PROCESS FOR PRODUCING AN ORGANIC SILVER CARBOXYLATE

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Field of Search...... 260/414, 430, 526 R

References Cited
UNITED STATES PATENTS
3,764,328 10/1973 Birkeland.......................... 96/67

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ABSTRACT

A process for producing a silver salt of an organic carboxylic acid which comprises mixing an aqueous silver nitrate solution or an aqueous silver complex solution with an organic carboxylic acid solution in the presence of a lead compound(s) and/or a mercury compound(s) to obtain the salt of the organic carboxylic acid. The product is employed in a thermally developable light-sensitive element.

18 Claims, No Drawings
PROCESS FOR PRODUCING AN ORGANIC SILVER CARBOXYLATE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process of producing a silver salt of an organic carboxylic acid (in the present specification the terms “silver salt of organic carboxylic acid,” and “organic silver carboxylate” refer to the reaction product of the process of the present invention between silver and the organic carboxylic acid. The former is generally used.) More particularly it relates to a process for producing a silver salt of an organic carboxylic acid having a fine grain size which is suitable for use in a thermally developable light-sensitive element. The present invention is directed to a process for producing silver salt of an organic carboxylic acid which comprises mixing an aqueous silver nitrate solution or an aqueous silver complex solution with a solution of an organic carboxylic acid in a solvent which is sparingly miscible with water, in which the organic carboxylic acid is soluble and the silver salt of an organic carboxylic acid and silver nitrate are hardly soluble to react, whereby the reaction of the organic carboxylic acid and silver ions is conducted in the presence of a mercury or lead compound(s).

2. Description of the Prior Art

It is described, for example, Japanese Pat. Publication No. 4921/68, Japanese Pat. Publication No. 4924/68, U.S. Pat. No. 3,589,901, U.S. Pat. No. 3,589,903, that a silver salt of an organic carboxylic acid can be employed in a thermally developable light-sensitive material.

The thermally developable light-sensitive material is substantially composed of a silver salt of an organic carboxylic acid, e.g., silver benenate, silver halide obtained by reacting a halide with the silver salt or silver halide separately prepared and a reducing agent. After the thermally developable light-sensitive material is exposed imagewise and heated, a silver image is obtained by the reaction of the silver salt of an organic carboxylic acid with the reducing agent which is caused by the action of the exposed silver halide upon heating.

We have now found that when the silver salt of an organic carboxylic acid has a small grain size in such a thermally developable light-sensitive material, the density of images increases and the resolving power is improved. This is assumed to be based on the fact that when a smaller grain size silver salt of an organic carboxylic acid is employed, the specific area of the grains becomes greater and as a result the area to react with the reducing agent increases so that the density of images also increases, and further, the grain size of the developed silver becomes small in the use of the silver salt of an organic carboxylic acid having a small grain size, so that the resolving power increases.

Apart from this assumption, it is known that the use of a silver salt of an organic carboxylic acid having a fine particle size as a silver salt of an organic carboxylic acid which can be similarly used in a thermally developable light-sensitive material increases the density of images and improves the resolving power. For instance, such is described in our Japanese Pat. Publication No. 30270/69.

In a thermally developable light-sensitive material, the light-sensitive material is usually merely heated after imagewise exposure to develop it, and other operations are omitted. That is, operations for silver halide photographic light-sensitive materials are not conducted such operations involving treating after development with a fixing solution containing a compound capable of forming a silver halide complex, e.g., sodium thiosulfate, to convert the undeveloped silver halide to a watersoluble silver complex which is washed with water to remove the silver complex and then fixed.

In other words, the silver salt of an organic carboxylic acid which is employed in a thermally developable light-sensitive material is not eliminated after development, unlike silver halide employed in a silver halide photographic light-sensitive material. Accordingly, a transparent photographic film cannot be formed when a silver salt of an organic carboxylic acid used in a thermally developable light-sensitive material is coated on a transparent film support. There are, of course, no difficulties in coating on opaque paper. As described above, in this regard thermally developable elements are different from silver halide photographic light-sensitive materials in which fixing is conducted after development where the coated layer which is opaque before development is developed, fixed and washed with water to remove silver halide, so that the light-sensitive material thus treated becomes transparent, even if silver halide having a coarse grain size is used in a silver halide photographic light-sensitive material.

Accordingly, a silver salt of an organic carboxylic acid having a fine grain size must be employed as the silver salt of an organic carboxylic acid used in the case that a transparent light-sensitive material coated layer is desired using a silver salt of an organic carboxylic acid in a thermally developable light-sensitive material.

Silver salts of an organic carboxylic acid have been prepared, e.g., by adding an aqueous silver nitrate solution to an aqueous solution of an organic carboxylate such as the sodium salt of an organic carboxylic acid, which is described, for instance, in the Examples of Japanese Pat. Publication No. 13554/66 and Japanese Pat. Publication No. 4924/68. According to this process, however, coarse spindle-like crystals in which the long side thereof is over several microns is obtained. Coating of such coarse silver salt of an organic carboxylic acid grains on, e.g., a transparent film support, gives an opaque coated layer. Further, insufficient image density is obtained since it is difficult to develop.

In order to eliminate the shortcomings in such conventional processes, a process has been provided which comprises incorporating a solution of a silver salt of an organic carboxylic acid in a water-immiscible solvent into an aqueous solution of an alkalisoluble silver complex to obtain silver salt of an organic carboxylic acid having fine grain size, which is described in U.S. Pat. No. 3,458,544.

The silver salt of an organic carboxylic acid in accordance with the above process is in the form of fine spindles having about a 1μ long side diameter so that a thermally developable light-sensitive material obtained from the silver salt of an organic carboxylic acid gives an image having a clear, high density after exposure and thermal development, while the coated layer is still somewhat opaque when coated on a transparent film support, and thus a transparent thermally developable photographic film can not be obtained.

SUMMARY OF THE INVENTION

The present invention is directed to a process of pro-
producing a silver salt of an organic carboxylic acid which comprises mixing an aqueous silver nitrate solution or an aqueous silver complex solution with a solution of an organic carboxylic acid in a solvent in which the organic carboxylic acid is soluble, both the silver salt of an organic carboxylic acid and silver nitrate are almost insoluble and with which water is sparingly miscible, to react the organic carboxylic acid with silver ions, the reaction being conducted in the presence of a mercury compound or a lead compound.

The inventors further found that a silver salt of an organic carboxylic acid having a grain size of less than 1 μ in diameter which is almost spherical can be obtained by the reaction of the organic carboxylic acid with silver ions in the preparation of the silver salt of an organic carboxylic acid having a fine grain size as described above when the reaction is conducted in the presence of a lead compound or a mercury compound. By the use of the silver salt of an organic carboxylic acid thus prepared in a thermally developable light-sensitive element, transparency in the coated layer so increases that a transparent thermally developable photographic film can be obtained on an industrial scale.

Comparing the amount of the silver salt of an organic carboxylic acid coated, the use of the silver salt of a fine grain size results in an increase in image density due to easier reduction of the silver salt of an organic carboxylic acid of a fine grain size as described above. In the process of this invention, a surface active agent may be present when reacting the organic carboxylic acid and the silver ion.

One object of the present invention thus lies in easily producing a silver salt of an organic carboxylic acid of fine grain size by which images having high resolving power can be obtained and which can be used to form a thermally developable light-sensitive element having a transparent coated layer.

Another object of this invention is to provide a process of easily producing fine-grained silver salts of organic carboxylic acids capable of preparing thermally developable photosensitive materials which give images having high density and excellent resolving power with a reduced amount of coated silver and which can have transparent coated layers.

A further object is to provide thermally developable photosensitive materials prepared by using such fine-grained organic silver carboxylates which give an image having less thermal fog, high image density and good contrast. The term "thermal fog" in this specification means the fog or black density formed when unexposed areas of the photosensitive material are heated. The formation of thermal fog is reduced in the thermally developable photosensitive material prepared by using the fine-grained organic silver carboxylates because, we believe, organic silver carboxylates produced by the process of this invention partially contain the lead compound or mercury compound. We are unsure if this is a reaction product or a mixture, but believe it is probably a mixture.

A further substantial benefit of the lead compound embodiment of the invention is that the process results in lowered toxicity as compared to the mercury compound embodiment, not only to workers but to the environment if such compounds are accidentally discharged, e.g., to fish, shellfish or humans if ingested.

DETAILED DESCRIPTION OF THE INVENTION

The silver complex salts are not particularly limited, though most preferred are the alkali soluble silver complexes having a dissociation constant higher than the silver salt of the organic carboxylic acid, e.g., a silver ammonium complex, a silver amine complex (e.g., the silver complexes of methyl amine or ethyl amine) and the like.

The lead and mercury compounds must be completely soluble in water or organic solvents and must yield lead or mercury ions in solution. Preferred materials are the inorganic lead or mercury compounds or lead or mercury compounds of organic acids.

Specific examples of mercury compounds which can be used in the present invention include mercuric nitrate, mercuric acetate, mercuric sulfate, mercuric bromide, mercuric iodide, etc. Further, there can also be used organic mercury compounds such as mercuric phenyl acetate, methyl mercuric chloride, ethyl mercuric chloride, phenyl mercury p-toluene sulfanilide, benzyl mercury-p-toluene sulfanilide, mercuric chloranilate, 2-acetamido-1,3,4-thiadiazolyl-(5)-mercuric chloride, phenyl mercury dinaphthylmethane disulfonate, etc.

As the lead compounds suitably used in this invention, there are illustrated lead nitrate, lead acetate, lead carbonate, lead sulfate, lead phosphate, and lead halide but the use of lead nitrate is most preferable. Furthermore, organic lead compounds such as lead benzoate, lead citrate and lead lactate can also be used in this invention.

It is preferred to dissolve or disperse these mercury compounds and/or lead compounds in an aqueous solution of silver nitrate. Alternatively, a solution containing the mercury compound(s) and/or lead compounds(s) may be incorporated into a solution of the organic carboxylic acid.

Thus, it is within the scope of the present invention to use both a lead compound and a mercury compound simultaneously, or to use two or more of each of such compounds simultaneously.

As suitable organic carboxylic acids in accordance with the present invention, the silver salts thereof which are relatively stable to light are preferred silver salts of organic carboxylic acids (considered "comparatively stable" to light when upon long exposure to light it does not blacken, whereas a silver halide would blacken under the same conditions). For example, long chain aliphatic carboxylic acids having more than 10 carbon atoms are preferred, which are exemplified by capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, etc. Other organic carboxylic acids can, of course, be used. Mixtures of such acids can, of also be used.

Solvents which dissolve the organic carboxylic acid and hardly dissolve both the silver salt of an organic carboxylic acid and silver nitrate or silver complex and are further sparingly miscible with water, i.e., solvents for the organic carboxylic acids, include phosphoric acid esters, phthalic acid esters or carboxylic acid esters of alcohols or phenols which are liquid at normal temperature, or glycercin esters of higher fatty acids. There can also be used aromatic hydrocarbons.

Specific examples of such solvents are tricresyl phosphate, tributyl phosphate, monoocetyl dibutyl phosphate, diethyl phthalate, dibutyl phthalate, dimethyl
phthalate, dioctyl phthalate, dimethoxyethyl phthalate, amyl acetate, isooamyl acetate, isobutyl acetate, isopropyl acetate, ethyl acetate, 2-ethylbutyl acetate, butyl acetate, propyl acetate, diethyl sebacate, dibutyl sebacate, diethyl sebacate, diethyl succinate, ethyl formate, propyl formate, butyl formate, amyl formate, ethyl valerate, diethyl tartarate, methyl butyrate, ethyl butyrate, butyl butyrate, isoamyl butyrate, castor oil, benzene toluene, xylene, etc.

Preferred solvents which hardly dissolve the recited compounds are those which dissolve 1 percent by weight or less, most preferably 0.1 percent by weight or less, of the salt and of the silver nitrate or complex, which are 35 percent by weight or less, most preferably 10% by weight or less, soluble in water and most preferably in which the acids are completely soluble.

For instance, a solution of 3.4g of behenic acid in 100 ml of xylene is maintained at 60°C and 100 ml of an aqueous diluted nitric acid solution (pH 2.0 at 25°C) containing 0.1 g of mercuric nitrate is added thereto. To the mixture, 100 ml of an aqueous ammonium silver nitrate complex solution containing 1.7 g of silver nitrate which has been cooled at 0°C is added over 1 minute to react behenic acid with silver ion. Almost spherical crystals of silver behenate can thus be obtained, which have about a 0.2μ diameter.

In the case of using 100 ml of an aqueous diluted nitric acid solution (pH 2.0 at 25°C) without the addition of mercuric nitrate thereto, spindle-like crystals of silver behenate are obtained which have about a 0.7 - about 1μ long side and about a 0.05 - about 0.1μ short side.

Similarly, when 100 ml of diluted aqueous nitric acid solution (pH of 2.0 at 25°C) containing 0.5 g of lead nitrate is added with stirring to a solution of 11 g of lauric acid in 100 ml of butyl acetate maintained at 10°C, and 50 ml of an aqueous solution of a silver nitrate-ammonium complex salt containing 8.5 g of silver nitrate cooled to 0°C is added to the above mixture over a one minute period to cause the reaction of lauric acid and silver ions, almost spherical silver laureate crystals having a diameter of about 0.1 micron are obtained.

However, when the above process is conducted under the same conditions while using 50 ml of a diluted aqueous nitric acid solution (pH of 2.0 at 25°C) without lead nitrate, only spindle shaped crystals of silver laureate having a short side diameter of about 0.05-0.1 micron and a long side diameter of about 0.7-1 micron is obtained (the term spindle shape denotes a shape similar to a sausage link).

The fine crystals of the silver salt of an organic carboxylic acid thus obtained can be isolated by separating the solvent layer containing the silver salt of an organic carboxylic acid from the aqueous layer, e.g., by decantation, to remove the aqueous layer and then repeating washing with water until watersoluble silver nitrate, mercuric nitrate and/or lead nitrate and nitric acid are eliminated.

Thereafter, the solvent layer of organic carboxylic acids in which fine crystals of the silver salt of an organic carboxylic acid are present is washed using a solvent for undesired materials such as the organic carboxylic acid and reaction solvent, e.g., methanol as a solvent for the unreacted behenic acid and xylene. In order to rapidly conduct washing, for example, centrifugal separation is suitable.

The fine crystals of the silver salt of an organic carboxylic acid thus obtained which have been thoroughly washed are dispersed in, e.g., a solution of polyvinyl butyral, e.g., using a ball mill, to prepare a thermally developable lightsensitive material. In this case, surface active agents may be incorporated therein to improve the dispersion.

It is not entirely clear, in view of the limitations of current analytical techniques, exactly how the additives of the present invention provide a superior silver salt of an organic carboxylic acid, i.e., it is not clear whether these materials are present as ions, metals or compounds. Accordingly, to describe the elements produced therewith, reference to the process should be made for both the lead and mercury compound embodiments.

The organic carboxylic acid silver salt produced by the process of the present invention is, of course, used in a thermally developable light-sensitive element, as has been heretofore described. The organic carboxylic acid silver salts produced in accordance with the present invention offer superior results as compared to the prior art when used in any thermally developable system as heretofore described. However, especially preferred results are obtained when the organic carboxylic acid silver salt produced in accordance with the present invention is used in elements as described below.

A thermally developable light-sensitive material obtained using the fine crystals of the silver salt of an organic carboxylic acid thus obtained comprises the following components on a support: (1) the fine crystals of the silver salt of an organic carboxylic acid obtained in accordance with the present invention, (2) a silver halide, preferably one which is in situ prepared by the reaction of the silver salt of an organic carboxylic acid with an inorganic or organic halide, (3) a compound as a reducing agent which can provide silver images by reducing the silver salt of an organic carboxylic acid upon heating in the presence of exposed silver halide and (4) a binder.

The preferred inorganic halides are those represented by the formula MxN, where M is H+, NH4+, or a metal, X is Cl-, Br-, or I-, and n is the valence of M, e.g., hydrogen bromide, hydrogen iodine, ammonium bromide, ammonium iodide, ammonium chloride, or where M is a metal such as strontium, cadmium, zinc, tin, titanium, sodium, barium, iron, cesium, lanthanum, copper, calcium, nickel, magnesium, potassium, aluminum, antimony, gold, cobalt, mercury, lead, beryllium, lithium, manganese, gallium, indium, rhodium, ruthenium, palladium, iridium, platinum, thallium, bismuth, etc., which can be used alone or in mixture.

Furthermore, organic halogen compounds such as chlorotrichloromethyl, bromotrichloromethyl, 2-bromo-2-methyl propane, 2-bromo-butyrate, 2-bromo-ethanol, di chlorobenzophenone, iodoform, bromoform, and 4-bromocarbonate can be used.

The silver halides per se used include silver chloride, silver bromide, silver bromoiodide, silver chloroiodide, silver chlorobromide and silver iodide. However, as indicated, highly preferred are the silver halides formed by reaction of the inorganic or organic halide with the silver salt of the organic carboxylic acid.

Among these light-sensitive silver halides we can use coarse grained or fine grained ones with emulsions of very small particles being especially preferred.
The emulsions which contain the light-sensitive silver halide can be made by any method which is widely known in the photographic field, for example, emulsions formed by the single jet method, double jet method, a Lipmann emulsion, by the ammonia method, and can use thiocyanate or thiourea ripened emulsions and the emulsions which are described in U.S. Pat. Nos. 2,222,264, 3,320,069 and 3,271,857.

The silver halide which used in this invention is generally used in a chemically sensitized silver halide emulsion, e.g., sensitized by reducing agents such as sulfur or selenium compounds, with gold or platinum sensitizers or with palladium compounds, or combinations thereof. Preferred sensitization methods are shown in U.S. Pat. Nos. 2,623,499; 2,399,083; 3,297,447; and 3,297,446.

The above mentioned compounds in component (2), can be used singly or in combinations of two or more thereof.

The amount of component (2) added is preferably about 0.001 - 0.5 mol per 1 mol of the silver salt of organic carboxylic acid. If the amount of component (2) is too much less than this extent, sensitization is bad, and if too much greater this becomes the cause of blacking of non-image portions and also lowers the contrast of image portions.

The reaction of the inorganic or organic halide and the silver salt of an organic carboxylic acid generally proceeds quite easily, and in practice the stoichiometric amount of halide is mixed with the silver salt of an organic carboxylic acid system (polymer dispersion) and well agitated for a short period of time, e.g., on the order of 5 seconds.

To illustrate the relative non-criticality of the conditions generally guidelines are: 0° - 80°C. better yet 10° - 60°C, 1 sec - 3 hours, longer times generally being unnecessary, mixing at atmospheric pressure.

The preferred reducing agents are substituted phenols, substituted or non substituted bisphenols, substituted or non substituted naphthols, di- or poly-hydroxy benzenes, di- or polyhydroxynaphthalenes, hydroquinone mono-ether, reducing sugar, 5-hydroxy-2-hydroxyethyl-m-phenyl-pyrene, pyrazoline-5-one, 4-isopropyltoluylene, where typical substituents are alkyl (C₁ - C₄) alkoxy (C₁ - C₆), phenyl, halogen, amino, alkyl substituted amino. (C₁ - C₆ benzyl, hydroxy-alkyl, acetyl, nitro, etc.

Reducing agents used in this invention must form silver images when heated under the catalysis of exposed silver halide to reduce the organic carboxylic acid silver salt.

Specific examples of useful reducing agents are hydroquinone, methylhydroquinone, chlorohydroquinone, 1-methoxyhydroquinone, phenylhydroquinone, hydroquinone mono-sulfonic acid, t-octylhydroquinone, t-butylhydroquinone, 2,5-dimethoxyhydroquinone, 2,6-dimethoxyhydroquinone, methoxyhydroquinone, ethoxyhydroquinone, p-methoxyphenol, p-ethoxyphenol, hydroquinone mono-benzyl ether, catechol, 1,2,3-trihydroxybenzene, 1,3-dihydroxybenzene, p-amino phenol, o-aminophenol, N-methyl-p-aminophenol, 2-methoxy-4-aminophenol, 2,4-diaminophenol, 2,4-hydroxyethyl-4-aminophenol, p-t-butylphenol, p-t-aminophenol, p-cresol, 2,6-di-t-butyl-p-cresol, p-acetophenol, o-phenylphenol, 1,4-dimethoxyphenol, 3,4-xylanol, 2,4-xylanol, 2,6-dimethoxyphenol, 1-amino-2-naphthol-6-
sodium sulfonate, 1-naphthylamine-7-sulphonic acid, 1-hydroxy-4-methoxy-naphthalene, 1-hydroxy-4-ethynaphthalene, 1,4-dihydroxynapthalene, 1,3-dihydroxynapthalene, 1-hydroxy-4-ethynapthalene, 1,4-dihydroxynapthalene, 1,3-dihydroxynapthalene, 1-hydroxy-4-aminonapthalene, 1,5-dihydroxynapthalene, 1-hydroxy-2-phenyl-4-methoxynapthalene, 1-hydroxy-2-methyl-4-methoxynapthalene, α-naphthol, β-naphthol, 1,1'-dihydroxy2,2'-binaphthyl, 4,4'-diethoxy-1,1'-dihydroxy2,2'-binaphthyl, bis(2-hydroxy-1-naphthyl) methane, bisphenol A, 1.1'-bis(2-hydroxy-3,5-dimethyl phenyl)-3,5,5-trimethyl hexene, 2,4,4-trimethyl pentylbis(2-hydroxy-3,5-dimethylphenyl) methane, bis(2-hydroxy-3,5-di-t-butyl-5-methylphenyl) methane, bis(2-hydroxy-3,5-di-t-butylphenyl) methanol, 4,4'-methylene bis(3,5-di-t-butylphenol), 4,4'-methylene bis(2-t-butyl-4-ethylphenol), 2,6-bis(2-hydroxy-3,4butyl-5-methyl benzyl) 4-methylphenol, 3,3',5',5'-tetra-t-butyl-4,4'-dihydroxy-diphenyl, p-oxypheylglycine, N,N-diethyl-p-phenylenediamine, furon, benzoin, dihydroxyacetone, glyceraldehyde, rhodinic acid tetrahydroxquinone, propyl gallate, methyl gallate, hydroxy tetrin acid, N,N-di(2-ethoxyethyl) hydroxylamine, glucose, lactose, bis(3-methyl-4-hydroxy-5-t-butylphenol)-sulfide, 3,5-di-tbutyl-4-hydroxybenzyl-dimethylamine, a.a'-(3,5-di-t-butyl-4-hydroxyphenyl)dimethylether.

Combinations of more than two kinds of these reducing agents can be used at one time.

Suitable reducing agents are decided by the combination with the organic carboxylic acid silver salt. For example, higher fatty acid silver salts such as behenic acid silver are hard to reduce, so strong reducing agents, such as 4,4'-methylene bis-(3-methyl-5-t-butylphenol), one of the bis phenols is preferred. On the other hand, for an organic carboxylic acid silver salt which is easily reduced, like silver laureate, substituted phenols like p-phenyl phenol are preferred.

As the amount of the reducing agent used in this invention varies depending upon the organic carboxylic acid silver salt and the reducing agent it is difficult to set an all encompassing range, but generally 0.1 - 0.5 moles thereof per mole of organic carboxylic acid silver salt is preferred.

Components (1), (2) and (3) above are dispersed in a binder and coated on a support. Alternatively, one can coat on the support as separate components. The binder can be a cellulose derivative, synthetic polymer, etc. Specific examples are gelatin, phthalated gelatin, polyacrylic acids, polyvinyl butyrate, cellulose acetate-propionate, polymethyl methacrylate, polyvinyl pyrrolidone, polyvinyl chloride, chlorinated rubbers, polyisobutylene, butadiene-styrene copolymers, vinyl chloride-vinyl acetate copolymers, copolymers of vinyl acetate and vinyl chloride and malonic acid, polyvinyl alcohol, polyacetic vinyl material, benzyl cellulose, cellulose acetate cellulose propionate, cellulose acetate phthalate and the like.

If desired, mixtures of two or more kinds of the above binders can be used. The amount of the binder is preferably 4/1- 1/4 (weight ratio) to the organic carboxylic acid silver salt.
If component (1) or (3) is a relatively high molecular weight material which functions as a binder, a separate binder can be omitted.

Typical supports are, cellulose nitrate films, organic cellulose ester films, polyvinyl acetal films, polystyrene films, polyethylene terephthalate films, polycarbonate films, glass, paper and metals.

Preferred ratios of all components in the element are thus silver halide (the inorganic halide reacts substantially stoichiometrically to yield silver halide): 0.001 mol - 0.5 mol/mol of organic carboxylic silver salt; reducing agent 0.1 mol - 5 mol/mol of organic carboxylic silver salt; binder: organic carboxylic silver = 4/1 - 1/4 (weight); The light sensitive layers(s) will generally be 1μ - 15 μ thick, preferably 3μ - 10μ thick. The exposed layers are simply developed by heating at 100°C - 180°C, preferably 120°C - 160°C, for 1 sec. - 60 sec. preferably 2 sec. - 2 sec. Exposure is usually a contact printing or stretch printing at ambient conditions. The thermally developable light-sensitive layer can further contain an agent for blackening the image such as mercapto compounds, azolethiones or phthalaziones; organic carboxylic acids as a development accelerating agent; compounds which afford basicity upon heating, e.g., amine betaines or water containing inorganic hydrides which lose water upon heating; photolytic reducing agents e.g., when using an arsenic acid ester, a compound which accelerates photolysis thereof, exemplified by benzil; and spectral sensitizers which sensitizes to long wavelength light, e.g., merocyanine dyes having a thiohydantoin or a rhodamine nucleus.

It has been found that not only can a transparent coated layer be obtained, but also images having high density and high resolving power can be formed using a silver salt of an organic carboxylic acid of a fine grain size in accordance with the present invention in thermally developable light-sensitive elements as described in Japanese Pat. Publications No. 4924/65, 22,185/70 and 41,865/71 and U.S. Pat. No. 3,589,901 and U.S. Pat. No. 3,589,903.

The fine grained silver salt of an organic carboxylic acid of the present invention is especially advantageous for providing remarkably good images without the use of compounds which afford basicity upon heating or development accelerating agents such as aliphatic carboxylic acids, etc., that is by using a thermally developable light-sensitive element comprising a support having thereon a silver salt of an organic carboxylic acid of fine grain size, a light-sensitive silver halide, a reducing agent and a binder. Needless to say, it is preferred to add a color toning agent, a compound capable of affording basicity upon heating and a development accelerating agent in the case that images of higher quality are required.

The absolute amount of silver salt of an organic carboxylic acid present is that necessary to provide a discernable image upon exposure and development. In view of the fact that the visual acuity of users will vary over a wide range, usually a minimum of about 1/1000 mol /m² of support will be advisable, with no better results being provided by using more than about 1/10 mol /m² as compared to about 1/10 mol /m². On a commercial scale, to provide a density safety factor, coating well be at 1/300 - 1/50 mol /m².

The characteristics of the present invention will be summarized below. The use of the silver salt of an organic carboxylic acid, having a fine grain size gives images of higher density as compared to the use of a conventional silver salt of an organic carboxylic acid having a coarse grain size, and it is sufficient to use the fine grained silver salt of an organic carboxylic acid in a smaller amount to obtain the image of the same density so that a decrease in cost can be attained. In addition, preparation operations can be improved since it becomes easy to disperse the silver salt of an organic carboxylic acid in a polymer binder due to the fine grain size thereof. Further, it is unnecessary to add a compound which affords basicity upon heating or an acid so that improved storage capability of the product before treatment is obtained.

Applying the fine grains of the silver salt of an organic carboxylic acid thus obtained to a thermally developable lightsensitive element as described above, the defects with the use of coarse grains can be eliminated and a dispersion of crystalline grains in a high molecular weight binder can be provided in a simple manner.

The thermally developable light-sensitive material which is prepared using the silver salt of an organic carboxylic acid according to the present invention gives images of high density and high resolving power in which the coated layer becomes transparent.

Furthermore, comparing the case of producing the fine-grained silver salt of an organic carboxylic acid by the reaction of an organic carboxylic acid and silver ions in the presence of a mercury compound as opposed to a lead compound, the mercury compounds have strong toxicity, and thus the lead compound embodiment increases the ease of working, which results in lowering the danger to workers and the danger of environmental pollution upon reactant or reaction product accidental disposal.

Also, in the case of the above-mentioned process using a mercury compound, the mercury compounds should be prevented from being mixed with other photosensitive materials since mercury compounds have a strong desensitizing action thereon and this point is improved in the lead embodiment process of this invention.

The exact ratios of various components in the reaction system are not overly critical so long as a balance of essential components in the system exists. Excellent results are obtained on a commercial scale, however, when the following balance of components is observed:

<table>
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<tr>
<th>Components</th>
<th>Ratio</th>
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<tr>
<td>organocarboxylic acid/solvent</td>
<td>10/1-1/1000, preferably 2/1-1/1000 (weight)</td>
</tr>
<tr>
<td>organocarboxylic acid/silver nitrate or complex salt</td>
<td>4/1-1/4, preferably 2/1-1/2 (molar)</td>
</tr>
<tr>
<td>organocarboxylic acid/lead and/or mercury compound</td>
<td>2/1-1000/1, preferably 10/1-100/1 (molar)</td>
</tr>
</tbody>
</table>

The conditions of mixing the solution containing silver ions with a solution of the organic carboxylic acid are not limited to any specific values, but varying concentrations of the solutions, temperatures of the solutions, rates of mixing, conditions of stirring and kinds of solvents, depending upon the desired grain size, can be used. The general rule is that higher concentrations, lower temperatures, rapid mixing and rapid stirring give smaller grains. Further, the dispersion can be im-
proved using ultrasonic waves or surface active agents. Generally, however, excellent results are obtained when the process temperature is \(-30^\circ C \sim +80^\circ C\), more preferably \(-5^\circ C \sim +60^\circ C\). The pressure is typically 1 atmosphere, and while this is not limiting there is little merit to operation at sub- or super atmospheric pressure. The process time is merely that needed to complete the reaction, usually 1 sec - 1 hour, preferably 30 sec - 30 minutes is used, with the intermediate times being more common.

The silver salt of an organic carboxylic acid of the present invention is spherical or substantially spherical as opposed to the spindle or semi-tube shaped silver salt of an organic carboxylic acid of the prior art. While variable with process conditions, following the guidelines of this specification one can obtain a silver salt of an organic carboxylic acids of superior effect of a diameter of 0.01 - 1 \(\mu\), with best results in element use being obtained when the silver salt of an organic carboxylic acid has a diameter of 0.1 - 0.5 \(\mu\).

The invention will now be explained with reference to the following specific examples.

**EXAMPLE 1**

Two solutions were made by dissolving 3.4 g of behenic acid in 100 ml of tricresyl phosphate at 60°C. The solutions were maintained at 60°C (Solutions A). A solution was prepared by dissolving 0.1 g of mercuric nitrate in 100 ml of an aqueous diluted nitric acid solution which was adjusted with nitric acid to pH 2.0 at 25°C (Solution B). An identical solution was prepared except for replacing the 0.1 g of mercuric nitrate by 0.1 g of lead nitrate (Solution B'). Solution B was combined with one Solution A sample and Solution B' was combined with the other Solution A sample to give Solution A/B and A/B', which were then individually processed following the technique below. To the combined solutions was added, while maintaining at 60°C, an aqueous solution which was prepared by adding ammonia water to about 80 ml of an aqueous solution containing 1.7 g of silver nitrate to form a silver ammonium complex and adding water thereto to make the total amount 100 ml (pH = 11 at 25°C). After standing for 20 minutes at room temperature, the reaction liquid was separated into an aqueous layer and a tricresyl phosphate layer. After the removal of the aqueous layer, 400 ml of fresh water was added for washing and the operation was repeated three times. Thereafter, 400 ml of methanol was added to the tricresyl phosphate layer for washing. The resulting fine crystals of silver behenate were separated by centrifugal separation. Thus, 4.0 g of silver behenate was obtained, which was in the form of spherical grains having a diameter of about 0.1 \(\mu\) diameter, from the A/B system and the A/B' system.

**EXAMPLE 2**

The procedures of Example 1 were repeated except that the same amount of toluene was used in place of tricresyl phosphate. The amount of silver behenate obtained for the A/B1 and A/B2 system was 4.1 g, which were spherical grains having a grain size of about 0.3 \(\mu\) in diameter.

**EXAMPLE 3**

The procedure of Example 1 was followed except that the same amount of mercuric acetate was employed instead of mercuric nitrate and the same amount of lead carbonate was employed instead of lead nitrate. Silver behenate was obtained in an amount of 4.0 g, which had spherical grains having a grain size of about 0.5 \(\mu\) in diameter for the mercury run and about 0.2 \(\mu\) for the lead run.

**EXAMPLE 4**

Using silver behenate as obtained in Example 2 from the A/B1, and A/B2, runs and silver behenate obtained as in Example 2 but without the addition of mercuric nitrate or lead nitrate (spindle like grains having a long diameter of about 1 \(\mu\) and a short diameter of about 0.05 \(\mu\)) respectively, light-sensitive compositions for thermal development having the following formulation were prepared and each of them was coated in a dry thickness of 8 \(\mu\) (same in all Examples) on a transparent polyethylene terephthalate film support to give a light-sensitive element for thermal development.

**Polymer Dispersion of the silver salt**

<table>
<thead>
<tr>
<th>Solution</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solution of 0.6 g. of zinc bromide and 0.9 g of zinc iodide in 20 ml of methanol</td>
</tr>
<tr>
<td></td>
<td>Acetone solution containing 0.2 wt% of benzenezolidine thiohydantoin sensitizing dye</td>
</tr>
<tr>
<td></td>
<td>Methyl cellulose solution containing 10 wt% of phthalazinone</td>
</tr>
</tbody>
</table>

Preparation of the polymer dispersion of the silver salt. To 40 ml of an isopropyl alcohol solution containing 4 g. of polyvinyl butyral was added 5 g. of the silver salt and they were stirred for 4 hours by means of a ball mill to prepare the polymer dispersion for the mercuric nitrate embodiment and for 1 hour for the lead nitrate embodiment.

The light-sensitive element thus prepared was exposed (10^5 lux-same in all Examples) to a tungsten lamp through a transparent negative original having gradation and heated at 120°C for 30 seconds for the mercuric nitrate embodiment and for 20 seconds for the lead nitrate embodiment, to obtain positive images having gradation. The density of the images, resolving power and transparency of the coated layer are shown in the table below.

In the case of using silver behenate obtained in accordance with the present invention, the ratio of maximum density and resolving power increased, the coated layer became transparent, and hence a desirable transparent light-sensitive element for thermal development was obtained. By the term "the ratio of maximum density" is meant the ratio of the maximum densities of the images given by both methods, i.e., the maximum densities of the image obtained using the silver salt prepared by the use of the mercury compound (or the lead compound) to the maximum density of the image obtained using the silver salt prepared without using the mercury or lead compound the density of the latter being denoted by 1.0. Needless to say, the weight of silver behenate coated per unit area was substantially identical in all cases.
3,887,597

TABLE

<table>
<thead>
<tr>
<th>Grain size</th>
<th>Use of Silver Behenate Obtained without the Addition of Mercuric Nitrate or Lead Nitrate</th>
<th>Use of Silver Behenate Obtained in the Presence of Mercuric Nitrate</th>
<th>Use of Silver Behenate Prepared Using Lead Nitrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spindles having a long side of 1μ</td>
<td>1.0</td>
<td>3.0</td>
<td>2.5</td>
</tr>
<tr>
<td>Spherical grains having a diameter of 0.3μ</td>
<td>&gt;10</td>
<td>&gt;10</td>
<td></td>
</tr>
<tr>
<td>Spherical Grains having a Diameter of 0.3μ</td>
<td>65%</td>
<td>85%</td>
<td>85%</td>
</tr>
<tr>
<td>Coated (g. Ag/m²)</td>
<td>1.1</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

* The transmittance is denoted by the value measured at 500 nm using a spectrophotometer.
** No difference in results whether ball milled for 1 or 4 hours or exposed 20 or 30 seconds.

EXAMPLE 5

In 100 ml. of butyl acetate was dissolved 10 g. of laurie acid at 60°C, and the solution was then cooled to 10°C. A solution was prepared by dissolving 0.25 g. of mercuric nitrate in 100 ml. of an aqueous diluted nitric acid solution which was adjusted with nitric acid to pH 2.0 (25°C), and the both solutions were mixed together. The solution mixture was maintained at 10°C. An aqueous solution which was obtained by adding ammonia water to a solution of 8.5 g. of mercuric nitrate in about 80 ml. of water to convert to a silver ammonium complex and further adding water to make the whole 100 ml. (pH = 11 at 25°C) was added to the solution mixture. Allowed to stand for 20 minutes at room temperature, the reaction liquid was separated into an aqueous layer and a butyl acetate layer.

After the removal of the aqueous layer, 400 ml. of fresh water was added to the remaining liquid for washing. Thereafter, the microcrystals of silver laurate thus formed were separated by a centrifuge. The amount of silver laurate was 14 g., and possessed spherical grains of about 0.1μ in diameter.

EXAMPLE 6

Using silver laurate as obtained in Example 5 and silver laurate obtained as in Example 5 but without the addition of mercuric nitrate (spindle-like grains having a long side diameter of about 1μ and a short side diameter of about 0.05μ), respectively, light-sensitive compositions for thermal development having the following formulation were prepared and each of them was coated on a transparent polyethylene terephthalate film support to give a light-sensitive element for thermal development.

Preparation of the polymer dispersion of the silver salt.

To 40 ml. of an isopropyl alcohol solution containing 4 g. of polyvinyl butyral was added 5 g. of the silver salt and they were stirred for 4 hours by means of a ball mill to prepare the polymer dispersion.

The light-sensitive element thus prepared was exposed to a tungsten lamp through a transparent negative original having gradation and heated at 120°C for 20 seconds to obtain positive images having gradation. The density of the images, resolving power and transparency of the coated layer are shown in the table below. In the case of using silver laurate obtained in accordance with the present invention, the ratio of maximum density and resolving power increased, the coated layer became transparent, and hence a desirable transparent light-sensitive element for thermal development was obtained. By the term “the ratio of maximum density” is meant the ratio of maximum densities of the image obtained by both methods, i.e., the maximum density of the image obtained using the silver salt prepared by the use of the mercury compound to the maximum density of the image obtained using the silver salt prepared without using the mercury compound, the density of the latter being denoted as 1.0. Needless to say, the weight of silver laurate coated per unit area was substantially identical in both cases.

TABLE

<table>
<thead>
<tr>
<th>Grain size</th>
<th>Use of Silver Laurate Obtained without the Addition of Mercuric Nitrate</th>
<th>Use of Silver Laurate Obtained in the Presence of Mercuric Nitrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spindles having a long side of 1μ</td>
<td>1.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Spherical Grains having a diameter of 0.3μ</td>
<td>&gt;10</td>
<td>&gt;15</td>
</tr>
<tr>
<td>Coated (g. Ag/m²)</td>
<td>65%</td>
<td>90%</td>
</tr>
</tbody>
</table>

Polymer dispersion of the silver salt
Methanol solution containing 5 wt% of ammonium bromide
Chloroform solution containing 0.2wt% of a benzoxazolylidene rhodamin sensitizing dye

Preparation of the polymer dispersion of the silver salt.

To 40 ml. of an isopropyl alcohol solution containing 5 wt% of phthalazine
Methyl cellosolve solution containing 25 wt% of p-methoxyphenol

Preparation of the polymer dispersion of the silver salt.
To 40 ml. of an isopropyl alcohol solution containing 4 g. of polyvinyl butyral was added 5 g. of the silver salt and they were stirred for 4 hours by means of a ball mill to prepare the polymer dispersion.

The light-sensitive element thus prepared was exposed to a tungsten lamp through a transparent negative original having gradation and heated at 120°C for 20 seconds to obtain positive images having gradation. The density of the images, resolving power and transparency of the coated layer are shown in the table below. In the case of using silver laurate obtained in accordance with the present invention, the ratio of maximum density and resolving power increased, the coated layer became transparent, and hence a desirable transparent light-sensitive element for thermal development was obtained. By the term “the ratio of maximum density” is meant the ratio of maximum densities of the image obtained by both methods, i.e., the maximum density of the image obtained using the silver salt prepared by the use of the mercury compound to the maximum density of the image obtained using the silver salt prepared without using the mercury compound, the density of the latter being denoted as 1.0. Needless to say, the weight of silver laurate coated per unit area was substantially identical in both cases.

TABLE
When the same procedure as in Example 1 was followed but using the same amount of lead carbonate in place of lead nitrate, 4.0 g of silver benenate was obtained as almost spherical grains having a diameter of about 0.2 micron.

**EXAMPLE 8**

The same procedure as in Example 1 was followed but using the same amount of lead lactate in place of lead nitrate, whereby 4.1 g of silver benenate as almost spherical grains having a diameter of about 0.5 micron was obtained.

**EXAMPLE 9**

When the same procedure as in Example 1 was followed but using the same amount of lead acetate in place of lead nitrate, 4.0 g of silver benenate as almost spherical grains having a diameter of about 0.5 micron was obtained.

**EXAMPLE 10**

11 g of lauric acid was dissolved in 100 ml of butyl acetate at 60°C and then the solution was cooled to 10°C. Then, a solution prepared by dissolving 0.5 g of lead nitrate in 100 ml of diluted aqueous nitric acid solution (pH = 2.0 at 25°C) was mixed with the solution prepared above by means of a stirrer.

While maintaining the temperature of the mixed solution at 10°C, 50 ml of an aqueous solution (pH = 11 at 25°C) prepared by adding aqueous ammonia to a solution of 8.5 g of silver nitrate in about 40 ml of water to form a silver-ammonia complex and then adding water to the complex salt solution was added to the mixed solution prepared above with stirring, whereby precipitates containing silver laurate were obtained. When the reaction product was allowed to stand for 20 minutes at room temperature, the product separated into an aqueous phase and a butyl acetate phase.

The aqueous phase was first removed and the butyl acetate phase was washed by adding 400 ml of water. After repeating the washing operation three times, the butyl acetate solution phase was washed with 400 ml of methanol. By recovering the fine crystals of silver laurate formed by a centrifugal separator, 14 g of fine granular silver laurate was obtained. The silver laurate thus obtained was of almost spherical form, having a diameter of about 0.1 micron.

**EXAMPLE 11**

Two kinds of thermally developable photosensitive compositions having the following compositions were prepared using the silver laurate produced in Example 10 in one and using silver laurate of a spindle grain shape having a long side of about 1 micron and a short side of about 0.05 micron prepared by the same procedure as in Example 10 without using lead nitrate in the other. Each composition was coated on a transparent polyethylene terephthalate film to give a thermally developable photosensitive material.

<table>
<thead>
<tr>
<th>polymer dispersion of the silver salt ammonium bromide (5% by weight of methanol solution) chloroform solution containing 0.2% by weight of benzoxazoldione rhodamine sensitizing dye:</th>
<th>45 ml</th>
<th>1 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>phthalazine (5 wt% methylcellulose solution)</td>
<td>2 ml</td>
<td></td>
</tr>
<tr>
<td>p-phenylphenol (35 wt% methylcellulose solution)</td>
<td>8 ml</td>
<td></td>
</tr>
</tbody>
</table>

The above described polymer dispersion of the silver salt was prepared by adding 5 g of the silver salt to a 40 ml isopropyl alcohol solution containing 4 g of polyvinyl butyral and stirring the mixture by means of a ball mill for 1 hour to disperse the silver salt. When each of the photosensitive films thus prepared was exposed through a negative transparency to a tungsten lamp and heated at 120°C for 20 seconds, a positive image having varying gradation was obtained. The image density, the resolving power, and the transparency of the coated layer were observed, the results of which are shown in the following table. As is clear from the results, in the case of using the silver laurate prepared by the process of this invention, a transparent thermally developable photosensitive film of improved maximum density ratio and resolving power which had a transparent coated layer was obtained. The maximum density ratio was about the same as in Example 4. Of course, the coated amount of silver laurate per unit area of the thermally developable photosensitive film was substantially the same in both cases.

**TABLE**

<table>
<thead>
<tr>
<th>Grain size</th>
<th>Maximum density ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Obtained using Silver Laurate Prepared without</td>
<td>1.0</td>
</tr>
<tr>
<td>Obtained using Silver Laurate Prepared using</td>
<td>2.3</td>
</tr>
<tr>
<td>Lead Nitrate spherical having a long side of 1.0μ</td>
<td></td>
</tr>
<tr>
<td>Lead Nitrate spherical having a diameter of 0.1μ</td>
<td></td>
</tr>
</tbody>
</table>

* The transmittance is denoted by the value measured at 500 μm using a spectrophotometer.
EXAMPLE 12

The effect of lead nitrate was measured according to a process similar to the one shown in the examples of U.S. Pat. No. 3,458,544, that is, silver benenate was prepared in the following manner: 1.7 g of benheic acid was dissolved in 500 ml of benzene at 60°C and the solution kept at 60°C. Then, 0.1 of lead nitrate dissolved in 500 ml of diluted aqueous nitric acid solution (pH = 2.0 at 60°C) was mixed with the solution prepared above with stirring at 60°C.

While maintaining the mixed solution at 60°C, 50 ml of an aqueous solution (pH = 9.0 at 25°C) prepared by adding aqueous ammonia to 40 ml of an aqueous solution containing 0.85 g of silver nitrate to form a silver-ammonium complex salt, adding water to the complex salt solution, and adjusting the temperature of the solution to 25°C, was added with stirring to the abovementioned solution mixture, whereby precipitates containing silver benenate were formed. When the reaction product was allowed to stand for 20 minutes at room temperature, it separated into a aqueous phase and a benzene phase. The aqueous phase was first removed and the benzene solution phase was washed with 400 ml of water followed by decantation. After repeating the washing operation three times, the benzene solution phase was washed with 400 ml of methanol by means of a centrifugal separator and the fine crystals of silver benenate thus formed were recovered, whereby 2.0 g of silver benenate of a spherical form having a diameter of about 0.5 micron was obtained.

For the sake of comparison, silver benenate was also prepared in an identical manner but for using 500 ml of diluted aqueous nitric acid solution (pH = 2.0 at 60°C) without lead nitrate in place of the diluted aqueous nitric acid solution containing lead nitrate in the above process. Only coarse, spindle shaped crystals of silver benenate having a long side of 2 microns and short side of 0.1 micron were obtained.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. In a process of producing silver salt of a long chain aliphatic carboxylic acid which comprises mixing an aqueous silver nitrate solution or an aqueous silver complex solution with a solution of a carboxylic acid in a solvent in which said carboxylic acid is soluble, both said silver salt of the carboxylic acid and silver nitrate are almost insoluble and with which water is sparingly miscible, to react said carboxylic acid with silver ions, the improvement which comprises conducting said reaction of the carboxylic acid with silver ions in the presence of a mercury compound and/or lead compound.
butyrate, isoamyl butyrate, castor oil, benzene, toluene and xylene.

11. The process of claim 4 wherein the lead compound is used alone.

12. The process of claim 4 wherein the mercury compound is used alone.

13. The process of claim 4 wherein the lead and mercury compounds are used together.

14. The process of claim 4 wherein said carboxylic acid is selected from the group consisting of behenic acid and lauric acid.

15. The process of claim 4 wherein said solvent is selected from tricresyl phosphate, butyl acetate or benzene.

16. The process of claim 11 wherein said lead compound is lead nitrate.

17. The process of claim 12 wherein said mercury compound is selected from the group consisting of mercuric nitrate, mercuric acetate, mercuric sulfate, mercuric bromide, mercuric iodide, mercuric phenyl acetate, methyl mercuric chloride, ethyl mercuric chloride, phenyl mercuric-p-toluene sulfanilide, benzyl mercuric-p-toluene sulfanilide, mercuric chloranilate, 2-acetamino-1,3,4-thiadiazolyl-(5)-mercuric chloride and phenyl mercuric dinaphthylmethane disulfonate.

18. The process of claim 1 wherein said silver salt of the carboxylic acid has a grain size of less than 1 micron in diameter and is substantially spherical.