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# POLYHYDROXY-SPIRO-BIS-INDANE PHOTOGRAPHIC TANNING AGENT

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## ABSTRACT OF THE DISCLOSURE

This invention relates to the use of polyhydroxy-spiro-bis-indane tanning agents in silver halide photography.

Tanning developing agents have been incorporated in photographic emulsions and developers for many years. However, soluble tanning developing agents such as pyrocatechol and hydroquinone are subject to disadvantages such as fogging during aging, loss of speed during aging, and diffusion throughout the gelatin causing tanning of the contiguous nonimage areas. Some water-insoluble tanning agents in addition to the disadvtanges listed, are further limited because of sublimation during aging to yield unstable sensitometric properties and because they harden the unexposed emulsion and impair wash-off. It is, therefore, an object of this invention to provide new tanning agents which minimize or eliminate these unwanted effects.

This invention in its broadest sense encompasses developing a photosensitive silver halide in the presence of an alkyl hydroxy-spiro-bis-indane having ortho or para-sustituted hydroxyl groups in at least one of the aromatic rings. This group of compounds can be incorporated in the photosensitive silver halide emulsion, in the processing solution, or as an auxiliary layer in a multiple layer photosenstvie element, and has been found to have good developing properties for exposed or latent silver halide images and an excellent tanning action on water permeable colloids, especially gelatin.

In practicing a preferred embodiment of this invention, a suspensoid, a colloidal system having solid particles dispersed therein, is prepared by neutralizing an alkaline solution containing up to about 5% by weight of the agent 3,3,3′,3′-tetramethyl-5,6,5′,6′-tetrahydroxy-spiro-bis-indane, thereinafter referred to as indane (I), gelatin in amounts of approximately 1 to 10% and a water-miscible solvent for indane (I), e.g., 2-methoxyethanol in amounts of 0 to 10%, (all percentages being by weight). The resulting mixture is then mixed with an unhardened gelatino-silver halide emulsion such that the effective concentration of indane (I) is in the range of approximately 0.01 mole to 0.3 mole of indane (I) per mole of silver halide. The photosensitive silver halide emulsion containing indane (I) is then coated on a matted support as disclosed in assignee's pending applications, Moede Ser. Nos. 339,849, Jan. 24, 1964, now Patent No. 3,353,-958, and Moede et al. 517,894, Jan. 3, 1966. After exposure through a negative to actinic radiation, the photosensitive element containing the tanning agent, indane (I), is processed in an alkaline medium, usually a 5% aqueous potassium carbonate solution. Indane (I) develops the silver image and its oxidized form tans the gelatin in the image area while in the nonimage area, which is removed by washing in warm water, no tanning occurs. After washing in water, there remains a tough tanned silver-gelatin image in relief on the matted support.

This invention is further illustrated by but not intended to be limited to the following examples wherein the percentages are by weight.



## EXAMPLE I

An unhardened gelatino-silver chloride emulsion containing 1.5 moles of silver chloride and 50 grams of gelatin was coagulation washed and redispersed in the presence of 125 grams of gelatin by the process disclosed in Moede U.S. Patent 2,772,165, Nov. 27, 1956. The following additions were then made to the emulsion at 100° F.:

(1) 18 grams of a 10% aqueous solution of the sodium salt of N-coco-β-aminopropionate, "coco" representing a mixture of the high molecular weight hydrocarbon radicals corresponding to those present in the esters in coconut oil including in order of decreasing concentration, lauryl, myristyl, palmityl, caprylyl, capryl and oleyl,
(2) 250 grams of a 10% aqueous tartrazine solution, (C.I. 640, where C.I. refers to F. M. Rowe's Colour Index, 1st edition, Society of Dyes and Colourists, 1924),
(3) 75 grams of a 6% aqueous sodium dodecyl sulfate solution,
(4) 75 grams of a 6% aqueous hydroxylamine hydrochloride, and
(5) A mixture containing 50 grams of 3,3-tetramethyl-5,6,5′,6′-tetrahydroxy-spiro-bis-indane, 400 ml. of dimethyl formamide, 250 ml. of ethyl alcohol, and 600 ml. of water.

The resulting emulsion was coated on a subbed, matted polyester support as described in assignee's pending patent application, Ser. No. 339,849 filed on Jan. 24, 1964. The emulsion coating was at a level of 20 mg. of AgCl/dm.$^2$. The coated emulsion was then allowed to dry.

The photosensitive element exhibited the following sensitometric and physical properties:

| | Relative speed | $D_{max}$ | Fog | | Melting point of coated emulsion in water (° F.) |
|---|---|---|---|---|---|
| | | | 1 min. dev. | 3 min. dev. | |
| Fresh | 100 | 2.80 | .02 | .05 | 96 |
| Aged 7 days at 120° F. and 65% relative humidity | 97 | 3.03 | .03 | .07 | 104 |

After exposure through a negative to a carbon arc source for one minute, the element was developed for one minute in a 68° F., 5% aqueous potassium carbonate developer. The nonimage area was then easily washed off in warm water. The water washing left a tough, tanned relief image on the matted surface of the support.

## EXAMPLE II

Example I was repeated except that prior to development, the exposed photosensitive element was water washed for five minutes in water at 70° F. After this washing, development was carried on as in Example I. The procedure demonstrated the nonwandering or nonmigratory characteristics of indane (I) as was evidenced by the final tanned distinct relief image on the matted support.

## EXAMPLE III

Example III demonstrates that the alkyl hydroxy-spiro-bis-indane having ortho or para-substituted hydroxyl groups on the aromatic rings may be incorporated in the developer solution rather than the emulsion layer.

An unhardened slow, contact speed gelatino-silver chloride emulsion was coated at a level of 25 mg. of AgCl/dm.$^2$ on a subbed, matted acrylic layer prepared by the process disclosed in application Ser. No. 339,849.

The emulsion was exposed to a negative as in Example I.

A developer solution A was prepared as follows.

Solution A:

| | Gm. |
|---|---|
| Sodium carbonate (anhyd.) | 10 |
| 3,3,3',3'-tetramethyl-5,6,5',6'-tetrahydroxy-spiro-bis-indane | 1 |
| Water to make 1000 ml. | |

The exposed photosensitive element was developed in solution A for one minute at 68° F. The exposed area developed and tanned while the unexposed area exhibited no tanning effect or development. The unexposed area was washed off in warm water leaving a gelatin-silver image in relief on the matted surface, of the support.

To further demonstrate the tanning characteritsics of indane (I), the same emulsion as used in Example III was exposed and developed as was done in the first half of this example except that the developer did not contain any of the tanning agent, indane (I). There was no image development in the plain carbonate developer thus indicating the usefulness of indane (I) as a tanning agent and as a developer which reduces exposed silver halide to silver.

## EXAMPLE IV

The following suspensoid was prepared.

Suspensoid A:

| | | |
|---|---|---|
| 3.3% aqueous gelatin | gm. | 150 |
| 3 M NaOH | ml. | 2.5 |
| 10% aqueous $Na_2SO_3$ | gm. | 1.0 |
| 3,3,3',3'-tetramethyl-5,6,5'6'-tetrahydroxy-spiro-bis-indane 2-methoxyethanol solution (1 gm. indane (I)/6 ml. of 2-methoxyethanol) | ml. | 6.0 |

The components of suspensoid A were mixed, resulting in a hazy mixture. To produce a clear greenish-blue mixture with a pH of 11.5, 1 ml. of 3 M NaOH was added to the mixture. The mixture was slowly neutralized with 6.5 ml. of 1.5 N $H_2SO_4$ producing a pH of 6.5 and a precipitate of indane (I).

The following were then added to the precipitated suspensoid A:

| | Gm. |
|---|---|
| 20% aqueous gelatin | 150 |
| Washed AgCl emulsion (mole of AgCl) | 0.15 |
| 2% methanol solution of phenylbiguanide mercaptobenzothiazole | 20 |
| 10% ethanol solution of propyl gallate | 20 |
| Aqueous tartrazine (C.I. 640) | 25 |
| Sodium lauryl sulfate | 7.5 |
| Aqueous hydroxylamine sulfate | 3.5 |
| N-coco-β-aminopropionate (the same mixture as in Example I) | 1.8 |

The resulting emulsion, having a pH of 5.8 was then coated on a matted support as in Example I. The coated emulsion was then aged, exposed and developed as in Example I. The sensitometric and physical properties were as follows:

| | Relative speed | $D_{max}$ | Fog | | Melting point (° F.) |
|---|---|---|---|---|---|
| | | | 1 min. dev. | 3 min. dev. | |
| Fresh | 100 | 3.12 | .07 | .25 | 89 |
| Accelerated aging (as in Example I) | 90 | 2.73 | .06 | .15 | 90 |

The unexposed areas exhibited good wash-off properties leaving a tanned, tough, relief image on the matted support.

## EXAMPLE V

The following suspensoid was prepared.

Suspensoid B:

| | | |
|---|---|---|
| Component 1— | | |
| 7.2% aqueous gelatin | gm. | 1725 |
| 10% aqueous $Na_2SO_3$ | gm. | 17 |
| 3 M NaOH | ml. | 25 |
| Component 2— | | |
| 2-methoxyethanol | ml. | 186 |
| Methanol | ml. | 194 |
| Phenylbiguanide Mercapto benzothiazole | gm. | 4 |
| Propyl gallate | gm. | 20 |
| 3,3,3',3'-tetramethyl-5,6,5',6'-tetrahydroxy-spiro-bis-indane | gm. | 10 |

Component 2 was added to component 1 and the resulting mixture was then slowly neutralized, during a 3-minute period, with 115 ml. of 0.3 M $H_2SO_4$, yielding a suspensoid of indane (I), phenylbiguanide mercaptobenzothiazole, and propyl gallate.

The following were then added to suspensoid B:

| | | |
|---|---|---|
| Washed AgCl emulsion | moles | 1.5 |
| 10% aqueous tartrazine (C.I. 640) | gm. | 250 |
| 6% aqueous sodium dodecyl sulfate | gm. | 75 |
| 6% aqueous hydroxylamine sulfate | gm. | 75 |
| 10% aqueous N-coco-β-aminopropionate (same mixture as in Example I) | gm. | 18 |

The resulting photosensitve emulsion was then coated on a matted support as in Example I. The coated emulsion was aged and imagewise exposed as in Example I.

A developer was prepared as follows.

Developer C:

| | Gm. |
|---|---|
| Distilled water | 989 |
| $K_2CO_3$ (anhyd.) | 32.2 |
| NaOH | 3.1 |
| $K_2SO_3$ (anhyd.) | 4.9 |
| KBr | 0.21 |
| 1-phenyl-5-mercaptotetrazole | 0.04 |

The exposed photosensitive element was developed in developer C, forming an image in less than 15 seconds. The unexposed area was easily washed off in 90° F.-water after a 15-second immersion in the developer. There was no change in wash-off properties after a 20-minute bath in developer C. The sensitometric properties after one-minute development in developer C were as follows:

| | Relative speen | $D_{max}$ | Fog | | Melting Point (° F.) |
|---|---|---|---|---|---|
| | | | 1 min. dev. | 3 min. dev. | |
| Fresh | 100 | 2.22 | .02 | .03 | 98 |
| Accelerated aging (same as Example I) | 90 | 1.81 | .01 | .02 | 96 |

After washing, a tanned, relief image remained on the support.

## EXAMPLE VI

Example V was repeated except that the matted support was replaced in turn by the following:

(a) Polyethylene terephthalate with a gelatin sublayer,
(b) Paper,
(c) Electrical discharge treated matte-filled polyester base as described in application Ser. No. 517,894.

Results similar to those of Example V were obtained.

## EXAMPLE VII

Example V was repeated except that ⅓ of the gelatin in the photographic emulsion was replaced with a gelatin-polymer component prepared by copolymerizing 8 parts

of vinylidene chloride and 8 parts of methyl acrylate in the presence of 84 parts of gelatin, as disclosed in Example I of assignee's pending application, Ser. No. 339,849 filed Jan. 24, 1964 now Patent No. 3,353,958. Prior to coating the emulsion on a matted support as in Example V, 400 gm. of a 5% aqueous hydroquinone solution were added to the emulsion. Aging, exposing, developing, and testing were the same as in Example I. The emulsion containing the tanning agent indane (I) exhibited the following sensitometirc properties:

| | Relative speed | $D_{max}$ | Fog | | Melting point (° F.) |
|---|---|---|---|---|---|
| | | | 1 min. dev. | 3 min. dev. | |
| Fresh | 100 | 3.57 | .02 | .19 | 96 |
| Accelerated aging (as in Example I) | 92 | 2.90 | .04 | .15 | 115 |

The incorporation of hydroquinone in the emulsion yielded an increased $D_{max}$ but an increase in melting point also resulted. Image toughness and wash-off properties were superior to those obtained when using hydroquinone without any indane (I). Similar results were obtained when the gelatin of Example V was replaced by a 100% gelatin-polymer component.

## EXAMPLE VIII

Example I was repeated except that all ingredients were reduced to 1/10 to the scale in Example I and addition (5) was a mixture of 4 grams of indane II, 32 ml. of dimethyl formamide, 25 ml. of ethyl alcohol and 48 ml. of water. Indane II was prepared according to the procedure of Fisher, Furlong and Grant in J. Am. Chem. Soc., 58: 820–2 (1936), Example VI.

The emulsion coating was at a level of 45 mg. of AgCl/dm.$^2$ and exhibited the following sensitometric and physical properties:

| | Relative speed | $D_{max}$ | Fog | | Melting point of coated emulsion in water (° F.) |
|---|---|---|---|---|---|
| | | | 1 min. dev. | 3 min. dev. | |
| Fresh | 100 | 3.25 | .04 | .07 | 94 |
| Aged 7 days at 120° F. and 65% relative humidity | 96 | 2.84 | .04 | .10 | 102 |

After exposure through a negative to a carbon arc source for one minute, the photosensitive element was developed for one minute in 5% aqueous potassium carbonate developer at 68° F. The nonimage area was then easily washed off in farm water leaving behind a tough, tanned relief image on the matted surface of the support.

As mentioned earlier, the preferred tanning development agent of this invention is 3,3,3',3'-tetramethyl-5,6,5',6'-tetrahydroxy-spiro-bis-indane (indane I). Indane (I) can be prepared by contensation of catechol with acetone such as the process disclosed by Baker, J. Chem. Soc., 1934, pp. 1678–81. Satisfactory results were obtained using 3,3,3',3' - tetramethyl - 4,6,7,4,6',7' - hexahydroxy-1,1'-spiro-bis-indane (indane II). Indane II can be prepared by the condensation of polyhydric phenols with acetone as disclosed by Fisher, Furling, and Grant, J. Am. Chem. Soc., 58: 820–22, (1936). Other alkyl hydroxy-spiro-bis-indanes where the hydroxyls are ortho or para-substituted in the aromatic rings can be prepared as described in German Patent 1,092,648. Such compounds can be used in the same amounts as indane (I).

The tanning development agent is usually added to the emulsion as a suspensoid. The novel process for making a suspensoid is not limited to that disclosed in the examples as other techniques such as those listed in books on colloidal chemistry can be used to prepare a suspensoid of polyhydroxy-spiro-bis-indanes. Furthermore, such indanes can also be added to the emulsion directly as a solute in a water-miscible organic solvent or as a solute in the oil phase of an oil-water dispersion. The novel tanning developing agents of this invention may be used in all conventional hardened or unhardened photographic emulsions. Similarly, such indanes may be used in the developers or in combination with other developers. These indanes may also be used in processing mediums such as pods or packets for inverse transfer systems. These indanes, e.g., I and II, may be added to auxiliary layers of the photographic system and may be used alone or in combination with other nontanning or tanning developing agents, e.g., alkyl gallates and hydroquinone.

The silver halide emulsion may be selected from well known emulsions containing silver chloride, silver bromide, and silver iodide or mixtures thereof. The use of this class of novel tanning development agents is particularly useful in wash-off type emulsions, or precipitated and coagulated washed emulsions such as those disclosed in assignee's U.S. Patent 2,772,165 by Moede.

The preferred binder for use with this novel tanning development agent is gelatin. However, in place of gelatin other natural or synthetic water-permeable organic colloid binding agents susceptible to cross linked quinone tannage can be used. Such agents include water-permeable or water-soluble polyvinyl alcohol and its derivatives, e.g., partially hydrolyzed polyvinyl acetates, polyvinyl ethers, and acetals containing a large number of extra linear —$CH_2CHOH$— groups; hydrolyzed interpolymers of vinyl acetate and unsaturated addition polymerizable compounds such as maleic anhydride, acrylic and methacrylic acid ethyl esters, and styrene. Suitable colloids of the last mentioned type are disclosed in U.S. Patents, 2,276,322, 2,276,323 and 2,347,811. The useful polyvinyl acetals include polyvinyl acetaldehyde acetal, polyvinyl butyraldehyde acetal and polyvinyl sodium o-sulfobenzaldehyde acetal. Other useful colloid binding agents include the poly-N-vinyl lactams of Bolton U.S. Patent 2,495,918, the hydrophilic copolymers of N-acrylamidoalkyl betaines described in Shacklett U.S. Patent 2,833,650 and hydrophilic cellulose ethers and esters.

In addition to the matted supports disclosed in assignee's pending patent, Ser. No. 339,849, filed Jan. 24, 1964, and 517,894, filed Jan. 3, 1966, the film support for the emulsion layers used in the novel process may be any suitable transparent plastic. For example, the cellulosic supports, e.g., cellulose acetate, cellulose triacetate, cellulose mixed esters, etc. may be used. Polymerized vinyl compounds, e.g., copolymerized vinyl acetate and vinyl chloride, polystyrene, and polymerized acrylates may also be mentioned. The film formed from the polyesterification product of a dicarboxylic acid and a dihydric alcohol made according to the teachings of Alles, U.S. Patent 2,779,684, and the patents referred to in the specification of that patent. Other suitable supports are the polyethylene terephthalate/isophthalates of British Patent 766,290 and Canadian Patent 562,672 and those obtainable by condensing terephthalic acid and dimethyl terephthalate with propylene glycol, diethylene glycol, tetramethylene glycol or cyclohexane 1,4-dimethanol (hexahydro-p-xylene alcohol). The films of Bauer et al. U.S. Patent 3,052,543 may also be used. The above polyester films are particularly suitable because of their dimensional stability.

In addition to the adjuvants used to make a suspensoid of indane (I), e.g., water miscible solvents such as methoxy-ethanol, various adjuvants may be added to the emulsion. These include surfactants such as sodium dodecyl sulfate, auxiliary developers, and other tanning agents such as propyl gallate, alkyl gallates, and hydroquinone. The emulsion can contain dyes, e.g., tartrazine (C.I. 640); toners, e.g., phenyl biguanide mercapto benzothiazole, and similar compounds such as those disclosed in assignee's U.S. Patent 2,668,113; hardeners, e.g., chrome alum, formaldehyde; matting agents; optical brightening agents; image color modifiers; sensitizers; optical sensitizers; etc.

The use of tanning development agents such as indane

(I) are especially beneficial in making reproductions of drawings, maps, line copy, half tones, etc., wherein a reproduction can be easily revised by drawing on the matte surface and/or wet erasing the relief image. The use of an agent such as Indane (I), having ortho or para-substituted hydroxyl groups on the aromatic rings is especially useful with any binder that is subject to quinone tannage.

Indane (I) has specific advantages over the use of other tanning development agents. It is nonvolatile. This is important when the agent is added to the photographic product at the time of manufacture for it does not cause product instability through volatilization during aging as does catechol and tertiary butyl catechol.

Furthermore, indane (I) and its oxidation product are nonmigratory. This limits the tanning effect during development to the image area and does not cause wandering to the contiguous nonimage area. This property provides excellent wash-off definition.

Similarly, the silver image can be removed by bleaching in a known manner and elements containing indane (I) can be used for well known process of dye imbibition.

A further advantage exists because the oxidized form of indane (I) forms an excellent tanning agent and forms very tough images rapidly. This is required in wash-off products or in the formation of relief images for photochemical copying methods.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows.

I claim:

1. A process which comprises developing an exposed silver halide emulsion in the presence of a polyhydroxy-spiro-bis-indane.

2. A process which comprises developing a latent silver halide image in a water-permeable colloid binding agent in an aqueous alkaline developer solution containing a polyhydroxy-spiro-bis-indane.

3. A suspension of light-sensitive silver halide grains in a water-permeable colloid, said suspension containing per mole of silver halide about 0.01 mole to about 0.3 mole of a polyhydroxy-spiro-bis-indane.

4. A suspension as defined in claim 3 wherein said colloid is gelatin.

5. A suspension as defined in claim 3 wherein said colloid is a mixture of gelatin and a vinylidene chloride/alkyl acrylate copolymer.

6. A suspension as defined in claim 3 wherein said colloid is a mixture of gelatin and a vinylidene chlorine/methyl acrylate copolymer.

7. A suspension as defined in claim 3 wherein said indane is 3,3,3',3'-tetramethyl-5,6,5',6'-tetrahydroxy-spiro-bis-indane.

8. A suspension as defined in claim 3 wherein said indane is 3,3,3',3'-tetramethyl-4,6,7,4',6',7'-hexahydroxy-1,1'-spiro-bis-indane.

9. A suspension as defined in claim 3 wherein said colloid is gelatin and said indane is 3,3,3',3'-tetramethyl-4,6,7,4',6',7'-hexahydroxy-1,1'-spiro-bis-indane.

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