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PHOTOGRAPHIC PROCESSES USING A STABILIZING COMPOSITION COMPRISING A GLUCOSIDE OF A PHENOLIC HYDROXYL COMPOUND

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20 Claims. (Cl. 96—29)

The present invention relates to photography and more particularly to processes and products for protecting color diffusion transfer images from the deteriorating effects of sunlight, ultraviolet light, etc.

One object of this invention is to provide color diffusion transfer images having enhanced stability to sunlight.

Another object is to provide processes for obtaining such stability.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and order of one or more of such steps with respect to each of the others and the product possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

U.S. Patent No. 2,983,606, issued to Howard G. Rogers, May 9, 1961, discloses and claims processes wherein dye developers (i.e., compounds which are both dyes and silver halide developing agents) are used to form color transfer images. In such processes, a photosensitive element is exposed to create therein a latent image. The latent image is developed in the presence of a dye developer and an imagewise distribution of unreacted dye developer, from which the positive image may be created, is formed. At least a portion of said unreacted dye developer is transferred to a superposed image-receiving element to create thereon a positive image. The processes are preferably carried out by disposing the dye developer in the photosensitive element prior to exposure, and causing it to be solubilized therefrom by an alkaline processing liquid which is applied between the superposed photosensitive element and image-receiving element. As the process proceeds, the exposed silver halide is reduced to metallic silver and the portions of the dye developer which are oxidized as a result of the silver development, are substantially immobilized in developed areas. At least a portion of the unreacted dye developer is imbibed on a superposed image-receiving layer to create thereon the positive dye image. The positive dye image is preferably viewed by stripping the photosensitive element from the image-receiving layer.

The above-mentioned alkaline processing liquid comprises an aqueous solution of an alkali-metal hydroxide, e.g., sodium hydroxide, cesium hydroxide, or potassium hydroxide.

The image-receiving elements used in such processes generally comprise an opaque or transparent support coated with an image-receiving layer of a dyeable material which is permeable to the alkaline aqueous processing

solution. In the past, film-forming materials such as polyvinyl alcohol, gelatin and nylons (linear polyamides), such as N-methoxymethyl polyhexamethylene adipamide, have been used as the dyeable materials.

The color fastness of the color photographic images produced in such processes, upon prolonged exposure to sunlight, ultraviolet light, etc., often leaves something to be desired. The copending application of Howard G. Rogers, Serial No. 93,309, filed March 6, 1961 (now U.S. Patent No. 3,239,338, issued March 8, 1966), discloses a borate ion treatment of such color images, when the image-receiving layers comprise at least in part polyvinyl alcohol, polyvinyl alcohol copolymers or derivatives of polyvinyl alcohol having unreacted hydroxyl groups.

It has now been found that good image stability to light, in many instances to a substantially greater degree than by prior art methods, may be obtained by associating a glucoside of a phenolic hydroxyl with the image dyes. The glucoside of a phenolic hydroxyl may be conveniently applied to the colored image by immersion, swabbing, coating, spraying, flowing, etc. When desired, the solution may also comprise a film-forming polymer such, for example, as gelatin, polyvinyl alcohol, polyvinylpyrrolidone, ethyl cellulose, nylon, etc., which will serve as a protective surface coating for the image. In addition, the solution may include other stabilizing agents such, for example, as ultraviolet absorbers, the above-noted borate ions, or anhydroenneaheptitol. In a preferred embodiment, the glucoside of a phenolic hydroxyl compound is applied from aqueous solutions. When desired, such aqueous solutions may contain organic solvents such, for example, as methanol, acetone, etc., to provide for rapid drying of the image surface. It has also been found that such protection can be imparted to color images on a wider range of materials used as image-receiving elements. For example, when the dyeable image-receiving layer comprised gelatin, nylon, gelatin-poly-4-vinylpyridine, etc., enhanced stability of the colored images thereon was obtained after treatment in accordance with this invention.

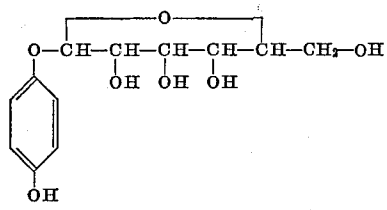
The dye developers, from which the images are formed, may also be defined as compounds which contain in the same molecule both the chromophoric system of a dye and also a silver halide developing function. By "a silver halide developing function" is meant a grouping adapted to develop exposed silver halide. A preferred silver halide developing function is a hydroquinonyl group. Other suitable developing functions are o-dihydroxyphenyl radicals. In general, the developing function includes a benzenoid developing function. Numerous examples of representative dye developers are given in the previously mentioned U.S. Patent No. 2,983,606 and in applications noted therein.

The processes of this invention have been found especially useful in stabilizing transfer images formed from azo and anthraquinone dye developers.

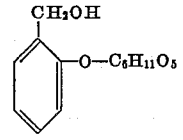
As mentioned above, the stabilizers of this invention are glucosides of phenolic hydroxyls. Such compounds are naturally occurring materials although some have now been synthesized. The sources and physical properties of such compounds are set forth in the Merck Index, 7th edition.

By the term "glucoside of a phenolic hydroxyl" is meant a glucoside attached through a phenolic oxygen to the hydroxyl-containing compound.

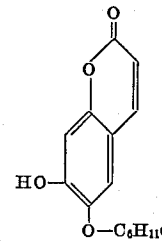
As examples of glucosides of phenolic hydroxyls useful in the process of this invention, mention may be made of the following:



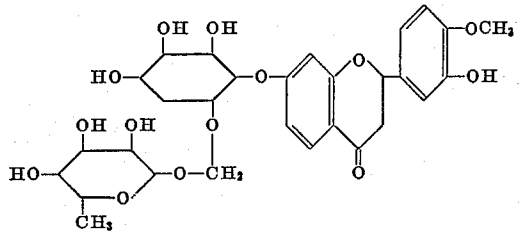
Arbutin (hydroquinone-β-D-glucopyranoside)



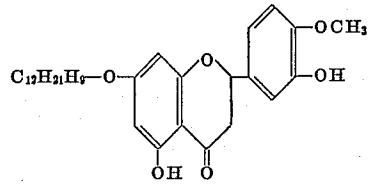
Salicin (saligenin-β-D-glucopyranoside)



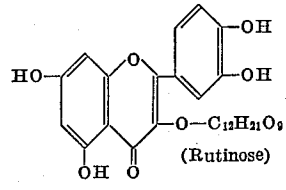
Esculin (6,7-dihydroxycoumarin-6-glucoside)



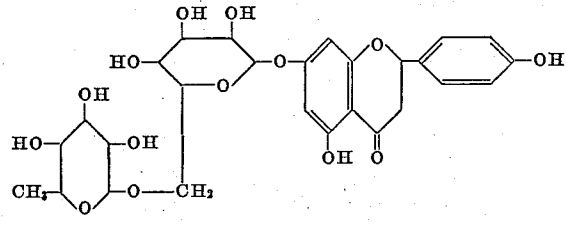
Hesperidin (hesperitin-7-rhamnoglucoside)



Neo-hesperidin



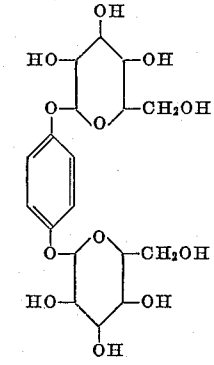
Rutin (3,3',4',5,7-pentahydroxyflavone-3-rutinoside)



Naringen (naringenin-7-rhamnoglucoside)

Although the compounds illustrated above are natural products, it should be understood that compounds for use within the scope of this invention are not limited to those derived from natural sources; synthetic materials may also be used. As an example of a synthetically prepared

glucoside of a phenolic hydroxyl, mention may be made of hydroquinone bis-glucoside:



In addition to stabilizing color images by application per se from aqueous solutions, the stabilizers of this invention provide an increased stabilization effect when used in combination with one or more materials such as boric acid and other sources of borate ions in aqueous solutions, as disclosed in the above-noted application of Howard G. Rogers, a saccharide, e.g., fructose or anhydroenneaheptitol, and the di-ortho-tolylguanidine salt of dicatechol borate. In a particularly useful embodiment of this invention, the glucoside of a phenolic hydroxyl is used in combination with boric acid, and the di-ortho-tolylguanidine salt of dicatechol borate. As mentioned above, the stabilizing compositions of this invention may also contain a film-forming material, e.g., polyvinyl alcohol, ethyl cellulose, polyvinylpyrrolidone, nylon, polyethyl methacrylate, etc.

The amount of the glucoside of a phenolic hydroxyl compound used will vary wih many factors such, for example, as the original color fastness of the dye developers, the amount of sunlight the colored image will be exposed to during its life expectancy, the solubility of the glucosides, yellowing of the color image, etc. The amount of stabilizer employed to provide protection may be referred to as an effective amount, i.e., an amount effective to give the desired protection, and it will be understood that such an amount will vary with many factors, such as mentioned above, and can be readily determined through color fading tests which will be hereinafter described. For example, the preferred stabilizer, arbutin, provides enhanced stability and protection to sunlight to color prints when used in a range of from 1 to 20% when used alone in aqueous solution and 1 to 8% of the total composition when used in combination with boric acid. However, in addition to solubility problems of the compounds, when used close to the upper limits of concentration, a yellowing of the color image may occur with some of these compounds, particularly after extended periods of time which detracts from the esthetic quality of the print. The preferred percentages of arbutin are 4 to 6% when used alone and 5 to 7% when used in combination with boric acid. The preferred ratio of arbutin to boric acid is 2 to 1.

The following nonlimiting examples illustrate the preparation of image-receiving elements for use in the processes of the present invention:

Example I

A subcoated film support was coated with a 2:1 mixture of polyvinyl alcohol and poly-4-vinylpyridine containing a small amount of 1-phenyl-5-mercaptotetrazole.

Example II

A subcoated film support was coated with a 2:1 mixture of gelatin and poly-4-vinylpyridine containing a small amount of 1-phenyl-5-mercaptotetrazole.

Example III

A subcoated film support was coated with a 5:5:1

solution of polyvinyl alcohol, p-trimethylammonium benzaldehyde p-toluenesulfonate partial acetal of polyvinyl alcohol and poly-N-methoxymethyl polyhexamethylene adipamide containing a small amount of 1-phenyl-5-mercaptotetrazole.

Example IV

A subcoated film support was coated with a solution of poly-N-methoxymethyl polyhexamethylene adipamide.

The image-receiving elements prepared in the above-described manner were used in diffusion transfer processes employing multilayer photosensitive elements prepared in a manner similar to that disclosed in the above-mentioned U.S. Patent No. 2,983,606. In general, the photosensitive elements comprised a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum; said emulsions having disposed in separate alkali-permeable layers behind them, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. The particular dye developers employed in the photosensitive elements were (1) 1,4 - bis - [α-methyl-β-(2',5'-dihydroxyphenyl)-ethylamino]-anthraquinone (a cyan dye developer), (2) 2 - [p - (2',5' - dihydroxyphenethyl) - phenylazo] - 5 - n-propoxy-1-naphthol (a magenta dye developer), and (3) 1 - phenyl - 3 - n - hexylcarbamyl - 4 - [p - (hydroquinonyl-ethyl)-phenylazo]-5-pyrazolone (a yellow dye developer). Areas of the photosensitive were exposed to (1) blue and green light only, (2) red and blue light only, and (3) red and green light only. After the transfer process, the image-receiving elements were swabbed with the desired stabilizing solution.

The following nonlimiting examples illustrate the preparation of the stabilizing compositions within this invention.

Example V

An aqueous solution of 10% arbutin and 6% boric acid was prepared.

Example VI

An aqueous solution of 5% arbutin and 3% boric acid was prepared.

Example VII

An aqueous solution was prepared comprising:

	Percent
Arbutin	15
Boric acid	8
Di-ortho-tolylguanidine salt of dicatechol borate	0.2

Example VIII

A 50:50 methanol/water solution was prepared comprising:

	Percent
Arbutin	6
Polyvinylpyrrolidone	10
Boric acid	3
Di-ortho-tolylguanidine salt of dicatechol borate	0.2

Example IX

A 50:50 methanol/water solution was prepared comprising:

	Percent
Salicin	6.3
Polyvinylpyrrolidone	10
Boric acid	3
Di-ortho-tolylguanidine salt of dicatechol borate	0.2

Example X

An aqueous solution was prepared comprising:

	Percent
Arbutin	5
Polyvinyl alcohol	10
Boric acid	2
Di-ortho-tolylguanidine salt of dicatechol borate	0.2

Example XI

A solution was prepared as in Example VIII using 6.25% esculin in place of arbutin.

Example XII

A solution was prepared as in Example VIII using 6% neohesperidin in place of arbutin.

Example XIII

A solution was prepared as in Example VIII using 3% rutin in place of arbutin.

Example XIV

A solution was prepared as in Example VIII using 3% naringen in place of arbutin.

Example XV

A solution was prepared as in Example VIII using 1% hesperidin in place of arbutin.

Example XVI

A 50:50 methanol-water solution was prepared comprising:

	Percent
Esculin	10
Polyvinylpyrrolidone	10
Boric acid	6
Di-ortho-tolylguanidine salt of dicatechol borate	0.2

The effectiveness of the processes of this invention was shown by (1) measuring, by reflectance, the integral densities of the transfer images using a green filter, (2) subjecting the images to an accelerated fading test in which the images were exposed (over saturated NaCl) to a xenon arc, and (3) again measuring the integral densities after 20, 40 and 100 hours of exposure to the xenon arc to show the percentage of magenta fading. The test procedure involved applying the composition to the image-receiving element immediately after the formation of the image and swabbing another image-receiving element approximately 4 hours after exposure. The results appear in tabular form below in comparison with a water swab.

Image-Receiving Element (Example No.)	Swabbing Composition	Percent Fading					
		Immediate Swab, Hours of Exposure			Delayed Swab, Hours of Exposure		
		20	40	100	20	40	100
1	Water Swab	55	56	90	45	71	94
1	6% Arbutin (in water)	17	31	38	30	37	57
1	10% Arbutin (in water)	31	17	37	26	28	[1] 39
1	6.3% Salicin (in water)	17	27	63	22	42	86
1	3% Naringen (in water)	26	40	49	33	58	71
1	Stabilizing Composition of Example V.	13	21	34	20	35	50
1	Stabilizing Composition of Example VI.	11	26	34	20	49	67
1	Stabilizing Composition of Example VII.	22	19	20	31	30	[2] 46
1	Stabilizing Composition of Example VIII.	22	29	27	20	35	49

Image-Receiving Element (Example No.)	Swabbing Composition	Percent Fading					
		Immediate Swab, Hours of Exposure			Delayed Swab, Hours of Exposure		
		20	40	100	20	40	100
1	Stabilizing Composition of Example IX.	19	37	39	32	45	63
1	Stabilizing Composition of Example X.	−2	0	24	1	−1	[2] 50
1	Stabilizing Composition of Example XI.	17	62	68	30	40	63
1	Stabilizing Composition of Example XII.	15	19	26	24	40	[3] 43
1	Stabilizing Composition of Example XIII.	14	24	46	20	38	[3] 88
1	Stabilizing Composition of Example XIV.	30	41	48	33	53	[3] 58
1	Stabilizing Composition of Example XV.	22	52	52	26	39	52
1	Stabilizing Composition of Example XVI.	20	26	47	23	51	67
2	6% Arbutin (in water)	14	30	45	33	47	60
2	6.3% Salicin (in water)	50	64	78	44	70	86
2	3% Naringen (in water)	49	76	73	50	77	82
2	Stabilizing Composition of Example VIII.	36	51	58	42	56	55
2	Stabilizing Composition of Example IX.	18	65	78	46	73	81
2	Stabilizing Composition of Example XIV.	62	72	72	62	71	75
3	6% Arbutin (in water)	51	72	74	53	72	77
3	6.3% Salicin (in water)	73	91	89	77	87	91
3	Naringen (in water)	40	79	82	59	82	87
3	Stabilizing Composition of Example VIII.	40	52	56	37	49	55
3	Stabilizing Composition of Example IX.	42	64	86	45	61	73
3	Stabilizing Composition of Example XIV.	49	63	69	51	68	72
4	6% Arbutin (in water)	48	92	88	62	93	89
4	6.3% Salicin (in water)	96	100	96	98	100	100
4	3% Naringen (in water)	39	96	61	92	100	96
4	Stabilizing Composition of Example VIII.	62	79	82	71	81	79
4	Stabilizing Composition of Example IX.	84	95	93	85	94	90
4	Stabilizing Composition of Example XIV.	78	91	91	80	91	87

[1] Browning.
[2] Color change.
[3] Yellowed.

The glucoside of a phenolic hydroxyl compound also can be applied to the color image during processing, i.e., by dissolving said compound from a layer of the film unit or by including said compound in the alkaline processing composition. A swab or other means of application of a glucoside of phenolic hydroxyl compound may or may not be used in addition to the glucoside in the processing composition. An example of such an aqueous processing composition is:

	Percent
Sodium hydroxide	5.17
Hydroxyethyl cellulose	4.5
Benzotriazole	2.3
N-benzyl-α-picolinium bromide	2.3
Sodium thiosulfate	1.15
Arbutin	2

It should be noted that, while sodium hydroxide is the preferred alkaline material in liquid processing solutions, other alkali metal hydroxides, e.g., cesium hydroxide and potassium hydroxide also may be used.

Particularly beneficial results with regard to color image stability have been noted when a glucoside of a phenolic hydroxyl is used in the liquid processing composition in conjunction with image-receiving elements containing a polymeric acid layer and disclosed and claimed in the copending application of Edwin H. Land, Serial No. 234,864, filed November 1, 1962. The use of such a liquid processing composition containing a glucoside of a phenolic hydroxyl with the above-mentioned image-receiving element of Edwin H. Land, Serial No. 234,864 is disclosed and claimed in the copending application of Howard G. Rogers, Serial No. 247,864, filed December 28, 1962.

In some of the coating compositions, a yellowing of the color image was noted after extended exposure to the xenon arc. Where such yellow was especially severe, it has been noted in the above table. Stabilizing compositions that did not result in yellowing or resulted in only a low degree of yellowing are therefore preferred. It should be noted that the protective characteristics of the materials are greater than those that could be attributed to ultraviolet absorption by the above-described yellowing condition of the colored image. Other phenomena such as color change other than that due to the magenta fading have been noted in the above table to indicate aberrations in the reported data.

It should be noted that the above-described wet xenon arc test is an extremely severe test used as a rapid indication of the stabilizing characteristics of the various compositions. A factor inherent in such a test must be noted: the age of the lamp element, which will determine the intensity of the light and, to some extent, the rate of fading. Therefore, in order to determine precisely, eliminating the lamp variable, the relative merits of one stabilizing composition over another, the samples are run simultaneously.

It has also been found that the stabilizing effects of treatment with the stabilizers and stabilizing compositions of this invention appear to be increased where the transfer process has been performed in the presence of a quaternary ammonium compound, e.g., N-β-phenethyl-α-picolinium bromide or N-benzyl-α-picolinium bromide, as disclosed in the copending application of Howard G. Rogers, Serial No. 50,851, filed August 22, 1960 (now U.S. Patent No. 3,173,786, issued March 16, 1965). An increased stabilizing effect has also been observed where the transfer process has been effected in the presence of such a quaternary ammonium compound in combination

with a substituted hydroquinone auxiliary silver halide developing agent, particularly 4'-methylphenyl-hydroquinone.

Since certain changes may be made in the above product and process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. In a process of forming a photographic image in color wherein an exposed silver halide emulsion is developed in the presence of a dye developer to provide a predetermined distribution of unoxidized dye developer, said dye developer being a compound which is both a dye and a silver halide developing agent, and wherein at least part of said distribution of said unoxidized dye developer is transferred from said emulsion to a superposed image-receiving layer to provide a dye image thereon, the improvement which comprises increasing the stability of said dye image by treating said dye images, subsequent to their formation, with a stabilizing composition comprising a glucoside of a phenolic hydroxyl compound.

2. A process as defined in claim **1** wherein said glucoside of a phenolic hydroxyl compound is applied to said image from an aqueous solution.

3. A process as defined in claim **1** wherein said glucoside of a phenolic hydroxyl compound is applied to said image from a methanol-water solution.

4. A process as defined in claim **1** wherein said stabilizing composition contains boric acid.

5. A process as defined in claim **1** wherein said stabilizing composition contains a film-forming material.

6. A process as defined in claim **1** wherein said stabilizing composition contains di-ortho-tolylguanidine salt of dicatechol borate.

7. A process as defined in claim **1** wherein said glucoside of a phenolic hydroxyl compound is arbutin.

8. A process as defined in claim **1** wherein said glucoside of a phenolic hydroxyl compound is salicin.

9. A process as defined in claim **1** wherein said glucoside of a phenolic hydroxyl compound is esculin.

10. A process as defined in claim **1** wherein said glucoside of a phenolic hydroxyl compound is neo-hesperidin.

11. A process as defined in claim **1** wherein said glucoside of a phenolic hydroxyl compound is rutin.

12. A process as defined in claim **1** wherein said glucoside of a phenolic hydroxyl compound is naringen.

13. A process as defined in claim **1** wherein said glucoside of a phenolic hydroxyl compound is hesperidin.

14. A process which comprises the steps of permeating an exposed photosensitive element, including a silver halide emulsion, with an alkaline liquid processing composition, providing said composition with a glucoside of a phenolic hydroxyl compound, developing said exposed silver halide emulsion and forming an imagewise distribution of an unoxidized dye developer, and transferring at least a portion of said glucoside of a phenolic hydroxyl and of said dye developer to an image-receiving layer in superposed relationship with said exposed silver halide emulsion.

15. The process as defined in claim **14** wherein said glucoside of a phenolic hydroxyl compound is arbutin.

16. In a process of forming a photographic image in color wherein an exposed silver halide emulsion is developed in the presence of a dye developer to provide a predetermined distribution of unoxidized dye developer, and wherein at least a portion of said dye developer is transferred from said emulsion to a superposed image-receiving layer to provide a dye image thereon, the improvement which comprises associating a glucoside of a phenolic hydroxyl compound with said dye image whereby the stability of said dye image is enhanced.

17. The process as defined in claim **16** wherein said image-receiving layer comprises a film-forming material selected from the group consisting of polyvinyl alcohol, polyvinyl alcohol copolymers, derivatives of polyvinyl alcohol having unreacted hydroxyl groups, gelatin and nylon.

18. The process as defined in claim **16** wherein said glucoside of a phenolic hydroxyl compound is arbutin.

19. A photographic dye image comprising a layer containing an imagewise distribution of a dye developer, said dye developer having associated therewith a glucoside of a phenolic hydroxyl compound in a concentration effective to reduce fading of said dye image by exposure to light.

20. A photographic dye image as defined in claim **19**, wherein said glucoside of a phenolic hydroxyl compound is arbutin.

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