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(54) Two-side imageable photothermographic paper.

(57) Two-side coated paper dry silver photothermographic imaging elements suffer from bubbling on the second coated side. The use of polyvinylacetate as part of the binding media for the second coated emulsion has been found to reduce the problem.

TWO-SIDE IMAGEABLE PHOTOTHERMOGRAPHIC PAPER

Background of the Invention

1. Field of the Invention

The present invention relates to dry silver photothermographic imaging elements and in particular to dry silver photothermographic imaging elements comprising an opaque substrate having imageable photothermographic layers on both sides of the substrate.

2. Background of the Art

Silver halide photothermographic imaging materials, often referred to as "dry silver" compositions because no liquid development is necessary to produce the final image, have been known in the art for many years. These imaging materials basically comprise a light insensitive, reducible silver source, a light sensitive material which generates silver when irradiated, and a reducing agent for the silver source. The light sensitive material is generally photographic silver halide which must be in catalytic proximity to the light insensitive silver source. Catalytic proximity is an intimate physical association of these two materials so that when silver specks or nuclei are generated by the irradiation or light exposure of the photographic silver halide, those nuclei are able to catalyze the reduction of the silver source by the reducing agent. It has been long understood that silver is a catalyst for the reduction of silver ions and the silver-generating light sensitive silver halide catalyst progenitor may be placed into catalytic proximity with the silver source in a number of different fashions, such as partial metathesis of the silver source with a halogen-containing source (e.g., U.S. Pat. No. 3,457,075), coprecipitation of the silver halide and silver source material (e.g., U.S. Pat. No. 3,839,049), and any other method which intimately associates the silver halide and the silver source.

The silver source used in this area of technology is a material which contains silver ions. The earliest and still preferred source comprises silver salts of long chain carboxylic acids, usually of from 10 to 30 carbon atoms. The silver salt of behenic acid or mixtures of acids of like molecular weight have been primarily used. Salts of other organic acids or other organic materials such as silver imidazolates have been proposed, and U.S. Pat. No. 4,260,677 discloses the use of complexes of inorganic or organic silver salts as image source materials.

In both photographic and photothermographic emulsions, exposure of the silver halide to light produces small clusters of silver atoms. The imagewise distribution of these clusters is known in the art as the latent image. This latent image generally is not visible by ordinary means and the light sensitive article must be further processed in order to produce a visual image. The visual image is produced by the catalytic reduction of silver ions which are in catalytic proximity to the specks of the latent image.

Research Disclosure 17029, "Photothermographic Silver Halide Systems," published June 1978, pp. 9-15, gives a brief history of photothermographic systems and discusses attempts to provide color to them. Many of these previously discussed patents and other art such as U.S. Patent Nos. 4,022,617; 3,180,731 and 3,761,270 are noted as relevant to the subject of providing dye density and color images to photothermographic emulsions.

F. M. Cerquone, R. S. Gabrielsen and R. H. Willis, U.S. Patent No. 4,021,240, issued May 3, 1977 show multiple layers in column 22, lines 7 to 65 and column 23, line 1 to 57. Interlayers of polyvinyl alcohol were used to preserve the integrity of the color-forming layers. Other hydrophilic polymers, such as gelatin, were also found useful. The use of other synthetic polymeric binders alone or in combination as vehicles or binding agents and in various layers was described. Useful resins such as poly(vinyl butyral), cellulose acetate butyrate, polymethyl methacrylate, ethyl cellulose, polystyrene, polyvinyl chloride, chlorinated rubber, butadiene-styrene copolymers, vinyl chloride-vinyl acetate copolymers; copolymers of vinyl acetate, vinyl chloride, and maleic acid and poly(vinyl alcohol) were cited.

U.S. Patent No. 4,460,681 discloses a color photothermographic element in which color forming layers are separated by barrier layers to prevent migration of components between layers which would reduce the color separation.

Summary of the Invention

The imageable article of the present invention comprises a substrate having on both sides thereof at least one dry silver photothermographic emulsion layer in which the binder for the emulsion layer comprises above 2.0% and usually at least 2.5% by weight of polyvinyl acetate.

Detailed Description of the Invention

It is sometimes desirable to provide imaging elements which have the capability of providing independent images on opposite sides of a support base. Usually such a construction requires little more than providing imaging systems on both sides of a base and assuring that the imaging exposure performed on one side does not expose the other side. In attempting to provide dry silver photothermographic elements with photothermographic media on both sides of a paper substrate, blister defects were encountered in the second coating. This phenomenon has previously been encountered in the coating of both sides of a paper substrate with organic solvent media. One proposed solution to the problem was disclosed in U.S. Patent No. 3,674,534 as coating of many thin layers to build up to the desired final thickness. This is very expensive and time-consuming and is not practical with many types of coating materials.

Conventional photothermographic chemistry is usually constructed as one or two layers on the same side of a substrate. Single layer constructions must contain the silver source material, the silver halide, the developer and binder as well as optional additional materials such as toners, coating aids and other adjuvants. Two-layer constructions on the same side of a substrate must contain silver source and silver halide in one emulsion layer (usually the layer adjacent substrate) and the other ingredients in the second layer or both layers. In the present invention it is preferred to use single layer chemistry on each side of a substrate. It is possible to use two-layer chemistry by forming a first layer and coating it with the second layer chemistry, by putting the second layer chemistry in the binder layer, or by coating a traditional second layer over the first layer.

The silver source material, as mentioned above, ordinarily may be any material which contains a reducible source of silver ions. Silver salts of organic acids, particularly long chain (10 to 30, preferably 15 to 28 carbon atoms) fatty carboxylic acids are preferred in the practice of the present invention. Complexes of organic or inorganic silver salts wherein the ligand has a gross stability constant between 4.0 and 10.0 are also useful in the present invention. The silver source material should constitute from about 20 to 70 percent by weight of the imaging particles. Preferably it is present as 30 to 55 percent by weight.

The silver halide may be any photosensitive silver halide such as silver bromide, silver iodide, silver chloride, silver bromoiodide, silver chlorobromoiodide, silver chlorobromide, etc., and may be added to the article in any fashion which places it in catalytic proximity to the silver source. The silver halide is generally present as 0.75 to 15 percent by weight of the layer, although larger amounts are useful. It is preferred to use from 1 to 10 percent by weight silver halide in the particle and most preferred to use from 1.5 to 7.0 percent.

The silver halide may be provided by in situ halidization or by the use of pre-formed silver halide. The use of sensitizing dyes for the silver halide is particularly desirable. These dyes can be used to match the spectral response of the emulsions to the spectral emissions of intensifier screens. It is particularly useful to use J-banding dyes to sensitive the emulsion as disclosed in U.S. Patent No. 4,476,220.

The reducing agent for silver ion may be any material, preferably organic material, which will reduce silver ion to metallic silver. Conventional photographic developers such as phenidone, hydroquinones, and catechol are useful, but hindered phenol reducing agents are preferred. The reducing agent should be present as 1 to 20 percent by weight of the imaging layer. In a two-layer construction, if the reducing agent is in the second layer, slightly higher proportions, of from about 2 to 20 percent tend to be more desirable.

Toners such as phthalazinone, phthalazine and phthalic acid are not essential to the construction, but are highly desirable. These materials may be present, for example, in amounts of from 0.2 to 5 percent by weight.

The binder may be selected from any of the wellknown natural and synthetic resins such as gelatin, polyvinyl acetals, polyvinyl chloride, cellulose acetate, polyolefins, polyesters, polystyrene, polyacrylonitrile, polycarbonates, and the like. Copolymers and terpolymers are, of course, included in these definitions. The polyvinyl acetals, such as polyvinyl butyral and polyvinyl formal, and vinyl copolymers, such as polyvinyl acetate/chloride are particularly desirable. The binders are generally used in a range of from 20 to 75 percent by weight of the particle, and preferably about 30 to 55 percent by weight.

The binder for the photothermographic layer coated onto the paper substrate as the second coated photothermographic system must contain above 2.0% and usually at least 2.5% or preferably at least 3% by weight of total solids in the dry layer as polyvinyl acetate (PVAc). The polyvinyl acetate may be present as a homopolymer or copolymer. If present as a copolymer, the PVAc units should comprise at least 2.5% or 3% by weight of the total solids in the imaging layers of the system (not just the copolymer unless only the copolymer is used) as the binder. It is preferred to use polymeric additives having at least 5% or at least 10% by weight of total solids as PVAc. It is sometimes desirable to use at least 50% by weight units of PVAc or even 100% and most preferable to use PVAc homopolymers as the additive.

As previously noted, various other adjuvants may be added to the photothermographic particle of the present invention. For example, toners, accelerators, acutance dyes, sensitizers, stabilizers, surfactants, lubricants, coating aids, antifoggants, leuco dyes, chelating agents, binder crosslinking agents, and various other well-known additives may be usefully incorporated in either the particle or continuous layer. The use of acutance dyes matched to the spectral emission of an intensifying screen is particularly desirable. A particularly useful chemistry which can be present in the layer binder is stabilization chemistry, and particularly image stabilization chemistry. Crosslinking agents, either active or thermally latent, for the particle binder or the binder in the photosensitive layer can be present in the layer binder. Other standard addenda such as coating aids, antifoggants, accelerators, toners, and acutance dyes may be present in the layer binder.

The effect of the polyvinylacetate polymer is believed to be that of a moderator of the vapor transmission of the coated layers, thus avoiding the defect produced by escaping vaporized gases blistering and otherwise deforming the plastic film that is formed on the substrate. The observed defect is not due to poor wetting of the substrate by the coating media, as coatings applied with and without PVAc resin wet the paper and form a continuous film upon it with apparent equal ability. The blister defects are observed to occur as the wet film is dried down to its solid components and the solvents are released. The PVAc may be present as homopolymers, copolymers, graft copolymers, block copolymers, and the like. High levels of ethylene or polyvinylchloride in the polymer would not be desirable as that should have the effect of decreasing the permeability of the PVAc.

Example 1

Five levels of "AYAF" PVAc polymeric resin (Union Carbide Company) were tested in a Dry Silver photothermographic formulation. The coatings were applied to the reverse side of a paper substrate ("SP 7772 paper, Simpson Paper Co.) which had already been coated with a similar photothermographic formulation, except that no PVAc resin was contained in that precoated silver imaging layer. The formulation is shown below:

Silver salt (silver soap) premix (percentages):

2-Butanone	52.4%	
Toluene	17.8	
Acetone	17.0	
Polyvinylbutyral resin	.5	(B-76 resin, Monsanto Co.)
"Half soap"	4.0	(Silver behenate/stearate and the respective fatty acids, approximately 1:1 molar ratio)
"Full soap"	8.3	(Substantially silver behenate and silver stearate)

The listed silver dispersion was mixed for one-half hour on a Cowles mixer and then homogenized to produce a fine particle dispersion of the silver salt in the solvent.

Silver Dispersion Formula:

1)	Silver "soap" homogenate	297.0 gms
2)	Toluene	102.0 gms
3)	2-Butanone	44.8 gms
4)	Polyvinylbutyral (B-76) resin > Mix 10 minutes	.9 gms
5)	Mercuric chloride in methanol > Mix 60 minutes	6.0 ml (.026 gms HgC12/ml)
6)	Polyvinylbutyral (B-76) > Mix 40 minutes	54.0 gms
7)	Permanox WSO antioxidant > Mix 15 minutes	11.4 gms
8)	Polymethylmethacrylcate resin (Rohm and Haas A-21, 30% solids) > Mix 10 minutes	42.0 gms

At this point, the batch was split into five 100 gram samples. To each of the samples was added the following solutions of AYAF polyvinylacetate resin in acetone:

Sample Identification	gms of Acetone	gms AYAF/Acetone solution (20% AYAF by weight)
A	10.00 gms	0.00 gms
B	8.75	1.25
C	7.50	2.50
D	5.00	5.00
E	0.00	10.00

The acetone/AYAF solutions were combined in a vial and added to each sample batch with agitation. The respective amounts of AYAF PVAc polymeric resin added to the five 100 gram samples of the silver dispersion were 0, .25, .5, 1.0, and 2.0 grams (in Samples A, B, C, D, and E, respectively). These levels equate to (respectively) 0, 1.2, 2.4, 4.7, and 9.4% polyvinylacetate relative to the total dry solids left in the coating after the solvents have been removed by the drying process.

The five finished dispersions were then coated on the uncoated side of the aforementioned paper base. The wet coating thickness was metered with a knife coating head set at 4.0 mils (102 microns).

The coatings were transported into a 'Blue M' oven on a moving web and dried at 77° C. for 2.5 minutes. The evaluation of the sample coatings is noted below:

Sample	Coating uniformity of side coated per example:
A	Numerous blister defects visible
B	" "
C	Blisters much reduced, still a few present (e.g. 3 blisters noted on a 4' x 6" sample (10.24 x 15.24 cm)
D	Very few blisters (e.g. 1 blister visible in a 4" x 6" sample (10.16 x 15.24 cm)
E	No blisters

Example 2

Various polyvinylacetate resins were added to the silver soap dispersion identified in Example 1. These resins were added as a solution in acetone. The silver soap dispersion, which when coated provides the silver image forming layer, is disclosed below.

1)	Silver salt homogenate	297.0 gms
2)	Toluene	102.0 gms
3)	2-Butanone	38.2 gms
4)	Polyvinylbutyral (B-76) resin	.9 gms
	> Mix 10 minutes	
5)	Mercuric chloride in methanol	6.0 ml (.026 gms HgC12/ml)
	> Mix 60 minutes	
6)	Polyvinylbutyral (B-76)	58.2 gms
	> Mix 40 minutes	
7)	Permanox WSO antioxidant	11.4 gms
	> Mix 15 minutes	
8)	Polymethylmethacrylcate resin (Rohm and Haas A-21, 30% solids)	42.0 gms
	> Mix 10 minutes	

Additionally, Victoria Pure Blue dye was added as a colorant to make detection of the blister defects easier in the white unprocessed sheet samples. The above dispersion was coated on side two of a base paper (Simpson SP 7772 39# paper) which had been previously coated on side one with the silver soap dispersion noted in Example 1.

The silver dispersion was split into 100 gram portions to which were added various polyvinylacetate polymers or copolymers. The listing of those samples appears below:

Sample	PVAc Polymer	Ammount Added to 100 gms	Solution Concentration
1	None--Control	---	---
2	Gelva V1.5 (Monsanto)	1.5 gm	10%/Acetone
3	AYAA (Union Carbide Corp)	1.5 gm	20%/Acetone
4	AYAF (UCC)	1.5 gm	20%/Acetone
5	AYAT (UCC)	1.5 gm	20%/Acetone
6	Mowilith 60 (Hoechst-Celanese)	2.0 gm	20%/Acetone
7	Mowilith Ct5 (Hoechst-Celanese)	2.0 gm	20%/Acetone
8	Elvax 150 (DuPont)	1.5 gm	10%/Toluene

Note: PVAc resins 2-6 are homopolymers;
sample #7 is a polyvinylacetate-crotonic acid copolymer;
sample #8 is a polyvinylacetate-ethylene copolymer.

The finalized dispersions were coated at 4.0 mils (102 microns) with a notched bar coater and dried for 2 minutes at 77° C in a modified Blue M oven. The dried coatings were evaluated for blister type defects and were compared with the control sample. The evaluations of the samples are shown below.

Rating scale
1) Acceptable uniformity, free of defects
2) Marginal uniformity, blisters very small and/or extremely low in frequency
3) Blisters noticeable, larger and/or greater frequency than level 2
4) Blisters widespread throughout coating
5) Severe, widespread blisters, worst-case condition

Sample	PVAc Polymer	Ammount Added to 100 gms	Uniformity Rating
1	None--Control	---	5
2	Gelva V1.5 (Monsanto)	1.5 gm	2
3	AYAA (Union Carbide Corp)	1.5 gm	1
4	AYAF (UCC)	1.5 gm	1
5	AYAT (UCC)	1.5 gm	1
	Mowilith 60 (Hoechst-Celanese)	2.0 gm	3
6	Mowilith Ct5 (Hoechst-Celanese)	2.0 gm	4
7	Elvax 150 (DuPont)	1.5 gm	3

Example 3

Polyvinylacetate polymers are also found to improve the coating uniformity of other coated layers cast from solutions for two sided photothermographic constructions. For instance, it is common to overcoat the silver image forming layer with a protective topcoat, which may also contain elements of the activating chemistry for the total construction. These topcoats also suffer defects of blisters and open coat voids when applied to a two-sided sheet construction in which both sides have already been coated with the silver imaging layer. The use of polyvinylacetate resins as a coating aid in such two sided constructions is again found to improve coating uniformity, to the point of eliminating such defects.

While differences have been noted in the improvement of coating uniformity with various PVAc resins used with a particular formulation, they have been observed to in general effect an improvement in coating uniformity.

In this example a plastic overcoat formulation was tested with various levels of several different polyvinylacetate resins. The PVAc resins differed by manufacturer and molecular weight. The formulation of the premix is listed below:

Overcoat Formulation:	Amount (gms)
Acetone	850.00
2-Butanone	450.00
Cellulose acetate resin 398-6 (Eastman Chemicals)	68.75
Silica premix*	125.00
Phthalazine	6.30
4-Methylphthalic acid	4.35

*Silica Premix:	Amount (gms)
Acetone	87.50
2-Butanone	27.50
Cellulose acetate resin 398-6	6.25
Degussa OX-50 fumed silica	3.75

This overcoat was applied over the silver imaging layer of a previously coated two-sided construction in which the silver layers had been applied to each side of a paper base (SP 7774 60# paper, Simpson Paper Co.) and dried to form continuous, defect free coatings on each side. The silver imaging media was similar to that described in Example 1, with 1.5% by weight AYAF polyvinylacetate resin (Union Carbide Co.) To 100 gram portions of the above premix, the following resins were added and dissolved with a mechanical shaker prior to coating of the overcoat:

Sample	PVAc Polymer	Amount Added to 100 gms Overcoat
1	None-Control	---
2	Gelva V1.5 (Monsanto	1 gm
3	" "	2 gm
4	" "	3 gm
5	" "	4 gm
6	AYAF (Union Carbide)	1 gm
7	" "	2 gm
8	" "	3 gm
9	" "	4 gm
10	AYAT (Union Carbide)	1 gm
11	" "	2 gm
12	" "	3 gm
13	" "	4 gm
14	Mowilith 60 (Hoechst-Celanese)	4 gm
15	Mowilith Ct5 (hoechst-Celanese)	4 gm

All the above samples were PVAc homopolymers, with the exception of Mowilith Ct5, which is a PVAc-Crotonic acid copolymer. In all cases, the PVAc polymer was the minor resin relative to the cellulose acetate formula weight percent.

The overcoat formulations were coated at 3.4 mils (85 microns) wet orifice on a notched bar coater and dried for 1.5 minutes at 77° C.

The coated samples were evaluated for freedom from coating defects that would normally be encountered when coating this solvent-based formulation over a paper substrate having both sides already coated with the thermoplastic silver imaging layers. To provide maximum visibility of the defects, the samples were exposed to a light source (Olix Al 121 ultraviolet printer with Kokomo filter, 8 second exposure) and thermally developed (3M Model 9014, six seconds processing at 132° C). The evaluations of those samples appear below.

Rating Scale:

1) Acceptable image--no visible blisters or voids in the overcoat
2) Marginal image--very small blisters or void defects visible
3) Unacceptable image--small, scattered blisters and coating voids visible
4) Unacceptable image--blisters and voids larger and more widespread, most likely visible on both white as well as black areas of the image
5) Unacceptable image--severe blisters and voids, of largest size and greatest, most widespread frequency

Sample	PVAc Polymer	Amount Added to 100 gm	Observed Defects (Rating)*
1	None--Control	---	5
2	Gelva V1.5 (Monsanto)	1 gm	4
3	" "	2 gm	4
4	" "	3 gm	5
5	" "	4 gm	3
6	AYAF (Union Carbide)	1 gm	4
7	" "	2 gm	3
8	" "	3 gm	2
9	" "	4 gm	2
10	AYAT (Union Carbide)	1 gm	4
11	" "	2 gm	3
12	" "	3 gm	2
13	" "	4 gm	1
14	Mowilith 60 (Hoechst-Celanese)	4 gm	1
15	Mowilith Ct5 (Hoechst-Celanese)	4 gm	3

With this formulation, the harder, higher molecular weight PVAc polymers (AYAT, Mowilith 60) were found to yield the greatest coating uniformity. The lower molecular weight, softer polymers (Gelva V1.5, Mowilith Ct5) were significantly poorer in their ability to function as a coating aid for this formulation. All samples were able to improve the coating, however, with respect to the control.

Example 4

The experimental series of polyvinylacetate levels described in Example 1 was later repeated on a different paper substrate. In the second series, a 60# base sheet made by Simpson Paper Co. was tested. This second sheet was identified as "SP 7773" paper, and differed from SP 7772 in several aspects: SP 7773 was not opacified with titanium dioxide, it was manufactured with a high solids latex size press coating, it utilized an aluminum chloride (rather than aluminum sulfate) flocculating agent, and it was greater in caliper (as expected, given its higher basis weight).

The procedure for the silver dispersion batch preparation was identical to that listed in Example 1, except that the mixing time after the addition of mercuric chloride was only twenty minutes.

The addition of AYAF was accompanied by compensating weight addition of acetone, as listed in Example 1. The levels of AYAF resin added to Samples A, B, C, D, and E were respectively 0, .25, .5, 1.0, and 2.0 grams per 100 grams of silver imaging media, as was the case in Example 1.

The coating conditions were the same as indicated in Example 1, with the finished silver dispersion coated on each side of the SP 7773 base. The resulting coating uniformity with the five levels of AYAF addition are listed below.

Sample	AYAF Level	Coating Uniformity of Second Side* Coated
A	0.00 gms	Numerous blister defects visible
B	0.25 gms	Numerous blister defects visible
C	0.50 gms	Very few blisters (0 to 1 blisters on 4"x6" samples (10.16cm x 15.24cm)
D	1.00 gms	No blisters
E	2.00 gms	No blisters

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*As expected, the first side coated was blister free in all cases

Examples 1 and 4 establish .5 grams of AYAF added to 100 grams of the silver dispersion as a threshold for effective reduction of blistering during coating and drying of the silver imaging layer. This equates to a percentage of about 2.4%, based on the solid components of the dried coating media. The minimum effective level is expected to be additionally affected, however, by drying conditions, applied media coating weights, and by solvent holdout, density, and water content of the substrate.

Claims

1. A two-side imageable photothermographic element comprising:
   a) a paper substrate, and
   b) on each side of said paper substrate at least one layer of a photothermographic imaging system which comprises binder, light-sensitive silver halide, a light-insensitive silver source material, and a reducing agent for silver ion,

   at least one of said at least one layer of said photothermographic imaging system having an imaging layer the total solids of which comprises more than 2% by weight of polyvinyl acetate.

2. The element of claim 1 wherein said polyvinyl acetate is present as a polymer having at least 50% by weight of its units derived from vinyl acetate.

3. The element of claim 1 wherein said polyvinyl acetate is present as a homopolymer of polyvinyl acetate.

4. The element of claim 1 wherein said imaging layer comprises at least 2.5% by weight of polyvinyl acetate.

5. The element of claim 1 wherein said imaging layer comprises at least 3% by weight of polyvinyl acetate.

6. A process for making the two-side imageable photothermographic element of claim 1 comprising:
   a) providing a paper substrate,
   b) coating one side of said paper substrate with at least one layer comprising binder, light-sensitive silver halide, light-insensitive silver source materials, and a reducing agent for silver ion,
   c) drying said at least one layer coated in step b),
   d) coating a second at least one layer onto the uncoated side of said paper substrate, said second at least one layer comprising light-sensitive silver halide, a light-insensitive silver source material, a reducing agent for silver ion, and binder comprising more than 2% by weight of said second at least one layer of polyvinyl acetate, and
   e) drying said second at least one layer coated in step d).

7. The process of claim 6 wherein said second at least one layer comprises at least 2.5% by weight of

polyvinyl acetate.

8. The process of claim 6 wherein said second at least one layer comprises at least 3% by weight of polyvinyl acetate.

9. The process of claim 6 wherein said second at least one layer comprises at least 5% by weight of polyvinyl acetate.

10. The process of claim 6 wherein said second at least one layer comprises at least 5% to less than 50% by weight of polyvinyl acetate.