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PHOTOGRAPHIC ANTI-HALATION LAYERS

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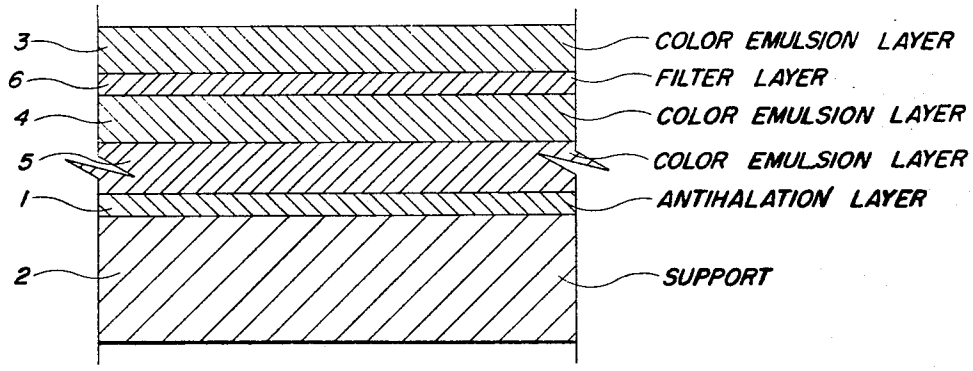

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PHOTOGRAPHIC ANTI-HALATION LAYERS

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This invention relates to photographic elements and more particularly relates to antihalation components of photographic elements.

It is desirable to have in photographic products some form of antihalation layer which absorbs light in order to avoid undesirable reflections from the film base or from interfaces between the emulsion layer or layers and the film which if not avoided causes additional diffused exposure of the silver halide emulsion.

Among the more recent methods used for preventing halation is the use of dye-containing pelloids, the so-called gray silver underlayer, and the carbon black dispersed in a polymeric or colloidal binder. The use of gray silver suffers from requiring substantial amounts of silver to provide an acceptable density for use as an antihalation layer, and the use of carbon black dispersed in a binder is particularly disadvantageous because of the resulting contamination of the solutions used in processing the exposed photographic element.

Furthermore, when dye layers are used, the neutral density which is desired has usually required two or three dyes to obtain a neutral adsorption of the light. This is particularly important in color processes requiring a neutral density layer such as that disclosed in Millikan's patent application Ser. No. 159,057, filed Dec. 13, 1961, now abandoned.

In some of the antihalation methods used heretofore, an antihalation layer, containing, for instance, pigments or dyes or carbon black is coated on the reverse side of the film base or support. Normal processing of the exposed film in an alkaline developer solution causes the anti-halation layer to be dissolved away, thus contaminating the developer solution.

It has been desirable to find a material with a neutral color which would act as anti-halation material when used as an undercoat but which could be processed to a transparent film in normal photographic processing without contaminating the processing solutions. Such an antihalation material must be compatible with the light sensitive elements, such as a silver halide emulsion, and should not appreciably affect the speed of the emulsion when utilized as a contiguous layer.

I have now discovered that an advantageous antihalation material is Carey Lea silver toned neutral by treatment with an ionic compound comprising palladium, platinum or gold. Carey Lea silver is very finely divided colloidal metallic silver. A method for its preparation is described in Example 1 hereof.

One object of this invention is to provide a photographic element having incorporated therein an anti-halation layer in which the light absorbing layer can be made transparent during normal photographic processing. An additional object is to provide an anti-halation material which is compatible with a light sensitive silver halide emulsion and which does not have an appreciable effect on the speed of the silver halide emulsion when used as an anti-halation undercoat. Another object is to provide an anti-halation undercoat having a greater density and being made from readily available materials. A further object is to provide an anti-halation material which may be readily bleached to a transparent layer without physical removal in the normal photographic processing using an oxidizing bleach.

This discovery is unexpected in view of the prior art's

teaching that the toning of a silver image produces a color other than neutral, such as a sepia tone, which is entirely unsuitable for use in an antihalation layer. It is furthermore unexpected that Carey Lea silver particles could be toned neutral and that such neutral particles are more effective an antihalation material than the gray silver used heretofore.

In one embodiment, my invention comprises an antihalation composition for use with photographic elements comprising Carey Lea silver toned neutral black with an ionic compound comprising palladium, platinum or gold or mixtures thereof. Such ionic compounds may comprise simple salts, such as $PdCl_2$, $AuCl_3$, or $Pt(CN)_2$, or it may comprise a compound having the noble metal as part of a complex anion, such as potassium chloropalladite, or chloroplatinic acid. Noble metal compounds containing a halogen are desirable and of the halogens, chlorine and bromine are advantageously used as elements in the noble metal compounds. The noble metal of such compound may be at any positive valence, such as Pd^{++} or Pd^{++++}. I prefer to use potassium chloropalladite to tone Carey Lea silver.

For use as an antihalation agent, it is normal to dispose the toned Carey Lea silver in a binder of the kind conventionally used in preparing silver halide emulsions, such as colloids, including gelatin, casein or zein, and synthetic polymeric substances such as polyvinyl alcohol, polyacrylates, hydrolyzed cellulose esters or cellulose ethers. In the event that the antihalation layer is to be used on the back of a film support, the binder could be one of those removable in an alkaline solution, such as cellulose acetate or phthalate, polyvinyl phthalate, or polyacrylate.

In another embodiment, my invention comprises a photographic element having a support (or base) which has coated thereon at least one light sensitive silver halide emulsion coating and at least one antihalation layer containing Carey Lea silver toned neutral with an ionic noble metal compound wherein the noble metal is palladium, platinum or gold. Such photographic elements may be adapted for either black-and-white photography or color photography and may have a plurality of light sensitive silver halide emulsion layers. They may also have one or more antihalation layers, for instance, an antihalation layer on each side of the support. Any of the conventional supports may be used, such as cellulose acetate, paper, glass, metals such as aluminum as is used in lithography, a polyester such as polyethylene terephthalate, polystyrene and polyolefins such as polyethylene.

The support may be given a preparatory treatment in order to improve adhesion, such as an electron bombardment, oxidation or flame treating, or other known treating techniques.

In an additional embodiment, my invention involves the process of neutral toning Carey Lea silver by mixing a liquid suspension of Carey Lea silver with an aqueous solution of the aforesaid noble metal compounds. The toning of the Carey Lea silver occurs very rapidly upon mixing the solution and the suspension. It is desirable that the liquid solution also contain some gelatin or other binder in which the toned Carey Lea silver is to be dispersed when applied as an anti-halation layer. After the toning of the Carey Lea silver, additional binder may be added to the resulting mixture.

The ratio of noble metal compound to Carey Lea silver may be varied widely, from about a chemical equivalent ratio of about 1:10 to about 3:1. The chemical equivalent weight of the noble metal is calculated from the molecular weight and the valence of the metal. Advantageously sufficient noble metal compound is used, taking into account the valence of the noble metal, to oxidize a sub-

stantial portion of the metallic Carey Lea silver to ionic silver. An excessive amount of the noble metal compounds is undesirable, not only from an economic standpoint but because there may be adverse side effects in the further manfacture of the photographic element or its processing after exposure. The amount of neutral toned Carey Lea silver, usually expressed as milligrams per square foot of surface area of the support of the photographic element, to be used varies depending upon the character of the support, the character of the binder in which the Carey Lea silver is dispersed and the intended use of the photographic element. Illustratively, sufficient toned Carey Lea silver is used to provide in the range of from about five to about one hundred milligrams per square foot of support area.

It will also be understood that the antihalation materials herein dscliosed may be used with advantage in a diffusion transfer system where the light sensitive emulsion is coated on a paper support. It may also be used in colloid transfer systems and in the formation of lithographic plates where the emulsion is coated on a support which precludes the use of an antihalation layer which must be removed in its entirety.

The light sensitive emulsions which may be used with the toned Carey Lea silver anti-halation material of this invention may be sensitized chemically or spectrally employing compounds heretofore known for such sensitization. Such material may also be used with light sensitive acid polymer layers as disclosed in U.S. Patent No. 2,948,-610; light sensitive cinnamic acid ester polymers disclosed in U.S. Patent No. 2,690,966, bichromate sensitized material such as those disclosed in U.S. Patent No. 2,448,861; the light sensitive layers described in U.S. Patent No. 3,903,800; and in the product described in U.S. Patent No. 2,607,683.

These anti-halation layers are particularly valuable when used with color emulsions, particularly those that have dye-forming couplers contained therein which react with the oxidation products of a paraphenylene diamine type developing agent. They may also be used with the color type emulsions in which the dye-forming coupler is supplied from the processing solution. In these processes, it is conventional to use a bleach step such as a ferricyanide bleach in removing the silver image. This bleach step bleaches the Carey Lea silver anti-halation layer rendering it transparent, but permitting such layer to remain as part of the photographic element. It will be appreciated that such anti-halation layers can be used whether the color element is on an opaque support such as paper or whether it is on a transparent support such as film base. It is also useful in conventional multi-layer photographic elements, and in those color processes where the multilayer color element is used to produce the colored print by diffusion to a mordanted receiving sheet, although in this particular adaption it would not be necessary to bleach the Carey Lea silver anti-halation layer.

The annexed drawing illustrates diagrammatically a photographic element comprising a neutral toned Carey Lea silver anti-halation layer made and used in accordance with this invention. The anti-halation layer **1**, comprising neutral toned Carey Lea silver dispersed in gelatin, is disposed on a cellulose acetate film support **2**. On top of the antihalation layer **1**, are a plurality of color layers **3**, **4** and **5** which comprise light sensitive silver halide gelatin emulsions containing dye-forming couplers, each layer of which is sensitized to a respective light range so that the resulting element will contain images in the cyan, magenta and yellow colors. A conventional filter layer **6** is interposed between color layers **3** and **4** and comprises a dispersion in gelatin of untoned Carey Lea silver having its natural yellow color.

It is to be understood that, although the photographic element depicted in the drawing is a multi-layered product intended for color photography, a photographic element intended for black and white photography might comprise merely support **2**, anti-halation layer **1**, and a light sensitive silver halide emulsion layer disposed in the position of layer **5**, but not having the dye couplers used to make color layers.

The following examples are intended to illustrate my invention but not to limit it in any way.

EXAMPLE 1

An anti-halation using underlayer coating was prepared as follows, using the method of preparing the Carey Lea silver (CLS) described by Luppo-Cramer, Koll. Zeitschrift, vol. 8, page 240 (1911).

To 140.0 milliliters of a 10-percent dextrin solution were added 40.0 milliliters of a 10-percent sodium hydroxide solution. One hundred milliliters of a 10% (all percentages are by weight unless otherwise stated) silver nitrate solution were then added at 40° C. with stirring. After 2 hours, 280.0 milliliters of methanol were added and the mixture was allowed to stand for 1 hour. The supernatent liquid was then decanted and the silver particles redispersed in 140.0 milliliters of distilled water. The resulting solution contained 16.0 to 21.0 milligrams of Carey Lea silver per milliliter.

To 5.0 milliliters of the above solution the following were added:

	Ml.
Potassium chloropalladite (1%) in water	1.0
Nitric acid (0.3 N)	2.0
Gelatin (10%) in water	8.0

A hardener and coating aid were also included. This solution was then coated at 4.7 cc. per square foot over a cellulose acetate support.

A portion of the anti-halation underlayer prepared as aforesaid was bleached and rehalogenated for 3 to 5 seconds at room temperature in the following solution:

	Grams
Potassium ferricyanide	100
Potassium bromide	20
Water to make 1 liter.	

A part of the section treated in the above solution was bathed for 1 minute at room temperature in Kodak F–5 hardener and fixing solution. This conventional photographic processing sequence eliminated the opacity of the anti-halation layer without removing it or contaminating the processing solution.

EXAMPLE 2

An alternative formula was used for preparing anti-halation layers from Carey Lea silver toned neutral with potassium chloroplatinite (K_2PtCl_4). The preparation was as follows:

Nuclei solution

	Ml.
Carey Lea silver (aqueous solution prepared as described in Example 1)	25.0
K_2PtCl_4 (1%) in water	75.0
Gelatin (5%) at 40° C.	100.0

The coating solution was the foregoing nuclei solution plus a coating aid and hardener.

These anti-halation layers were all coated from a common melt over cellulose acetate support as follows:

Coating Number	Gelatin Coverage, mg./ft.²	Mg./ft.² CLS	Mg./ft.² K_2PtCl_4	Transmission Density
1	100	12.48	15.00	.28
2	150	18.72	22.50	.34
3	200	24.96	30.00	.42

EXAMPLE 3

In this and the subsequent examples, the Carey Lea silver was an aqueous solution prepared as described in Example 1.

At room temperature the following were combined:

	Ml.
Aqueous Carey Lea silver dispersion	1.5
Distilled water	15.0
K_2PdCl_6 solution (6.5%)	10.0
Gelatin (5%)	10.0

A hardener and coating aid were included.

A coating was prepared by pouring the above solution onto the subbed side of a cellulose acetate support, draining the excess solution, and then allowing the coating to dry at room temperature.

EXAMPLE 4

This example illustrates the preparation of a layer containing Carey Lea silver toned neutral with potassium chloroplatinate (K_2PtCl_6), instead of the chloropalladate as was used in Example 3.

At room temperature the following were combined:

	Ml.
Carey Lea silver dispersion	3.0
Distilled water	30.0
K_2PtCl_6 solution (1.0%)	12.0
Gelatin (5%)	10.0

A hardener and coating aid were included.

A coating was prepared by pouring the above solution onto the subbed side of a cellulose acetate support, draining the excess solution, and then allowing the coating to dry at room temperature.

EXAMPLE 5

This example represents an improved formula for preparing a layer containing Carey Lea silver toned ueutral with potassium chloropalladite (K_2PdCl_4).

At room temperature the following were combined:

	Ml.
Carey Lea silver dispersion	3.0
Distilled water	30.0
K_2PdCl_4 solution (1.0%)	12.0
Gelatin (5%)	10.0

A hardener and coating aid were included.

A coating was prepared with the above solution employing the same technique as described in Examples 3 and 4.

EXAMPLE 6

This example illustrates the toning of Carey Lea silver with gold chloride ($AuCl_3$).

At room temperature the following were combined:

	Ml.
Carey Lea silver dispersion	3.0
Distilled water	30.0
$AuCl_3$ solution (1%)	3.0
Gelatin (5%)	10.0

A hardener and coating aid were included.

A coating was prepared in the same manner as in Examples 3, 4 and 5.

Where it is desired to prepare an anti-halation layer for use with a material wherein the anti-halation layer will eventually be removed, a density as high as 1.0 may be desirable. Such densities can be achieved by anti-halation layers prepared according to my invention at coverages up to 100 mg. per square foot of treated Carey Lea silver. For those applications wherein the anti-halation layer may remain as part of the finished product, densities as low as 0.15 may be desirable. Such density results from a coverage of about 5–10 mg. per square foot of modified Carey Lea silver. Thus, the coverage range may be from about 5 mg. per square foot Carey Lea silver to 100 mg. per square foot.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can

be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A photographic element comprising a support having thereon at least one light sensitive coating and having on the same support at least one layer comprising Carey Lea silver toned neutral with ionic compound comprising a noble metal selected from the class consisting of palladium, platinum and gold.

2. A photographic element comprising a support having thereon at least one light sensitive layer and having on the same support at least one layer comprising neutral toned Carey Lea silver which has been toned with a compound comprising a complex halogen-noble metal anion in which said noble metal is selected from the class consisting of palladium, platinum, and gold.

3. A photographic element comprising a support having at least one light sensitive layer and having on the same support at least one anti-halation layer comprising Carey Lea silver toned neutral with an aqueous solution of a halide of a noble metal selected from the class consisting of palladium, platinum and gold.

4. A photographic element comprising a support having at least one light sensitive coating and at least one anti-halation layer comprising Carey Lea silver toned neutral with an ionic compound comprising a noble metal selected from the class consisting of palladium, platinum and gold, in which said noble metal is at its lowest positive valence.

5. A photographic element comprising a support having at least one light sensitive coating and at least one anti-halation layer comprising Carey Lea silver toned neutral with an ionic palladium compound.

6. A photographic element comprising a support having at least one light sensitive coating and at least one anti-halation layer comprising Carey Lea silver toned neutral black with a chloropalladite compound.

7. A photographic element comprising a support having at least one light sensitive coating and at least one anti-halation layer comprising Carey Lea silver toned neutral black with a chloroplatinate compound.

8. A photographic element comprising a support having at least one light sensitive coating and at least one anti-halation layer comprising Carey Lea silver toned neutral black with an alkali metal chloropalladite.

9. A photographic element comprising a support having at least one light sensitive coating and at least one anti-halation layer comprising Carey Lea silver toned neutral black with gold trichloride.

10. A photographic element comprising a support having at least one light sensitive coating and at least one anti-halation layer comprising Carey Lea silver toned neutral black with palladium dichloride.

11. A photographic element comprising a support having thereon at least one light sensitive coating and at least one anti-halation layer comprising Carey Lea silver toned neutral black with an ionic compound comprising a noble metal selected from the class consisting of palladium, platinum, and gold wherein the chemical equivalent ratio of the noble metal compound used to the Carey Lea silver is in the range of about 1:10 to about 3:1.

12. A photographic element comprising a support having a plurality of silver halide emulsion layers each containing dye coupling compounds and having disposed adjacent to said support an anti-halation layer comprising Carey Lea silver toned neutral with an ionic compound comprising a noble metal selected from the class consisting of palladium, platinum and gold.

13. An anti-halation composition for use with photographic elements comprising Carey Lea silver toned neutral with an ionic compound comprising a noble metal selected from the class consisting of palladium, platinum and gold.

14. An anti-halation composition for use with photo-

graphic elements comprising Carey Lea silver toned neutral with an ionic compound comprising palladium.

15. An anti-halation composition for use with photographic elements comprising Carey Lea silver toned neutral with an ionic compound comprising a complex halogen-noble-metal-containing anion in which said noble metal is selected from the class consisting of palladium and platinum.

16. An anti-halation composition for use with photographic elements comprising a dispersion in gelatin of Carey Lea silver toned neutral with a compound comprising as its anion $PdCl_4^=$.

17. An anti-halation composition for use with photographic elements comprising a dispersion in gelatin of Carey Lea silver toned neutral with an alkali metal chloropalladite.

18. An anti-halation composition for use with photographic elements comprising a dispersion in gelatin of Carey Lea silver toned neutral with an alkali metal chloroplatinate.

19. An anti-halation layer composition for use with photographic elements comprising Carey Lea silver toned neutral by contacting the Carey Lea silver within the

range of from about 0.1 to about 3 chemical equivalents with a noble metal in an ionic compound comprising a noble metal selected from the class consisting of palladium, platinum and gold per chemical equivalent of said Carey Lea silver.

20. An element comprising a support having thereon at least one layer comprising Carey Lea silver toned neutral black with an ionic compound comprising a noble metal selected from the class consisting of palladium, platinum and gold.

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