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RECORDING MATERIAL CONTAINING CLUSTER SILVER COMPOUNDS

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15 Claims

ABSTRACT OF THE DISCLOSURE

Recording material sensitive to electromagnetic radiation and or high energy elementary particles comprising a silver-containing layer in which the silver is present as a cluster silver compound having a proportion of the silver atoms thereof arranged in a plurality of layers of mono-atomic thickness with metal-metal bonds existing between the silver atoms of any one layer; and recording process using the same. The silver ketenide containing silver atoms arranged in mono-atomic layers is preferably prepared by the reaction of silver acetate and acetic anhydride in pyridine.

This invention relates to photographic recording materials consisting of or including a layer containing a silver compound, and particularly relates to photographic recording materials wherein the said silver compound contains silver atoms arranged and associated in a manner hereinafter referred to as "cluster silver." The term "compound" used herein and in the claims hereof in relation to "cluster silver" includes simple compounds and complexes thereof with other compounds.

There has been an increasing interest in metal "cluster" compounds in which the metal atoms thereof are arranged and associated with each other in a way which is different from the arrangement in conventional compounds of such metals. Recent work (E. T. Blues and D. Bryce-Smith, Discuss Faraday Soc., 1969, 47) has shown that silver and silver compounds having anomalous properties may be obtained, for instance by reacting silver salt with acetic anhydride, possibly in the presence of a tertiary base, possibly followed by a heating step. It was suggested that such compounds (e.g. complexes) are consistent with a "silver ketenide" structure $\text{Ag}_2\text{C}_2\text{O}$ and furthermore that such compounds may contain silver clusters (cluster silver) having metal-metal bonding, possibly involving sheets of silver atoms. Further work has confirmed this hypothesis (E. T. Blues et al., Chem. Soc., Chemical Communications 1970, 699-701) wherein silver ketenide prepared by the reaction of silver salts with ketene, or with acetic anhydride in the presence of pyridine or triethylamine, is shown by X-ray and electron diffraction analysis to have a structure wherein silver atoms are in mono-atomic layers, the distance between silver atoms in a layer being 2.84 Å., and a strong direct bond exists between the silver atoms. The inter-layer separation may vary. Thus for silver ketenide the inter-layer distance is 5.856 Å., and for silver ketenide/pyridinate complex the inter-layer distance is approximately twice this value. The layers are separated by ketenide (C_2O) groups.

Recent work has indicated that the "cluster silver" configuration in cluster silver compounds comprises an arrangement of silver atoms in mono-atomic layers which is generally but not exclusively characterized by at least a proportion of the silver atoms being separated from each other, by a distance of less than 3.0 Å.

Silver ketenide and silver ketenide complexes may be

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converted to other silver compounds or complexes by ligand exchange, and in such other silver compounds or complexes at least a proportion of the silver atoms retain the "cluster silver" configuration of silver ketenide. Thus "cluster silver" halides may be produced by the reaction of silver ketenide complexes with a halide salt to provide a precipitate of the cluster silver halide or complexes thereof. By this means cluster silver chloride, cluster silver bromide and cluster silver iodide may be obtained. Such cluster silver halide or complexes may owe their anomalous properties to a residual proportion of silver ketenide associated therewith.

The term "cluster silver compounds" used in the present specification and claims is hereby defined as silver compounds (which term includes simple compounds or complexes thereof with other compounds) wherein at least a portion of the silver atoms are arranged in a plurality of layers of mono-atomic thickness, and wherein metal-metal bonds exist between the silver atoms of any one layer.

It has now been discovered that a useful photographic recording material is provided by a recording element containing one or more cluster silver compounds as hereinbefore defined. Preferably the cluster silver compounds are applied in or to a sheet material e.g. in a binder layer.

Particular cluster silver compounds are silver ketenide, complexes of silver ketenide with certain tertiary bases as hereinafter described, complexes of silver ketenide or silver ketenide/tertiary base with a complexing compound e.g. a salt, for instance silver chloride, silver bromide or silver iodide, and cluster silver salts, e.g. cluster silver chloride, bromide and iodide.

The binder may be a hydrophilic binder, e.g. a water-soluble colloid of the type used in silver halide emulsion layers, preference being given to gelatin; or an organophilic binder i.e. a binder soluble in organic solvents, for example polyvinylbutyral, which may be used in association with a hydrophilic binding agent e.g. acting a dispersing agent or protective colloid. Useful in that respect are hydrophilic colloids that are soluble in water and in a lower alkanol e.g. methanol. A suitable binding agent combination contains polyvinylbutyral and poly-N-vinylpyrrolidone. Organophilic binding agents may be applied for a solution in an organic solvent or as a dispersion from an aqueous medium e.g. as a latex.

Suitable organophilic binding agents are known from electrophotographic recording materials containing dispersed photoconductive pigments. In cases wherein the recording layer needs a particular good mechanical strength cross-linked binding agent structures may be formed. The layer of binder containing cluster silver compound(s) may be a self-supporting layer or such a layer on a support.

The recording material according to the invention on exposure to electromagnetic radiation, e.g. visible light or infrared radiation, or exposure to high-energy electromagnetic radiation, is capable of forming an image in the exposed areas. On exposure to appropriate radiation a print-out image may be obtained, or a latent image which may be developed. For example by using a compound having reducing properties as e.g. contained in a conventional photographic silver halide developer.

Cluster silver compounds for incorporation in the binder for use according to the invention may be produced by any of the methods described in United States patent application 21,539 or in the Chem. Soc. Chemical Communications publication hereinbefore referred to.

Silver ketenide has the empirical formula $\text{Ag}_2\text{C}_2\text{O}$ and is considered to have a structural arrangement as set forth on page 700 of the Chemical Society Chemical Communications publication.

In particular such cluster silver complexes may be prepared by contacting a compound of conventional sil-

ver with a carboxylic acid anhydride, the reactants being selected so that at least one of the reactants contains a $-\text{CH}_2-\text{CO}-$ group, whereby a yellowish or yellowish-red precipitate of complex is formed, and separating the said complex. The separated complex is preferably treated with an aqueous medium or methanol, or by heating, or a combination of both, for such a combination of time and temperature that the complex develops a magnetic susceptibility which is field-dependent.

The particular silver compound and the particular organic anhydride used are selected so that a yellowish or yellowish-red product is formed in the reaction medium. Subject to the said test for suitability, specific classes and specific examples of silver compounds which may be used to form the said yellowish or yellowish-red complexes containing cluster silver for use according to the invention include the following.

Silver salts of monocarboxylic acids, e.g. formate, acetate, trimethyl acetate, trifluoroacetate, propionate, isobutyrate or lactate, or unsaturated acids e.g. acrylate; or aromatic acids, e.g. benzoate and phenylacetate.

Silver salts of polycarboxylic acids, e.g. oxalate, malonate, succinate, or adipate, or unsaturated acids, e.g. maleate or fumarate; or aromatic acids, e.g. phthalates.

Silver salts of sulphonic acids, e.g. methane sulphonate, benzene sulphonate or toluene p-sulphonate.

Miscellaneous organic salts, e.g. silver naphthenate and phenylacetylde.

Silver salts of inorganic acids, e.g., sulphate, nitrate, nitrite, carbonate, fluoride, perchlorate, tetrafluoroborate, hexafluorophosphate.

Miscellaneous inorganic compound, e.g. silver oxide or hydroxide.

Conventional silver metal may be used as a starting material in the presence of a reagent that converts the silver to a silver compound as hereinbefore described, e.g. nitric acid or peracetic acid.

Certain conventional silver compounds may not in practice produce the required yellowish or yellowish-red complex when reacted with an organic anhydride according to the invention, and their unsuitability may be recognised by their failure of the reaction medium to develop a yellow or reddish-yellow complex. Such compounds include silver halides (other than silver fluoride), silver pseudo halides and silver sulphide.

Anhydrides which may be used in the said preparation to produce the yellowish or yellowish-red complex include anhydrides of monocarboxylic acids, e.g. acetic anhydride, propionic anhydride, n-butyric anhydride, n-valeric anhydride, iso-valeric anhydride, caproic anhydride, caprylic anhydride and lauric anhydride. Anhydrides of an unsaturated monocarboxylic acid may be used, e.g. acrylic anhydride. Mixed anhydrides of organic acids or organic and inorganic acids may be used, for instance acetic-isovaleric anhydride, acetic butyric anhydride, acetyl chloride, and acetyl fluoride.

In carrying out the initial reaction to form the yellow or yellowish-red complex, it is necessary that the said $-\text{CH}_2-\text{CO}-$ group be present in at least one of the reagents. For example the said $-\text{CH}_2-\text{CO}-$ group may be present as the acetate group in silver acetate starting material, or may be present in the organic anhydride. Thus suitable combinations of reactants are silver acetate and benzoic anhydride or silver benzoate and acetic anhydride. Such combinations as silver benzoate and benzoic anhydride may not however be used, as such a combination does not include a $-\text{CH}_2-\text{CO}-$ group.

In the reaction to produce the said yellow or yellowish-red silver complex, carboxylic acid(s) are formed from the starting materials. For instance with silver acetate and acetic anhydride, acetic acid is the major by-product, and as such tends to inhibit the formation of the said complex and should therefore preferably be removed during the course of the reaction, for instance by frac-

of a large molar excess of the anhydride component based on the silver reactant, e.g. from 20:1 to 40:1, whereby the carboxylic acid is diluted and its inhibitory effect decreased.

The reaction may be carried out under air or an inert atmosphere for example argon. Nitrogen is not an inert gas, as nitrogen may enter the product.

The reaction between the silver compound and the organic anhydride may if required, be effected at an elevated temperature between 80°C . and the boiling point of the reactants, preferably above 130°C ., and particularly by refluxing the reaction medium.

An alternative procedure for effecting the reaction, which is a preferred method, permits the reaction to be effected rapidly and with good yields at room temperature. Said preferred method comprises effecting said reaction between the silver compound and the organic anhydride in the presence of at least one tertiary amine.

Specific examples of tertiary amines which may be used in the said preferred method include quinoline, isoquinoline, N,N-dimethyl aniline, 2,3-dimethyl quinoline, 2,6-dimethyl quinoline, N,N-dimethyl-o-toluidine, N-methyl pyrrolidine, 2-methyl quinoline, 5-methyl quinoline, α -picoline, β -picoline, γ -picoline, pyridine, quinoline, trimethylamine, triethylamine, triisobutylamine, N-methylpiperidine, N-methylmorpholine and diazabicyclooctane.

Certain very weak tertiary bases, for example triphenylamine, may not however exert a significant effect on the reaction rate, and the selection of suitable tertiary amines may readily be determined by experiment. A useful tertiary amine is a trialkylamine, e.g. trimethylamine or triethylamine. Silver ketenide derived from ketene and silver acetate or from acetic anhydride and silver acetate, in the presence of triethylamine, has particularly light-sensitive properties. Particularly useful complexes are those of silver ketenide with either silver chloride or silver bromide. If silver ketenide is contacted with a solution of silver chloride or silver bromide in concentrated ammonia at room temperature, mixed complexes of halide and ketenide are obtained which are particularly sensitive. Thus the silver bromide complexes are sensitive to visible and infra-red light.

A particularly preferred method of forming silver ketenide comprises reacting silver acetate and acetic anhydride in the presence of pyridine. One variant of the said method is to suspend the silver acetate in the silver anhydride and to add pyridine drop-wise to the suspension at room temperature (20°C .) whilst stirring. By this means a pyridinate complex is formed. Silver ketenide may be obtained from the pyridinate by heating, preferably with acetic anhydride, whereby pyridine is removed. Alternatively, products for use according to the present invention may be obtained by contacting the pyridinate with a hydroxyl group containing compound, e.g. methanol or water.

Silver ketenide has absorption maxima at about 445 and 468 nm. and shows light sensitivity at these wavelengths.

However simultaneous exposure to shorter wavelength radiation may decrease sensitivity, i.e. blue and UV-radiation either may inhibit or reverse the darkening process.

The photosensitive compounds used in recording materials and processes according to the present invention may be spectrally sensitized with compounds and according to recording techniques known to those skilled in the art of preparing silver halide photographic materials.

The presence of silver ketenide in materials obtained by the various methods as hereinbefore described may be removed by distillation, or its effect minimized by the presence tested by exposing the material e.g. suspended on glass wool, with hydrogen chloride gas diluted with nitrogen to prevent detonation of the complex. Ketene gas is first produced, followed by acetyl chloride.

The following examples of the invention are provided.

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Example 1

A silver iodide/silver ketenide complex was prepared in a first stage by heating under reflux under argon in the dark a mixture of silver acetate with an excess of acetic anhydride. In a second stage 21 g. of the obtained silver ketenide product were heated with 23 g. of methyl iodide, in 200 ml. of n-hexane for six weeks in the dark. The resulting yellow product was filtered, washed with pentane and dried. Yield: 29.5 g. of silver iodide/silver ketenide complex.

4 g. of the complex thus obtained were dispersed in a liquid mixture of 70 g. of a 10% by weight solution in methanol of polyvinylbutyral (average molecular weight 38,000-45,000 containing 80% of acetal groups) and 10 g. of a 10% by weight solution of poly-N-vinylpyrrolidone (average molecular weight 40,000) in methanol. The dispersion thus obtained was diluted with 52 ml. of methanol and thereafter applied to a photographic paper at such a loading that the formed layer contained said complex in an amount corresponding with 33 g. of silver per sq. m. of paper, and the layer dried.

The thus obtained photosensitive recording material was exposed for 185 sec. through a line image. The recording layer received 109,000 lux emitted by tungsten incandescent lamps in correspondence with the optically clear image parts of the original. A print-out image was obtained having a maximum optical density of 0.64 measured in reflection. The minimum density was 0.18.

The procedure was repeated using conventional silver iodide or silver bromide instead of the silver iodide/silver ketenide complex, the silver iodide and silver bromide being used in corresponding amounts, and the following optical density values were respectively obtained.

	D _{max.}	D _{min.}
AgI.....	0.10	0.10
AgBr.....	0.20	0.10

EXAMPLE 2

Preparation of silver ketenide from the reaction of silver acetate and acetic anhydride, in the presence of pyridine

20 g. of silver acetate was dissolved in 80 ml. of pyridine, and 200 ml. of acetic anhydride slowly added at 20° C. with stirring. On standing for 10 minutes a yellow precipitate had formed.

The yellow precipitate was filtered off and washed with acetic anhydride, and the solid thus obtained introduced into a 500 ml. flask with 150 ml. of acetic anhydride. The mixture was then slowly heated until all the pyridine was driven off and only acetic anhydride was being distilled over. The product complex was then filtered off, washed with methanol, and a slurry formed with acetone, and the slurry washed with methanol and ether being filtered after each washing.

The dried yellow product analyzed as Ag₂C₂O, and consisted of silver ketenide, the silver atoms of which were arranged in monoatomic sheets, as shown by X-ray analysis.

The magnetic susceptibility of the silver ketenide was measured in different magnetic fields at 22° C., using a Gouy balance, and was found to be weakly field dependent.

2 g. of the said complex were added to 20 ml. of water and dispersed in 80 ml. of a 10% by weight aqueous solution of gelatin.

The obtained dispersion was coated at a loading of 1 g. of complex per sq.m. onto a baryta coated photographic paper base. The thus obtained layer was dried at 30° C. and had a yellow appearance.

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The dried recording layer was contact-exposed for 2 min. with normal daylight using a step wedge having a constant 0.2 as original.

The exposed recording layer was developed at 20° C. in a developing liquid having the following composition:

	G.
p-Methylaminophenol sulphate	1.5
Hydroquinone	6
10 Anhydrous sodium sulphite	50
Anhydrous sodium carbonate	32
Potassium bromide	2
Water to 1000 ml.	

15 The developed wedge image representing 15 reproduced steps was fixed in a fixing liquid having the following composition:

	G.
20 Sodium thiosulphate	200
Anhydrous sodium sulphite	12
Potassium disulphite (K ₂ S ₂ O ₅)	12
Water to 1000 ml.	

25 After 30 min. rinsing and drying a stable wedge print of black silver on a white image background was obtained.

We claim:

1. A recording material sensitive to electromagnetic radiation and/or high energy elementary particles comprising a layer of a binder medium containing a cluster silver compound which is yellow to reddish yellow in color and comprises silver ketenide, a complex of silver ketenide with a tertiary base, a complex of silver ketenide with silver chloride, silver bromide, silver iodide or mixture thereof or a complex of silver ketenide with a tertiary base and with silver chloride, silver bromide, silver iodide or mixtures thereof, said cluster silver compound being characterized in that at least a portion of the silver atoms are arranged in a plurality of layers of mono-atomic thickness with direct metal-metal bonds between the silver atoms of a given layer, the distance between any silver atom in such layer and the nearest silver atom being generally less than about 3 Å.

2. A recording material according to claim 1, wherein said layer contains a hydrophilic binding agent.

3. A recording material according to claim 2, wherein the hydrophilic binder is a water-soluble colloid.

4. A recording material according to claim 3, wherein the hydrophilic binder is gelatin.

5. A recording material according to claim 1, wherein said layer contains an organophilic binding agent.

6. A recording material according to claim 1, comprising a support carrying said layer.

7. A recording material according to claim 1, wherein said cluster silver compound is obtained by reacting a silver salt with a carboxylic acid anhydride, at least one of the reactants being selected to contain a —CH₂—CO— group, whereby a yellowish or yellowish-red complex is precipitated, and separating the said complex.

8. A recording material according to claim 7, wherein said separated complex is contacted with a hydroxyl group containing compound.

9. A recording material according to claim 7, wherein the carboxylic acid anhydride is acetic anhydride.

10. A recording material according to claim 7, wherein the said reaction is carried out in the presence of a tertiary amine.

11. A recording material according to claim 10, wherein the said tertiary amine is a trialkylamine.

12. A recording material according to claim 10, wherein the said tertiary amine is pyridine.

13. A recording material according to claim 7, wherein the said reaction is carried out in the presence of silver chloride, bromide or iodide, or a mixture thereof.

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14. A recording method which comprises image-wise exposing a layer comprising in a binder medium a cluster silver compound which is yellow to reddish yellow in color and comprises silver ketenide, a complex of silver ketenide with a tertiary base, a complex of silver ketenide with silver chloride, silver bromide, silver iodide or mixtures thereof or a complex of silver ketenide with a tertiary base and with silver chloride, silver bromide, silver iodide or mixtures thereof, said cluster silver compound being characterized in that at least a portion of the silver atoms are arranged in a plurality of layers of mono-atomic thickness with direct metal-metal bonds between the silver atoms of a given layer, the distance between any silver atom in such layer and the nearest silver atom being generally less than about 3 Å., to electromagnetic radiation and/or high energy elementary particles resulting in the formation of a recorded image in said layer.

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15. A recording method according to claim 14, wherein the image is developed by means of a reducing compound.

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