

[54] **PHYSICALLY DEVELOPABLE COPY
MEDIUM WITH PHOTOCONDUCTORS AND
COMPLEXING AGENT**

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96/95 R**

[56] **References Cited**

UNITED STATES PATENTS

3,645,736 2/1972 Mowat 96/48 PD
3,647,439 2/1972 Bass 96/48 PD

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[57] **ABSTRACT**

This invention relates to a copy medium capable of transmitting ultraviolet radiation comprising a photo-

sensitive layer having a photoconductive material such as titanium dioxide and certain complexing agents incorporated in a binder. The photosensitive material, upon exposure to activating radiation in an image pattern, becomes reversibly activated in the image pattern. The reversibly activated portions are then capable of causing a chemical reaction which permits development and formation of an irreversible image by physical development such as by contact with a chemical redox system, an aqueous solution of silver nitrate and a suitable photographic reducing agent being an example thereof. The copy medium of the invention is characterized by having a photosensitive layer of reduced photoconductor coat weight without the expected decrease in sensitometric characteristics such as reduced image optical density. The reduced coat weight of photoconductor is made possible by the addition of the complexing agent to the photosensitive material. A copy medium having a photosensitive layer of reduced photoconductor coat weight is an advantage as it permits more efficient use of the copy medium for various applications such as use as a diazo master wherein the medium must transmit radiation which is absorbed by the photoconductor e.g., ultraviolet radiation. Another advantage of reduced photoconductor coat weight is reduced manufacturing costs as a result of more efficient use of photoconductor and associated spectral sensitizing dyes.

46 Claims, No Drawings

PHYSICALLY DEVELOPABLE COPY MEDIUM WITH PHOTOCONDUCTORS AND COMPLEXING AGENT

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a reversibly activatable copy medium having a photosensitive layer characterized by a reduced photoconductor coat weight.

2. Description of the Prior Art

In U.S. Pat. No. 3,380,823, there is disclosed a photographic system wherein a photosensitive material is exposed to an image to be recorded and there is formed a latent image which can be subsequently made visible by treatment with a developing material. The photosensitive material generally is a pigment such as titanium dioxide, zinc oxide, or other photoresponsive material coated onto a suitable substrate in a binder. After the material has been exposed to an image, it is developed with a physical developer comprising first contact with an ion-containing, image-forming material such as a silver salt solution followed by contact with a solution of a suitable reducing agent such as a photographic reducing agent to form a visible, developed image.

The aforesaid copy medium is useful for a variety of purposes such as data storage, lithographic masters and the like. For such use, the diazo master must be translucent and transmit ultraviolet radiation. It cannot be opaque. A difficulty with the use of the copy medium of the above referenced patent is that the photosensitive material, to provide an image of satisfactory optical density, must be used in relatively heavy coat weights, e.g., typically 5 to 10 grams per square meter. With these relatively high coat weights, and due to the nature of the materials employed, e.g., titanium dioxide, the photosensitive layer is relatively opaque to radiation which decomposes diazonium compounds and therefore unsuitable for use as a diazo master.

Attempts have been made in the prior art to make a thin, visibly transparent layer of a photosensitive material from radiation-sensitive titanium dioxide. Such a transparent layer is disclosed in U.S. Pat. No. 3,409,429 incorporated herein by reference. In this patent, there is disclosed a radiation-sensitive titanium dioxide surface suitable for the production of photographic images formed by heating a titanium containing surface in an oxidizing atmosphere at a temperature between about 400°C and about 900°C. The titanium containing surface is a film of a titanium compound selected from the group of hydrolyzable titanium esters and polymers thereof. In accordance with the patent, a photographic transparency is prepared by exposing a transparent copy medium comprising a transparent substrate having a coating of the thin transparent radiation-sensitive film of titanium dioxide to a pattern of activating radiation, thereby rendering the titanium dioxide chemically reactive in the portions corresponding to the image pattern of radiation, and then developing the chemically reactive portions of the titanium dioxide by contact of at least the reactive portions with image forming materials to form an irreversible image corresponding to the image pattern. The photographic transparency at this stage comprises a visibly transparent substrate having a coating of a transparent film consisting essentially of titanium dioxide and including

portions of different optical densities defining an image pattern.

The method described in U.S. Pat. No. 3,409,429 provides a visibly transparent, image-bearing print useful for many applications. However, it cannot be formed on paper because of the high temperatures required which would cause decomposition of a paper substrate. Instead, a thin metal support is used. Such a thin, visibly transparent copy medium would not be suitable for use as a diazo master such as the copy medium of the subject invention described in greater detail below. For example, where a metal support is used, the copy medium would only be poorly transparent to ultraviolet radiation as is required for diazo copying. Also, diazo masters are generated in rapid access recording devices which devices typically use physical developers comprising two separate stable solutions, one being the metal ion solution and the other being the photographic developer. The copy medium of Pat. No. 3,409,429 must be developed by a unitary physical developer in order to obtain images of adequate optical density, e.g., 1.2 reflection optical density. Consequently, such a copy medium would not be suitable for a rapid access recording device.

In co-pending U.S. Pat. application Ser. No. 76,279 filed Sept. 28, 1970, now U.S. Pat. No. 3,700,437, there is provided a photographic imaging medium comprising a transparent support, a pellucid film of a particulate photosensitive semi-conductor thereon, preferably having a thickness of about ½ mil or less and a transparent film over said pellucid film to decrease light diffraction thereon. The semi-conductor preferably has an average particle size of about 300μ or less in diameter and preferably is present on the imaging medium in an amount per unit area of about 3 grams per square meter, (g/m²) or less. The transparent coating over the pellucid film of the particulate semi-conductor decreases the diffraction of light at the surface of the imaging medium thereby increasing its transparency.

The transparent imaging medium described above also would not be suitable for use as a diazo copy medium as contemplated with the copy medium to be described in greater detail below because of the low concentration of semi-conductor material. Hence, with such a copy medium, the density of the developed image would not be sufficient because for use as a diazo master, good image density is required-e.g., 1.2 reflection optical density.

As will be described in detail below, a translucent copy medium having desirable sensitometric and spectral transmission properties suitable for use as a diazo master is provided by the invention described herein by a photosensitive layer of a photo-sensitive material and one or more of certain complexing agents dispersed in a binder which photosensitive layer has a reduced coat weight of photosensitive material.

The addition of various complexing agents to certain pigments to avoid discoloration is not new in the art and such addition to a titanium dioxide pigment is described in U.S. Pat. No. 3,390,961. According to this patent, complexing agents are added to increase color stability of the titanium dioxide. It is disclosed in said patent that metal impurities such as iron and copper and occasionally manganese and chromium are associated with the titanium dioxide and they tend to precipitate on its surface discoloring the same. In accor-

dance with the patent, this discoloration is avoided by the addition of complexing agents to an aqueous slurry of the titanium dioxide during manufacture. The complexing agents are selected so as to form soluble complexes with the metal ion impurities thus preventing their precipitation on the surface of the pigment. The pigment grade titanium dioxide disclosed in said patent is formulated primarily for use in metal coating enamels rather than for the formation of copy media of the type described herein.

The addition of various amines to photographic systems comprising a photoconductor to increase sensitivity to activating radiation, is taught in co-pending U.S. Pat. application Ser. No. 251,671, filed May 9, 1972, in the name of Samuel Stein, and entitled, "Photoconductor Copy Medium of Improved Response and Processes Using This Medium." The amine compounds used in said application are those that do not normally act to reduce reducible metal ions.

SUMMARY OF THE INVENTION

The subject invention provides a copy medium containing less photoconductor per unit area than is normally permissible which copy medium is thus capable of transmitting ultraviolet radiation while providing an image having excellent sensitometric and spectral transmission properties including good optical image density. The copy medium is thus well suited for use as a diazo master. One potential use is a master for use in copy processes. For example, the imaged medium of this process is translucent enough to be utilized for contact printing with a second photosensitive copy medium such as a diazo copy medium, i.e., contacted with the second medium and exposed to activating radiation for the second medium. The imaged medium is also opaque enough to be exposed by a reflection exposure onto the second copy medium, such as a silver halide copy medium. It is also possible to make corrections on the imaged copy medium of this invention prior to using it to expose a second copy medium. Corrections such as additions and deletions are very easily made on the preferred titanium dioxide medium because of the good properties for use for writing on with a pen or pencil and also the fact that the titanium dioxide remaining in the copy medium can be dark adapted and reused for its photosensitive properties as disclosed in U.S. Pat. No. 3,390,989, incorporated herein by reference.

According to the invention, the copy medium comprises a photosensitive layer having a photosensitive material such as titanium dioxide and a complexing agent such as ethylenediamine-tetraacetic acid or triethanolamine incorporated in a binder which photosensitive material, upon exposure to activating radiation in an image pattern, becomes reversibly activated in said image pattern. The reversibly-activated pattern is capable of causing a chemical reaction which permits development or formation of irreversible images by contact with a physical developer such as a chemical redox system exemplified by an aqueous solution of silver nitrate and a photographic reducing agent therefor.

The photosensitive layer is made translucent to ultraviolet radiation by decreasing the coat weight of the photosensitive material. Thus, where the coat weight in the prior art is typically 5 to 10 grams per square meter, for the copy medium described herein, the coat weight

preferably does not exceed 4 grams per meter and preferably is within the range of 1 to 3 grams per square meter.

It would be expected that a reduced coat weight would result in a developed image of poor optical density (in the absence of prolonged development) and this does in fact happen in the absence of the aforesaid complexing agent. However it is an unexpected discovery of this invention that the coat weight can be reduced to the extent described above without loss of image optical density when the complexing agent is substituted in part for the photosensitive material which is omitted.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The copy medium of this invention comprises a substrate having a photosensitive layer thereover comprising a photosensitive material and a suitable complexing agent dispersed in a binder, said photosensitive layer having a coat weight not exceeding 4 grams of photosensitive material per square meter.

The photosensitive material suitable for formation of the photosensitive layer is preferably a photoconductor which becomes activated upon exposure to activating radiation and is thereby capable of causing a chemical reaction in the exposed area. The preferred photoconductors are the metal containing photoconductors such as compounds of a metal and a non-metallic element of Group VIA of the Periodic Table such as oxides, including zinc oxide, titanium dioxide, zirconium dioxide, germanium dioxide, indium trioxide, and tin oxide; metal sulfides such as cadmium sulfide, zinc sulfide, and tin disulfide; and metal selenides such as cadmium selenide. Metal oxides are the preferred photoconductors of this Group and titanium dioxide is the preferred metal oxide because of unexpectedly good results. Titanium dioxide having an average particle size less than about 250 millimicrons and which has been treated in an oxidizing atmosphere at a temperature between about 200°C and 950°C for from about 0.5 hours to about 30 hours is especially preferred, more especially, that titanium dioxide produced by the high temperature pyrolysis of a titanium halide.

Also useful as photosensitive material are the metal halides. Such materials include the silver halides, such as silver chloride, silver bromide, silver chlorobromide, silver chlorobromiodide, etc., thallous halides, and mercurous halides.

Also useful in this invention as photoconductors are certain fluorescent materials. Such materials include, for example, compounds such as silver activated zinc sulfide, zinc activated zinc sulfide, zinc activated zinc oxide, manganese activated zinc phosphate, an admixture of copper sulfide, antimony sulfide and magnesium oxide, and cadmium borate.

While the exact mechanism by which the photoconductors work is not known, it is believed that exposure of photoconductors or photocatalysts to activating means causes an electron or electrons to be transferred from the valence band of the photoconductor or photocatalyst to the conductance band of the same or at least to some similar excited state whereby the electron is loosely held, thereby changing the photoconductor from an inactive form to an active form. If the active form of the photoconductor is in the presence of an electron accepting compound, a transfer of electrons will

take place between the photoconductor and the electron accepting compound, thereby reducing the electron accepting compound. Therefore a simple test which may be used to determine whether or not materials have a photoconductor or photocatalytic effect is to mix the material in question with an aqueous solution of silver nitrate. Little, if any, reaction should take place in the absence of light. The mixture is then subjected to light. At the same time a control sample of an aqueous solution of silver nitrate alone is subjected to light, such as ultraviolet light. If the mixture darkens faster than the silver nitrate alone, that material is a photoconductor.

It is evident that the gap between the valence and the conducting band of a compound determines the energy needed to make electron transitions. The more energy needed, the higher the frequency to which the photoconductor will respond. It is known to the art that it is possible to reduce the band-gap for these compounds by adding a foreign compound as an activator which either by virtue of its atomic dimensions or by possessing a particular electronic forbidden zone structure or through the presence of traps as donor levels in the intermediate zone between the valence and the conduction band stresses the electronic configuration of the photoconductive compound, thereby reducing its band-gap and thus increasing its ability to release electrons to its conduction band. Phosphors almost necessarily imply the presence of such activating substances. The effect of such impurities may be such as to confer photoconductivity upon a compound which intrinsically is non-photoconductive. The (Cr-Sr)S phosphors are believed to be an example of this group. On the other hand, excessive impurity content can interfere with a compound acting as a photoconductor, as above described.

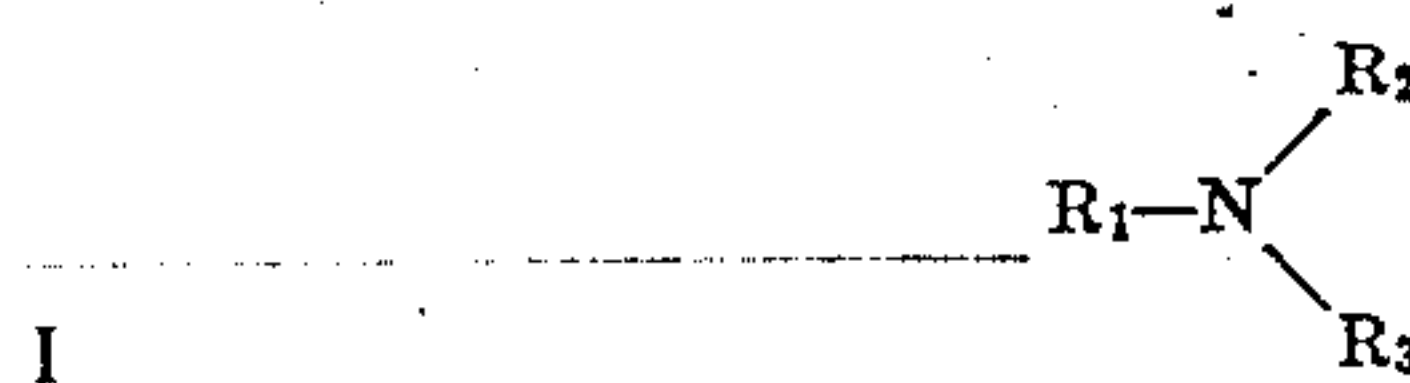
The photoconductors may be sensitized to visible and other wavelengths of light by foreign ion doping, addition of fluorescent materials and/or by means of sensitizing dyes. Bleachable dyes useful for sensitizing photoconductors include, for example, the cyanine dyes, the dicarbocyanine dyes, the carbocyanine dyes, and the hemicyanine dyes. Additional dyes which are useful for sensitizing photoconductors are the cyanine dyes described on pages 371-429 in "The Theory of Photographic Process" by C.E. Kenneth Mees published by McMillan Company in 1952. Other useful dyes include those known to the art as triphenylmethane dyes such as crystal violet and basic Fuchsin, diphenylmethane dyes such as Auroamine O, and Xanthene dyes such as Rhodamine B.

As noted above, the photosensitive layer of the invention has a reduced photoconductor coat weight without loss in sensitometric properties due to the addition of certain complexing agents to the photosensitive layer. The complexing agents suitable for this purpose are believed to be those capable of forming a complex with the metal ion of a physical developer used to develop the image under developing conditions. For example, a typical physical developer would be an aqueous solution of silver nitrate having a pH of about 4.5 followed by a separate developing solution having a pH of about 7. The complexing agent used in the photosensitive layer would then be one capable of forming a complex with silver within the pH range of about 4.5 to about 7. The kinetics of complex formation believed to be such that the complex is formed upon contact of the

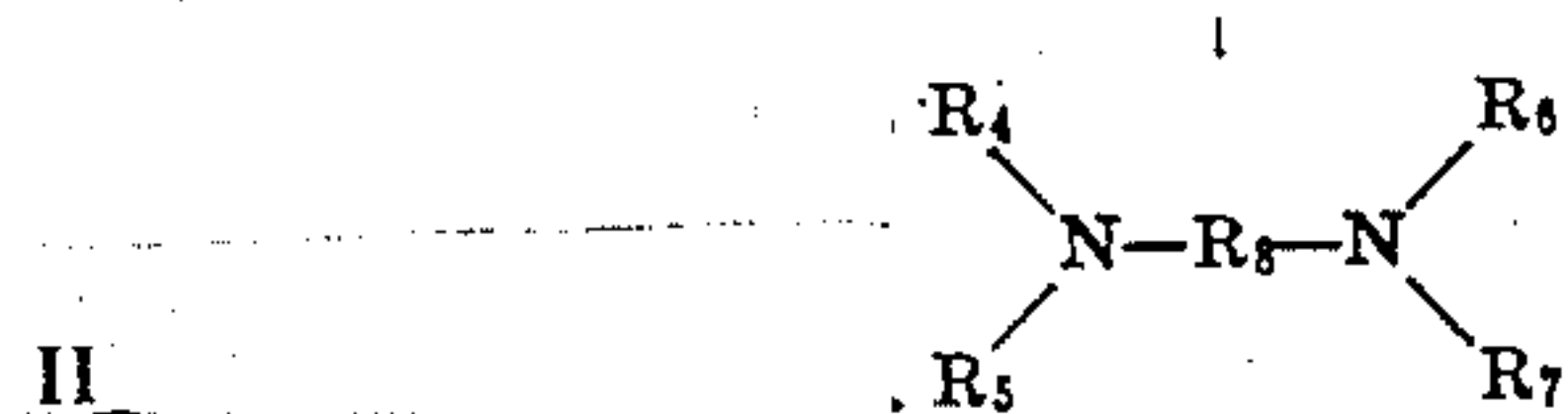
metal ion of the physical developer with the complexing agent.

Though not wishing to be bound by theory, it is believed that the complexing agent holds more of the metal from the first solution of the two solution physical developer in the photosensitive layer than would otherwise be available. Upon subsequent contact with a reducing agent, this additional metal ion is available for reduction to metallic form and hence, an image of enhanced optical density is formed.

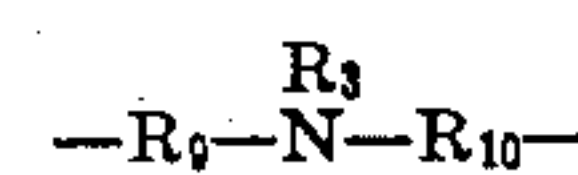
It should be apparent that the complexing agent used is dependent upon the physical developer selected (the metal ion, reducing agent, pH of the solutions and treatment times). From the above discussion, it would be within the ordinary skill of the art to select suitable complexing agents within the above guidelines. However, preferred complexing agents conform to the following structural formulas:



where R_1 and R_2 are selected from the group of carboxylic acid radicals such as $-\text{COOH}$, $-\text{CH}_2\text{COOH}$ and $-\text{C}_2\text{H}_5\text{COOH}$ and their alkali metal or ammonium salts, and alkanol radicals such as $-\text{CH}_2\text{OH}$ and $-\text{C}_2\text{H}_4\text{OH}$, and R_3 is selected from the group of R_1 and R_2 and also hydrogen, alkyl including cycloalkyl such as $-\text{CH}_3$, $-\text{C}_2\text{H}_5$ and C_5H_{11} ; aryl such as benzyl, and alkylene oxide; and



where R_4 , R_5 , R_6 and R_7 are the same as R_3 provided that at least two of R_4 , R_5 , R_6 and R_7 are carboxylic acid radicals or their alkali metal or ammonium salts; and R_8 is selected from the group of alkylene, arylene, alkylene oxide or



where R_3 is as defined above and R_9 and R_{10} are alkylene groups.

Examples of compounds falling within the structural formula identified as I above include triethanolamine, nitrilotriacetic acid, iminodiacetic acid, N-(2-hydroxyethyl)-iminodiacetic acid, nitrilotripropionic acid and the like. Examples of compounds falling within the formula identified as II above are as follows: ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, 1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid, 1,3-diamino-2-hydroxypropane-N,N,N',N'-tetraacetic acid, 1,2-diaminopropane-N,N,N',N'-tetraacetic acid, [ethylenbis(oxyethylenenitrilo)] tetraacetic acid, ethylenediamine-N,N'-diacetic acid, and the alkali metal and ammonium salts thereof.

While the above compounds and their alkali metal and ammonium salts are suitable for purposes of this invention dependent upon the actual physical developer used, in the preferred embodiment of this invention where either silver or copper is used as the metal ion in essentially neutral solution, it has been found that the organic amine complexing agents exemplified by ethylenediaminetetraacetic acid [EDTA] and ni-

triloticacetic acid [NTA] and their alkali metal salts are most beneficial.

The photosensitive material and the complexing agent are coated onto a carrier sheet by use of a binder. Preferably, though the binders may be translucent they are preferably transparent so as not to interfere with the transmission of light therethrough. Preferred binders are organic resins such as butadiene-styrene copolymer, poly(alkylacrylates) such as polymethylmethacrylate, polyamides, polyvinyl acetate, polyvinyl alcohol and polyvinyl pyrrolidone.

The inert carrier sheet upon which the complexing agent and photoconductor are deposited is any suitable backing of sufficient strength and durability to satisfactory serve as a reproduction carrier. Preferred carriers are sufficiently translucent or transparent to ultraviolet radiation to permit use of the copy media as a diazo master. Thus, suitable materials include glass or metal, plastic such as poly-(ethyleneterephthalate) (MYLAR), cellulose acetate, and paper such as wood or rag fiber paper with or without transparentizing resins.

The coat weight of the light sensitive layer is the weight of the light sensitive material in the photosensitive layer over a given area, defined herein in terms of grams per square meter. In the prior art, it was conventional to use from 5 to 10 grams per square meter of a light sensitive material such as titanium dioxide. However, this much titanium dioxide in the photosensitive layer renders the same opaque to ultraviolet radiation and unsuitable for use as a diazo master even when coated on a transparent support such as Mylar. In order to obtain a light sensitive layer sufficiently translucent for use as a diazo master, using titanium dioxide as an example, the coat weight cannot exceed four grams per square meter and preferably, is between 1½ and 3 grams per square meter. Another disadvantage of a high coat weight is the expense due to the high content of the photoconductor such as the titanium dioxide and also, the accompanying high content of expensive spectral sensitivity dyes as required. The dry thickness of this layer preferably does not exceed one-half mil.

As noted above, the sensitometric properties of the light sensitive layer are retained even though the coat weight is reduced by the addition of a complexing agent to the light sensitive layer. The amount of complexing agent is dependent upon many facts such as the specific light sensitive material used, the specific complexing agent used, the specific physical developing system used, and the like. In general, sufficient complexing agent is used to provide an image having a reflection optical D_{max} of at least 1.0 and preferably 1.2. For purposes of a guideline only, this D_{max} value is generally obtained from about 0.1 to 50 percent by weight complexing agent, based upon the weight of light sensitive material in the light sensitive layer, though from 2 to 20 percent by weight complexing agent is preferred. However, it should be apparent that for any specific combination of light sensitive material, physical developer and complexing agent, some minimal testing would be necessary to determine the optimum amount of complexing agent for optimum properties.

The photosensitive material and the complexing agent are dispersed in a binder and coated onto the carrier substrate. The ratio of the photosensitive material and complexing agent to binder in the photosensitive layer is not critical. Preferably, the ratio of photosensitive material and complexing agent to binder varies

from 1 part by weight to about 50 parts by weight per part by weight of binder, and more preferably falls within the range of from about 2 parts by weight to about 6 parts by weight per part by weight of binder.

The manner of imaging and developing the copy medium of this invention is in accordance with prior art procedures. Thus, the copy medium is exposed to a suitable source of irradiation. Irradiation sources which are useful for producing the initial latent image include any activating electromagnetic radiation. Thus, actinic light, x-rays, or gamma rays are effective in exciting the photosensitive or photoconductive material. Beams of electrons and other particles of low mass may be also used in the place of the ordinary forms of electromagnetic radiation for forming an image according to this invention. These various activating means are designated by the term "activating radiation."

After exposure to activating radiation, the copy medium is developed with a two solution physical developer, e.g., a first solution of metal ions and a second solution of a reducing agent therefor. The copy medium contacts the two solutions in sequence. Physical developers useful are image-forming materials which will cause build-up in the exposed areas of the copy medium. Physical developers which are useful are those such as described in U.S. Pat. Nos. 3,152,973 and 3,576,631, incorporated herein by reference. These physical developers include an oxidizing agent and a reducing agent in separate solutions. The oxidizing agent is generally the image-forming component of the image-forming material and is preferably a reducible metal compound. The reducing agent may in certain cases function as the image-forming component of the physical developer. Either organic or inorganic oxidizing agents may be employed as the oxidizing component of the image-forming material. Preferred oxidizing agents comprise the reducible metal ions having at least the oxidizing power of cupric ion and include such metal ions as Ag^+ , Hg^{+2} , Pb^{+4} , Au^{+1} , Au^{+3} , Pt^{+2} , Pt^{+4} , Ni^{+2} , Sn^{+2} , Pb^{+2} , Cu^{+1} , and Cu^{+2} .

The reducing agent component of the physical developers of this invention are inorganic compounds such as the oxalates, formates, and ethylenediaminetetraacetic complexes of metals having variable valence; and organic compounds such as hydroxybenzenes, aminophenols, and aminoanilines. Also, tetracyanoethane and ascorbic acid may be used as reducing agents in this invention. Suitable specific reducing compounds include hydroquinone or derivatives thereof, o- and p-aminophenol, p-methylaminophenol sulfate, p-hydroxyphenyl glycine, o- and p-phenylenediamine, 1-phenyl-3-pyrazolidone, alkali and alkaline earth metal oxalates and formates.

Additionally, the physical developers may contain organic acids or alkali metal salts thereof, which can react with metal ions to form metal complex anions. Further, the developers may contain other ingredients to improve image formation, stability of the developer solution and other properties found to be desirable in this art.

The invention will be better understood by reference to the following examples:

EXAMPLE 1

A paper composed of 100 percent cotton fibers and rendered translucent by impregnation with a resin fol-

lowed by calendaring was coated with an emulsion of the following composition:

Disperant	12 grams
Na ₃ EDTA	78 grams
Titanium dioxide	784 grams
Dye sensitizer	9 grams
polyvinyl alcohol	216 grams
water	3900 grams

The pH is adjusted to 7.0 with nitric acid.

The above formulation on a dry weight basis has a photosensitive layer containing 10 percent Na₃EDTA based on titanium dioxide. The weight ratio of titanium dioxide and Na₃EDTA together to polyvinyl alcohol ratio was 4:1. The coat weight was 3 grams of titanium dioxide per square meter of paper.

The so prepared copy medium was exposed and processed in an automatic machine through which the paper is conveyed by pairs of rotating rollers. The velocity of the paper during processing is about 22 feet per minute. The processor is divided into three compartments. In the first compartment there is an activating solution containing silver nitrate which is applied to the paper and removed by a pair of squeegee rollers, of which the lower roller is partially submerged in the activator solution. The second compartment contains two pairs of squeegee rollers which apply and remove a de-

veloping solution. The activating and developing solutions together comprise a physical developer. The third compartment contains a stabilizing solution. Wire guides cause the paper to become momentarily submerged in this stabilizing solution and a pair of squee-

gee rollers wring excess stabilizing solution from the print as it exits the processor. The effective dwell times in the activating, developing and stabilizing compartments of the processor are typically 0.25, 0.7 and 0.9 second, respectively and in all cases, less than a total of

5 seconds.

Using the apparatus described above, the copy medium was exposed to a 500 watt tungsten bulb and de-

veloped in the processor. The activating solution was a 0.33 normal silver nitrate solution having a pH of about 4.6. The developing solution was a Metol solution having a pH of about 7. The stabilizing solution was a thio-sulfate ion solution. The developed image had a reflection D_{max} of about 1.12 and contained 0.16 grams of silver per square meter.

EXAMPLE 2

The procedure of Example 1 was repeated, but the Na₃EDTA was omitted and titanium dioxide content increased to 862 grams. In this way, the solids content in the photosensitive layer was maintained at 862 grams and the ratio of pigment to binder was maintained at 4:1. After coating, the titanium dioxide coat weight was 3 grams per square meter. Following development as in Example 1, D_{max} , was found to be 1.03 and silver content was reduced to about 0.13 grams per square meter.

EXAMPLE 3

The procedure of Example 1 was repeated with variation in the Na₃EDTA content. The sum of the titanium dioxide and Na₃EDTA contents was maintained at 862 grams and the final pH was maintained at 7.0. The results obtained are as follows:

Sample	wt. Na ₃ EDTA/ wt. TiO ₂ ×100	Coat Weight gTiO ₂ /m ²	D_{max}	% Change from control D_{max}
A	control	3.0	1.03	—
B	0.1	3.1	1.05	+2
C	1.0	2.9	1.05	+2
D	10.0	3.0	1.12	+9
E	control	2.2	0.95	—
F	20.0	2.2	1.12	+18
G	20.0	1.4	0.97	+2

EXAMPLE 4

The procedure of Example 3 was repeated substituting trisodium nitrilotriacetic acid (Na₃NTA) for EDTA. The results obtained are as follows:

Sample	wt. Na ₃ NTA/ wt. TiO ₂ ×100	Coat Weight gTiO ₂ /m ²	D_{max}	% Change from control D_{max}
A	control	2.5	.88	—
B	0.1	2.5	.94	+7
C	1.0	2.6	.94	+7
D	10.0	2.8	1.00	+15

EXAMPLE 5

The procedure of Example 3 was repeated substituting triethanolamine (TEA) for the EDTA. The results obtained are as follows:

Sample	wt. TEA/ wt. TiO ₂ ×100	Coat Weight gTiO ₂ /m ²	D_{max}	% Change from Control D_{max}
A	control	3.5	1.05	—
B	0.1	3.4	1.03	-2
C	1.0	3.2	1.03	-2
D	10.0	3.1	1.10	+5

From the above, it can be seen that useful results were obtained when the content of the complexing agent was as low as 0.1 percent that of the TiO₂.

In all of the above examples, the copy medium so formed was sufficiently translucent to permit its use as a diazo master.

EXAMPLE 6

The emulsion of Example 1 was prepared both with and without the EDTA, and both variants were coated onto the paper substrate described in Example 1 at a wide range of coat weights. The papers were then exposed and processed as described in Example 1. The results obtained were as follows:

Coat Weight grams TiO ₂ per. sq. m.	Reflection D _{max} without EDTA	Reflection Dmax with 10 Wt% EDTA
1.0	0.80	0.85
1.3	0.82	0.96
1.5	0.84	1.00
2.0	0.91	1.09
2.5	0.96	1.14
3.0	0.99	1.17
4.0	1.06	1.2+
5.0	1.14	1.2+

EXAMPLE 7

The procedure of Example 6 was repeated except that the EDTA content of the emulsion containing EDTA was 20 weight percent of the titanium dioxide. The results obtained were as follows:

Coat Weight grams TiO ₂ per sq. meter	Reflection D _{max} without EDTA	Reflection D _{max} with 20 wt.% EDTA
1.0	0.80	1.07
1.3	0.82	1.10
1.5	0.84	1.13
2.0	0.91	1.16
2.5	0.96	1.18
4.5	1.10	1.2+

These results show that a coat weight of 4.5 grams per square meter is required to obtain a D_{max} of 1.10 in the absence of EDTA, but only 1.3 grams per square meter with 20 weight percent EDTA. The EDTA permitted a reduction in coat weight of 71 percent. When the two samples having D_{max} of 1.10 were used as masters for making diazo prints, both provided diazo prints of equal quality, but the diazo print could be run 65 percent faster when the sample containing EDTA was used as a printing master.

Similar results to those achieved above were obtained when the ratio of the weight of titanium dioxide and complexing agent to the weight of the binder is 6 to 1.

EXAMPLE 8

Two emulsions were prepared, both identical except that one contained 20 grams of trisodium EDTA per 100 grams of titanium dioxide, while the other emulsion contained no EDTA. The pH of both emulsions was adjusted to 7.0. Both emulsions were coated onto an opaque paper, having a basis weight of 61 pounds per 3,300 square feet, at a variety of coat weights. After exposure and processing as described in Example 1, the maximum image optical density was measured with a Macbeth RD-100 reflection densitometer. The results obtained were as follows:

Coat Weight grams TiO ₂ per sq. meter ²	without EDTA	D _{max} with EDTA
3.0	0.91	1.19
6.0	1.09	—

Thus, addition of EDTA resulted in a higher D_{max} at half the coat weight. The reduction in coat weight halved the cost of the coating.

EXAMPLE 9

An emulsion was made with the following formulations:

TiO ₂	175 g
TiO ₂ Dispersant	10 g
Na ₂ EDTA.2H ₂ O	7.3 g
Na ₃ EDTA.H ₂ O	20.7 g
Spectral Sensitizing dye	1 g
Polyvinyl alcohol	50 g
water	801 g

No pH adjustment was required.

A coating was applied on the substrate described in Example 1 with a coat weight of 2.1 gTiO₂/m². Processing was performed as in Example 1 and resulted in a D_{max} of 1.16.

EXAMPLE 10

An emulsion described in Example 9 was coated on a matte-surfaced, 4 mil thick polyester film with a coat weight of 3.3 g TiO₂/m². Processing was performed as in example 1 and resulted in an image with a D_{max} of 1.18 and neutral image color. A similar coating with the same coat weight, but without the EDTA complexing agent resulted in an image with a D_{max} of 0.95 and a brownish image color.

I claim:

1. A copy medium that transmits ultraviolet radiation comprising a support and a photosensitive layer on said support, said photosensitive layer comprising an inorganic photosensitive photoconductor material and a complexing agent able to complex a reducible metal ion contained in a physical developer composition used to develop said copy medium to thereby produce an image having an enhanced photographic density in the thus physically developed copy medium said photosensitive layer having a coat weight of the photosensitive photoconductor material not exceeding 4 grams per square meter of the support.

2. The copy medium of claim 1 where the photosensitive photoconductor material is a silver halide.

3. The copy medium of claim 1 wherein said photosensitive photoconductor material is a metal oxide of a Group VIA metal.

4. The copy medium of claim 3 where said photosensitive photoconductor material is titanium dioxide.

5. The copy medium of claim 4 where said titanium dioxide and complexing agent are dispersed in a binder.

6. The copy medium of claim 5 where the ratio of titanium dioxide and complexing agent to binder varies

between 1 part titanium dioxide and complexing agent to 1 part binder to 50 parts titanium dioxide and complexing agent to 1 part binder.

7. The copy medium of claim 5 where the ratio of titanium dioxide and complexing agent to binder varies between about 2 parts titanium dioxide and complexing agent to 1 part binder and 12 parts titanium dioxide and complexing agent to 1 part binder.

8. The copy medium of claim 5 where the ratio of titanium dioxide and complexing agent to binder is about 6:1.

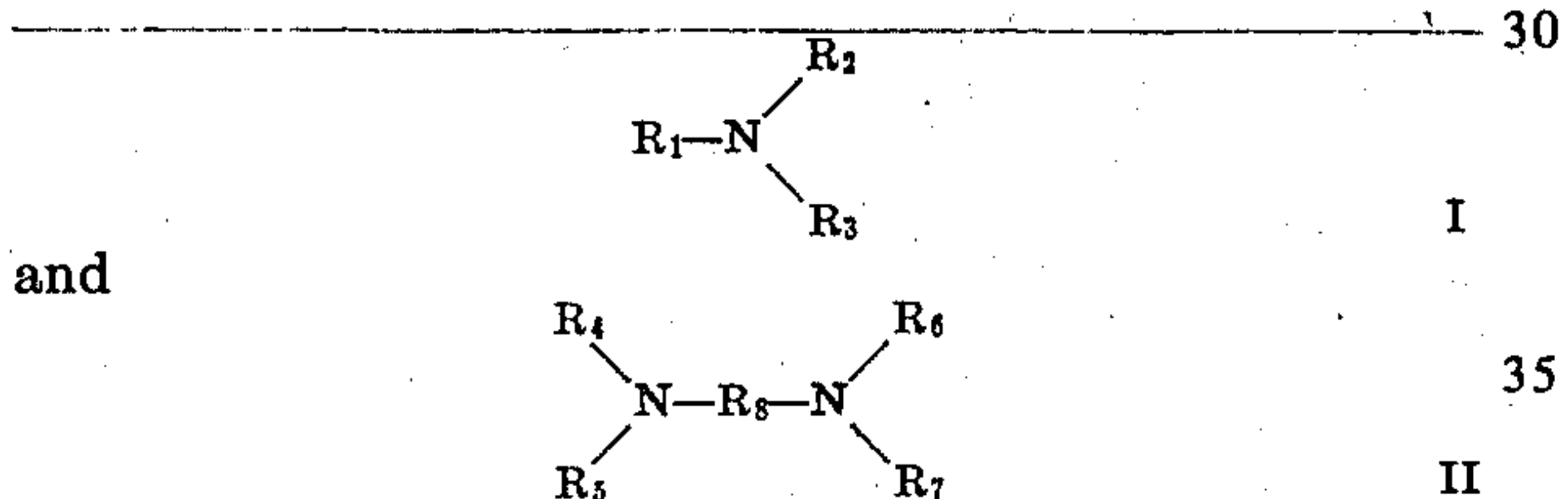
9. The copy medium of claim 5 where the photosensitive layer has a dry thickness not exceeding one-half mil.

10. The copy medium of claim 4 where the coat weight of titanium dioxide in the photosensitive layer varies between 1½ and 3 grams per square meter of support.

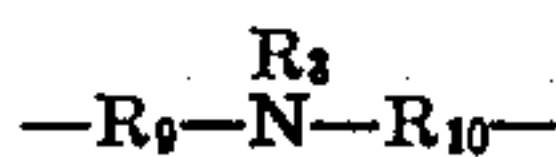
11. The copy medium of claim 4 where the complexing agent comprises from 1 to 50 percent by weight of the total of the titanium dioxide and the complexing agent.

12. The copy medium of claim 11 where the complexing agent comprises from 2 to 30 percent by weight of the total of the titanium dioxide and complexing agent.

13. The copy medium of claim 12 where the complexing agent is selected from the group of



where R_1 and R_2 are selected from the group of carboxylic acid radicals and their alkali metal and ammonium salts, and alkanol radicals; R_3 is selected from the group of R_1 and R_2 , and also, hydrogen, alkyl including cycloalkyl, aryl and alkylene oxide; R_4 , R_5 , R_6 and R_7 are the same as R_3 provided that at least two of R_4 , R_5 , R_6 and R_7 are carboxylic acid radicals or their alkali metal or ammonium salts; and R_8 is selected from the group of alkylene, arylene, alkylene oxide,



where R_3 is as defined above and R_9 and R_{10} are alkylene groups.

14. The copy medium of claim 13 where the complexing agent conforms to formula I and is selected from the group of triethanolamine, nitrilotriacetic acid, iminodiacetic acid, N-(2-hydroxyethyl)-iminodiacetic acid, nitrilotripropionic acid and the alkali metal and ammonium salts.

15. The copy medium of claim 13 where the complexing agent conforms to formula II and is selected from the group of ethylenediaminetetraacetic acid, diethylenetriaminopentaacetic acid, 1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid, 1,3-diamino-2-hydroxypropane-N,N,N',N'-tetraacetic acid, 1,2-diamino-propane-N,N,N',N'-tetraacetic acid, [ethylenebis(oxyethylene-nitrilo)] tetraacetic acid, ethylenediamine-N,N'-diacetic acid, and the alkali metal and ammonium salts thereof.

16. The copy medium of claim 13 where the complexing agent is selected from the group of ethylenediaminetetraacetic acid and nitrilotriacetic acid and their alkali metal and ammonium salt.

17. The copy medium of claim 13 where the complexing agent is ethylenediaminetetraacetic acid or its alkali metal or ammonium salts.

18. The copy medium of claim 13 where the complexing agent is nitrilotriacetic acid or its alkali or metal ammonium salts.

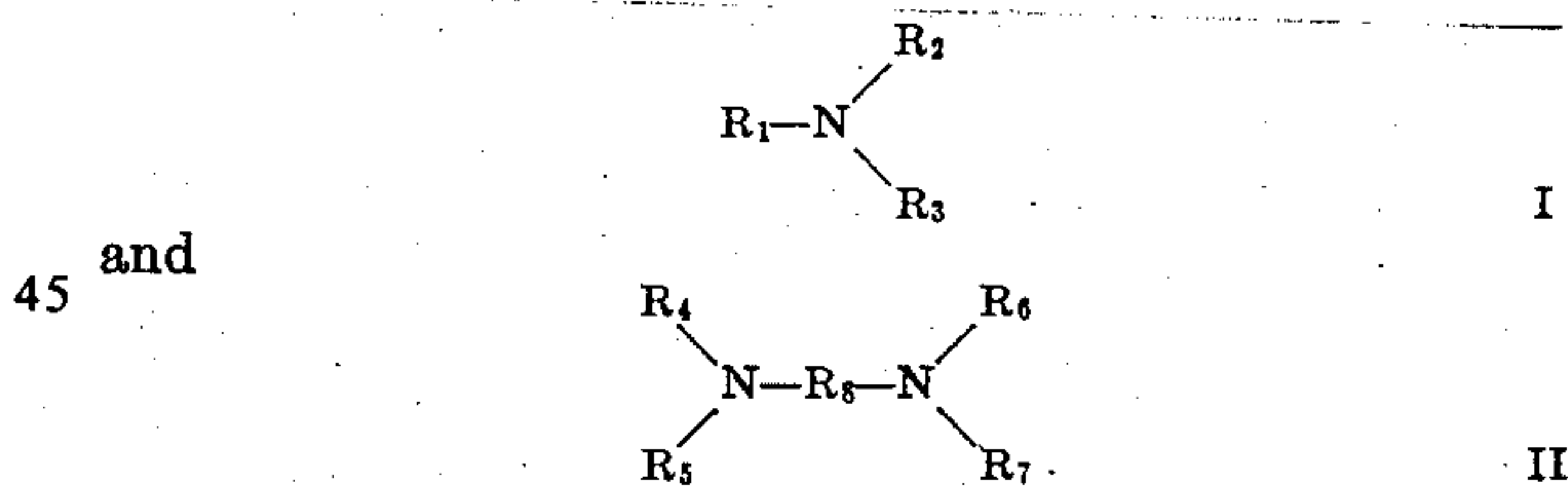
19. A copy medium capable of transmitting ultraviolet radiation comprising a transparent or translucent support and a photosensitive layer, said photosensitive layer comprising titanium dioxide and a complexing agent for silver dispersed in a translucent or transparent binder, said complexing agent comprising from 1 to 50 percent by weight of the total of said titanium dioxide and said complexing agent, the ratio of said titanium dioxide and complexing agent to said binder being between 2 parts titanium dioxide and complexing agent per part binder and 12 parts by weight titanium dioxide and complexing agent per part binder, the coat weight of said titanium oxide over said support not exceeding about 4 grams per square meter of said support.

20. The copy medium of claim 19 where said complexing agent comprises 2 to 30 percent by weight of the total of said titanium dioxide and complexing agent.

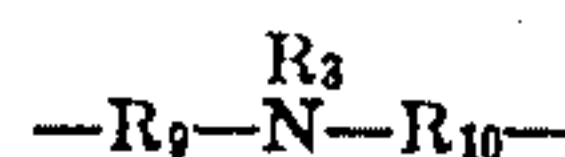
21. The copy medium of claim 19 where the ratio of said titanium dioxide and complexing agent to said binder is about 6 parts titanium dioxide and complexing agent per 1 part of binder.

22. The copy medium of claim 19 where the coat weight of said titanium dioxide over said support varies between 1½ and 3 grams per square meter.

23. The copy medium of claim 19 where the complexing agent is selected from the group of



where R_1 and R_2 are selected from the group of carboxylic acid radicals and their alkali metal and ammonium salts, and alkanol radicals; R_3 is selected from the group of R_1 and R_2 , and also, hydrogen, alkyl including cycloalkyl, aryl and alkylene oxide; R_4 , R_5 , R_6 and R_7 are the same as R_3 provided that at least two of R_4 , R_5 , R_6 and R_7 are carboxylic acid radicals or their alkali metal or ammonium salts; and R_8 is selected from the group of alkylene, arylene, alkylene oxide,



where R_3 is as defined above and R_9 and R_{10} are alkylene groups.

24. The copy medium of claim 23 where the complexing agent conforms to formula I and is selected from the group of triethanolamine, nitrilotriacetic acid, iminodiacetic acid, N-(2-hydroxyethyl)-iminodiacetic acid, nitrilotripropionic acid and the alkali metal and ammonium salts.

25. The copy medium of claim 23 where the complexing agent conforms to formula II and is selected from the group of ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, 1,2-diaminocyclohexane-N,N,N',N',-tetraacetic acid, 1,3-diamino-2-hydroxypropane-N,N,N',N',-tetraacetic acid, 1,2-diaminopropane-N,N,N',N',-tetraacetic acid, [ethylenebis(oxy-ethylenenitrilo)] tetraacetic acid, ethylenediamine-N,N'-diacetic acid, and the alkali metal and ammonium salts thereof.

26. The copy medium of claim 23 where the complexing agent is selected from the group of ethylenediaminetetraacetic acid and nitrilotriacetic acid and their alkali metal and ammonium salts.

27. The copy medium of claim 1 as a diazo master.

28. The copy medium of claim 13 as a diazo master.

29. The copy medium of claim 19 as a diazo master.

30. The copy medium of claim 26 as a diazo master.

31. The copy medium of claim 19 where the dry thickness of the photosensitive layer does not exceed one-half mil.

32. The method of forming a diazo master comprising the steps of exposing the copy medium of claim 1 to a source of radiation and contacting the so exposed copy medium with a physical developer comprising a first solution of reducible metal ions and then a second solution of a reducing agent therefor.

33. The process of claim 32 where the reducible metal ions are selected from the group consisting of Ag^+ , Hg^{+2} , Pb^{+4} , Au^{+1} , Au^{+3} , Pt^{+2} , Pt^{+4} , Ni^{+2} , Sn^{+2} , Pb^{+2} , Cu^{+1} , and Cu^{+2} .

34. The process of claim 33 where the solution of reducible metal ions is a solution of silver ions.

35. The process of claim 32 where the reducing agent is selected from the group consisting of o- and p-aminophenol, p-methylaminophenol sulfate, p-hydroxyphenyl glycine, o- and p-phenylenediamine, 1-phenyl-3-pyrazolidone, alkali and alkaline earth metal oxalates and formates.

36. The process of claim 32 where the total contact time of the copy medium with both the solution of the reducible metal ions and the complexing agents does

not exceed 5 seconds.

37. The process of claim 32 where the total contact time of the copy medium with both the solution of the reducible metal ions and the complexing agent does not exceed 2 seconds.

38. The method of copying comprising the steps of (1) exposing the copy medium of claim 19 to a source of radiation, (2) contacting the so exposed copy medium with a physical developer comprising a first solution of reducible metal ions and a second solution of a reducing agent therefor, and (3) using the thus prepared imaged medium to expose a second photographic copy medium to thereby produce a copy of the imaged medium.

39. The process of claim 38 where the reducible metal ions are selected from the group consisting of Ag^+ , Hg^{+2} , Pb^{+4} , Au^{+1} , Au^{+3} , Pt^{+2} , Pt^{+4} , Ni^{+2} , Sn^{+2} , Pb^{+2} , Cu^{+1} , and Cu^{+2} .

40. The process of claim 39 where the solution of reducible metal ions is a solution of silver ions.

41. The process of claim 38 where the reducing agent is selected from the group consisting of o- and p-aminophenol, p-methylaminophenol sulfate, p-hydroxyphenyl glycine, o- and p-phenylenediamine, 1-phenyl-3-pyrazolidone, alkali and alkaline earth metal oxalates and formates.

42. The process of claim 38 where the total contact time of the copy medium with both the solution of the reducible metal ions and the complexing agents does not exceed 5 seconds.

43. The process of claim 38 where the total contact time of the copy medium with both the solution of the reducible metal ions and the complexing agents does not exceed 2 seconds.

44. The process of claim 43 wherein the exposure of the second copy medium is performed by contact printing.

45. The process of claim 44 wherein the second photographic copy medium comprises a diazo copy medium which is then developed to form a visible image.

46. The process of claim 38 comprising the additional step of adding or deleting material from the imaged copy medium of step (2) prior to the exposure of the second copy medium.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,791,829 Dated February 12, 1974

Inventor(s) Phillip G. Creter

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 33, delete "300 μ " and insert in its place--
300 m μ --.

Column 4, line 42, delete "expecially" and insert in its place--
especially--.

Column 7, line 19, delete "sch" and insert in its place--such--.

Column 12, lines 59 and 60, after "oxide" delete--of a Group VIA
metal--.

Column 15, line 46, delete "complexing" and insert in its
place--reducing--.

Column 16, line 4, delete "complexing" and insert in its
place--reducing--.

Column 16, line 26, delete "anf" and insert in its place--
and--.

Column 16, line 29, delete "complexing" and insert in its
place--reducing--.

Column 16, line 33, delete "complexing" and insert in its
place--reducing--.

UNITED STATES PATENT OFFICE Page 2
CERTIFICATE OF CORRECTION

Patent No. 3,791,829 Dated February 12, 1974

Inventor(s) Phillip G. Creter

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 15, line 46 and Column 16, line 29, "agents"
should read -- agent --.

Signed and sealed this 11th day of March 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks