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(54) **Reducing silver sludging during photographic processing.**

(57) The deposition of a silver-containing sludge on a radiation-sensitive material having a layer of a silver halide emulsion on one surface thereof is prevented or inhibited by providing the material with a surface coating comprising a hydrophillic colloid having dispersed within it particles of wax having a mean diameter of 6 to 25 $\mu$ m, and developing the material with an alkaline solution. The specification also discloses a processing solution composition which comprises a mercapto compound and an anionic surfactant preferably alkylphenoxy polyalkylene oxy phosphoric acid sludge retardation is more effective when using a combination of the material and the processing solution.

Field of the Invention

The present invention relates to sludge-resistant light-sensitive materials containing silver halide emulsions and to methods for developing them which result in reduced silver sludge.

Background of the Invention

The phenomenon of "silver sludge" is the deposition on a silver halide containing photographic material of reduced (i.e. metallic) finely divided silver particles via the processing solution during development. This sludge causes black smudge marks on the developed photographic material and accumulates on the conveyor belts and transport rollers of automatic photographic material processing apparatus. The sludge problem is aggravated by the incorporation in the development medium of silver solvents (which are often used); by high development temperatures; and by spent (not fresh) developing solutions.

Various ways of reducing silver sludge have been proposed. For example, compounds which form insoluble and non-reducible silver salts have been added to developing solutions. Such compounds include 5,5'-bis-1,2,4-triazolin-3-thiones, and derivatives thereof; 1,3,4-thiadazole-2-thiols and derivatives thereof; 2-mercapto-1,3,4-thiadazoles and a variety of other mercapto compounds including substituted 1-phenyl-5-mercaptotetrazoles (Belgian Patent No. 606,550; British Patent No. 1,120,963; U.S. Patent No. 3,212,892; French Patent No. 1,470,235; British Patent No. 1,471,554 and European Patent Application No. 223,883). Unsubstituted 1-phenyl-5-mercaptotetrazole has also been used (U.S. Patent No. 3,173,789). Finally, other sulfur containing compounds have been used such as dithiooctanoic acid, o-mercapto benzoic acid, aliphatic mercaptocarboxylic acids, L-thiazolidine 4-carboxylic acid, other divalent sulfur compounds, 2-mercaptobenzoxazole, 2-mercapto benzimidazole et al. (U.S. Patent Nos. 3,318,701; 3,628,955; British Patent No. 1,144,481; Japanese Application No. 36029/77; *J. Photogr. Sci.* 13:1233, 1965; *Photogr. Sci. Eng.* 20:2120, 1976).

To date, the performance of these compounds in preventing sludge has not been satisfactory. Among the reasons advanced for their failure have been

- formation of high amounts of insoluble silver salts which contaminate the light-sensitive materials and processing solutions (U.S. Patent No. 4,310,622);
- necessity to use high amounts of these compounds many of which have development-restraining properties and thus adversely affect the speed (sensitivity) of the photographic material (EP 223883);
- short-term antisludging effectiveness sometimes attributed to oxidation of the antisludging compounds (U.S. Patent No. 4,310,622); and
- aggravation of the sludge problem after a short period of sludge reduction (U.S. Patent No. 4,310,613; 3,769,015).

Other attempts to reduce sludging have focused on the incorporation in the photographic materials (or in the developing or processing solutions) of various surfactants (such as anionic alkylphenoxy polyalkyleneoxy phosphate esters) which are said to improve the antisludge properties of certain substituted phenyl mercaptotetrazoles (EP 223,883).

Nevertheless, a need has persisted in the field for reducing or eliminating the sludge problem (i.e. for substantially increasing the footage of light-sensitive materials that can be developed in a given amount of processing solution, especially materials containing a paper support, before sludge becomes a problem).

Wax particles have been used in protective layers of silver halide light-sensitive materials as matting agents. For example U.S. Patent No. 2,221,873 discloses a particulate wax matting agent dispersed in the top coat of photographic paper with the aid of a surfactant (dispersing agent). The particles of the wax are bigger than the silver halide grains.

U.S. Patent No. 4,820,615 discloses use of wax-containing coatings for photographic elements as lubricants to improve mechanical properties (slideability and scratch resistance). The '615 invention is directed to a photographic element containing a protective hydrophilic colloid layer which in turn contains beads (0.5-20 microns in average size) of a hydrophobic resinous polymer. The polymer beads are distributed throughout a water-insoluble wax. The effect of these resin/wax beads is said to be reduction of the friction coefficient of the coated surface.

To date, wax particles have not been used to combat the sludge problem.

Summary of the Invention

It has now been found that silver sludge can be effectively reduced or eliminated from developed silver halide light-sensitive materials (such as photographic paper or film) by coating these materials with a particulate wax dispersed in a hydrophilic colloid. Sludge reduction is even more effective if these materials are also proc-

essed in a processing solution (e.g. a developer) containing an amount of a surfactant and a mercapto compound effective in further reducing sludge without substantially affecting sensitivity of these materials. A processing solution containing a mercapto compound and a surfactant can also be used to develop a material that does not contain particulate wax.

Preferred are polyethylene homopolymeric wax particles. Among the mercapto compounds unsubstituted 1-phenyl-5-mercapto tetrazole is preferred. Preferred surfactants are those that decrease the surface tension of the processing solution below 230 dynes/cm<sup>2</sup>.

#### Detailed Description of the Invention

The polymeric waxes useful in this invention desirably have a molecular weight within the range from 1000 up to 10,000.

Preferred are polyalkylene homopolymeric waxes, such as polyethylene homopolymeric wax (e.g. ACUMIST® B and C Series sold by Allied Signal, Inc.).

The average particle size of these wax materials is desirably within the range of about >6 to about 25 microns preferably within the range of about >6 to about 18 microns. ACUMIST B-12 which has a mean particle size of 12 microns is particularly preferred.

The useful amounts of particulate wax are within the range of about 15 to about 80 grams/kg total hydrophilic colloid; preferably about 20 to about 40 g/kg total colloid. ("Total colloid" refers to the amount of colloid on the material, not only the colloid on the wax-bearing top layer.)

The particulate wax material of the present invention may be dispersed in the hydrophilic colloid by first forming an aqueous dispersion of the wax particles (using preferably a surfactant as a dispersing agent) and then mixing the dispersion with the colloid solution. By way of preferred (though non-limiting) example, a 15% dispersion of ACUMIST B-12 containing 0.13% surfactant and 0.06% bactericide is mixed with a gelatin solution containing about 15% gelatin by weight. The resulting colloid dispersion contains about 10% particulate wax material and about 7% gelatin by weight.

The hydrophilic colloid used as a binder for the silver halide emulsion or as a protective colloid to coat the light-sensitive emulsion layer (or layers) of the material is preferably gelatin but other hydrophilic colloids can also be used: For example, processed gelatin, gelatin derivatives, graft polymers of gelatin with other high-molecular weight materials; proteins such as albumin or casein; cellulose derivatives, such as hydroxymethyl or hydroxyethyl cellulose or cellulose sulfate; saccharide derivatives such as sodium alginate, starch derivatives such as polyglycoside dextrans; synthetic homopolymers and copolymers of polyvinyl alcohol, partial acetal polyvinyl alcohol, poly-n-vinyl pyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinyl imidazole, polyvinyl pyrazone, etc. can also be used. All of these materials are known and commercially available.

Processed gelatin includes without limitation lime-processed gelatin, acid-processed gelatin, hydrolyzed gelatin and enzyme-decomposed gelatin. Suitable gelatin derivatives include the reaction products of gelatin and various compounds such as acid halides, acid anhydrides, isocyanates, bromoacetic acid, alkane sulfones, vinyl sulfonamides, maleinimide compounds, polyalkylene oxides, epoxy compounds, phthalic anhydride or succinic anhydride. Specific examples of these gelatin derivatives are described in e.g., U.S. Patent Nos. 2,614,928, 3,132,945, 3,186,846 and 1,005,784, all incorporated by reference.

Examples of suitable gelatin graft polymers include those prepared by grafting a homopolymer or a copolymer of a vinyl monomer such as acrylic acid, methacrylic acid, the derivatives thereof (such as the esters or the amides thereof), acrylonitrile or styrene to gelatin. In particular, graft polymers prepared from polymers which are compatible with gelatin to some degree, such as those of acrylic acid, methacrylamide or a hydroxyalkyl methacrylate. Examples of those polymers are described in, e.g., U.S. Patent Nos. 2,763,625, 2,831,767 and 2,956,884. Typical synthetic hydrophilic high molecular weight materials are described in, e.g., German Patent Application (OLS) 2,312,708, U.S. Patent Nos. 3,620,751 and 3,879,205, all incorporated by reference.

The photographic emulsions used in the light-sensitive materials of this invention can be prepared using the well-known methods described in, e.g., P. Glafkides, *Chimie et Physique Photographique*, Paul Montel, Paris (1967), G. F. Duffin, *Photographic Emulsion Chemistry*, The Focal Press, London (1966), V. L. Zelikman et al., *Making and Coating Photographic Emulsions*, the Focal Press, London (1964), all incorporated by reference. These methods include the acid method, the neutral method, the ammonia method and others. Moreover, a soluble silver salt can be reacted with a soluble halogen salt using any of the single jet method, the double jet method and a combination thereof. The well-known method of forming grains in the presence of an excess of silver ions (the so-called "reverse mixing method") can also be used. The "controlled double jet method" (also called "controlled diffusion method") is preferred. According to this method, the pAg of the liquid phase (in which the silver halide is to be produced) is kept constant. This method can provide silver halide emulsions having a

regular crystal form and an almost uniform grain size.

The silver halide grains in the photographic emulsions used in this invention can have a relatively wide grain size distribution, but a narrow grain size distribution is preferred. In particular, the size of the silver halide grains amounting to 90% of the total, based on the weight or number of the grains, is preferably within  $\pm 40\%$  of the average grain size (such an emulsion is usually called a monodispersed emulsion). Grain size can be controlled by known techniques such as are disclosed in, e.g. U.S. Patents No. 3,271,157; No. 3,704,130; No. 3,574,628; No. 4,276,374 and No. 4,297,439 and in Research Disclosures RD No. 17643, December 1978 and 18716, November 1979, all incorporated by reference.

The individual reactants can be added to the reaction vessel through surface or sub-surface delivery tubes by gravity feed or by delivery apparatus for maintaining control of the pH and/or pAg of the reaction vessel contents, as illustrated by Culhane et al U.S. Patent No. 3,821,002, Oliver U.S. Patent No. 3,031,304 all incorporated by reference. In order to obtain rapid distribution of the reactants within the reaction vessel, specially constructed mixing devices can be employed, as illustrated by Audran U.S. Patent No. 2,996,287, McCrossen et al U.S. Patent No. 3,342,605, Frame et al U.S. Patent No. 3,415,650, Porter et al U.S. Patent No. 3,785,777, Saito et al German OLS No. 2,556,885 and Sato et al German OLS No. 2,555,364 all incorporated by reference. An enclosed reaction vessel can be employed to receive and mix reactants upstream of the main reaction vessel, as illustrated by Forster et al U.S. Patent No. 3,897,935 and Posse et al U.S. Patent No. 3,790,386, all incorporated by reference.

The grain size distribution of the silver halide emulsions can be controlled by silver halide grain separation techniques or by blending silver halide emulsions of differing grain sizes. The emulsions can include ammoniacal emulsions, as illustrated by Glafkides, Photographic Chemistry, Vol. 1, Fountain Press, London, 1958, pp. 365-368 and pp. 301-304; thiocyanate ripened emulsions, as illustrated by Illingsworth U.S. Patent No. 3,320,069; thioether ripened emulsions, as illustrated by McBride U.S. Patent No. 3,271,157, Jones U.S. Patent No. 3,574,628 and Rosecrants et al U.S. Patent No. 3,737,313 or emulsions containing weak silver halide solvents, such as ammonium salts, as illustrated by Perignon U.S. Patent No. 3,784,381 and Research Disclosure, Vol. 134, June 1975, Item 13452 all incorporated by reference. The method using ammonium salts is preferred.

The crystal form of the silver halide grains in the photographic emulsion may be regular (such as cubic or octahedral) or irregular (such as spherical or plate-like) or it may be a composite of these forms. The grains may comprise mixed grains having various crystal forms or core-shell grains.

The interior and the surface layer of the silver halide grain may be different or the grains may be uniform throughout. During the process of the formation or physical ripening of the grains, cadmium salts, zinc salts, lead salts, thallium salts, rhodium salts or complex salts thereof, iron salts or iron complex salts, and the like can be present, as can mixtures thereof. Preferred as such dopants, are rhodium or iridium salts or mixtures thereof.

Any silver halide or combination thereof can be used with silver bromide and silver chlorobromide being preferred.

Two or more of silver halide emulsions which are separately prepared can be mixed and then used, if desired.

After the formation of the precipitates or after physical ripening, the soluble salts are usually removed from the emulsion. For this purpose, the well known noodle washing method may be used. Alternatively, the flocculation method may be used. This method employs an inorganic salt having a polyvalent anion such as sodium sulfate, an anionic surface active agent, an anionic polymer (such as polystyrene sulfonic acid) or a gelatin derivative (such as an aliphatic acylated gelatin, an aromatic acylated gelatin or an aromatic carbamoylated gelatin). The removal of the soluble salts may be omitted, if desired.

The light-sensitive materials can contain a contrast-enhancing agent, such as a hydrazine or a hydrazine derivative. Acyl phenyl hydrazides and especially the "oxaly" phenyl hydrazides disclosed in U.S. Patent No. 4,686,167 or U.S. Patent No. 4,816,373 (Ohashi) (both incorporated by reference) are preferred.

The silver halide emulsions used in the present invention may be chemically sensitized. Processes for chemical sensitization of the silver halide emulsions which can be used include known sulfur sensitization, reduction sensitization and noble metal sensitization processes. In addition to sulfur sensitization, selenium, tellurium, rhenium or phosphorus sensitizers or combinations of these sensitizers can be used. Chemical ripening can be performed at pAg levels of from 5 to 10, pH levels of from 5 to 8 and at temperatures from 30° to 80°C.

These processes are described in references such as P. Glafkides, Chimie et Physique Photographique, Paul Montel, Paris (1967) or Zelikmann, Making and Coating Photographic Emulsions, The Focal Press, London (1964) or H. Frieser, Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden, Akademische Verlagsgesellschaft (1968). The disclosure of these references is incorporated by reference. In the noble metal sensitization processes, a gold sensitization process is a typical process where gold compounds or gold complexes are used.

Complexes of noble group VIII metals other than gold, such as those of platinum, palladium, osmium, rhodium or iridium, etc. can also be used as chemical sensitizers. A reduction sensitization process may be used if the process does not generate fog to a degree which causes practical difficulties (with or without the use of known antifoggants). A particularly preferred chemical sensitization process for the present invention is the use

Examples of sulfur sensitizing agents which can be used include not only sulfur compounds present in the gelatin per se, but also various sulfur compounds such as thiosulfates, thioureas, thiazoles or rhodanines, etc. Examples of suitable sulfur compounds are described in U.S. Patent Nos. 1,574,994, 2,410,689, 2,278,947, 2,728,668 and 3,656,955, all incorporated by reference. Typical examples of reduction-sensitizing agents include stannous salts, amines, formamidine sulfinic acid and silane compounds, methylchlorosilane, hydrazine derivatives, boranes such as aminoboranes, thiourea dioxide, hydrogen, and other boron hydrides such as cyanoborohydrides. Reduction sensitization can also be obtained by low pAg (less than 5) or high pH (greater than 8) treatment, as is well-known in the art.

Specifically contemplated is the combined use of several of the aforementioned chemical ripening techniques; in particular gold-sulfur sensitization combinations are highly preferred.

A photographic material used in this invention may contain an antifoggant incorporated therein. Examples of antifoggants which can be advantageously used in the materials of this invention are 1,2,4-triazole compounds substituted with a mercapto group at the 3-position, mercapto tetrazole compounds, benzotriazole compounds, 2-mercaptobenzimidazole compounds (which do not contain a nitro group), 2-mercaptopyrimidines, 2-mercaptothiazoles, 2-mercaptobenzothiazoles, benzothiazolium compounds (such as N-alkylbenzothiazolium halides, nitrobenzimidazole, substituted triazaindolizines (tetraazaindenes) or N-allylbenzothiazolium halides), and 2-mercapto-1,3,4-thiazoles. Combinations of the two or more of these antifoggants as well as of one or more of these antifoggants with auxiliary antifoggants such as a 6-nitrobenzimidazole, can also be used. It should be noted that if antifoggants are incorporated in the light-sensitive material according to the present invention they are generally in addition to, not instead of, antifoggants that may be incorporated in the processing solution.

It has been observed that both fog reduction and an increase in contrast are obtainable by incorporating in the light-sensitive material benzotriazole antifoggants. When the benzotriazole is located in the photographic element concentrations of  $10^{-4}$  to  $10^{-1}$ , preferably  $10^{-3}$  to  $3 \times 10^{-2}$ , mole per mole of silver are employed.

Useful benzotriazoles can be chosen from among conventional benzotriazole antifoggants, such as those disclosed by Land U.S. Patent No. 2,704,721 and Rogers et al U.S. Patent No. 3,265,498, both incorporated by reference. The preferred benzotriazoles for use in this invention are benzotriazole (that is, the unsubstituted benzotriazole compound), halo-substituted benzotriazoles (e.g., 5-chlorobenzotriazole, 4-bromobenzotriazole and 4-chlorobenzotriazole) and alkyl-substituted benzotriazoles wherein the alkyl moiety contains from about 1 to 12 carbon atoms (e.g., 5-methylbenzotriazole). 5-methylbenzotriazole is most preferred. The use of 5-methylbenzotriazole as an antifoggant is illustrated by Baldassari et al U.S. Patent No. 3,925,086, incorporated by reference.

The photographic emulsions used in this invention can be black and white or color and can be used for camera exposure. To insure good safelight protection safelight dyes and UV absorbing compounds can be used, such as those in U.S. Patents Nos. 3,533,794; 3,314,794 and 3,352,681, all incorporated by reference. Safelight dyes such as oxonols, hemioxonols, styryl dyes, merocyanine dyes and azo dyes can also be used, but preferably such dyes are easily removed or decolorized during processing (see U.S. Patents Nos. 2,274,782; 2,956,879; 3,423,207; 3,976,661 and 3,384,487, all incorporated by reference). Desensitizing dyes (see, e.g. U.S. Patent No. 3,501,307, incorporated by reference) can also be used.

The emulsions can be spectrally sensitized (e.g. to long blue, green, red or infrared) with at least one methine-type and/or other spectrally-sensitizing dye. Suitable sensitizing dyes include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly useful dyes are cyanine dyes, merocyanine dyes and complex merocyanine dyes. These dyes can contain, as a basic heterocyclic nucleus, any of the nuclei which are usually employed in cyanine dyes: a pyrroline nucleus, an oxazoline nucleus, a thiazoline nucleus, a pyrrole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, an imidazole nucleus, a tetrazole nucleus, a pyridine nucleus and the like; one of the above-described nuclei condensed with an alicyclic hydrocarbon ring; and one of the above-described nuclei condensed with an aromatic hydrocarbon ring, such as an indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a benzoselenazole nucleus, a benzimidazole nucleus and a quinoline nucleus. The carbon atoms of the above-described nuclei may be mono- di- or poly-substituted with such diverse substituents as alkyl, aryl, carboxy, sulfo, phenyl, alkoxy and halo, without limitation, and, optionally can be themselves further substituted.

The merocyanine dyes or complex merocyanine dyes can contain, as nucleus having a ketomethylene structure, a 5- to 6-membered heterocyclic nucleus such as a pyrazolin-5-one nucleus, a thiohydantoin nucleus, a 2-thioxazolidin-2,4-dione nucleus, a thiazolidin-2,4-dione nucleus, a rhodanine nucleus or a thiobarbituric acid nucleus.

5 Useful sensitizing dyes include those described in, e.g., German Patent No. 929,080, U.S. Patent Nos. 2,231,658; 2,493,748; 2,503,776; 2,519,001; 2,912,329; 3,656,959; 3,672,897 and 3,694,217, and British Patent No. 1,242,588, all incorporated by reference. The choice of a particular sensitizing dye or dyes depends on the end use of the photographic material as is well-known in the art.

10 These sensitizing dyes may be used individually or as a combination. A combination of sensitizing dyes is often employed particularly for the purpose of supersensitization. Typical examples of such combinations are described in, e.g., U.S. Patent Nos. 2,688,545; 2,977,229; 3,397,060; 3,522,052; 3,527,641; 3,617,293; 3,628,964; 3,666,480; 3,679,428; 3,703,377; 3,769,301; 3,814,609 and 3,837,862, and British Patent No. 1,344,281, all incorporated by reference.

15 The sensitizing dyes may be present in the emulsion together with dyes which themselves do not have any spectral sensitizing effects but exhibit a supersensitizing effect when used in combination with sensitizing dyes, or with other materials which do not substantially absorb visible light but exhibit a supersensitizing effect when used in combination with sensitizing dyes. Examples of such materials are dyes, heterocyclic mercaptans, styryl bases, "Q" salts (e.g. quaternary ammonium salts) and high-molecular weight sulfonic acids such as stilbenes. More specifically, examples include stilbene such as aminostilbene compounds preferably substituted with a nitrogen-containing heterocyclic ring group (e.g., those described in U.S. Patent Nos. 2,933,390 and 3,635,721), aromatic organic acid formaldehyde condensates (e.g., those described in U.S. Patent No. 3,743,510), azaindene compounds, and the like, can be present. The combinations described in U.S. Patent Nos. 3,615,613; 3,615,641; 3,617,295 and 3,635,721 are particularly useful. (The disclosure of all patents mentioned in this paragraph is incorporated by reference.)

25 A water-soluble dye may be present in any of the hydrophilic colloid layers in the photographic light-sensitive materials used in this invention, for example, as a filter dye or for prevention of light scattering, or for antihalation. Examples of these dyes include oxonol dyes, hemioxonol dyes, styryl dyes, merocyanine dyes, cyanine dyes and azo dyes. Of these dyes, oxonol dyes, hemioxonol dyes and merocyanine dyes are particularly useful. Specific examples of dyes which can be used are those described in British Patent Nos. 584,609 and 1,177,429, and U.S. Patent Nos. 2,274,782; 2,533,472; 2,956,879; 3,148,187; 3,177,078; 3,247,127; 3,540,887; 3,575,704; 3,653,905 and 3,718,472, all incorporated by reference.

30 An inorganic or organic hardener may be present in any of the hydrophilic colloid layers in the light-sensitive material used in this invention. These hardeners include, for example, chromium salts (such as chrome alum or chromium acetate), aldehydes (such as formaldehyde, glyoxal or glutaraldehyde), N-methylol compounds (such as dimethylolurea or methyloldimethylhydantoin), dioxane derivatives (such as 2,3-dihydroxydioxane), active vinyl compounds (such as 1,3,5-triacryloyl-hexahydro-s-triazine or bis(vinylsulfonyl)methyl ether), active halogen compounds (such as 2,4-dichloro-6-hydroxy-s-triazine), mucohalic acids (such as mucochloric acid or mucophenoxychloric acid), isoxazoles, dialdehyde starch, 2-chloro-6-hydroxytriazinylated gelatin and the like can be used individually or in combination. Specific examples of these compounds are described, e.g., U.S. Patent Nos. 1,870,354; 2,080,019; 2,726,162; 3,870,013; 2,983,611; 2,992,109; 3,047,394; 3,057,723; 40 3,103,437; 3,321,313; 3,325,287; 3,362,827; 3,539,664 and 3,543,292, British Patent Nos. 676,628; 825,544 and 1,270,578, German Patent Nos. 872,153 and 1,090,427, all incorporated by reference.

45 The light-sensitive materials of this invention may contain various known surface active agents for various purposes, e.g., as a coating aid, for preventing the generation of static charges, improving slip characteristics, improving emulsion dispersion, preventing adhesion, improving photographic characteristics (e.g., accelerating development, increasing contrast, sensitization), etc.

50 Examples of suitable surfactants are: nonionic surface active agents such as saponin (steroids), alkylene oxide derivatives (such as polyethylene glycol, polyethylene glycol/polypropylene glycol condensates, polyethylene glycol alkyl or alkylaryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or amides or silicone/polyethylene oxide adducts), glycidol derivatives (such as alkenylsuccinic acid polyglycerides or alkylphenol polyglycerides), aliphatic esters of polyhydric alcohols, alkyl esters of sucrose, urethanes or ethers; anionic surface active agents containing an acidic group such as a carboxy group, a sulfo group, a phospho group, a sulfuric acid ester group or a phosphoric acid ester group, such as triterpenoid type saponin, alkylcarboxylates, alkylsulfonates, alkylbenzenesulfonates, alkyl naphthalenesulfonates, alkyl sulfuric acid esters, alkyl phosphoric acid esters, N-acyl-N-alkyltaurines, sulfosuccinates, sulfoalkylpolyoxyethylene alkylphenyl ethers or polyoxyethylene alkylphosphates; amphoteric surface active agents such as amino acids, aminoalkylsulfonic acids, aminoalkylsulfuric acid esters, aminoalkylphosphoric acid esters, alkylbetaines, amineimides or amine oxides; and cationic surface active agents such as alkylamine

salts, aliphatic or aromatic quaternary ammonium salts, (such as pyridinium or imidazolium salts) or phosphonium or sulfonium salts containing an aliphatic or heterocyclic ring.

Specific examples of these surface active agents are those described in, e.g., U.S. Patent Nos. 2,240,472; 2,831,766; 3,158,484; 3,210,191; 3,294,540 and 3,507,660; British Patent Nos. 1,012,495; 1,022,878; 1,179,290 and 1,198,450, U.S. Patent Nos. 2,739,891; 2,823,123; 3,068,101; 3,415,649; 3,666,478 and 3,756,828, British Patent No. 1,397,218, U.S. Patent Nos. 3,133,816; 3,441,413; 3,475,174; 3,545,974; 3,726,683 and 3,843,368. Belgium Patent No. 731,126, British Patent Nos. 1,138,514; 1,159,825 and 1,374,780, U.S. Patent Nos. 2,271,623; 2,288,226; 2,944,900; 3,253,919; 3,671,247; 3,772,021; 3,589,906 and 3,754,924, all incorporated by reference. Specifically preferred is a mixture of saponin, nonionic surfactants such as aliphatic esters of polyhydric alcohols, and an anionic surfactant containing a sulfuric or phosphoric acid ester group.

The photographic emulsions used in this invention can contain a dispersion of a synthetic polymer which is insoluble or slightly soluble in water for the purpose of improving the dimensional stability, the development and the fixing and drying rates. Examples of polymers which can be used include polymers composed of one or more alkyl acrylates or methacrylates, alkoxyalkyl acrylates or methacrylates, glycidyl acrylates or methacrylates, acyl or methacrylamide, vinyl esters (for example, vinyl acetate), acrylonitrile, olefins and styrene, etc., and polymers comprising a combination of the above described monomers and acrylic acid, methacrylic acid, unsaturated dicarboxylic acids, hydroxyalkyl acrylates or methacrylates or styrenesulfonic acid, etc. For example, those compounds described in U.S. Patent Nos. 2,376,005; 2,739,137; 2,853,457; 3,062,674; 3,411,911; 3,488,708; 3,525,620; 3,607,290; 3,635,715 and 3,645,740, and British Patent Nos. 1,186,699 and 1,307,373, all incorporated by reference, can be used. A suitable amount of the polymer ranges from about 20 to 80% by weight based on the total weight of the hydrophobic colloid binders. Since high-contrast emulsions such as that used in this invention are suitable for the reproduction of line drawings and the dimensional stability is of importance for such a purpose, it is preferred to use the above-described polymer dispersion to be employed.

In addition to the components of the photographic emulsions and other hydrophilic colloid layers described above, it is appreciated that other conventional agents can be present. For example, the photographic elements can contain developing agents (described below in connection with the processing steps), development modifiers, plasticizers and lubricants, coating aids, antistatic materials, matting agents, brighteners and color materials, these conventional materials being illustrated in Paragraphs V, VIII, XI, XII and XVI of Research Disclosure, December 1978 Item 17643, all incorporated by reference. Preferably, the photographic emulsion also contains anti-ageing agents, useful to prolong the shelf life of the emulsion. Suitable anti-ageing agents (especially for rhodium-doped emulsions) include polyhydroxyspiro-bis-indane as disclosed in U.S. Patent No. 4,346,167 of E. Imatomi and preferably phenidone (up to 2 g/kg of emulsion) as disclosed in U.S. Patent No. 2,751,297 of G. Hood.

In forming photographic elements, the emulsion and other layers can be applied on photographic supports by various procedures, including immersion or dip coating, roller coating, reverse roll coating, air knife coating, doctor blade coating, gravure coating, spray coating, extrusion coating, bead coating, stretch-flow coating and curtain coating. High speed coating using a pressure differential is illustrated by Beguin U.S. Patent No. 2,681,294. Controlled variation in the pressure differential to facilitate coating starts is illustrated by Johnson U.S. Patent No. 3,220,877 and to minimize splicing disruptions is illustrated by Fowble U.S. Patent No. 3,916,043. Coating at reduced pressures to accelerate drying is illustrated by Beck U.S. Patent No. 2,815,307. Very high speed curtain coating is illustrated by Greiller U.S. Patent No. 3,632,374. Two or more layers can be coated simultaneously, as illustrated by Russell U.S. Patent No. 2,761,791, Wynn U.S. Patent No. 2,941,898, Miller et al U.S. Patent No. 3,206,323, Bacon et al U.S. Patent No. 3,425,857, Hughes U.S. Patent No. 3,508,947, Herzhoff et al U.K. Patent No. 1,208,809, Herzhoff et al U.S. Patent No. 3,645,773 and Dittman et al U.S. Patent No. 4,001,024. In simultaneous multilayer coating varied coating hoppers can be used, as illustrated by Russell et al U.S. Patent No. 2,761,417, Russell U.S. Patent Nos. 2,761,418 and 3,474,758, Mercier et al U.S. Patent No. 2,761,419, Wright U.S. Patent No. 2,975,754, Padday U.S. Patent No. 3,005,440, Mercier U.S. Patent No. 3,627,564, Timson U.S. Patent Nos. 3,749,053 and 3,958,532, Jackson U.S. Patent No. 3,933,019 and Jackson et al U.S. Patent No. 3,996,885. Silver halide layers can also be coated by vacuum evaporation, as illustrated by La Valle et al U.S. Patent Nos. 3,219,444 and 3,219,451.

The photographic emulsions are coated on conventional supports which do not undergo serious dimensional changes during processing. Typical suitable supports which can be used are a cellulose acetate film, a polystyrene film, a polyethylene terephthalate film, a polycarbonate film, a laminate thereof, paper, baryta paper, paper coated on laminated with a hydrophobic polymer such as polyethylene, polypropylene, etc. as are commonly used for photographic light-sensitive materials. Transparent supports can also be employed for certain end uses of the light-sensitive material. Transparent supports may be colored by adding a dye or a pigment thereto as described in J. SMPTE, 67, 296 (1958), or Cleare, U.S. Patent No. 3,822,131 (1984), incorporated

by reference. Where the adhesion between the support and the photographic emulsion layer(s) is insufficient, a subbing layer (an adhesive layer) that adheres to both the support and the photographic emulsion layer(s) can be employed. Also, in order to improve the adhesion, surface of the support may be subjected to a preliminary processing such as corona discharge, irradiation with ultraviolet light, flame treatment, etc. A suitable coating amount of silver is about 0.5 g/m<sup>2</sup> to about 10 g/m<sup>2</sup> of the support.

The photographic elements can be imagewise exposed with various forms of light energy, which encompass the ultraviolet, visible (e.g., actinic) and infrared regions of the electromagnetic spectrum as well as electron beam and beta radiation, gamma ray, X-ray, alpha particle, neutron radiation and other forms of corpuscular and wavelike radiant energy in either noncoherent (random phase) forms or coherent (in phase) forms, as produced by lasers ("flash exposure"). Exposures can be monochromatic, orthochromatic or panchromatic. Imagewise exposures at ambient, elevated or reduced temperatures and/or pressures, including high or low intensity exposures, continuous or intermittent exposures, exposure times ranging from minutes to relatively short durations in the millisecond to microsecond range and solarizing exposures, can be employed within the useful response ranges determined by conventional sensitometric techniques, as illustrated by T. H. James, *The Theory of the Photographic Process*, 4th Ed., Macmillan, 1977, Chapters 4, 6, 17, 18 and 23, incorporated by reference.

The photographic light-sensitive material of this invention can be photographically processed using known methods and known processing solutions. The processing temperature usually ranges from about 18° to about 50°C, but temperatures lower than about 18°C or higher than about 50°C may be used. This invention is particularly useful for the formation of an image by development in which a silver image is formed (a black-and-white photographic processing).

The processing liquids used for black-and-white photographic processing preferably contain, as a developing agent, aminophenols (such as N-methyl-p-aminophenol), 3-pyrazolidones (such as 1-phenyl-3-pyrazolidone), dihydroxybenzenes (such as hydroquinone) and other of the aforementioned developing agents. Specific examples of the useful developing agents include hydroquinone alone, hydroquinone plus N-methyl-p-aminophenol, hydroquinone plus 1-phenyl-3-pyrazolidone, and hydroquinone plus N-methyl-p-aminophenol plus 1-phenyl-3-pyrazolidone. (Developing agents can alternatively -- or in addition -- be included in the light-sensitive material itself.) Moreover, the processing liquids usually contain known antioxidants, alkali agents, pH buffers or the like and, if desired, a dissolving aid, a color toning agent, a development accelerator, a surface active agent, an anti-foaming agent, a water softener, a hardener, a tackifier, etc., may be present. An antifogging agent (such as an alkali metal halide or benzotriazole) may also be present in the processing solution developer. It should be noted that when the mercapto compounds of the present invention are used in the processing solution, they are preferably used in addition to other (preferably non-mercapto) antifoggants in amounts which have no significant effect on the sensitivity of the light-sensitive material. These amounts depend on the particular agent used but they are usually within the range of about 0.03 millimoles/l to about 0.85 millimoles/l. For example, PMT is employed in amounts within the range of about 20 mg/l to about 70 mg/l with about 40 mg/l being particularly preferred.

Development is preferably carried out using a processing solution containing more than about 0.15 mol/l of sulfite ions which serve to stabilize the processing solution. The pH of the processing solution is preferably about 10 to about 12.6.

Fixing solutions having a composition generally employed in the art can be used in the present invention. Not only thiosulfates and thiocyanates but also organic sulfur compounds known as fixing agents can be used as fixing agents in the present invention. Preferred examples of fixing agents which can be used in the fixing solution include water-soluble thiosulfates such as sodium thiosulfate, potassium thiosulfate, ammonium thiosulfate, etc., water-soluble thiocyanates such as sodium thiocyanate, potassium thiocyanate, ammonium thiocyanate, etc., water-soluble organic diol fixing agents containing an oxygen atom or a sulfur atom such as 3-thia-1,5-pentanediol, 3,6-dithio-1,8-octanediol, 9-oxo-3,6,12,15-tetrathio-1,17-heptadecanediol, etc., water soluble sulfur-containing organic dibasic acids and water-soluble salts thereof such as ethylene-bisthioglycolic acid and the sodium salt thereof, etc., imidazolidimethiones such as methylimidazolidimethione, etc. These agents described in L. F. A. Mason, *Photographic Processing Chemistry*, pages 187 to 188, Focal Press (1966).

A preferred developing system in accordance with the present invention contains a dihydroxybenzene (e.g. hydroquinone) developing agent, an antifogging agent (development restrainer), an alkanolamine such as diethylamino-propanediol, a source of sulfite ion such as sodium sulfite, and a pH modifier (preferably NaOH and/or Na<sub>2</sub>CO<sub>3</sub>) to adjust the pH. Known antifogging agents include the mercapto compounds having also antisludging properties, but use of other antifogging agents such as the triazoles mentioned above in the discussion of the light-sensitive materials is preferred. Benzotriazoles are particularly preferred. The reason for preferring antifogging agents that are not mercapto compounds is that the cumulative concentration of a mercapto compound may adversely affect sensitivity. A specific preferred developing system is set forth in the Examples below.

Suitable antisludging mercapto agents for incorporation in the processing solution include mercaptotetrazole compounds, mercaptotriazoles, mercaptothiadazoles, mercaptooxadiazoles, mercaptobenzimidazoles, mercaptobenzoxazoles, and mercapto benzthiazoles. Preferred are 1-phenyl-5-mercaptotetrazoles with the phenyl ring optionally mono or multisubstituted with one or more substituents including without limitation C<sub>1</sub>-C<sub>20</sub> alkyl (straight or branched) NHX wherein X is alkyl, aryl, alkaryl, aralkyl, alkarylalkyl or X is -SO<sub>2</sub>R or -COR with R having the same definition as X (except for -SO<sub>2</sub>R and -COR). However unsubstituted 1-phenyl-5-mercaptotetrazole is most preferred.

The foregoing mercapto compounds are well-known and can be synthesized by methods well-known in the art. (Also, many of them are commercially available.) For example, U.S. Patent Nos. 3,295,976; 3,212,892; 3,295,976 and British Patent No. 1,471,554 describe several such syntheses and are incorporated by reference.

The foregoing mercapto compounds can also be synthesized by well-known techniques, such as reaction of the appropriate alkylthiocyanate and sodium azide with dioxane in the presence of water, or condensation of a phenyl mercaptotetrazole with an organic acid chloride.

The amounts of mercapto compound to be incorporated in the processing solution should be generally within the range of about 0.03 to about 0.85 millimole/liter of processing solution. Preferred amounts are about 0.1 to about 0.5 millimoles/liter of processing solution. It is important that the particular amount used be effective to reduce sludging without substantially affecting speed. (A "substantial" effect on speed is for example a reduction by 1/6 stop.)

Most preferably, the processing solution will also contain one or more anionic surfactants in amounts which decrease the surface tension of the processing solution to below about 230 dynes/cm<sup>2</sup>. Preferred are alkylphenoxy polyalkylene oxy phosphoric acid (or sulfuric acid) esters and polyalkylene oxides (such as those having a molecular weight between about 200 and 4000).

The alkylphenoxy polyalkylene oxy phosphoric acid ester anionic surfactant is incorporated in the processing solution in an amount ranging from about 50 to about 1500mg/liter. Preferred amounts are 50 to 200 mg/liter. A particularly preferred surfactant combination is a mixture of nonylphenoxy polyalkylene oxy mono- and di-ester phosphate. The surfactants can be prepared according to methods well-known in the art (see, e.g. Anionic Surfactants, W.M. Linfield, Ed., Marcel Dekker Publ. New York 1976. pp. 509-511) or they are available commercially from e.g. Rhone Poulenc, (GAFC-710).

Addition of the foregoing anionic surfactants serves to further improve the antisludging effect. Preferably the particulate wax dispersion. is used on the photographic material and this material is also processed in a mercapto-compound containing solution preferably also containing one or more of the foregoing surfactants.

### Example 1

#### Formation of Silver Halide Emulsions:

A 91% chlorobromide (0.15 micron) cubic grain emulsion (Emulsion A) was prepared by simultaneously jetting, into a stirred 2% gelatin solution containing 0.015 mole/liter sodium chloride at 56°C, a silver nitrate solution, and a solution containing 8.7 mole% potassium bromide, 91.3 mole% sodium chloride and 0.05 millimole/liter or rhodium trichloride. After desalination the emulsion was redispersed with additional gelatin to produce a Ag/gel ratio of 1.11 and a gelatin concentration of 8.0%. The resulting emulsion was then sulfur-sensitized using methods well known in the art.

A pure bromide (0.20 micron) cubo-octahedral grained emulsion (emulsion B) was prepared by double jetting 3N solutions of silver nitrate and potassium bromide into a stirred 5% gelatin solution held at pH 4.0 and 52°C, such that the pAg was maintained at 8.3. Ten minutes into the make, sufficient sodium hexachlororhodate was introduced to produce an overall rhodium level of approximately 0.3 micromole per mole total silver. After desalination the emulsion was redispersed with additional gelatin to produce a Ag/gel ratio of 1.25 and a gelatin concentration of 8.2%. The resulting emulsion was chemically sensitized with conventional gold/sulfur techniques.

After the addition of appropriate coating aids, Emulsion A was coated on a photographic paper support at a silver coating weight of 0.68 g/m<sup>2</sup>, and emulsion B was similarly coated to produce a silver coat of 1.1 g/m<sup>2</sup>. The corresponding gelatin coating weights were 1.54 and 1.32 g gelatin/m<sup>2</sup>, respectively. Four sample coatings were prepared : each emulsion (A and B) was coated with surface formulations I-1 and I-2 :

Sample A-1 I-1  
Sample A-2 I-2  
Sample B-1 I-1  
Sample B-2 I-2

Formulation I-1 contained 4.6% gelatin, 0.4% of an anionic surfactant, and 0.1% of a silica matting agent (with mean particle size around 3 micron), and in addition, 60 g per kilogram surface gelatin of a polyethylene homopolymeric wax (ACUMIST B-12, made by Allied Signal, Inc., Morristown, NJ and having a mean particle size of 12 microns). The wax was added to the surface formulation as a 10% dispersion in a 7% aqueous gelatin medium.

Formulation I-2 did not contain wax but was otherwise identical to Formulation I-1.

The four samples (A-1, A-2, B-1 and B-2) were then developed in a developer (Developer Y) containing 27g hydroquinone, 80g sodium sulfite, 45g potassium carbonate, 18g sodium hydroxide, 3.3g sodium bromide, 1g ethylene diamine tetraacetic acid, sodium salt (EDTA), 0.12g 5-methyl benzotriazole and 5ml 3-diethylamino-1,2-propane diol at a pH of 12.0.

Silver sludging was assessed in this experiment as follows: Paper samples, with and without the aforementioned wax, were processed through an automatic processing machine which had been deliberately 'dirtyed'. In such cases, the paper samples without the wax material exhibited excessive silver sludge markings, whereas the paper samples containing the wax material, and processed alongside the wax-free papers, showed no evidence of silver sludge.

| SAMPLE        | SILVER SLUDGE LEVEL |
|---------------|---------------------|
| A-1           | None                |
| A-2 (Control) | Excessive           |
| B-1           | None                |
| B-2 (Control) | Excessive           |

## Example 2

The same types of coated samples as used in Example 1 were used as silver sludge test papers by processing in Developer Y (whose composition was given in Example 1) and in Developer X, a developer formulation derived from Developer Y by the addition of 1-phenyl-5-mercaptotetrazole (40mg/liter) and the surfactant mixture of nonylphenoxy polyalkylene oxy mono- and di-ester phosphate (166mg/liter). The mercaptotetrazole was dissolved in methanol prior to addition to the developing solution. To demonstrate the beneficial effect of both the wax and the developer additive a different test method was employed. An automatic processing machine in 'clean' condition was 'exhausted' by processing, without replenishment, unexposed photographic film, at 37°C, and periodically, about every 4.65 m<sup>2</sup> of processed film, photographic paper samples were processed to check for signs of silver sludge. In this manner the amount of processed film necessary to produce silver sludge on photographic paper was established. Parallel processing runs were performed with (Developer X) and without (Developer Y) PMT as the developer additive to determine its effect.

Thus, four coated paper samples (A-1, A-2, B-1 and B-2) were processed through the same processor, to check for signs of silver sludge. The results were as follows:

| SAMPLE | DEVELOPER X           | DEVELOPER Y (CONTROL) |
|--------|-----------------------|-----------------------|
| A-1    | > 46.5 m <sup>2</sup> | > 46.5 m <sup>2</sup> |
| A-2    | > 46.5 m <sup>2</sup> | > 7.5 m <sup>2</sup>  |
| B-1    | > 46.5 m <sup>2</sup> | > 46.5 m <sup>2</sup> |
| B-2    | > 46.5 m <sup>2</sup> | > 7.5 m <sup>2</sup>  |

The data contained in the table above refer to the amount of photographic film which may be processed through the (unreplenished) processing machine, before silver sludge becomes evident on the paper samples.

From these data, it is apparent that either one of the aspects of the present invention is sufficient to solve the sludge problem. However, use of both the wax on the paper and the mercapto compound in the developer is preferred.

Contrary to observations in the prior art, in the present developer there is no progressive aggravation of the sludging problem accompanying use of PMT. Moreover, PMT does not substantially affect speed (data not shown).

Example 3

To demonstrate the combined effect of PMT and wax particles, the same type of experiment as in Example 2 will be carried out but processing of A-1 and B-1 papers will continue in each developer. It will thus be demonstrated that the amount of paper coated with particulate wax that can be processed in Developer X will be at least 93 m<sup>2</sup>, i.e., considerably higher than the amount of wax-free paper that can be processed through Developer X before sludging becomes a problem.

**Claims**

1. A method for reducing the deposition of silver sludge on a radiation-sensitive material having a silver halide emulsion on at least one surface thereof, the method comprising:
  - providing on the material prior to development thereof an effective amount of a surface coating composition comprising a dispersion in a hydrophilic colloid of wax particles having a mean diameter within the range of 6 to 25  $\mu\text{m}$ , and
  - developing the material in an alkaline processing solution.
2. The method of Claim 1, wherein the wax has a molecular weight within the range from 1000 to 10,000 daltons.
3. The method of Claim 2, wherein the wax comprises homopolymeric polyethylene wax, and the colloid comprises gelatin.
4. The method of any preceding Claim, wherein the processing solution contains at least one silver halide solvent.
5. The method of any preceding Claim, wherein the processing solution contains an amount of a mercapto compound sufficient to further reduce sludging but insufficient to affect sensitivity of the radiation-sensitive material, and an amount of a surfactant sufficient to reduce the surface tension of the processing solution to below 230 dynes/cm<sup>2</sup>.
6. The method of Claim 5, wherein the mercapto compound is 1-phenyl-5-mercapto tetrazole.
7. The method of Claim 6, wherein the amount of 1-phenyl-5-mercaptotetrazole is within the range of 20 to 70 milligrams/litre of processing solution.
8. A light-sensitive material comprising a layer emulsion containing silver halide, and a surface layer comprising polyethylene wax particles dispersed in a hydrophilic colloid, the particles being in an amount sufficient to reduce the deposition of sludge on the material during subsequent processing of the material, and having an average size of 6 to 25  $\mu\text{m}$ .
9. The material of Claim 8, wherein the polyethylene wax has a molecular weight within the range of 1000 to 10,000 daltons.
10. The material of Claim 8 or 9, wherein the colloid is gelatin.
11. The material of any of Claims 8 to 10, wherein the wax particles are present in an amount from 15 to 80 grams of wax per kilogram of total colloid.
12. A method for reducing the deposition of silver sludge on a radiation-sensitive material having a silver halide emulsion on at least one surface thereof, the method comprising processing the material in a processing solution in the presence of a dihydroxybenzene developing agent, an alkanolamine, a pH modifier, sulfite ion, at least one antifoggant not comprising a mercapto compound, and a sludge-reducing agent comprising a mercapto compound and an anionic surfactant, the mercapto compound being present in an amount sufficient to reduce sludging but insufficient to affect significantly the sensitivity of the material, and the surfactant being present in an amount sufficient to reduce the surface tension of the processing solution to below 230 dynes/cm<sup>2</sup>.
13. The method of Claim 12, wherein the antifoggant is an alkali halide and/or a benzotriazole.

14. A processing solution for a light-sensitive material, solution comprising:
- a dihydroxybenzene developing agent;
  - an alkanolamine;
  - a pH modifier;
  - sulfite ion;
  - an antifoggant consisting of an alkali halide and/or benzotriazole;
  - a sludge-reducing agent comprising a mercapto compound in an amount sufficient to reduce sludge but insufficient to affect significantly the sensitivity of the light-sensitive material, and
  - a surfactant in an amount sufficient to reduce the surface tension of the solution to below 230 dynes/cm<sup>2</sup>.
15. The solution of Claim 14, wherein the dihydroxybenzene is hydroquinone, the alkanolamine is 3-diethylamino-1,2-propane diol, the pH modifier is sodium carbonate and/or sodium hydroxide, the alkali halide is sodium bromide, the benzotriazole is 5-methyl-benzotriazole, the mercapto compound is 1-phenyl-5-mercaptotetrazole, and the surfactant is a combination of nonylphenoxy polyalkyleneoxy monoester phosphates and diester phosphates.



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# EUROPEAN SEARCH REPORT

Application Number

EP 92 30 5303

| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                        |                                                    |                                                      |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------|------------------------------------------------------|
| Category                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | Citation of document with indication, where appropriate, of relevant passages                                                          | Relevant to claim                                  | CLASSIFICATION OF THE APPLICATION (Int. Cl.5)        |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | US-A-2 059 829 (ERWIN J WARD)<br>* the whole document *<br>---                                                                         | 1-3,8-11                                           | G03C1/76<br>G03C5/305<br>G03C1/95                    |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | GB-A-2 222 700 (ILFORD LIMITED)<br>* page 2, paragraph 2 - page 5, paragraph 5 *<br>* page 6, paragraph 2 - paragraph 4 *<br>---       | 1-3,8-11                                           |                                                      |
| D,Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | EP-A-0 223 883 (AGFA-GEVAERT NV)<br>* the whole document *<br>---                                                                      | 12-15                                              |                                                      |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | EP-A-0 203 521 (FUJI PHOTO FILM CO. LTD.)<br>* page 2, line 17 - page 4, line 2 *<br>---                                               | 12-15                                              |                                                      |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | EP-A-0 136 582 (MINNESOTA MINING AND MANUFACTURING CO.)<br>* page 4, line 1 - line 8 *<br>* page 5, line 26 - page 6, line 17 *<br>--- | 12-15                                              |                                                      |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | US-A-2 970 907 (JOSEPH SOTTYSIAK ET AL)<br>* column 2, line 33 - line 49 *<br>---                                                      | 1                                                  | TECHNICAL FIELDS<br>SEARCHED (Int. Cl.5)<br><br>G03C |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | US-A-3 121 060 (JEROME J DUANE)<br>* the whole document *<br>---                                                                       | 1                                                  |                                                      |
| D,X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | US-A-2 221 873 (JULIUS KNOEFEL)<br>* claims 1-7; figure 3 *<br>-----                                                                   | 1-3                                                |                                                      |
| The present search report has been drawn up for all claims                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                                                                                                        |                                                    |                                                      |
| Place of search<br>THE HAGUE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                                                                        | Date of completion of the search<br>21 AUGUST 1992 | Examiner<br>BOLGER W.                                |
| <p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone<br/>Y : particularly relevant if combined with another document of the same category<br/>A : technological background<br/>O : non-written disclosure<br/>P : intermediate document</p> <p>T : theory or principle underlying the invention<br/>E : earlier patent document, but published on, or after the filing date<br/>D : document cited in the application<br/>L : document cited for other reasons<br/>.....<br/>&amp; : member of the same patent family, corresponding document</p> |                                                                                                                                        |                                                    |                                                      |

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