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(54) Method for etching half-tone silver halide images and silver halide photosensitive material for half-tone image reproduction.

(57) A black and white silver halide photosensitive material for contact copying of dot (or line) images comprises a high-chloride fine-grain silver halide emulsion reactively associated with a compound selected from the group of thiazolium salt compounds, thiazole compounds and pyrazole compounds. Said compounds are preferably added to the silver halide emulsion in combination with a mercaptotetrazole compound. The photosensitive material allows, during the photomechanical etching process, a significant reduction in the area of the dots without causing a significant reduction of small dots.

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Method For Etching Half-Tone Silver Halide Images And Silver Halide Photosensitive Material For Half-Tone Image Reproduction.

FIELD OF THE INVENTION

The present invention relates to a method for etching half-tone silver halide images and to a silver halide photosensitive material for contact copying of half-tone (dot and line) images.

BACKGROUND OF THE ART

Silver halide photosensitive materials are commonly used in the photo-lithographic industry for making dot or line images, for example for use as color proofing films and contact papers.

It is common practice, for the purpose of adjusting the hue of a lithographic print, to submit the dot or line image (normally, the expression "dot image" includes also the meaning of "line image") to a process, called "dot-etching", which consists of a treatment with a solution of mild oxidizing agents to partially dissolve the metallic silver of dot or line images. The most commonly used etching solution employs a mixture of a ferricyanide and a thiosulfate and is known as Farmer's solution, but other oxidizing agents, such as permanganates, ceric salts, dichromates, persulfates, etc. may be used.

In the case of dot images, the loss of silver image at the edges of the dots results in a reduction in the dot percentage, that is the percentage of the total area which is covered by the half-tone dots and varies from 0% to 100%. The degree to which the dots can be etched is limited by the loss in density which inevitably occurs at the center of the dots during dot etching. The density of the center of the dots should not fall much below a value of 2, otherwise the quality of copies or printing plates produced from the original deteriorates. The degree to which a film may be usefully etched is also limited by the constraint that during the etching process the small dots, i.e. 10% to 20% dots, should not be completely lost but remain sufficiently large and dense to be copied. In order to improve the dot etching characteristics of silver halide films used for photolithography, it is common practice to increase the coating weight of silver halide. In this way the density loss at the dot center during etching may be reduced. However, the increased cost of the film resulting from the increased coverage of silver is a serious drawback. Also a very thick gelatin top coat over the silver halide emulsion has been disclosed in GB 2,108,693 as a method for improving the dot etching characteristics of photolithographic films. This method, however, has the disadvantage that any substantial increase in the gelatin content leads to an increase in the time required to dry the film after processing.

SUMMARY OF THE INVENTION

We have found a method for improving the photomechanical dot etching of a black and white silver halide photosensitive material for contact copying of dot or line images, wherein the image-wise exposed silver halide emulsion is developed in an alkaline developer solution and the silver image is subjected to dot etching by means of a silver halide oxidizing solution, the improvement being that a high-chloride fine-grain silver halide emulsion is used in reactive association with at least one compound selected from the group of thiazolium salt compounds, thiazole compounds and pyrazole compounds (preferably in combination with a mercaptotetrazole compound), said at least one compound being in an amount such that the dots area (particular reference can be made to dots of mid range size, such as, for example, 50% dots) can be reduced without causing a significant reduction in the dot percentage of the small dots (the etching, in fact, is most harmful to small dots. An undesirable significant reduction of small dots would be etching of a 10 percent dot to less than 3 percent).

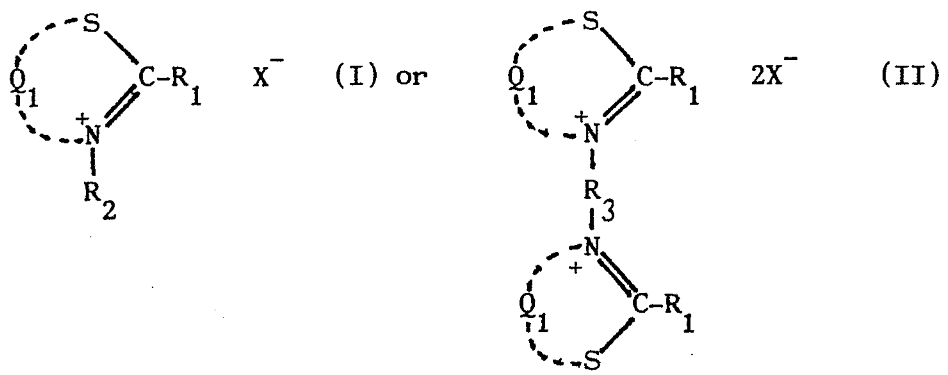
DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a method of photomechanical dot etching wherein an image-wise exposed silver halide photosensitive material for contact copying of line or dot images is developed in an alkaline developer solution and the silver image is subjected to dot etching by means of a silver halide oxidizing solution, in which the improvement consists of reactively associating a high-chloride fine grain silver halide emulsion with at least one compound selected from the group of thiazolium (including di-thiazolium) salt compounds, thiazole (including di-thiazole) compounds and pyrazole compounds, said compound being used in an amount such that the area reduction of the dots is affected without significantly impairing the dot percent of small dots. The term "high-chloride", as used in the present invention, is intended to refer to a silver halide having at least 60% of its molar halide content in chloride ions. The term "fine grain", as used in the present invention, is intended to refer to silver halide having an average grain size lower than 0.15 microns.

Preferably, the present invention relates to a method as described above, in which the selected compound is associated with the high-chloride fine-grain silver halide emulsion in combination with a mercaptotetrazole compound.

The following formulas (I), (II), (III), (IV) and (V) are given to better understand the chemical nature of the compounds of the present invention. Any substituents attached to them are to be reasonable in size and nature as not to impair their useful characteristics as stabilizers, antifoggants or toners as used to the purposes of the invention.

In general the thiazolium (including the di-thiazolium) salt compounds of the method of the present invention may correspond to general formulas I or II:

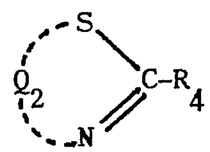


wherein R_1 represents hydrogen, a mercapto group, an aliphatic group or an aromatic group; Q_1 represents the atoms selected from the group consisting of nitrogen and carbon atoms necessary to complete a simple or fused 5-membered ring; R_2 represents an aliphatic group or an aromatic group, R_3 represents a divalent group and X^- represents an anion. The mercapto group represented by R_1 includes an alkylmercapto group, wherein the alkyl substituent preferably comprises 1 to 4 carbon atoms, such as methylmercapto, ethylmercapto, etc. The aliphatic groups represented by R_1 and R_2 include a straight or branched chain alkyl group, a cycloalkyl group, an alkenyl group, and an alkynyl group. Examples of straight or branched chain alkyl groups are alkyl groups having from 1 to 10, and preferably from 1 to 5 carbon atoms. Preferred examples include a methyl group, an ethyl group, a propyl group, a butyl group, etc. Also, the cycloalkyl group has generally from 3 to 10 carbon atoms and preferred examples thereof are a cyclopentyl group, a cyclohexyl an adamantyl group, etc. Also, examples of the alkenyl group include an allyl group, etc., and examples of the alkynyl group include a propargyl group, etc. The aliphatic groups represented by R_1 and R_2 may be substituted. Examples of the substituents for the aliphatic groups are an alkoxy group (e.g. a methoxy group, an ethoxy group, a propoxy group, a butoxy group, etc.), one or more halogen atoms (e.g. chlorine, bromine, fluorine, iodine, etc.), an alkoxycarbonyl group, an aryl group (e.g. a phenyl group, a halogen-substituted phenyl group, etc.), a hydroxy group, a cyano group, a sulfonyl group, etc.

Examples of the aromatic groups shown by R_1 and R_2 include a phenyl group, a naphthyl group bearing or not substituents (e.g. an alkyl group, an alkoxy group, a cyano group, a dialkylamino group, an alkoxycarbonyl group, a carboxy group, a nitro group, an alkylthio group, a hydroxy group, a sulfonyl group, a carbamoyl group, a halogen atom, etc., the alkyl groups thereof preferably including 1 to 5 carbon atoms). Preferred examples of the substituted groups are, for example, a p-methoxyphenyl group, an o-methoxyphenyl group, a tolyl group, a p-chlorophenyl group, an m-fluorophenyl group, etc. The divalent group represented by R_3 includes any divalent group, but preferably a cyclic hydrocarbon group such as an arylene group having 6 to 12 carbon atoms, e.g. an m-phenylene group, etc., an acyclic hydrocarbon group such as an alkylene group having 1 to 12 carbon atoms, e.g. a methylene group, an ethylene group, a trimethylene group, a decamethylene group, etc. The divalent group represented by R_3 can also be an aralkylene groups having a total of 8 to 10 carbon atoms. One to three of the carbon atoms of the group defined above for R_3 can be replaced by a hetero atom such as a nitrogen atom, a sulfur atom, an oxygen atom, etc. More preferably, R_3 is a divalent branched or straight chain alkylene group having 1 to 10 carbon atoms. Such chain can be substituted, for example, with one or more of an alkoxy group having 1 to 4 carbon atoms, such as a methoxy group, an ethoxy group, etc., a halogen atom such as a chlorine atom, a bromine atom, etc., a hydrogen atom, an acethoxy group, and the like. The simple or fused 5-membered ring, completed by Q_1 in formula (I) above, may be substituted by an alkyl group, such as a methyl group, an ethyl group, etc., an alkoxy group, such as a methoxy group, an ethoxy group, etc., an aryl group, such as a phenyl group, a benzyl group, etc., a halogen atom, such as chlorine, bromine, etc., an alkoxycarbonyl group, a cyano group, an amido group, etc. The ring fused on the 5-membered ring may be a simple or fused 6-membered ring including or not in its skeleton one or more nitrogen atoms such as, for example, benzene, |1,2-d| or |2,1-d| or |2,3-d|-naphthalene, 1- or 2- or 3-pyridine, pyridazine, pyrimidine and pyrazine.

Examples of X^- include chlorine, bromine, iodine, nitrate, sulfate, p-toluensulfonate, etc.

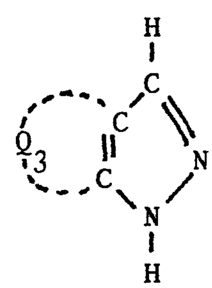
Still in general, the thiazole (including the di-thiazole) compounds of the present invention may correspond to general formula (III):



(III)

wherein Q_2 represents the atoms selected from the group consisting of nitrogen and carbon atoms necessary to complete a simple or fused 5-membered ring as described for the 5-membered ring of formula (I) and R_4 represents hydrogen, a mercapto group and an aliphatic or aromatic group as described for R_1 in formulas (I) and (II).

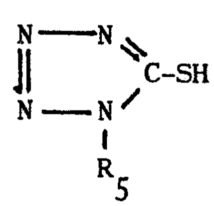
Still in general, the pyrazole compounds of the present invention may correspond to general formula (IV):



(IV)

wherein Q_3 represents a simple or fused ring as described for the 5-membered ring of formula (I).

Still in general, the mercaptotetrazole compounds to be combined with the above selected compound in reactive association with the high-chloride fine-grain silver halide emulsion according to the present invention, may correspond to general formula (V):



(V)

wherein R_5 represents an aliphatic or an aromatic group as described for R_1 and R_2 in formula (I).

Preferably, the high-chloride fine-grain silver halide emulsions according to the method of the present invention have an average grain size lower than 0.11 microns (the term "grain-size", as used herein, refers to the diameter of a circle which has the same area as the average projected area of the silver halide crystals viewed under an electron microscope). Still preferably, the high-chloride fine-grain silver halide emulsions according to the method of the present invention has a silver chloride content higher than 80 mole percent and more preferably higher than 90 percent. In particular, the preferred high silver chloride content emulsion is a silver chloro-bromide or a silver chloro-iodo-bromide emulsion. Still preferably, the compounds selected from the group above or their combination with the mercapto-tetrazole compounds, according to the method of the present invention, are associated with the high-chloride fine-grain silver halide emulsion in quantities ranging from 0.01 to 2 gram per mole of silver, more preferably from 0.05 to 0.5 gram per mole of silver.

According to another aspect, the present invention relates to a black and white silver halide photosensitive material, for contact copying of line or dot images, comprising, coated on a support, one or more hydrophilic colloidal layers, at least one of which is a silver halide emulsion layer, wherein the silver halide emulsion is a high-chloride fine-grain silver halide emulsion reactively associated with a compound selected from the group of thiazolium salt compounds, thiazole compounds and pyrazole compounds. Preferably, in the silver halide photosensitive material of the present invention, the selected compound is associated with the high-chloride fine-grain silver halide emulsion in combination with a mercaptotetrazole compound.

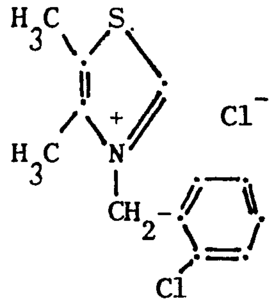
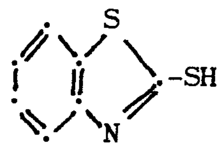
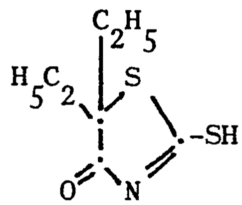
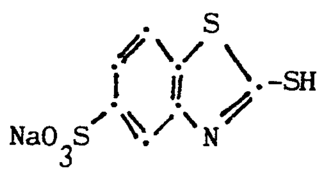
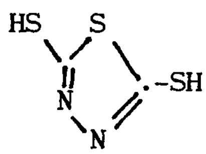
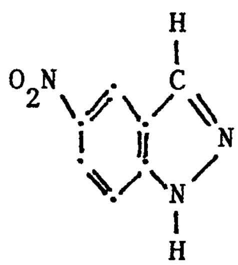
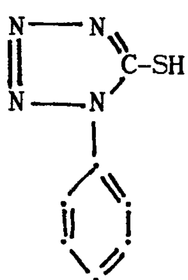
Generally, the thiazolium (including the di-thiazolium) salt compounds useful in the silver halide photosensitive material of the present invention correspond to the formulas (I) and (II) described above. Still in general the thiazole (including the di-thiazole) compounds correspond to the formula (III) described above. Still in general, the pyrazole compounds correspond to the general formula (IV) described above. Compounds selected within the formulas above may be combined, to prepare the silver halide photosensitive material of the present invention, with mercaptotetrazole compounds corresponding to the general formula (V) described above.

Such compounds, emulsion compositions and grain size are particularly chosen in a way as to reduce more than 10%, preferably at least 12%, of the dot percentage of a 50% dot without thereby causing either the dot percentage of a 10% dot to fall below 3% or the density of a 100% dot to fall below 2.0.

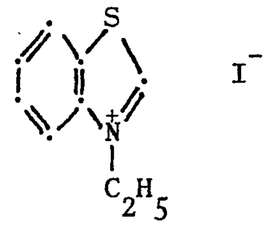
In fact, according to the present invention, the silver chloride content of the silver halide emulsion, the grain-size of the silver halide particles and the nature and amount(s) of the compounds (selected from the group of thiazolium salt compounds, thiazole compounds and pyrazole compounds and their combination with mercapto-tetrazole compounds) can be properly chosen to obtain the best results. Particularly, it has been found that the grain-size has a significant effect to the above purpose. Of course, the skilled in the art can arrange the emulsion with proper silver halide content, grain size of silver halide particles and amounts of the selected compouds to best operate the process depending upon his particular needs. To this purpose, a standard half-tone dot test target, as described hereinafter in the example, can be used to control the obtained results while changing the indicated parameters.

In a further aspect, the present invention refers to a dot etched photograph prepared by the dot etching method described above.

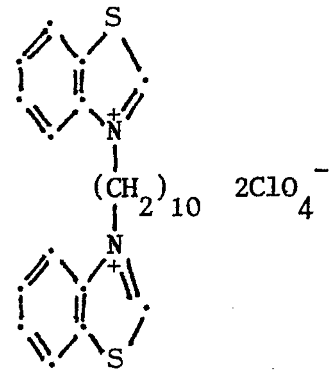
Specific examples of compounds corresponding to the general formulas above, which are useful in the method for dot etching and in the silver halide photosensitive material of the present invention are the following:

Compounds	Formula
1.	
2.	
3.	
4.	
5.	
6.	
7.	

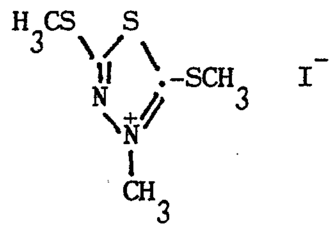
8.



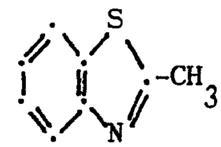
9.



10.



11.



When associated with the high-chloride fine-grain silver halide emulsion of the present invention (the term "associated with" is used to mean added to the coating composition including the silver halide emulsion used to form the silver halide emulsion layer, or added to a coating composition, not including the silver halide emulsion, used to form a non light-sensitive layer in a mutual relationship of permeability to water with the silver halide emulsion layer), the compounds of general formulas I, II, III and IV alone or in combination with the compounds of general formula V lead to a significant improvement in the dot etching characteristics of the coated emulsion. In particular the mid-range dot size is highly reduced without losing the small dots and decreasing the density of big dots.

It is well known that organic sulfur compounds, in particular thiols, act as inhibitors towards the bleaching of the silver image by bleaching solutions, as for example described in Phot. Sci. Eng., 11, (1967), p. 363, in Research Disclosure, 1972, 10233 and in US patent 3,705,803. This effect has been utilized, for example, for the protection of silver optical sound track of movie films while metallic silver is bleached from the color image. However, this effect is simply an overall inhibition of bleaching and gives no indication that bleaching of small dots (such as 10% dots) is inhibited to a larger extent than bleaching of mid-range dots (such as 50% dots). Indeed 1-phenyl-5-mercaptotetrazole compound, corresponding to compound 7 of the hereinbefore reported list, which is known to inhibit the overall bleaching, as described in Phot. Sci. Eng. reference above, is not effective on its own in the method and material of the present invention.

It is also well-known that many heterocyclic nitrogen and sulfur compounds including compounds of general structures I, II, III IV and V above, when added to the photographic emulsions produce a stabilizing or antifogging effect, as described by E.J. Birr in "Stabilization of Photographic Emulsions", Focal Press, London, 1974, Chapter 3. This effect does not generally depend on the type of the halide present in the emulsion, provided that the dissociation constant of the stabilizer-silver ion complex is lower than the solubility product of the silver halide. Also the antifogging effect does not depend on the grain size of the silver halide emulsion. In contrast, the improvement in dot etching produced by compounds of general formulas I, II, III or IV or their combination with compounds of general formula V appear to be more specific to fine silver halide emulsions containing a high percent of chloride.

It is further known that many photographic stabilizers including some compounds of structures I, II, III, IV and V particularly when added to pure silver chloride emulsions modify the form of the developed silver thereby giving the image a blue tone, such as described by P. Glafkidés in "Photographic Chemistry", Foutain Press, London, 1958, vol. I, page 380. Unlike the present invention, which requires very fine-grain emulsions, the image-toning effect occurs irrespective of the grain size of the silver halide.

The silver halide emulsions of the present invention are preferably of narrow grain-size distribution, but the invention is not limited to such emulsions. As stated before, the invention is restricted to very fine-grain silver halide emulsions, the major halide constituent being chloride and the minor, if present, being either bromide or iodide or both. Emulsions of very fine grain-size, such as the emulsions of the present invention, are often referred to as "Lippmann Emulsions". Methods for the preparation of such emulsions are well-known and are described for example by P. Glafkidés in "Photographic Chemistry", Fountain Press, London, 1958, vol. I, page 365.

The silver halide emulsions can optionally be sensitized with gold compounds, such as chloroaurates or gold chloride; salts of noble metals such as rhodium or iridium, sulfur compounds capable of producing silver sulfide by reacting with silver salts; and reducing substances such as stannous salts, amines and formamidine sulfinate. Furthermore, at the time of precipitation or physical ripening of the silver halide emulsion, salts of noble metals such as rhodium and iridium may also be present. The binder for the emulsion is preferably gelatin although part or all of this may be substituted by other synthetic or natural polymers as described in Research Disclosure, 1978, 17643, IX, for example, in order to improve the dimensional stability and the physical properties of the coated film.

Suitable antifoggants or stabilizers may be added to the coatings as described for example in the Research Disclosure above para. VI.

The emulsions may further contain additives, such as wetting agents, hardeners, filtering dyes, plasticizers, lubricants, matting agents, etc., as described in the Research Disclosure above. Additionally to the silver halide emulsion layer of the present invention coated onto a support, the photosensitive material may contain light unsensitive layers, such as a surface protective layer, an antihalation layer, an antistatic layer, etc. Said light insensitive layers can contain hydrophilic colloidal binders (e.g. gelatin), surface active agents, antistatic agents, matting agents, slipping agents, gelatin plasticizing agents, a polymer latex and so on.

Examples of supports preferably used in the photosensitive materials of the present invention include polyester films, such as a polyethylene terephthalate film and cellulose ester films, such as cellulose triacetate film.

The present invention does not put any particular restriction on the process for development of the photosensitive material. In general, any developing process (comprising the steps of developing, fixing and etching) used to process conventional photographic materials for use in the lithographic field can be adopted. Said development process may be performed manually or by using automatic developing machines, at processing temperatures generally in the range from 18 to 50°C, but not excluding temperatures outside that range.

The developing solution can contain any known developing agent. Examples of developing agents (which can be used alone or in mixtures) include dihydroxybenzenes (e.g. hydroquinone), aminophenols (e.g. N-methyl-p-aminophenol), 3-pyrazolidones (e.g. 1-phenyl-3-pyrazolidone), ascorbic acid, etc. In addition said developing solutions can contain preservatives, alkali agents, buffers, antifoggants, water softeners, hardeners, etc. A developing solution which can also be used in the present invention is the so-called lith developing solution, which comprises a dihydroxybenzene developing agent, an alkali agent, a small amount of free sulfite and a sulfite ion buffer (such as adducts of formalin and sodium bisulfite and of acetone and sodium bisulfite) to control the concentration of free sulfite and so on.

The fixing solution can have any conventionally used composition. Examples of fixing agents which can be used include thiosulfates, thiocyanates and organic sulfur compound which are known as fixing agents. The fixing solution can further contain water-soluble aluminium salts as hardeners.

Also the etching solution can have any conventionally used composition and for example the compositions described by C.E.K. Mees in "The Theory Of The Photographic Process", McMillan, 1954, pages 737-744. Specifically, an etching solution as a reducing component comprising a permanganate, a ferric salt, a persulfate, a cupric salt, a ceric salt, a hexacyanoferrate-(III), or a dichromate, independently or in combination and, optionally, an inorganic acid such as sulfuric acid, and an alcohol; or an etching solution comprising a reducing agent such as a hexacyanoferrate-(III), ethylenediaminotetraacetatoferrate-(III) or the like, and a silver halide solvent such as a thiosulfate, a thiocyanate, thiourea or a derivative thereof and, optionally, an inorganic acid such as sulfuric acid, can be used. Representative examples of etching solutions are Farmer's solution comprising potassium ferricyanide and sodium thiosulfate, an etching solution comprising a persulfate and potassium permanganate, an etching solution comprising a persulfate, an etching solution comprising a ceric salt, and so on.

There is no particular limitation as regards the composition of the etching solution and the processing conditions (temperature, time, etc.) to be used in the present invention. The etching of the whole surface can be carried out, as normal, by dipping the photosensitive material into the etching solution. Otherwise the etching solution may be applied locally, by using for example a brush, in order to etch a part of the image.

The present invention is now illustrated with more details making reference to the following examples.

EXAMPLE 1

A silver halide emulsion containing 98% silver chloride and 2%

silver bromide was prepared by adding an aqueous solution of silver nitrate (800 ml 2.5N) and an aqueous solution of mixed halides (17 ml 2.5N potassium bromide and 833 ml 2.5N potassium chloride) to a well-agitated solution of aqueous gelatin at 36°C over a period of 30 minutes by the conventional double-jetting technique.

The emulsion was coagulated by reducing the pH to 3.5 and adding sodium sulfate (800 ml 40% w/v). The emulsion was then washed in the conventional way and reconstituted with the addition of extra gelatin to give a final content of 80 g of gelatin per mole of silver.

The average grain-size of the emulsion was determined as 0.080 microns by examination under electron microscope. The emulsion was divided into portions which were prepared for coating with the addition of formaldehyde (hardener) and wetting agent. Further additions were made to the individual portions as indicated in Table 1, followed by coating onto polyester base which was backed with a green antihalation layer. The coatings were each conventionally exposed through a standard halftone dot test target made with a Crosfield Laser Scanner Model 640 Magnascan consisting of areas of dots ranging from 0 to 100% in 10% increments. The exposing source was a Philips HPM17 metal halide lamp. The coatings were developed in 3M RDC developer for 20 seconds at 40°C and fixed in 3M "Fixroll" fixer to give halftone images which were exact negative replicas of the test target.

The halftone dot images were cut into strips which were dipped into a ferricyanide bleach solution for a series of times from 30 seconds to 6 minutes, followed by rinsing in water.

The ferricyanide bleach solution was prepared as follows:

Solution A:	Potassium ferricyanide	37.5 g
	Water to make	500 cm^3
Solution B:	Sodium thiosulfate pentahydrate	480 g
	Water to make	2000 cm^3

For use, 1 part of Solution A was mixed with 4 parts of Solution B and 27 parts of water. The temperature was maintained at 20°C.

The strips were dried and the dot percentages of the bleached images were measured using a densitometer. The maximum etchability of a coating was taken as the reduction in dot percent which can be obtained on a 50% dot before either the measured percentage of a 10% dot falls below 3% or the density of a 100% dot falls below 2.0. The maximum etchability values are shown in Table 1.

Table 1

Coating Number	Compound added to emulsion	Quantity of compound added (g/mole silver)	Maximum etchability
1a (Comparison)	None	-	10%
1b (invention)	Compound 1	0.25	13%
1c (invention)	Compound 1 & Compound 7	0.25 0.07	16%
1d (comparison)	Compound 7	0.07	9%
1e (invention)	Compound 2 & Compound 7	0.20 0.07	15%
1f (invention)	Compound 3 & Compound 7	0.20 0.07	12%
1g (invention)	Compound 4 & Compound 7	0.20 0.07	12%
1h (invention)	Compound 5 & Compound 7	0.20 0.07	13%
1i (invention)	Compound 6	0.10	14%
1j (invention)	Compound 6 & Compound 7	0.10 0.07	15%
1k (invention)	Compound 8 & Compound 7	0.20 0.07	14%
1l (invention)	Compound 9 & Compound 7	0.20 0.07	12%
1m (invention)	Compound 10 & Compound 7	0.20 0.07	13%
1n (invention)	Compound 11 & Compound 7	0.20 0.07	14%

The results shown in Table 1 show the effectiveness of the compounds of structures I, II, III and IV in improving the etching characteristics of the coating and the further improvement resulting from the additional presence of a compound of structure V.

EXAMPLE 2

A series of silver halide emulsions of increasing grain size was prepared. The emulsions were all of 98% silver chloride, 2% silver bromide composition. The grain size of the emulsions was controlled by using the well-known techniques of altering the temperature, addition rates and quantity of silver and halide solutions. Each emulsion was split into two parts one of which was coated without further addition. The other part was added with Compound 1 (0.25 g/mole silver) and Compound 7 (0.07 g/mole silver). All the emulsions were coated and tested as described in Example 1.

The maximum etchability of the emulsion is shown in Table 2.

Table 2

Coating number	Grain size of silver halide (microns)	Compounds present	Maximum etchability
2a (invention)	0.09	1 + 7	16%
2b (comparison)	0.09	None	10%
2c (invention)	0.11	1 + 7	13%
2d (comparison)	0.11	None	10%
2e (comparison)	0.15	1 + 7	11%
2f (comparison)	0.15	None	11%

The results shown in Table 2 prove that the effectiveness of the additives of the invention in improving the etchability of the coating depends upon the grain size of the emulsion.

EXAMPLE 3

A series of silver halide emulsions was prepared by varying chlorobromide ratio and using a procedure like that described in Example 1. The emulsions had all a grain size ranging from 0.078 to 0.088 microns.

The emulsions were coated as said in Example 2 with and without the addition of Compounds 1 and 7. The maximum etchability of these coatings is reported in Table 3.

Table 3

Coating number	Halide ratio (Cl:Br)	Additions present	Maximum etchability
3a (comparison)	98:2	None	10%
3b (invention)	98:2	1 + 7	16%
3c (comparison)	90:10	None	10%
3d (invention)	90:10	1 + 7	13%
3e (comparison)	80:20	None	11%
3f (invention)	80:20	1 + 7	12%

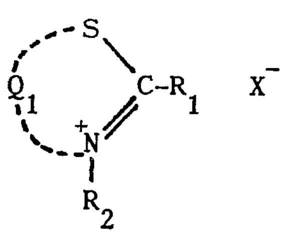
The results shown in Table 3 prove that the effectiveness of the compounds of the present invention in improving the etchability of the coating depends upon the chloro-bromide ratio of the emulsion.

CLAIMS:

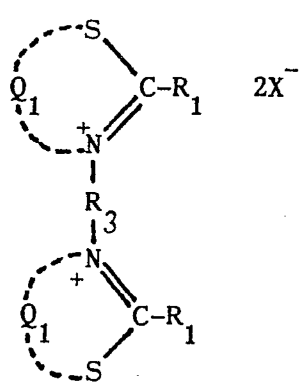
1. A method of photomechanical etching of a half-tone image wherein an image wise exposed silver halide photosensitive material to form half-tone dot images is developed in an alkaline developer solution and the developed silver image is subjected to dot etching by means of a silver halide oxidizing solution, the improvement consisting of reactively associating a high-chloride fine-grain silver halide emulsion in the photosensitive material with a compound selected from the group of thiazolium salt compounds, thiazole compounds and pyrazole compounds in an amount such that reduction in the area of the dots is caused without causing a significant reduction of small dots.

2. The method of photomechanical dot etching as claimed in claim 1, wherein the compounds selected from the class of thiazolium salt compounds, thiazole compounds and pyrazole compounds are associated with the high-chloride fine-grain silver halide emulsion in combination with a mercaptotetrazole compound.

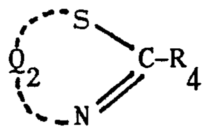
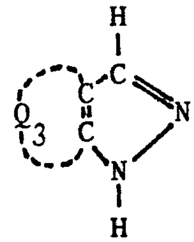
3. The method of photomechanical dot etching as claimed in claims 1 and 2 wherein said thiazolium salt, thiazole and pyrazole compounds correspond to the formulas :



(I)



(II)

 (III)  (IV)

wherein R_1 represents hydrogen, a mercapto group, an aliphatic group or an aromatic group, R_2 represents an aliphatic or aromatic group, R_3 represents a divalent group, R_4 represents hydrogen, a mercapto group, an aliphatic or an aromatic group; Q_1 and Q_2 represent the atoms selected from the group consisting of nitrogen and carbon atoms necessary to complete a simple or fused 5-membered ring, Q_3 represents the atoms necessary to form a fused ring and X^- represents an anion.

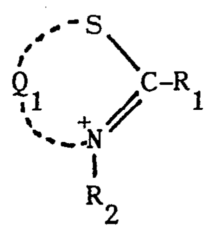
4. A black and white silver halide photosensitive material for contact copying of line or dot images comprising coated on a support one or more hydrophilic colloidal layers, at least one of which is a silver halide emulsion layer, wherein the silver halide emulsion is a high-chloride fine grain silver halide emulsion reactively associated with a compound selected from the group of thiazolium salt compounds, thiazole compounds and pyrazole compounds.

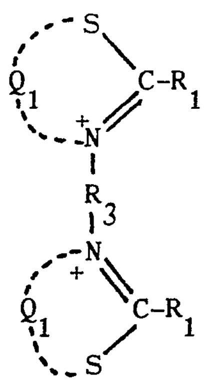
5. The silver halide photosensitive material for contact copying of line or dot images as claimed in claim 11, wherein the compounds selected from the group of thiazolium salt compounds, thiazole compounds and pyrazole compounds are associated with the silver halide emulsion in combination with a mercaptotetrazole compound.

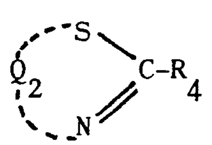
6. The silver halide photosensitive material for contact copying of line or dot images of claim 11 or 12, wherein the silver chloride content of the silver halide emulsion, the grain-size of the silver halide particles and the quantity of the compound selected from the group of thiazolium salt compounds, thiazole compounds and pyrazole

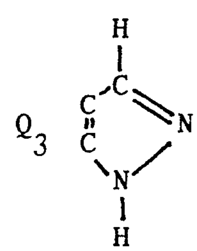
compounds and their combination with mercaptotetrazole compounds are chosen to operate the etching method by which the dot percentage of a 50% dot is reduced by more than 10% without thereby causing either the dot percentage of a 10% dot to fall below 3% or the density of a 100% dot to fall below 2.0.

7. The silver halide photosensitive material for contact copying of line or dot images as claimed in claim 11, wherein the thiazolium salt, the thiazole and pyrazole compounds correspond to the formulas:


X^- (I)


$2X^-$ (II)


(III)


(IV)

wherein R_1 represents hydrogen, a mercapto group, an aliphatic group or an aromatic group, R_2 represents an aliphatic or aromatic group, R_3 represents a divalent group, R_4 represents hydrogen, a mercapto group, an aliphatic or an aromatic group; Q_1 and Q_2 represent the atoms selected from the group consisting of nitrogen and carbon atoms necessary to complete a simple or fused 5-membered ring, Q_3 represents the atoms necessary to form a fused ring and X^- represents an anion.

8. The silver halide photosensitive material for contact cpying of line or dot images as claimed in claim 11, wherein the silver halide particles have a size of less than 0.15 microns.

9. The silver halide photosensitive material for contact copying of line or dot images as claimed in claim 11, wherein the silver halide is silver chlorobromide or silver chloro-iodo-bromide containing 60% mole silver chloride or more.

10. The silver halide photosensitive material for contact copying of line or dot images as claimed in claims 11 and 12, wherein the compounds selected from the group of thiazolium salt compounds, thiazole compounds and pyrazole compounds and their combination with mercaptotetrazole compounds are associated with the silver halide emulsion in quantities ranging from 0.01 to 2 grams per mole of silver.