United States Patent Office 3,488,707
Patented Jan. 6, 1970

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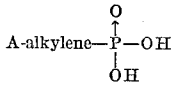
LIGHT-SENSITIVE SILVER HALIDE ELEMENTS CONTAINING PHOSPHONIC ACIDS

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No Drawing. Filed June 28, 1965, Ser. No. 467,717
Claims priority, application Great Britain, July 2, 1964, 27,345/64
Int. Cl. G03c 1/06
U.S. Cl. 96—67 4 Claims

ABSTRACT OF THE DISCLOSURE

Photographic light-sensitive material having a support, a light-sensitive silver halide emulsion layer, and optionally at least one other water-permeable layer adjacent the emulsion layer, one or more of such layers having incorporated therein a phosphonic acid of the formula:



wherein A is a carboxyl group, a phosphonic acid group, or a water-soluble salt thereof. Where another water-permeable layer contains the phosphonic or water-soluble salt thereof, that layer need not be necessarily arranged contiguously to the emulsion layer but can be separated by an additional water-permeable layer.

This invention relates to photographic light-sensitive silver halide materials containing compounds which prevent the formation of spots by the presence of particles of heavy metals and/or of heavy metal compounds.

Although an utmost care is taken in the manufacture of light-sensitive material, it is difficult to avoid completely the setting down of particles of heavy metals, such as iron particles, or of compounds of heavy metals, such as rust particles, onto the light-sensitive material. Said particles generally originate from the wearing and the corrosion of the coating machines, but also traces of these metals or metal compounds are sometimes present in the photochemicals used or may be present in the support such as a support of paper, film and glass upon which the light-sensitive emulsion is coated.

Said metal particles or particles of metal compounds are harmful particularly because they are chemically reactive, which means that they exert a secondary action upon the light-sensitive emulsion layer and aggravate the faults which are caused by the presence of said particles and which are mostly invisible by the unaided eye in such a way that according to the nature of the particle and the kind of the emulsion applied, light and dark spots become visible after treating the exposed light-sensitive material in the photographic baths.

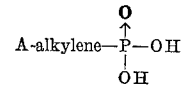
The metal particles in the photographic layers can be affected and the corrosion products formed can diffuse away from the central nucleus. These corrosion products can exert a sensitizing or a desensitizing action on the emulsion so that after the normal bath-treatment the photographic material shows black and white spots respectively. Furthermore most of these metals or their compounds can act as reductors and cause a spontaneous development which leads to black spots. On the contrary, other influences such as affection of the latent image and hindrance of the development lead to white spots. In all these cases the resulting spot is always larger than the dust particle which is the cause of this undesired

phenomenon. This can easily be checked e.g. by bleaching out with a usual bleaching agent the silver from the material showing the black spot. Nearly always the black spot disappears but in the centre a very small nucleus remains which can only be seen by enlarging.

Also fine metal particles or dust consisting of metal compounds which are present in a non-light-sensitive adjacent layer exert an equally disadvantageous influence on the upper- or underlying light-sensitive layer. The harmful corrosion products of the metal particles or the dissolved ingredients of the metal compounds indeed by diffusion can reach the light-sensitive layer to cause the above-mentioned faults.

Hitherto many compounds have already been proposed to prevent this formation of spots or at least to reduce such formation to a great extent. All these compounds, however, show one or more of the following disadvantages: an insufficient activity, an activity only in determined emulsions and in a well determined rather small pH range, and the occasioning of secondary effects on the silver halide emulsion layer such as desensitisation, fog formation and colouration.

Surprisingly it has now been found that the formation of spots as described above can practically completely be avoided when in at least one water-permeable layer lying at the same side of the support as the light-sensitive silver halide emulsion layer and/or in the support itself, at least one water-soluble phosphonic acid is present which corresponds to the following general formula:



wherein A represents a carboxyl group, a phosphonic acid group or a hydroxyl group. Also water-soluble salts of such phosphonic acids such as sodium, potassium, ammonium salts and amines are considered for the present invention.

These phosphonic acids and phosphonates are active in all kinds of light-sensitive silver halide material regardless the pH and the sensitivity of the silver halide emulsion layer; moreover, they are likely to exert also an antistatic and fog-depressing action on the light-sensitive material.

The phosphonic acids wherein A is a carboxyl group can be prepared among others by reaction of halocarboxylic acid esters with trialkyl phosphites followed by saponification of ester functions in acid medium. More particulars about this preparation can be found in Chem. Ber. (1924) 1023–1038 and (1927) 291–295, J. Am. Chem. Soc. (1946) 1103–1105 and J. Gen. Chem. U.S.S.R. (1927) 237 and (1929) 619. Suitable compounds wherein A is a carboxyl group can be found in Koslapoff, organophosphorus compounds, pp. 160–161. As particularly suitable can be mentioned

$HO_2C-CH_2-PO(OH)_2$—carboxymethylphosphonic acid

$HO_2C-CH(CH_3)-PO(OH)_2$—1-carboxymethylphosphonic acid

$HO_2C-CH_2-CH_2-PO(OH)_2$—2-carboxyethylphosphonic acid, and

$HO_2C-CH_2-CH_2-CH_2-PO(OH)_2$—3-carboxypropylphosphonic acid

A suitable phosphonic acid wherein A is a phosphonic acid group is methylenediphosphonic acid. This compound can be prepared by reaction of the diethyl ester of chloromethanephosphonic acid and triethyl phosphite followed by saponification of the ester function. Other suitable phosphonic acids wherein A is a phosphonic acid group can be prepared by reaction between an α,ω-dihalogenoalkane and a double molar quantity of triethyl phosphite followed by saponification of the ester function

in dilute acids. Further particulars of these preparing methods can be found in an article of K. Moedritzer and R. R. Irani, J. Inorg. Nucl. Chem. (1961) 297–304. Suitable phosphonic acids of this kind are among others ethylene-1,2-diphosphonic acid, propylene-1,3 - diphosphonic acid and butylene-1,4-diphosphonic acid.

The phosphonic acids according to the above-mentioned general formula wherein A is a hydroxyl group can be prepared by reaction of aldehydes or ketones with phosphorous acid or phosphorus trichloride. For further particulars about this method of preparation the J. Am. Chem. Soc. (1921) 1928–1935 and to the above-mentioned book of Kosolapoff, pages 129–132 are referred to. Compounds wherein A is a hydroxyl group are mentioned in said book on pages 156–157. In particular can be mentioned (1-hydroxyheptyl)-phosponic acid, [(1-hydroxy-1,3 - dimethyl)-butyl]-phosphonic acid and [(1-hydroxy-1-methyl)-ethyl]-phosphonic acid as suitable for being used according to the present invention.

Addition of hypophosphorous acid to aldehydes or ketones yields hydroxyphosphonic acids, but double addition yields dihydroxyphosphinic acids. The latter compounds too are effective in photographic silver halide material as spot-inhibiting compounds. Very suitable is, e.g., the addition product of hypophosphorous acid to pyruvic acid whereby di(1-carboxy - 1 - hydroxyethyl) - phosphinic acid is formed.

The compounds used according to the present invention can be present in different concentrations in the support, e.g., a paper support of the light-sensitive material and/or in at least one of the water-permeable layers lying at the same side of the support as the light-sensitive silver halide emulsion layer, in a way according to among others the compound chosen and the nature of the layer wherein the compound is present. Preferably the compounds according to the present invention are present in the light-sensitive silver halide emulsion layer itself and this in the most widely varying concentrations ranging from some mg. to 10 and more g. per sq. m. of light-sensitive material. For the case the compounds are not present in the light-sensitive layer but in another layer, they are active since they diffuse into said light-sensitive layer.

The phosphonic acids or salts are usually first dissolved, e.g., in water. The support can then be soaked with such solution for the case the compounds applied according to the invention are incorporated into the support. If, however, the compounds are incorporated into a water-permeable layer, their solution is usually added to the coating composition of the respective layer or layers.

In a photographic material, the compounds used according to the present invention have the advantage that they do not impair at all the pursued photographic properties, such as, e.g., contrast, sensitivity and stability. Consequently, these compounds can be incorporated into high-sensitive as well as into low-sensitive emulsions, into very contrasty as well as into low-contrast emulsions, into acid as well as into alkaline emulsions.

A further advantage is that the compounds according to the invention do not impair at all the other products used in the manufacture of light-sensitive materials such as dispersing agents, colour couplers. surface-active agents, optical brightening agents, antioxidising agents, sensitisers, fog-inhibiting agents, stabilisers, hardeners or plasticisers.

As a result, the compounds according to this invention can be used in all kinds of photographic negative and positive material, such as, e.g., printing material, X-ray film, graphic material, infrared-sensitive silver halide material and material for the application of the silver complex diffusion transfer process. Also in photographic light-sensitive material not containing silver halide or in photographic non-light-sensitive material, the phosphonic acids and/or their salts described can successfully be used for avoiding spots caused by particles of heavy metal compounds.

The following examples illustrate the present invention.

EXAMPLE 1

A not yet quite dry subbing layer applied to a cellulose triacetate support is dusted with finely divided iron powder. A strip A of this treated support is coated with a high-sensitive panchromatically sensitized silver bromide emulsion. A strip B of this treated support is coated with the same silver bromide emulsion to which, however, 3 g. of carboxymethylphosphonic acid were added per kg. of emulsion. After drying these two test strips they are exposed in such a way that after developing for 9 minutes at room temperature, fixing and rinsing, a density of 0.6 is obtained. For development a solution of the following composition is used:

Water	cc	800
Monomethyl-p-aminophenol sulphate	g	2
Sodium sulphite (cryst.)	g	200
Hydroquinone	g	4
Borax	g	2

Water to 1000 cc.

Both strips are rinsed for some seconds, whereafter they are fixed for 10 minutes in a solution of the following composition:

Sodium thiosulphate	g	200
Potassium metabisulphite	g	25

Water to 1000 cc.

The strips are then rinsed for 30 minutes in running water and finally dried. The strip A shows numerous black spots, whereas the strip B prepared according to the present invention possesses a uniform appearance and the same density all over its surface.

EXAMPLE 2

Example 1 is repeated but the carboxymethylphosphonic acid is replaced by a same amount of methylenediphosphonic acid.

EXAMPLE 3

Example 1 is repeated but the carbovymethylphosphonic acid is replaced by a same amount of butylene-1,4-diphosphonic acid.

EXAMPLE 4

Example 1 is repeated but the carboxymethylphosphonic acid is replaced by a same amount of (1-hydroxyheptyl)-phosphonic acid.

EXAMPLE 5

A strip of paper stock of usual photographic quality is coated with a baryta layer of the following composition:

50% aqueous suspension of barium sulphate	kg	2
10% aqueous solution of gelatin	cc	1000

The half A of this baryta-coated strip is coated with a light-sensitive contrasty silver bromide emulsion containing iron powder. After drying, this strip is exposed in such a way that after developing for 90 seconds, fixing and rinsing it shows a density of 0.6. For development a solution of the following composition is used:

Water	cc	800
Monomethyl-p-aminophenol sulphate	g	1.5
Sodium sulphite (cryst.)	g	50
Hydroquinone	g	6
Sodium carbonate (cryst.)	g	100
Potassium bromide	g	1

Water to 1000 cc.

This strip is rinsed for 5 seconds and then fixed for 10 minutes in a solution as described in Example 1, rinsed for 1 hour in running water and dried. The paper strip shows numerous white spots.

If, however, 4 g. of carboxymethylphosphonic acid are

added per kg. of the light-sensitive emulsion and if the latter is applied to the other half B of the baryta-coated strip and further treated as the half A, then this half B shows a uniform appearance without white spots.

EXAMPLE 6

Example 5 is repeated, but the carboxymethylphosphonic acid is replaced by a same amount of methylenediphosphonic acid.

EXAMPLE 7

Example 5 is repeated, but the carboxymethylphosphonic acid is replaced by a same amount of ethylene-1,2-diphosphonic acid.

EXAMPLE 8

Example 5 is repeated, but the carboxymethylphosphonic acid is replaced by a same amount of propylene-1,3-diphosphonic acid.

EXAMPLE 9

Example 5 is repeated, but the carboxymethylphosphonic acid is replaced by a same amount of butylene-1,4-diphosphonic acid.

EXAMPLE 10

Example 5 is repeated, but the carboxymethylphosphonic acid is replaced by a same amount of (1-hydroxy-heptyl)-phosphonic acid.

EXAMPLE 11

Example 5 is repeated, but the carboxymethylphosphonic acid is replaced by a same amount of [(1-hydroxy-1,3-dimethyl)-butyl]-phosphonic acid.

EXAMPLE 12

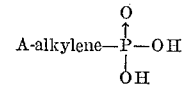
Example 5 is repeated, but the carboxymethylphosphonic acid is replaced by a same amount of [(1-hydroxy-1-methyl)-ethyl]-phosphonic acid.

EXAMPLE 13

Example 5 is repeated, but the carboxymethylphosphonic acid is replaced by a same amount of di(1-carboxy-1-hydroxy-ethyl)-phosphonic acid.

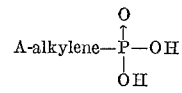
We claim:

1. A photographic light-sensitive material comprising a support, and a light-sensitive silver halide emulsion layer, said material containing a phosphonic acid corresponding to the following general formula:



wherein A represents a group selected from a carboxyl group or a phosphonic acid group.

2. A photographic light-sensitive material comprising a support, and a light-sensitive silver halide emulsion layer, said material containing a water-soluble salt of phosphonic acid corresponding to the following general formula:



wherein A represents a group selected from a carboxyl group or a phosphonic acid group.

3. The light-sensitive material of claim 1 wherein said material comprises at least one water-permeable layer in addition to said emulsion layer and lying on the same side of said support as said emulsion layer.

4. The light-sensitive material of claim 2, wherein said material comprises at least one water-permeable layer in addition to said emulsion layer and lying on the same side of said support as said emulsion layer.

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U.S. Cl. X.R.

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