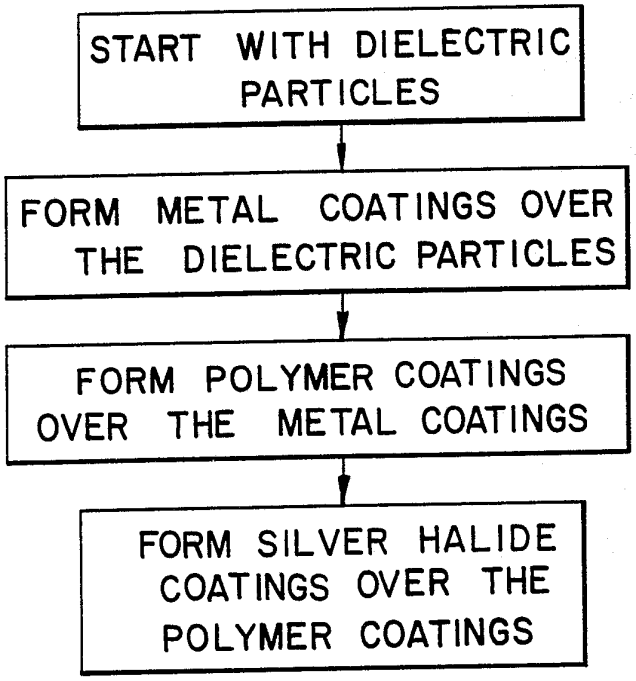
START WITH DIELECTRIC PARTICLES
FORM METAL COATINGS OVER THE DIELECTRIC PARTICLES
FORM POLYMER COATINGS OVER THE METAL COATINGS
FORM SILVER HALIDE COATINGS OVER THE POLYMER COATINGS

FIG.36

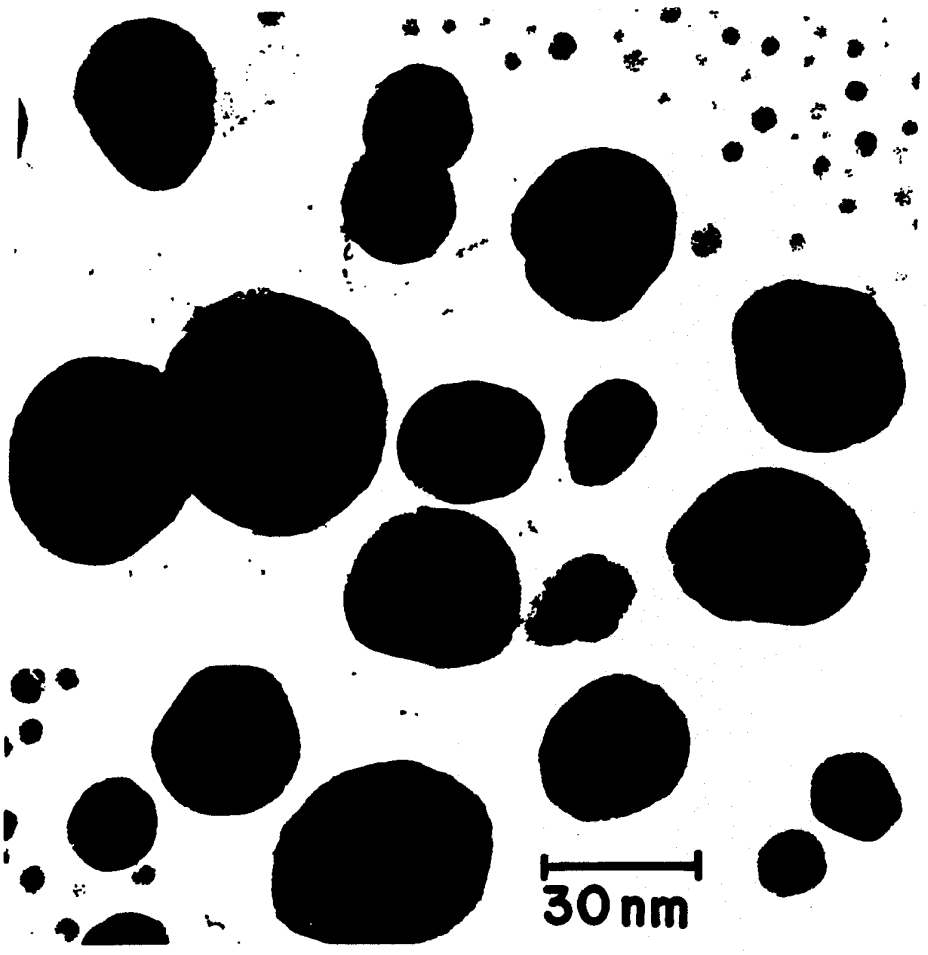

FIG. 37

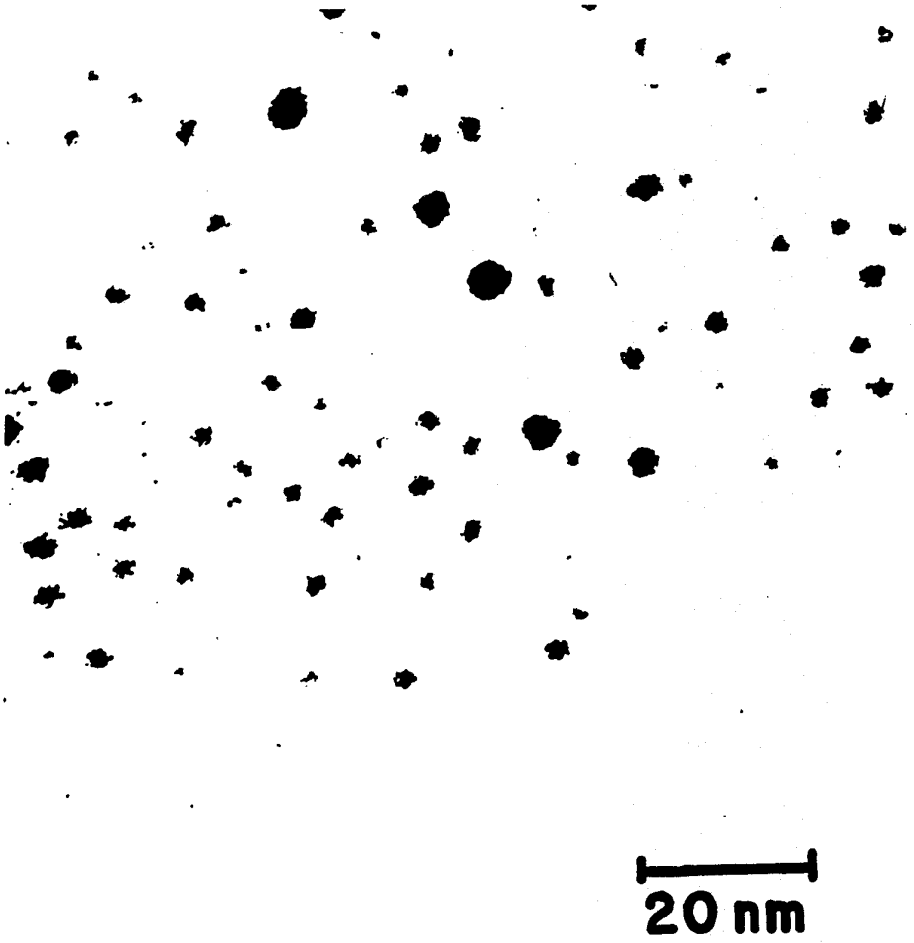

FIG.38

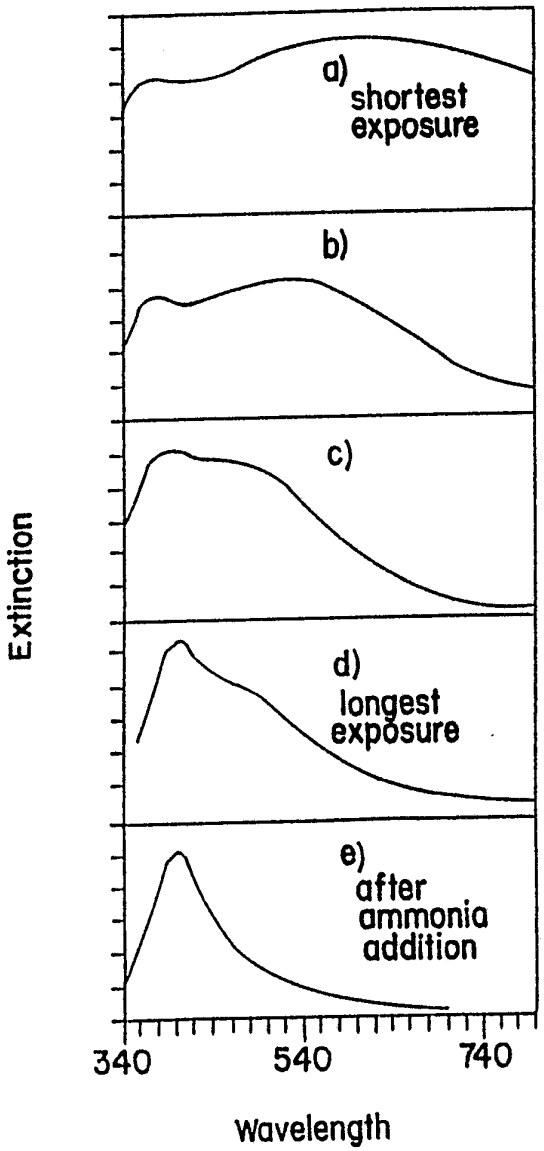
a)
shortest
exposure
b)
c)
d)
longest
exposure
e)
after
ammonia
addition
Extinction
340
540
740
Wavelength

FIG. 39

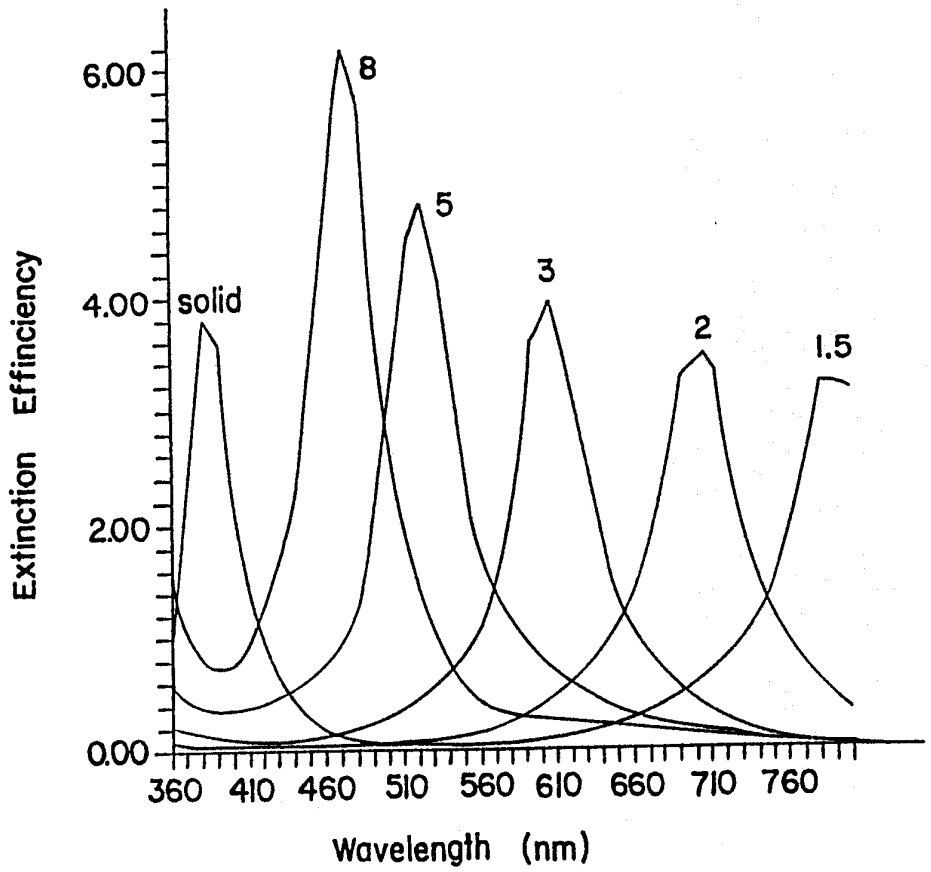
6.00
4.00
2.00
0.00
Extinction Effinciency
solid
8
5
3
2
1.5
360 410 460 510 560 610 660 710 760
Wavelength (nm)

FIG. 40

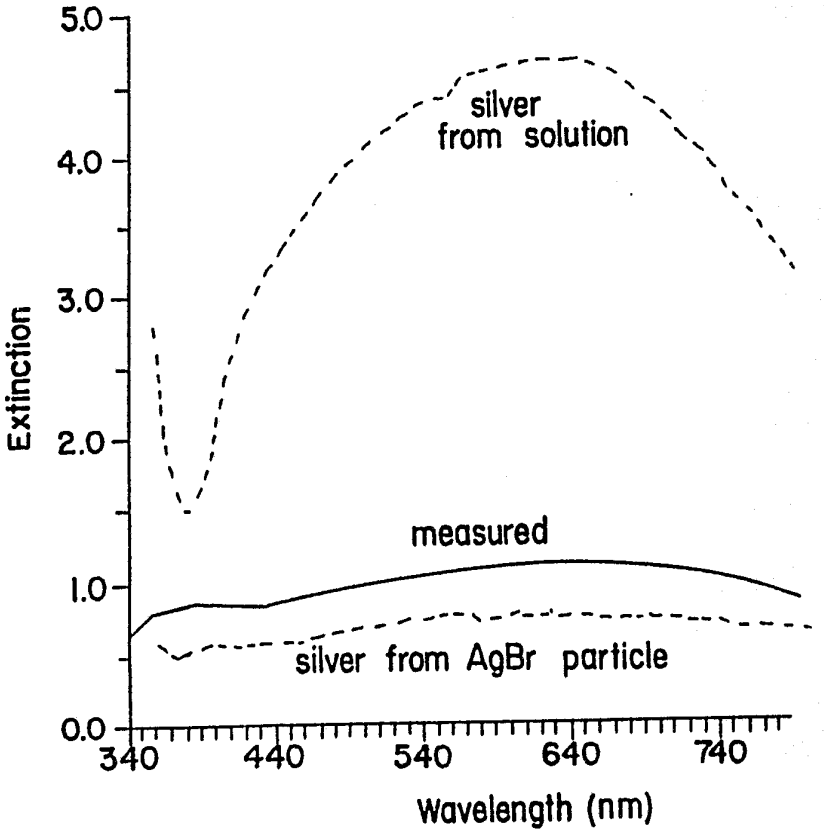
5.0
4.0
3.0
2.0
1.0
0.0
Extinction
silver
from solution
measured
silver from AgBr particle
340
440
540
640
740
Wavelength (nm)

FIG. 41

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/06008

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): G03C 1/00,1/72; G11B 5/00,7/00; B05D 7/00; B32B 5/16, 9/00,15/02 U.S. CL. 430/138; 369/13,283; 427/217,221

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S.	430/138, 567; 369/13, 280, 283, 284, 286, 288 427/217, 221; 428/402.24, 403, 404, 406, 407

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	US, A, 4,587,533 (NAKANE ET AL) 06 MAY 1986; See column 1, lines 16-24.	1-33
Y	US, A, 4,770,973 (KANDA ET AL) 13 SEPTEMBER 1988; See column 1, lines 48-50.	1-33
Y	JP, A, 63-244424 (TOSHIBA CORP.) 11 OCTOBER 1988; See abstract.	1-33
Y	JP, B, 1-25149 (SHARP KK) 16 MAY 1989 See abstract.	1-33
Y	JP, A, 1-189049 (NEC CORP.) 28 JULY 1989 See abstract.	1-33

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
04 DECEMBER 1990	04 FEB 1991
International Searching Authority	**Signature of Authorized Officer**
ISA/US	Hoa V. Le Hoa V. Le

Form PCT/ISA/210 (second sheet) (Rev.11-87)

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers . because they relate to subject matter [12] not required to be searched by this Authority, namely:

2. ☐ Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

3. ☐ Claim numbers_____, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

I. Claims 1-16, 20-24 drawn to a microcapsule, classified in Class 430 Subclass 138.

II. Claims 17-19 and 25-33 drawn to a method of storing and recording, classified in Class 369 Subclass 13.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application. Telephone Practice

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Con't. from Form PCT/ISA/210 supplemental sheet:

Group I, claims 1-16 and 20-24, which relates to microcapsules containing a light sensitive silver halide.

Group II, contains claims 17-19 and 25-33. Claims 17-19 relate to magnetized sensitive metal. Claims 25-33 relate to a method of storing and reading data using the material of claims 17-19.

Applicant has not provided any evidence that the silver halide containing microcapsules as claimed in claim 1 are magnetized and can be able to store or read a data. In the absence of demonstrating a single invention. The above groups of claim invention are lacking of unity under PCT Rule 13.