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2,983,605

PHOTOGRAPHIC PRODUCTS, PROCESSES, AND COMPOSITIONS

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No Drawing. Filed Jan. 31, 1955, Ser. No. 485,342

19 Claims. (Cl. 96—29)

This invention relates to photography and more particularly to products, compositions and processes for the development of photosensitive silver halide elements.

It is one object of the present invention to provide novel processes and compositions for the development of silver halide emulsions, in which colored developing agents are used to develop a latent photographic image.

Another object is to provide novel processes and compositions for the development of silver halide emulsions, in which the novel developing agent is capable of developing a photographic latent image and imparting a reversed or positive colored image of said latent image to a superposed image-receiving element.

A further object is to provide novel products, processes and compositions suitable for use in preparing monochromatic and multichromatic photographic images.

A still further object is to provide a method of changing the color properties of colored developing agents whereby colored developing agents of desired colors may be obtained from colored developing agents of similar chemical composition.

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

The invention accordingly comprises the processes 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 products and compositions 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.

The objects of this invention may be accomplished by the use of certain compounds hereinafter described, which possess the ability to function both as a dye and as a photographic developing agent. These compounds may therefore be referred to as dye developers.

The photographic processes and compositions disclosed herein are particularly useful in the treatment of a latent image present in a photosensitive element, such as an exposed silver halide emulsion, whereby a positive dye image thereof may be imparted to another element, herein referred to as an image-carrying or image-receiving element, as will be further described herein.

U.S. Letters Patent Nos. 2,559,643 and 2,647,049 to Edwin H. Land disclose examples of such diffusion transfer reversal processes wherein a photographic material, such as a photosensitive element comprising an exposed silver halide emulsion layer containing a latent image, is processed to impart to an image-carrying element a reversed or positive dye image of said latent image by permeating into said emulsion layer a suitable liquid processing composition and bringing said photosensitive element into superposed relationship with an appropriate image-receiving element.

In carrying out the process of this invention, a photosensitive element containing a silver halide emulsion is exposed and a liquid processing composition applied

thereto, as by immersing, coating, spraying, flowing, etc., in the dark, and the photosensitive element superposed, prior to, during or after wetting, on an image-receiving element. In a preferred embodiment, the photosensitive element contains a layer of the dye developer, and the liquid processing composition is applied to the photosensitive element in a uniform layer as this element is brought into superposed relationship with an image-receiving element. The liquid processing composition permeates the emulsion and provides a solution of the dye developer substantially uniformly distributed therein. As the solubilized dye developer develops the latent negative image to silver, its oxidation product is immobilized or precipitated in situ with said silver. This immobilization is apparently due, at least in part, to a change in the solubility characteristics of the dye developer upon oxidation, and especially as regards its solubility in alkaline solutions. It may also be due, in part, to a tanning effect on the emulsion by the oxidized dye developer. The unoxidized dye developer retains its solubility in the liquid processing composition, thereby providing an imagewise distribution of unoxidized dye developer, at least part of which is transferred, by imbibition, to a superposed image-receiving element, said transfer substantially excluding silver or oxidized dye developer. The latter element receives a depthwise diffusion, from the emulsion, of unoxidized dye developer without appreciably disturbing its imagewise distribution, thereby giving a reversed or positive, colored image of the developed negative image. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developer. If the color of the diffused dye developer is affected by changes in the pH of the image-receiving element, this pH may be adjusted in accordance with known techniques to provide a pH according to the desired color. Imbibition periods of approximately one minute have been found to give good results, but this contact period may be adjusted where necessary to compensate for variations in temperature or other conditions. The desired positive image is revealed by stripping the image-receiving element from the photosensitive element at the end of the imbibition period.

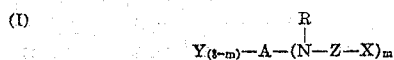
The novel dye developers disclosed herein may be utilized in the liquid processing composition, in the image-receiving element, or in the photosensitive element, as for example, in, on or behind the silver halide emulsion layer. When employed in either element, the dye developer becomes solubilized by the liquid processing composition as it permeates the element. In a preferred embodiment, a coating or layer of the dye developer is placed behind the silver halide emulsion layer, i.e., on the side of the emulsion layer adapted to be located most distant from the photographed subject when the photosensitive element is exposed. This coating of the dye developer is preferably also located on the side of the emulsion layer adapted to be most distant from the image-receiving element when in superposed relationship therewith. Placing the dye developer behind the emulsion layer, as in the preferred embodiment, has the advantage of providing increased contrast in the positive image, and also minimizes any light-filtering action by the novel colored dye developer. In this preferred embodiment, the dye developer coating may be applied by using coating solutions containing about 0.5 to 8%, by weight, of the dye developer. Similar concentrations may be used if the dye developer is utilized as a component of the liquid processing composition.

The liquid processing composition referred to above comprises at least an aqueous solution of an alkaline material, such as diethylamine, sodium hydroxide or sodium carbonate. In some instances, it may contain a minor amount of a conventional developing agent. If the liq-

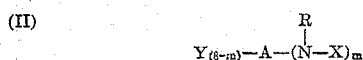
liquid processing composition is to be applied to the emulsion by being spread thereon, preferably in a relatively thin, uniform layer, it may also include a viscosity-increasing compound constituting film-forming material of the type which, when spread over a water-absorbent base, will form a relatively firm and relatively stable film. A preferred film-forming material is a high molecular weight polymer such as a polymeric, water-soluble ether which is inert to an alkaline solution, as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Other film-forming materials or thickening agents may be employed whose ability to increase viscosity is substantially unaffected when left in solution for a long period of time.

It has been discovered that dye developers having amino-nitrogen atoms as part of their chromophoric system may have their color properties altered by acylation of such amino-nitrogen atoms. This has been found to be particularly applicable to dye developers having amino-nitrogen atoms attached directly to the anthraquinone nucleus.

The novel dye developers which may be used to accomplish the objects of this invention may be represented by the formulae:



and



wherein:

A represents an anthraquinone nucleus;

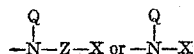
X represents an organic radical containing hydroxyl substituents imparting a silver halide developing function thereto;

R represents an acyl group, which may be aliphatic, e.g., acetyl, or aromatic, e.g., benzoyl;

Z is a bivalent organic radical containing at least one methylene ($-\text{CH}_2-$) group;

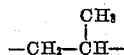
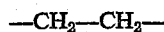
m is a positive integer less than 5; and

Each Y may be hydrogen, amino, alkyl, aryl, nitro, halogen, alkylamino, arylamino, aryloxy, alkoxy, hydroxyl, sulfonamido, carboxamido, carboxy, sulfo,

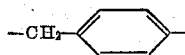


wherein Q may be hydrogen or alkyl.

The expression "bivalent organic radical" refers to organic radicals having the two free valences attached to different atoms. As examples of suitable bivalent organic radicals comprehended by the radical Z, mention may be made of alkylene radicals such as $-\text{CH}_2-$,



as well as bivalent radicals such as



It is also intended that Z may be saturated, unsaturated, such as $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$, or substituted, such as chloroalkylene or hydroxyalkylene. Experience has indicated that where Z is an alkylene group, best results are obtained by the use of a lower alkylene group, e.g., an alkylene group containing less than about six carbons, and preferably an ethylene ($-\text{CH}_2\text{CH}_2-$) group. Alkylene groups containing more carbons may be used, however, provided that the resulting dye developer is capable of being dissolved in the liquid processing composition described herein, and its oxidation product rendered immobile in the developed emulsion layer.

X has been defined as an organic group containing hydroxyl substituents which impart to it a silver halide developing function. Although, in a preferred embodiment, X contains a benzene nucleus substituted in the para positions, with respect to each other, by hydroxyl groups, this is intended to be illustrative only. Thus, for example, a silver halide developing function may be imparted to an aryl nucleus, by hydroxyl groups which are substituted in the ortho or para positions, with respect to each other, of a benzene nucleus, or in the 1,2 or 1,4 positions of a naphthalene nucleus. It is to be noted also that X may contain substituents other than those hydroxyl groups which supply the silver halide developing function so long as such substituents do not destroy the silver halide developing ability; such substituents include alkyl, hydroxyl, amino, halogen, etc. Reference is made to The Theory of the Photographic Process, C. E. K. Mees (1st Ed., 1942), The Macmillan Co., New York, N. Y., p. 342 et seq., for a discussion of the chemical constitution of silver halide developing groups.

Where the developing function possessed by X is supplied by hydroxyl groups, it may be desirable to protect these groups as by acylation, to avoid side reactions or oxidation. The protective groups are removed, as by hydrolysis, prior to photographic use.

The novel dye developers of this invention are preferably prepared by heating the corresponding amino compounds with the appropriate acid halide or acid anhydride. Other known methods of acylation may also be used, such as use of an ester or amide of the acid. By suitable control of reaction conditions and ratios of the acylating agent and the amino compound, acylation may be brought about at one or more amino-nitrogen atoms. It is also within the scope of this invention to introduce different acyl groups into a compound having more than one amino-nitrogen in the chromophoric system.

Acylation of amino-nitrogen atoms which are part of the chromophoric system has the effect of shifting the visible absorption band of the compound toward higher frequencies (shorter wave lengths). Thus, acylating one amino-nitrogen of the cyan 1,4-bis-[beta-(2',5'-dihydroxyphenyl)-ethylamino]-anthraquinone changes its color to a magenta and acylating both the amino-nitrogen atoms changes its color to an orange-yellow.

As examples of suitable amino-anthaquinone compounds which may be acylated in accordance with this invention, mention may be made of 1,4-bis-(2',5'-dihydroxyanilino)-anthraquinone and similar compounds as disclosed and claimed in the copending application of Elkan R. Blout and Myron S. Simon, Serial 449,514, filed August 12, 1954, now abandoned in favor of a continuation-in-part application Serial No. 849,727, filed October 30, 1959, and also compounds such as 1,4-bis-[beta-(2',5'-dihydroxyphenyl)-ethylamino]-anthraquinone and similar compounds as disclosed and claimed in the copending application of Elkan R. Blout, Marilyn R. Cohler, Milton Green, Myron S. Simon and Robert B. Woodward, Serial No. 478,922, filed December 30, 1954, now abandoned in favor of continuation-in-part applications Serial Nos. 824,785 and 824,786, filed July 3, 1959.

An example of a method of preparing a dye developer within the scope of this invention, and set forth as an illustration only, is:

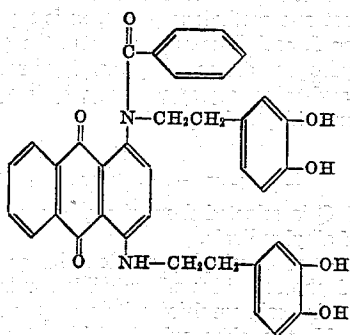
Example 1

1,4-bis-[beta-(3',4'-dihydroxyphenyl)-ethylamino]-anthraquinone and benzoyl chloride in 1:1 molar proportions are refluxed in approximately 10 volumes of acetone until the color change from cyan to magenta is complete. The acetone solution is then concentrated and the residue twice recrystallized from acetone-chloroform to obtain a 32% yield of N-monobenzoyl-1,4-bis-

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[beta - (3',4' - dihydroxyphenyl) - ethylamino] - anthraquinone of the formula:

(III)



This product sinters at 221-223° C., and melts at 229-232° C. It is soluble in aqueous alkali, moderately soluble in methanol and acetone, and very soluble in pyridine. In solution, it is an intense, bright magenta. Analysis of the product, based on the above formula, shows:

	O	H	N
Calculated.....	68.77	4.67	4.33
Found.....	68.6	4.6	4.1

An example of a photographic use of the dye developers of this invention, and set forth as an illustration only, is:

Example 2

A photosensitive element is prepared by coating a sub-coated cellulose acetate film base with a 4% aqueous gelatin solution. After this coating has dried, a coating is applied of a solution comprising 2 g. of the dye developer of Formula III as prepared in Example 1, above, in:

Cellulose acetate hydrogen phthalate	g--	4
Acetone	cc--	80
Methanol	cc--	20

A silver-iodobromide emulsion is applied after the above coating has dried. An image-receiving element is prepared by applying a polyvinyl butyral coating to a cellulose acetate coated baryta paper, followed by a coating of a solution comprising:

Nylon Type F8 (trade name of E. I. du Pont de Nemours & Co., Wilmington, Delaware, for N-methoxymethyl polyhexamethylene adipamide)	g--	4
Ethanol	cc--	85
Furfuryl alcohol	cc--	15

The photosensitive element is exposed and brought into superposed relationship with the image-receiving element as a liquid processing composition is spread between said elements. This liquid processing composition comprises:

Sodium hydroxide	g--	1.5
Water	cc--	100
Metol	g--	0.1
Sodium carboxymethyl cellulose (very high viscosity)	g--	4.5

After an imbibition period of approximately one minute, the image-receiving element is separated and contains a magenta positive image of the photographed subject.

A further example of a photographic use of a dye developer within the scope of this invention is:

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Example 3

A photosensitive element is prepared as described in Example 2, above, except that the dye developer coating solution comprises:

N - monobenzoyl - 1,4 - bis - [beta - (2',5' - dihydroxyphenyl)-ethylamino]-anthraquinone (prepared in a manner similar to that described in Example 1)	g--	3
Cellulose acetate hydrogen phthalate	g--	4
Acetone	cc--	80
Methanol	cc--	20

An image-receiving element is prepared by applying a polyvinyl butyral coating to a cellulose acetate coated baryta paper, followed by a coating of a solution comprising:

Nylon Type F8	g--	4
Ethyl alcohol	cc--	85
Furfuryl alcohol	cc--	15

The photosensitive element is exposed and brought into superposed relationship with the image-receiving element as a liquid processing composition is spread between said elements. This liquid processing composition comprises:

Water	cc--	100
Sodium carboxymethyl cellulose (very high viscosity)	g--	4.5
Sodium hydroxide	g--	2.0
Metol	g--	0.2
Potassium bromide	g--	0.2
Sodium carbonate	g--	2.0

After an imbibition period of approximately one minute, the image-receiving element is separated and contains a magenta, positive image of the photographed subject.

It will be noted that the liquid processing composition may, and in the above examples does, contain a minor amount of a conventional developer, such as Metol. The amount of this conventional developer used is insufficient to develop the latent image by itself, and merely serves to accelerate and possibly initiate the action of the dye developer.

The dye developers of this invention may be used also in conventional photographic processes, such as tray or tank development of conventional photosensitive films, plates or papers to obtain black and white, monochromatic or toned prints or negatives. By way of example, a developer composition suitable for such use may comprise an aqueous solution of approximately 1-2% of the dye developer, 1% sodium hydroxide, 2% sodium sulfite and 0.05% potassium bromide. After development is completed, any unreacted dye developer is washed out of the photosensitive element, preferably with an alkaline washing medium or other medium in which the unreacted dye developer is soluble. The expression "toned" is used to designate photographic images wherein the silver is retained with the precipitated dye, whereas "monochromatic" is intended to designate dye images free of silver.

It should be noted that the dye developers of this invention are self-sufficient to provide the desired color image and do not depend upon coupling reactions to produce the desired color. They thus provide a complete departure from conventional photographic color processes in which the color is produced by a coupling reaction involving the oxidized developing agent.

It will be apparent that, by appropriate selection of the image-receiving element from among suitable known opaque and transparent materials, it is possible to obtain either a colored positive reflection print or a colored positive transparency. Likewise, the inventive concepts herein set forth are adaptable for multicolor work by the use of special photographic materials, for example film materials of the type containing two or more photosensitized elements associated with an appropriate num-

ber of image-receiving elements and adapted to be treated with one or more liquid processing compositions, appropriate dye developers suitable to impart the desired subtractive colors being incorporated in the photosensitized elements or in the liquid processing compositions. Examples of such photographic materials are disclosed in the previously mentioned U.S. Patent No. 2,647,049 to Edwin H. Land.

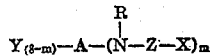
The inventive concepts herein set forth are also adaptable for the formation of colored images in accordance with the photographic products and processes described and claimed in the copending application of Howard G. Rogers, Serial No. 415,073, filed March 9, 1954, now abandoned in favor of a continuation-in-part application Serial No. 748,421, filed July 14, 1958, and also those set forth in the copending application of Edwin H. Land, Serial No. 448,411, filed August 9, 1954, now U.S. Patent No. 2,968,554, issued January 17, 1961.

In the preceding portions of the specification the expression "color" has been frequently used. This expression is intended to include the use of a plurality of colors to obtain black, as well as the use of a single black dye developer.

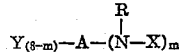
Since certain changes may be made in the above products, compositions and processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

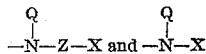
1. A photographic developer composition comprising an aqueous solvent, an alkaline material soluble therein, and a compound selected from the group consisting of:



and



wherein A is an anthraquinone nucleus, X is an organic radical selected from the group consisting of ortho- and para-dihydroxyphenyl and ortho- and para-dihydroxynaphthyl radicals, R is an acyl group of an organic carboxylic acid, Z is a bivalent hydrocarbon radical containing at least one methylene group, m is a positive integer less than 5, each Y is selected from the group consisting of hydrogen, amino, alkyl, aryl, nitro, halogen, alkylamino, arylamino, aryloxy, alkoxy, hydroxyl, sulfonamido, carboxamido, carboxy, sulfo,



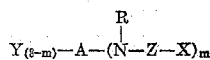
radicals, and Q is selected from the group consisting of hydrogen and alkyl radicals.

2. A photographic developer composition as defined in claim 1 wherein said X is a para-dihydroxyphenol radical.

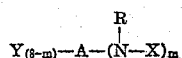
3. A photographic developer composition comprising an aqueous solvent, an alkaline material soluble therein, and N - monobenzoyl - 1,4 - bis - [beta - (3',4' - dihydroxyphenyl)-ethylamino]-anthraquinone.

4. A photographic developer composition comprising an aqueous solvent, an alkaline material soluble therein, and N - monobenzoyl - 1,4 - bis - [beta - (2',5' - dihydroxyphenyl)-ethylamino]-anthraquinone.

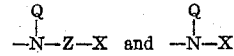
5. A process of developing a latent image contained in an exposed photosensitive silver halide emulsion which comprises treating said emulsion with an aqueous alkaline solution of a compound selected from the group consisting of compounds represented by the formulae:



and



wherein A is an anthraquinone nucleus, X is an aryl radical selected from the group consisting of ortho- and para-dihydroxyphenyl and ortho- and para-dihydroxynaphthyl radicals, R is an acyl group of an organic carboxylic acid, Z is a bivalent hydrocarbon radical containing at least one methylene group, m is a positive integer less than 5, each Y is selected from the group consisting of hydrogen, amino, alkyl, aryl, nitro, halogen, alkylamino, arylamino, aryloxy, alkoxy, hydroxyl, sulfonamido, carboxamido, carboxy, sulfo,

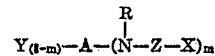


radicals, and Q is selected from the group consisting of hydrogen and alkyl radicals.

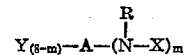
6. A process of developing a latent image contained in an exposed photosensitive silver halide emulsion which comprises treating said emulsion with an aqueous alkaline solution of N - monobenzoyl - 1,4 - bis - [beta - (3',4' - dihydroxy)-ethylamino]-anthraquinone for a time sufficient to develop the latent image to silver.

7. A process of developing a latent image contained in an exposed photosensitive silver halide emulsion which comprises treating said emulsion with an aqueous alkaline solution of N - monobenzoyl - 1,4 - bis - [beta - (2',5' - dihydroxyphenyl)-ethylamino]-anthraquinone.

8. In a process of forming a photographic image in color, the steps which comprise developing a latent image contained in an exposed silver halide emulsion with an aqueous alkaline solution containing a dye developer selected from the group consisting of:

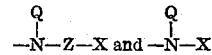


35 and



wherein A is an anthraquinone nucleus, X is an aryl radical selected from the group consisting of ortho- and para-dihydroxyphenyl and ortho- and para-dihydroxynaphthyl radicals, R is an acyl group of an organic carboxylic acid, Z is a bivalent hydrocarbon radical containing at least one methylene group, m is a positive integer less than 5, each Y is selected from the group consisting of hydrogen, amino, alkyl, aryl, nitro, halogen, alkylamino, arylamino, aryloxy, alkoxy, hydroxyl, sulfonamido, carboxamido, carboxy, sulfo,

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radicals, and Q is selected from the group consisting of hydrogen and alkyl radicals, to thereby provide in said emulsion layer a predetermined distribution of unoxidized dye developer, and transferring at least part of said distribution of unoxidized dye developer by imbibition from said emulsion layer to an image-receiving element in superposed relationship with said emulsion to impart to said image-receiving element a reversed, positive dye image of the developed image.

9. A process as defined in claim 8 wherein said aqueous alkaline solution contains an accelerating developer.

10. The process as defined in claim 8, wherein said X is a para-dihydroxyphenyl radical.

11. The process as defined in claim 8, wherein said dye developer is N-monobenzoyl-1,4-bis-[beta-(3',4'-dihydroxyphenyl)-ethylamino]-anthraquinone.

12. The process as defined in claim 8, wherein said dye developer is N-monobenzoyl-1,4-bis-[beta-(2',5'-dihydroxyphenyl)-ethylamino]-anthraquinone.

13. The process as defined in claim 8, wherein said dye developer is disposed, prior to exposure, in the photosensitive element comprising said exposed silver halide emulsion, and the solution containing said dye developer is formed by permeating said photosensitive element with

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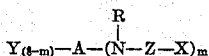
an aqueous alkaline liquid capable of solubilizing said dye developer.

14. The process as defined in claim 13, wherein said liquid is introduced by being spread in a substantially uniform layer between said photosensitive element and said image-receiving element as said elements are brought into superposed relationship.

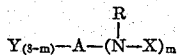
15. The process as defined in claim 14, wherein said liquid contains a thickener for increasing viscosity and for facilitating the spreading thereof between said photosensitive element and said image-receiving element.

16. The process as defined in claim 8, wherein said dye developer is dissolved in an aqueous alkaline solution prior to application thereof to said exposed emulsion.

17. In a photographic product comprising a plurality of layers including a layer containing a silver halide emulsion and having a silver halide developer disposed in at least one layer, the feature of having said silver halide developer be a compound selected from the group consisting of:



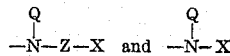
and



wherein A is an anthraquinone nucleus, X is an aryl radical selected from the group consisting of ortho- and

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para-dihydroxyphenyl and ortho- and para-dihydroxynaphthyl radicals, R is an acyl group of an organic carboxylic acid, Z is a bivalent hydrocarbon radical containing at least one methylene group, m is a positive integer less than 5, each Y is selected from the group consisting of hydrogen, amino, alkyl, aryl, nitro, halogen, alkylamino, arylamino, aryloxy, alkoxy, hydroxyl, sulfonamido, carboxamido, carboxy, sulfo,



radicals, and Q is selected from the group consisting of hydrogen and alkyl radicals.

18. A photographic product comprising a silver halide emulsion and N - monobenzoyl - 1,4 - bis - [beta - (3',4'-dihydroxyphenyl)-ethylamino]-anthraquinone.

19. A photographic product comprising a silver halide emulsion and N - monobenzoyl - 1,4 - bis - [beta - (2',5'-dihydroxyphenyl)-ethylamino]-anthraquinone.

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UNITED STATES PATENTS

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1,660,090	Perkin et al.	Feb. 21, 1928
2,123,375	Mieg et al.	July 12, 1938
2,192,891	Borst	Mar. 12, 1940
2,559,643	Land	July 10, 1951

UNITED STATES PATENT OFFICE
CERTIFICATION OF CORRECTION

Patent No. 2,983,605

May 9, 1961

Richard S. Corley

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 30, for "monomchromatic" read -- monochromatic --; column 2, line 37, for "miately" read -- mately --; column 4, lines 46 and 55, for "-anthaquinone" each occurrence, read -- -anthraquinone --; same column, line 51, after "Serial" insert -- No. --; column 5, line 54, for "Pant" read -- Pont --; column 7, line 55, for "para-dihydroxyphenol" read -- para-dihydroxyphenyl --; column 8, line 20, for "dihydroxy" read -- dihydroxyphenyl --.

Signed and sealed this 24th day of October 1961.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents