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3,365,293

PHOTOGRAPHIC DIAZOTYPE FILMS COMPRISING FLUORESCENT ULTRAVIOLET ABSORBERS

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No Drawing. Continuation-in-part of application Ser. No. 369,104, May 21, 1964. This application Nov. 29, 1965, Ser. No. 510,379

Claims priority, application Switzerland, June 6, 1963, 7,120/63

7 Claims. (Cl. 96—75)

This application is a continuation-in-part of our pending patent application Ser. No. 369,104 filed on May 21, 1964, now abandoned.

This invention relates to a process for the production of diazotype films, that is, positive copy films for photographic purposes, as well as to the diazotype films produced by this process.

The use of light-sensitive layers containing diazo compounds on paper, cellulose films and cellulose acetate films for the production of photoprints is known. Such diazotype layers have been used up to the present mainly for the copying of outline drawings and documents, while, because of their high contrast, they are not normally suitable for the reproduction of photographic pictures or motion picture films having many half tones.

In order to reduce the excessively high contrast of such diazotype layers it has been suggested to expose these layers only to such rays of the visible spectrum for which the diazo compounds in the layer have a lesser than their maximal absorptivity, while excluding from the light used for exposure that region of the spectrum for which the respective diazo compounds possess maximal absorption; however, this has been achieved only by providing special means for filtering the light used for exposure.

Another problem which occurs particularly in the production of motion picture films for projection, is the production of durable films which do not tear.

As the diazo salts suitable for diazotype processes are water-soluble and have good affinity to cellulose, diazotype films were initially produced on substrata of unesterified cellulose. Such films, however, have insufficient tensile strength and tear easily. Attempts have, therefore, been made to incorporate the diazo salt into a gelatin layer and to apply the latter to cellulose acetate substrata which, although they are of sufficient tensile strength and do not tear, do not themselves absorb the diazo salts, in a similar manner as is employed in the production of motion picture films on the basis of the silver bromide process.

However, such composite gelatine/cellulose acetate films cannot be stored without elaborate humidity control, for the gelatin layer, i.e. the layer containing the picture, has a tendency to peel off and to re-adhere to the cellulose acetate layer in a displaced, i.e. distorted way, in the course of time and due to varying humidity of the atmosphere, thereby becoming unusable.

For these reasons, it is conventional to hydrolyze a top layer at the surface of cellulose acetate substrata and to apply light-sensitive diazo salts to the cellulose hydrate top layers of these films. According to this process, the gradation of the diazotype layer is improved by prolonged ageing, e.g. during 2 to 3 months. As cellulose acetate material, preferably cellulose-2½ acetate is used as it is more easily and much more rapidly hydrolyzed than cellulose triacetate.

The incorporation of certain organic compounds such as optical bleaching agents, which are used in developers in an after-treatment to improve the appearance of exposed diazotype prints was not considered feasible, in

contrast to their inclusion in photographic emulsions, since such incorporation would lead to impairment of the light sensitivity of the diazotype layers and to interfering reactions between the optical bleaching agents and the diazotype compounds.

Processes incorporating diazo compounds in a gelatin layer applied to a cellulose base paper and treating the exposed diazotype material using developers containing optical bleaching agents are, for instance, described in British Patent 700,798, to Van der Grinten et al.

The above processes as well as other known processes such as that described in British Patent 910,038 to General Aniline & Film Corporation, of New York, N.Y., wherein fluorescent or phosphorescent dyestuffs incorporated in the surface of a paper, film or cloth base, are coated with a light-sensitive diazotype one- or two-component material with or without intermediate application of a layer of light colored pigment, to inhibit "quenching," serve the purpose of increasing the contrast of the resulting prints and also of increasing the printing speed. Increased contrast means, however, a steeper photographic gamma, and, consequently, such photographic diazotype material is rendered unsuitable for the reproduction of motion picture films.

In contrast thereto, it is an object of the present invention to provide novel diazotype films for photographic purposes which films are tear-proof, durable, and possess a greatly improved gradation which permits the reproduction of photographic pictures or motion picture films having many half tones.

The term "improved gradation" as used in this specification and in the appended claims means that the gradations of density obtained with films according to the invention approach the ideal photographic gamma of 1, i.e. corresponding to an angle of the curve of 45°, more closely than hitherto known diazotype films, and thus approach and/or attain that of a silver-gelatin film.

It is another object of the invention to provide diazotype films for the above-stated purposes which are ready for use immediately, without requiring any ageing.

It is a further object of the invention to provide diazotype films for the above-stated purposes, which films permit the copying of half tones from photographic pictures or motion picture films without requiring means for filtering the light used for exposure.

It is finally an object of the invention to provide a process for producing diazotype films suitable for fulfilling the above purposes and possessing the above-stated advantageous features.

The above-stated objects as well as others which will become apparent in the following description of our invention, have been realized in the diazotype photographic films according to the invention which comprise, as illustrated in the accompanying drawing,

(a) A film base consisting essentially of cellulose ester, such as cellulose acetate, namely cellulose di-acetate, cellulose tri-acetate or, preferably, cellulose 2½-acetate; cellulose nitrate, or mixed esters of cellulose such as cellulose acetate-propionate, cellulose acetate-butyrate and the like cellulose lower alkanoates,

(b) A top layer on and substantially integral with said film base which top layer consists at least in its major portion or entirely of cellulose hydrate and has a thickness of about 5 microns to, preferably, not more than 10 microns, and

(c) A mixture of

(i) A light-sensitive aryl-diazonium compound of the type conventionally incorporated in diazotype material, and

(ii) As a light-filtering agent, an anionic, non-coloring organic compound substantive to cellulose hydrate possess-

ing green-blue, blue or violet fluorescence, of the type conventionally used as bleaching agents, which mixture is present in said top layer in a state of fine dispersion, preferably in a state of solid emulsion or solid solution, and in amounts of from about 0.2 to 3 grams, preferably 0.8 to 1.2 g., per square meter of film surface of said top layer of said light filtering agent and 0.02 g. to 0.2 g. per square meter of top layer surface of said diazonium compound, the weight ratio of the diazo compound to the light filtering agent in the top layer being preferably about 1:10 to 1:15.

These novel photographic diazotype films are produced according to the invention by a first process which comprises:

(a) Hydrolyzing a top layer of a cellulose alkanoate base of the type described above, to a depth of at least about 5 microns, and preferably not more than 10 microns, by subjecting either one or both sides of the said base material to the attack of a hydrolyzing bath which contains per liter preferably about 2 to 20 g. of alkali metal hydroxide or alkaline earth metal hydroxide, particularly sodium hydroxide or potassium hydroxide, and preferably 0.5 to 5 g. of the above-described pure, concentrated fluorescent light-filtering compound which is substantive to cellulose hydrate as defined and, optionally, a wetting and dispersing agent which is stable to alkali, e.g. a fatty alcohol sulfate. Depending on its hydrolyzability, the cellulose acetate substrate is continuously treated in this solution for from about 2 to 20 minutes at about 40 to 95° C., excess bath liquid is removed, and the film rinsed in cold water and dried.

(In lieu of applying the fluorescent light-filtering agent simultaneously with the hydrolyzing agent in the hydrolysis bath, the former can also be applied in a separate bath following the formation of the hydrolyzed top layer.)

(b) Applying the cationic, light-sensitive aryl diazonium compound to the top layer of the cellulose ester substrate already containing the light-filtering agent, in the dark or in a yellow light, using conventional methods, and in sufficient concentration to incorporate the above-defined effective amount in the said top layer, namely of about 20 to not more than 100 g. and preferably about 40 to 60 g. of diazo compound per liter.

The contrast of the diazotype layers according to the invention is surprisingly satisfactorily but not excessively decreased i.e. their gradation is decisively improved by the treatment according to the invention, without requiring any previous ageing of the light-sensitive film.

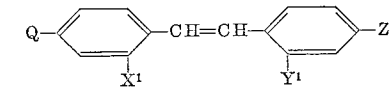
As has been mentioned hereinbefore, fluorescent compounds have been used in the past in order to brighten the substrate after the diazo compound had been incorporated therein and in developing the diazotype material. For this purpose, amounts of 0.1 to maximally 0.2% by weight calculated on the amount of entire film material were incorporated into the top layer, in the case of cellulose acetate films, or into the entire body of the substrate in the case of paper.

In the instant invention, the above-defined fluorescent compounds are used for an entirely different purpose, namely for effecting a filtration of ultraviolet light, thus avoiding the known use of separate filters. Moreover, these filtering substances surprisingly increase the affinity of the cellulose hydrate of the top layers for the diazo compounds which must be incorporated thereinto, according to the process according to the invention, subsequent to the treatment of the substrate, whereby the top layer of the latter is hydrolyzed and the fluorescent compounds are incorporated into the hydrolyzed top layer.

This permits in turn keeping the top layer thinner, namely at about 5 to 10 microns, and thus further improving the gradation of the film while leaving the tensile strength of the film unaffected. A thinner film is a prerequisite for a better gradation. To decrease light sensitivity does not mean as a matter of course an improvement in gradation. If that were so, a less sensitive diazo compound should afford better gradation. That is not the case. Such less sensitive diazo compound would only require longer exposure without any improvement in gradation.

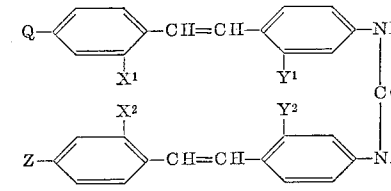
As a further advantage resulting from the above surprising effect, the tensile strength of the whole substrate is hardly affected. In addition, just because of the increased absorption power of the cellulose hydrate layer for diazo salts, sufficient amounts of light-sensitive diazo salts can be applied to this cellulose hydrate layer with a relatively diluted aqueous diazo solution of the concentration given above, which causes a further reduction of the contrast, i.e. an improved gradation.

Particularly suitable as light-filtering compounds usable according to the invention which are substantive to cellulose hydrate are soluble salts of a compound having acid, salt-forming groups, which compound, in its free acid form, is of the formula



(I)

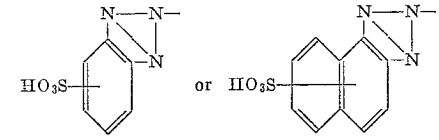
or of the formula



(II)

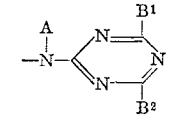
in which formulas

Q represents a radical of the formula



or

a radical of the formula



wherein

A represents hydrogen or lower alkyl,

B^1 represents an arylamino radical wherein "aryl" is an unsubstituted mononuclear or dinuclear carbocyclic aryl radical or such radical substituted with non-color-imparting, non-water-decomposable substituents;

Which substituents are, in particular, sulfo, carboxy, lower alkyl, lower alkoxy, chloro, bromo, fluoro, sulfamyl, carbamyl, sulfamyl which is N-substituted by lower alkyl, hydroxy-lower alkyl, lower alkoxy-lower alkyl, hydroxy-lower alkoxy-lower alkyl, sulfophenyl or carboxy-phenyl, or lower alkyl-sulfonyl-sulfamyl, carbamyl which is N-substituted by lower alkyl, hydroxy-lower alkyl, lower alkoxy-lower alkyl, hydroxy-lower alkoxy-lower alkyl, sulfophenyl or carboxyphenyl, lower alkyl-sulfonyl, hydroxy-lower alkyl-sulfonyl, lower alkanoylamino, N-lower alkanoyl-N-lower alkyl-amino, lower alkoxy-carbonyl-amino, or benzothiazolyl-(2')- in p-position to the —NH— moiety of the arylamino radical;

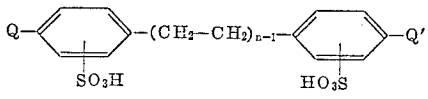
B^2 represents hydrogen, lower alkyl, lower alkoxy, hydroxy-lower alkoxy, lower alkoxy-lower alkoxy, amino, lower alkyl-amino, hydroxy-lower alkylamino, lower alkoxy-lower alkylamino, carboxy-lower alkylamino, sulfo-lower alkylamino, pyrrolidino, piperidino, morpholino or sulfophenylamino;

Z represents the above-described groupings represented by Q as well as hydrogen, chlorine, bromine, fluorine or lower alkyl; and

One of X^1, X^2, Y^1 and Y^2 represents an $-SO_3H$ group, And each of the other X's and Y's represents hydrogen, a lower alkyl, a lower alkoxy or the $-SO_3H$ group.

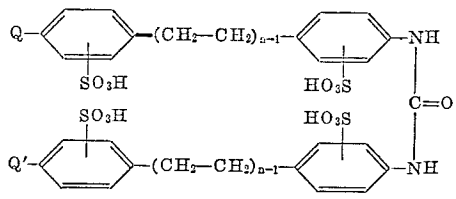
Preferably, both X and Y are $-SO_3H$.

Other anionic, non-coloring, green-blue, blue to violet fluorescent compounds which are substantive to cellulose hydrate and usable in the photographic diazotype materials according to the invention are benzidine and dibenzyl derivatives falling under the formulas



(III)

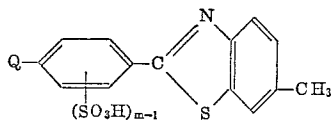
and



(IV)

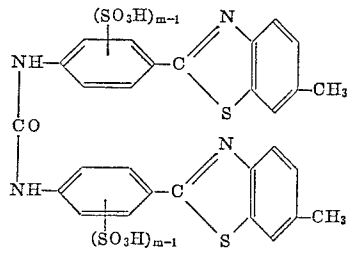
wherein Q and Q' have the meanings given hereinbefore for Q and are identical, and *n* is an interger ranging from 1 to 2;

or they are dihydro-p-toluidine derivatives falling under the formulas



(V)

and



(VI)

wherein:

m is an interger ranging from 1 to 2, and

Q has the meaning given hereinbefore.

In the above light-filtering agents of Formulas I to VI inclusive which possess a triazinyl-(2)-amino group as Q or Z, that radical must be substituted in one of its positions 4 and 6 by a phenylamino radical as defined hereinbefore in order to be usable in the diazotype photographic materials according to the invention.

Water-soluble salts, in particular sodium, potassium or ammonium salts of the above-defined stilbene derivatives in which the terminal groupings Q and Z are identical are particularly readily available and are, therefore, preferred.

Suitable water-soluble cationic, light sensitive aryldiazonium compounds for use in the process according to the invention are those wherein "aryl" represents from one to two six-membered carbocyclic aromatic rings, i.e. benzene, napthalene or diphenyl nuclei, bearing substituents selected from the group consisting of

Hydrogen, N-lower alkyl-amino, N,N-di-lower alkyl-amino, N-(hydroxy-lower alkyl)-amino, morpholino, piperidino, lower alkoxy, chloro, bromo, benzyloxy, N-phenyl-carbomyl, carboxy, lower alkoxy-carbonyl, sulfo, lower alkyl-sulfonyl, sulfamyl, N-lower alkyl-sulfamyl, N,N-di-lower alkyl-sulfonyl, N-phenyl-sulfamyl, N-phenyl-N-lower alkyl-sulfamyl, phenylamino, chlorophenylamino, bromophenylamino and carboxyphenylamino, lower alkoxy-carbonyl-phenylamino, sulfo-phenylamino, lower alkyl-sulfonyl-phenylamino, lower alkoxy-sulfonyl-phenylamino, sulfamyl-phenylamino, N-lower alkyl-sulfamyl-phenylamino, N,N-di-lower alkyl-sulfonyl-phenylamino, N-phenyl-sulfamyl-phenylamino, N-phenyl-N-lower alkyl-sulfamyl-phenylamino,

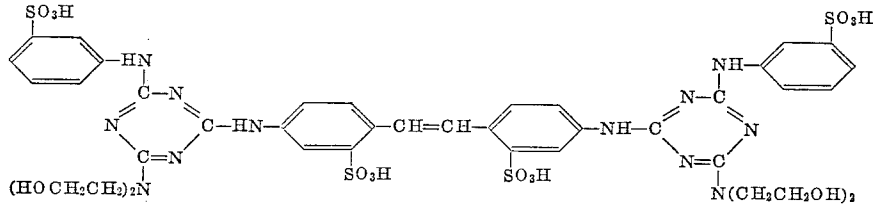
And the polycondensation product of formaldehyde and phenylamino-benzene diazonium chloride with about 2 to 20 repetitive units,

And double salts of the above with zinc chloride and cadmium chloride.

The following non-limitative examples illustrate the invention. The temperatures are given therein in degrees centigrade. Percentages are given by weight unless expressly stated otherwise; "g" stands for "gram" and "ml" for "milliliter".

Example 1

The surface of a cellulose-2½-acetate film having a 52% acetic acid content is saponified for 4 minutes at 65° with a solution which, per litre of water, contains 50 ml. of sodium hydroxide solution of 40° Bé, 3 g. of sodium salt of oleyl polyglycol ether sulphate (with 3 to 4 CH_2CH_2—O— groups) and 1.5 g. of the compound of the formula



The film is then passed through a second tank of flowing cold water, then squeezed out and dried by warm air at 60–70°.

In a darkened room with a yellow light, the film is then passed through a coating device which, by a rubber roller rotating in the diazo solution, applies a solution of 50 g. of the diazo salt of p-aminodiphenylamine which is free of nitrogen oxides, 25 g. of thiourea, 5 g. of stearyl polyglycol ether (with 20 CH_2CH_2—O— groups) and 5 g. of acetic acid per litre, to one side of the film.

The film is immediately dried with 30°-warm air and packed while excluding light.

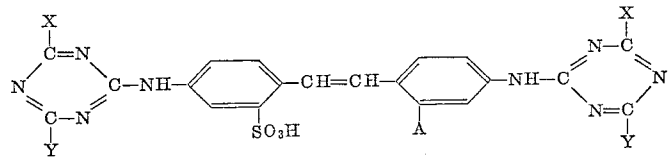
This film is well suited for copying positive motion picture films in a conventional copying machine with a mercury vapor or xenon lamp.

After exposure, the film is continuously developed for one second at 90° in a solution which contains 38 g. of monosodium phosphate, 80 g. of disodium phosphate, 20 g. of sodium formate, 10 g. of sodium tartrate, 10 g. of phloroglucine, 4.5 g. of resorcinol and 4 g. of napththol in 1250 ml. of water, and then rinsed cold and dried.

Positive copies with well graded half tones and a maximal black density of 2.3 are obtained. If the same film is exposed under a continuous tone stepwedge, then the individual grey shades are obtained in better gradation than when there is no blue fluorescent compound.

Positive copies having similarly good properties are obtained when, with otherwise the same procedure, the substantive fluorescent light-filtering compound of the formula given in the above example is replaced by one of the compounds defined hereinafter in the following Tables I and II and/or when the diazonium compound used in the above example is replaced by an equimolar amount of one of the diazonium compounds listed in Table III.

TABLE I.—GENERAL FORMULA



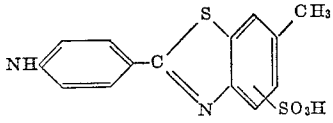
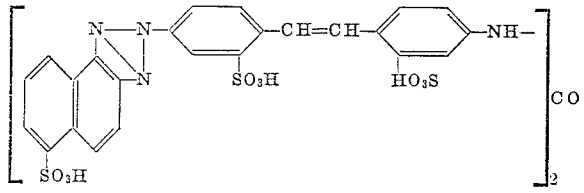
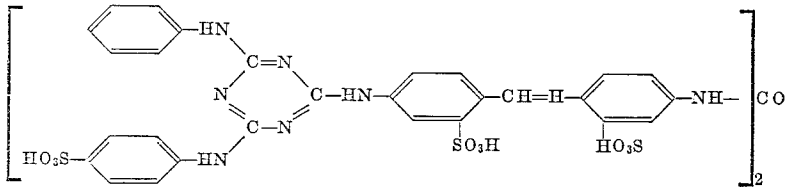
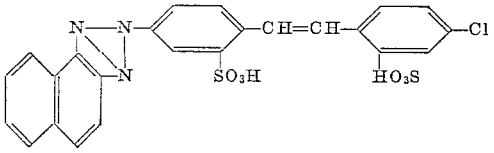
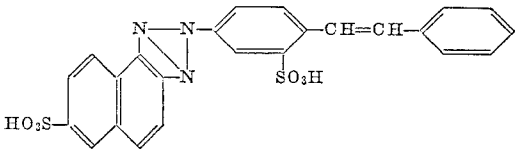
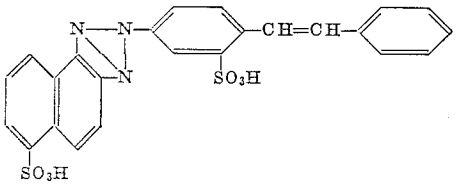
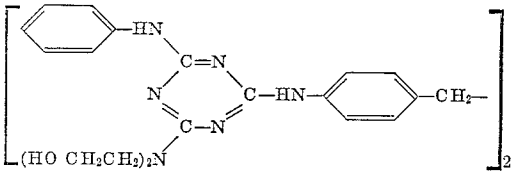
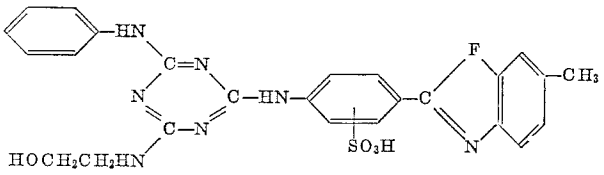
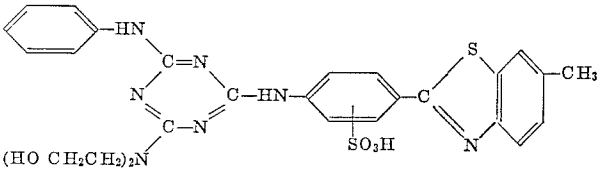
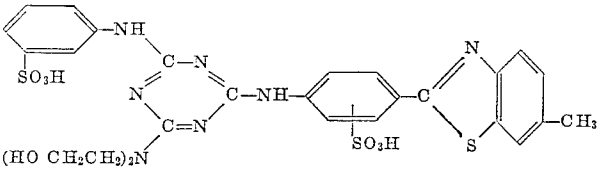
Example No.	X	Y	A
2	—NH—C$_6$H$_4$—SO$_3$H	—NH—C$_6$H$_5$	SO$_3$H
3	—NH—C$_6$H$_5$	—OCH$_3$	SO$_3$H
4	Same as Ex. 3	—NH—CH$_2$—CH(OH)—CH$_3$	SO$_3$H
5	do	—NH—C$_2$H$_5$	SO$_3$H
6	do	—N(CH$_3$)CH$_2$CH$_2$OH	SO$_3$H
7	do	—NH(CH$_2$)$_3$OCH$_3$	SO$_3$H
8	do	—OCH$_2$CH$_2$OH	SO$_3$H
9	do	—N(CH$_2$CH$_2$OH)$_2$	SO$_3$H
10	do	—NH(CH$_2$)$_2$OCH$_3$	SO$_3$H
11	—NH—C$_6$H$_3$(SO$_3$H)	—N(CH$_3$)CH$_2$CH$_2$OH	SO$_3$H
12	—NH—C$_6$H$_5$	—NH—CH$_2$CH$_2$OH	SO$_3$H
13	—NH—C$_{10}$H$_6$—SO$_3$H	—NH—CH$_2$CH$_2$OH	SO$_3$H
14		—NH—CH$_2$CH$_2$OH	SO$_3$H
15	—NH—C$_6$H$_4$—SO$_3$H	—N(CH$_3$)CH$_2$CH$_2$OH	SO$_3$H
16	—NH—C$_6$H$_3$(SO$_3$H)	—N(CH$_3$)CH$_2$CH$_2$OH	OCH$_3$
17	Same as Ex. 16	—N(CH$_3$)CH$_2$CH$_2$OH	CH$_3$
18	do	—N(CH$_2$CH$_2$OH)$_2$	CH$_3$
19	—NH—C$_6$H$_4$—COOH	—N(CH$_2$CH$_2$OH)$_2$	—SO$_3$H
20	—NH—C$_6$H$_3$(SO$_3$H)—CH$_3$	—N(CH$_2$CH$_2$OH)$_2$	—SO$_3$H
21	—NH—C$_6$H$_5$	—NH—CH$_2$COOH	—SO$_3$H
22	—NH—C$_6$H$_3$(SO$_3$H)$_2$	—NH—C$_6$H$_5$	—SO$_3$H
23	—NH—C$_6$H$_4$—SO$_3$H	—N(CH$_3$)CH$_2$CH$_2$OH	H

TABLE II

Ex. No.	Compound
23a	
24	
25	
26	
27	
28	
29	
30	
31	

If the compounds given in the above examples are not included in the saponification bath and otherwise the same procedure as given in Example 1 is followed, then only a maximal black density of at most 1.5 and much higher contrast are obtained.

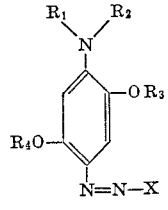
If after saponifying without the addition of the fluorescent compounds given in the examples, the concentration of the diazo salt is increased to 100 g. per litre, then the maximal black density of the positive copies is only improved to an inconsiderable extent.

If the fluorescent compounds given in the above examples are not added to the saponification bath but the cellulose acetate substate is treated for 15 minutes at 65° therein instead of for 4 minutes and afterwards the substrate is coated with 100 g. of diazo salt per litre in the same way, then after exposure and development, similar black densities as mentioned in Example 1 are obtained. However, the cellulose acetate layer becomes thinner by the longer saponification time which becomes undesirably apparent in the reduction of its tensile strength:

	Per 35 mm. film width	
	Tensile strength, kg.	Breaking tension, Percent
Saponification for 4 minutes	34	40
Saponification for 15 minutes	26.5	21

TABLE III

(a) The compounds as defined in German Auslegeschrift 1,163,675, published Feb. 20, 1964, of the formula



wherein:

R_1 represents lower alkyl or benzyl,

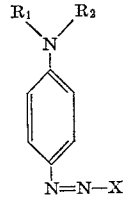
R_2 represents lower alkyl,

Each of R_3 and R_4 represent alkyl of from 1 to 5 carbon atoms,

X represents an acid radical, and

R_1 and R_2 together with a nitrogen atom to which they are linked also represent a 5-membered or 6-membered heterocyclic ring.

(b) The compounds of the formula



wherein

R_1, R_2 and X have the aforesaid meanings, especially p-diazo-N-ethyl-N-benzyl-aniline nitrate and the other diazos described in British Patent No. 700,798.

(c) The compounds listed on page 5 of Bristish Patent No. 871,216.

According to another aspect of the present invention, it has been found that the fluorescent compounds, which enable the excessively high contrast of the diazotype material to be reduced and so bring out the desirable half tones, can also be replaced by non-fluorescent UV-absorbers for polymeric plastics.

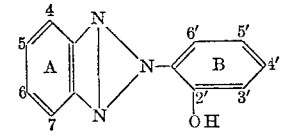
These substances not only have the desirable effect of reducing the excessively high contrast but also counteract the yellowing of the diazotype copies obtained. Because of this additional effect, they can also be used together with the fluorescent compounds employed under the first aspect of the invention described hereinbefore; films treated with blue fluorescent and non-fluorescent UV-absorbers produce diazotype copies the background of which is favourably affected by the fluorescent light and the stability in use of which is favourably affected by the UV-absorber.

Similar compounds used conventionally in the plastics industry from the classes of 2-hydroxyphenyl benzotriazoles, 2-hydroxyphenyl aryl ketones, 2-hydroxyphenyl triazines and 2-hydroxy xanthones can be used as stable UV-absorbers. Due to their hydroxyl function, these compounds are soluble in the aqueous-caustic alkali saponification liquor and they draw onto the cellulose hydrate layer from aqueous-alkaline or from organic-aqueous or purely organic solution; in this connection the 2-hydroxyphenyl benzotriazoles are distinguished by good stability and sufficient substantivity.

All the other steps in the process correspond to those under the first aspect of the invention; in particular, in the second aspect, the blue to violet fluorescent compounds more closely defined under the first invention aspect can also be optionally used.

The diazotype films for positive copies according to this second aspect of the invention are characterized by an acceptable reproduction of the half tones of the subject and by good wear in use, particularly by improved stability to yellowing of the copies.

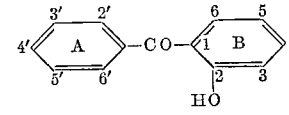
Non-coloring and non-fluorescent, light stable UV absorbers correspond, for example, to the formula



VII

In this formula, the ring A can be substituted, e.g. by chlorine, lower alkyl, alkoxy, alkylsulphonyl groups, carboxylic acid ester and amide groups, sulphonic acid ester and amide groups as well as by acylamino groups; the ring B can be substituted, e.g. by chlorine, lower alkyl, alkoxy, acylaminomethyl acylamino groups, cycloalkyl and phenyl groups as well as, in the 5'-position, by carboxylic acid ester groups.

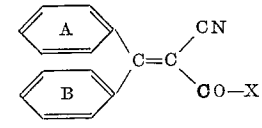
Another class of non-coloring, light stable UV absorbers corresponds to the formula



VIII

In this formula, the ring A can be substituted by chlorine, lower alkyl and alkoxy groups, aryloxy groups as well as, in the 2'- and/or 4-position, by hydroxyl groups; the ring B can be substituted by chlorine, lower alkyl groups, in the 4-position by alkoxy groups or the hydroxyl group and, in the 3- or 5-position, by a benzoyl group.

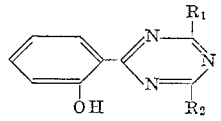
A third class of light stable, non-coloring UV absorbers corresponds to the formula



IX

In this formula X represents an optionally substituted alkoxy, alkylamino or dialkylamino group and the benzene rings A and B can be substituted, e.g., by chlorine, lower alkyl and alkoxy groups.

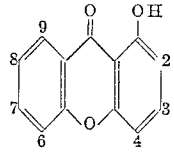
A fourth class of non-coloring UV absorbers corresponds to the formula



X

In this formula X represents an optionally substituted alkyl, phenyl or 2-hydroxyphenyl group; R_2 represents the same as R_1 with the condition that when R_1 is o-hydroxyphenyl, R_2 can also be an optionally substituted alkoxy, alkylthio or alkylamino group; the benzene rings can optionally be substituted by chlorine, lower alkyl and alkoxy groups as well as by a second hydroxyl group in the m-position to the first hydroxyl group.

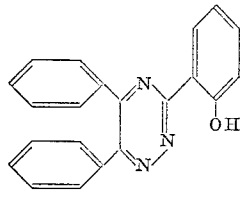
A further class of light stable, non-coloring UV absorbers corresponds to the formula



XI

In this formula, chlorine and alkyl groups can be substituents in the 2- to 9-positions and alkoxy and hydroxyl groups can be substituents in the 3-, 7- and 9-positions.

Aonther class of light stable, non-coloring UV absorbers corresponds to the formula



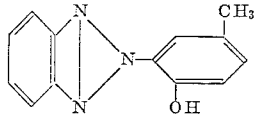
XII

wherein the phenyl rings can be substituted by chlorine, alkyl and alkoxy groups.

Further details are given in the following non-limitative examples which illustrate the second aspect of the invention. Parts and percentages are given therein by weight and the temperatures are in degrees centigrade.

Example 32

(a) The surface of a cellulose-2½-acetate film having a 52% acetic acid content (calculated on the weight of the cellulose acetate) is saponified for 4 minutes at 65° with a solution which, per litre of water, contains 17 g. of sodium hydroxide 100%, 2 g. of luaryl alcohol sulphate and 2.5 g. of the compound



The film is then rinsed with cold, softened water, treated for 2 minutes at 35° with a solution of 5 ml./litre of formic acid, again rinsed and dried in a stream of 60–70° warm air.

In a darkened room with a yellow light, the film is then passed through a coating device which, by a rubber roller rotating in the diazo solution, applies a solution of 50 g. of 4-diazo-2-ethoxydiphenylamine which is free of nitrogen oxides, 25 g. of thiourea, 5 g. of stearyl polyglycol ether (with 20 ethyleneoxy groups) and 5 g. of acetic acid per litre of water.

The film is immediately dried with 30° warm air and packed while excluding light.

This film is well suited for copying positive ciné films in a usual copying machine with a mercury vapour or xenon lamp.

After exposure, the film is continuously developed for 5 seconds at 90° in a solution which contains, per litre of water,

20 g. of prim. potassium phosphate,
20 g. of sodium formate,
3 g. of phloroglucinol,
1.2 g. of resorcinol
0.75 g. of β-naphthol, previously dissolved in 10 ml. of ethanol,
5 g. of sodium hydroxide 100%.

The film treated with the coupling component is then rinsed cold and dried.

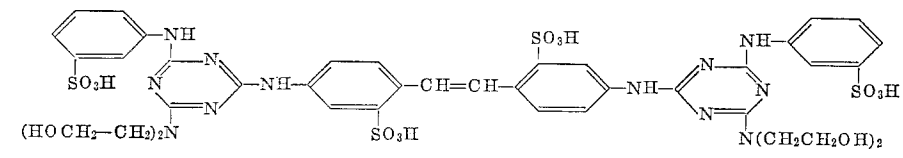
Positive copies having well graded half tones and a maximal black density of 2.3 are obtained.

Similar results are obtained if, in this example with otherwise the same procedure, the same amount of the following compounds are used:

(b) 2-(2'-hydroxy-3',5'-dimethylphenyl)-benzotriazole,
(c) 2-(2'-hydroxy-3'-methyl-5'-tert. butylphenyl-benzotriazole,
(d) 2-(2'-hydroxy-3'-tert. butyl-5'-methylphenyl-benzotriazole,
(e) 2-(2'-hydroxy-4',5'-dimethylphenyl)-1,2,3-benzotriazole,
(f) 2-(2'-hydroxy-5'-methylphenyl)-5-methyl-benzotriazole,
(g) 2-(2'-hydroxy-3',5'-dimethylphenyl)-5-methylbenzotriazole,
(h) 2-(2'-hydroxy-3'-methyl-5'-tert. amylphenyl)-5-methyl-benzotriazole,
(i) 2-(2'-hydroxy-3'-tert. amyl-5'-methylphenyl)-5-methyl-benzotriazole,
(j) 2-(2'-hydroxy-4',5'-dimethylphenyl)-5-methylbenzotriazole,
(k) 2-(2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole,
(l) 2-(2'-hydroxy-5'-methylphenyl)-5-fluorobenzotriazole,
(m) 2-(2'-hydroxy-5'-methylphenyl)-5-trifluoromethylbenzotriazole,
(n) 2-(2'-hydroxy-5'-methylphenyl)-5-sulphonic acid dimethylamide benzotriazole,
(o) 2-(2'-hydroxy-5'-methylphenyl)-5-methylsulphonyl benzotriazole,
(p) 2-(2'-hydroxy-5'-methylphenyl)-5-benzoylaminobenzotriazole,
(q) 2-(2'-hydroxy-5'-methoxyphenyl)-benzotriazole,
(r) 2-(2'-hydroxy-5'-ethoxyphenyl)-benzotriazole,
(s) 2-(2'-hydroxy-4'-β-hydroxyethoxy-phenyl)-benzotriazole,
(t) 2-(2'-hydroxy-5'-chlorophenyl)-benzotriazole,
(u) 2-(2'-hydroxy-5'-methylphenyl)-5-carboethoxybenzotriazole,
(v) 2-(2'-hydroxy-5'-tert. butylphenyl)-5-methylsulphonyl-benzotriazole.

Example 33

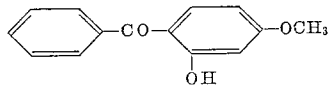
A cellulose-2½-acetate film is passed, in a continuous apparatus, through a saponification liquor of the same composition as that in Example 32 but which, in addition to 2.5 parts of 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, also contains 1.5 g. of the UV-absorber of the formula



Afterwards, the film is finished in the same way as described in Example 32. A diazotype film having similar properties is obtained. Instead of the 2-(2'-hydroxyphenyl)-benzotriazole compound mentioned above, one of the other compounds listed in Example 32 can be used.

Example 34

(a) A cellulose acetate film is continuously saponified at 70° in a solution of the composition described in Example 32 but which, instead of the benzotriazole compound, contains 2 g. of the following compound



On emergence of the film from the saponification bath it is squeezed out and, without rinsing, passed through a second tank containing a 50° warm solution of 20 ml./litre of formic acid. Afterwards, the film is thoroughly rinsed with cold water, dried and, as described in Example 32 treated with a light-sensitive diazonium compound.

A diazotype film is obtained which, on exposure and coupling, satisfactorily reproduces the half tones of the subject.

(b) Similar results are obtained if, in this example, the 4-methoxy-2-hydroxy-benzophenone is replaced by the corresponding amount of 2-hydroxybenzophenone or 4-ethoxy-2-hydroxybenzophenone.

We claim:

1. A diazotype photographic positive copy film, comprising

(a) a film base consisting essentially of cellulose alkanoate,

(b) a top layer on and substantially integral with said film base which top layer consists in its major portion of partially hydrolyzed cellulose acetate and has a thickness of from about 5 to 10 microns and contains in fine dispersion therein

(i) a cationic light-sensitive aryl diazonium compound suitable as diazotype developable component, and

(ii) an anionic, cellulose hydrate-substantive, non-color-imparting greenish-blue to violet fluorescing compound selected from the group consisting of the sulfonated stilbenes, sulfonated dehydrothiotoluidines, sulfonated diphenyls and sulfonated dibenzyls which are capable of decreasing the contarst of the said aryl diazonium compound sufficiently to adjust the photographic gamma of said film material closer to 1, and have a maximum light-absorptivity in the ultraviolet range between about 300 and 390 millimicrons.

2. A diazotype photographic positive copy film as defined in claim 1, wherein, component (i) is present in amounts ranging from about 0.02 to 0.2 grams per square meter, and component (ii) is present in amounts ranging from about 0.2 to 3 grams per square meter, of film surface.

3. A diazotype photographic film as defined in claim 1, wherein the film base consists essentially of cellulose 2½-acetate.

4. A diazotype photographic film as defined in claim 1, wherein the film base consists essentially of a member selected from the group consisting of cellulose di-acetate, cellulose tri-acetate, cellulose 2½-acetate, cellulose propionate, cellulose butyrate, cellulose nitrate and mixed cellulose lower alkanoates.

5. A diazotype photographic film as defined in claim 1, wherein the weight ratio of said diazonium compound to said light filtering agent is in the range of about 1:10 to 1:15.

6. A diazotype photographic positive copy film as defined in claim 1, wherein said fluorescing compound (ii) is a sulfonated stilbene possessing, per molecule, from one to not more than two stilbene nuclei and from one to not more than two s-triazinyl-(2)-amino radicals linked to the stilbene nucleus via said amino grouping, the 4-position of which s-triazinyl grouping is occupied by a mononuclear carbocyclic arylamino substituent and the 6-position of which s-triazinyl ring is free from aryl-containing substituents.

7. A diazotype photographic positive copy film as defined in claim 1, wherein said fluorescing compound (ii) is a sulfonated stilbene possessing, per molecule, from one to not more than two stilbene nuclei and from one to not more than two s-triazinyl-(2)-amino radicals linked to the stilbene nucleus via said amino grouping, at least one of the positions 4 and 6 of which s-triazinyl grouping is occupied by a mononuclear carbocyclic arylamino substituent.

References Cited

UNITED STATES PATENTS

2,027,688	1/1936	Hagedorn	96—87 X
2,333,809	11/1943	Nadeau et al.	96—84
2,591,309	4/1952	Slifkin et al.	96—75
2,685,511	8/1954	Nadeau et al.	96—75
2,700,043	1/1955	Baum et al.	96—82 X
2,713,055	7/1955	Baum et al.	96—82 X
2,792,303	5/1957	Sanders et al.	96—75 X
2,893,866	7/1959	Haefeli	96—87 X
2,933,390	4/1960	McFall et al.	96—84
2,976,259	3/1961	Hardy	96—84 X
3,008,995	3/1961	Hoeschele et al.	96—84 X
3,069,268	12/1962	Herrick	96—75 X
3,072,585	1/1963	Milionis et al.	96—84 X
3,127,270	3/1964	Wilson	96—82 X
2,245,628	6/1941	Von Poser et al.	96—47

FOREIGN PATENTS

12,084	7/1963	Japan.
492,795	9/1938	Great Britain.
910,038	11/1962	Great Britain.

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