

1

3,102,811

PROCESS FOR PRODUCING IMAGES, USING LIGHT SENSITIVE AROMATIC 1,2-DIALDEHYDES AND ELEMENTS THEREFOR

Arthur Livingston Barney, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Filed Apr. 7, 1960, Ser. No. 20,549

12 Claims. (Cl. 96-48)

This invention relates to a new process for the direct production of positive copies, and to actinic light-sensitive elements useful therein.

The direct production of positive facsimile images, e.g., duplication of office correspondence, business records, and the like, either singly or in substantial numbers forms a significant and rapidly expanding part of the present economy. There are several commercial duplicating systems which operate satisfactorily but all exhibit some undesirable facet. Thus, systems based on the diazo process use either aqueous developers or gaseous ammonia, both of which complicate handling. Furthermore, the copies fade, and only translucent originals with text on one side can be copied. Other systems based on controlled dye transfer from a sensitized dye-containing master also produce only a few copies and careful judgment by the operator is required. Furthermore, the sensitive layer is based on a silver salt and accordingly the paper is expensive.

Another system is based on the photoconductivity of a charged selenium metal plate with the image being developed by a powder which is taken up in the non-exposed and still charged areas of the plate. This pattern of the resinous developer powder is transferred to a paper sheet and subsequently fixed by heat or solvent treatment. Defects include dirty background and non-uniform areas, resulting from the tendency of the developing particles to adhere to the blank areas of the copy paper, and the necessity of carefully protecting against high humidity in view of the electrostatic nature of the process.

Another system, based on a heat activatable color-forming composition, uses infrared radiation to give heat buildup and image formation in the copy sheet in areas corresponding to the dark areas of the master. Substantially uniform contact between the master and the copy sheet is required. Also careful control is needed to prevent the color-forming ingredients from reacting ahead of time. Both factors severely limit versatility. To obtain a copy with material containing text matter on both sides, the reflex copy method must be used. In his procedure, the activating radiation passes through the copy sheet support, which must therefore be substantially transparent not only to the infrared radiation but also to light in the visible range so that the mirror image produced can be read through the paper support. Such support materials are not cheap and exhibit poor physical properties, being sleazy and floppy, thus making the copy difficult to handle and store.

Finally, there are several copy processes based on conventional high contrast silver halide/gelatin photographic systems. While these work adequately and are satisfactorily versatile in the types of material which can thereby be copied, they all require conventional photographic solution processing, albeit carried out integrally in the copy machine. This means the necessary formulation of photographic solutions, constant care, and required high machine cleanliness for satisfactory operation. Furthermore, in being based on silver halide photographic systems, the processes are obviously not as cheap as is desired.

An object of this invention is to provide a new process

2

for the formation of images. Another object is to provide such a process which is simple and dependable. Yet another object is to provide such a process which is free from the objectionable problems of prior art procedures referred to above. A further object is to provide new photosensitive elements, e.g., films, plates and papers for use in the new process of this invention. Still further objects will be apparent from the following description of the invention.

The novel process provided by the present invention comprises (1) exposing to actinic radiation, imagewise, a photosensitive element comprising a support having in operative association therewith an aromatic dialdehyde having the two aldehyde groups attached to adjoining aromatic ring carbon atoms and (2) developing the exposed element by treating it with an ammonium salt (preferably non-oxidizing) until a visible image forms in the unexposed areas. The exposure to actinic radiation, preferably a source of actinic light emitting a significant amount of radiation in the ultraviolet (UV) region (2500-3000 A.), should be carried out for a sufficient period of time to cause a chemical change in the aromatic dialdehyde in the exposed areas. Usually the period of exposure will vary from about 1/10 to about 15 minutes and the period of development from 1 second to 5 minutes depending upon the developing procedure used.

The aromatic dialdehydes used in accordance with the invention have the two aldehyde groups attached to aromatic ring carbon atoms in the ortho position to each other and may be termed aromatic vicinal dialdehydes, but for convenience are herein designated as aromatic 1,2-dialdehydes.

Since the color as well as the depth and the ease of development thereof are influenced by the substituents, if any, present on aromatic ring carbon of the dialdehydes, certain dialdehydes are more suitable than others for certain purposes. For a given aromatic 1,2-dialdehyde, the color and the depth and ease of development thereof can be determined readily by pressing a small quantity of dialdehyde between sheets of paper treated with ammonium acetate (see Example III Type A following) and placing the assembly on a hot plate at 125-135° C. for 10-15 seconds, whereby the characteristic color for the particular dialdehyde will appear.

In general, in the photosensitive elements used in accordance with the invention the aromatic dialdehyde is used in such amount that at least 0.25 mg./dm.² is deposited on or impregnated in the support (flexible or rigid) which should be non-reactive with the dialdehyde.

The novel photosensitive elements provided by the invention comprise a layer of a transparent organic polymer binder for the aromatic dialdehyde. This binder may be the support itself, e.g., a self-supporting film of regenerated cellulose, or it may be a layer of transparent polymer binder on the surface of a separate support.

Suitable sources of actinic light in the ultraviolet range include carbon arcs, mercury vapor arcs, fluorescent lamps with special ultraviolet emitting phosphors, mercury resonance lamps, and photographic flood lamps. The lamps, e.g., mercury vapor arcs or sunlamp type, can be used at a distance of 8-10 inches from the light-sensitive layer. However, the lamps can be placed even closer to the photosensitive layer provided care is taken to prevent overheating of the layer. This is especially important with elements containing an integral developer component.

The originals, which can be copied by this new direct positive-forming process, can vary widely and include process or continuous tone transparencies, either negative or positive, or conventional line or halftone text matter on the usual carriers, e.g., typed text matter on paper, and the like. The only requirement for the character of

the originals which can be copied by this process is that the text matter therein be an effective screen or absorber for the actinic light for the process, generally the light in the medium UV range, and that the carrier or support in which the text matter appears be transparent to or reflective of this actinic radiation, so as to allow modulation of the incident actinic radiation which is transmitted or reflected to the sensitized copy sheet.

The aromatic 1,2-dialdehyde forming the lightsensitive complementary color-forming reactant for use in the present copy process and in the new copy elements comprising the said aldehyde in operative association with the binder or support, and optionally a sensitizer therefor, can be put in said operative association with suitable carriers in many ways. For instance, in the case of the solid aromatic 1,2-dialdehydes, the required concentrations of the material may be carried on the required support simply as a layer of the solid on the uppermost surface of the support, which may be readily achieved by simply dusting the solid aromatic 1,2-dialdehyde on the support. In the case of those aromatic 1,2-dialdehydes which under normal conditions are liquids, the copy sheets may be made by simply dipping the support in the aromatic dialdehyde, or, in the case of the higher boiling, less readily absorbed aromatic liquid 1,2-dialdehydes, they may be simply spread on the surface of the suitable support. In the case of the liquid aromatic 1,2-dialdehydes which are readily absorbed by the more porous suitable carriers, the copy elements for the present process can be readily achieved simply by dipping and thereby impregnating the suitable support in the liquid aromatic 1,2-dialdehyde. Generally speaking, better results are achieved when the aromatic 1,2-dialdehyde is put into operative association with the requisite support carried or dispersed in a suitable binder transparent to the actinic radiation such as polyvinyl alcohol, ethyl cellulose, and the like. In general any resin, natural or synthetic, that is transparent to the radiation actinic for the system and that does not contain groups which react with the aromatic 1,2-dialdehyde to give the color prematurely can be used as the binder. Suitable resins include polyvinyl chloride, vinyl chloride/vinyl acetate copolymers, polyvinyl acetate, polymethyl methacrylate, polystyrene, polyvinyl butyral, polyvinylpyrrolidone, styrene/butadiene copolymers (high styrene), alcohol-soluble superpolyamides, polyethylene oxide, chlorinated rubber, shellac, zein, agar, cellulose esters, and the like. Some natural proteins such as casein and gelatin react with the aromatic 1,2-dialdehyde to give dark materials similar to those obtained in the developing reaction and, therefore, cannot be used as binders. Some synthetic polymers may contain peroxide residues which oxidize part of the 1,2-dialdehyde. This may require that additional amounts of the aldehyde be added to the mix in order to obtain the desired image density.

The nature of the support for use in forming the copying elements useful in the broad new copy process can vary widely. They can be rigid or flexible, and preferably are the latter. Glass plates and other solid supports are suitable for preparing the copying elements useful in the broad copying invention process. Because of greater flexibility, the flexible sheet materials are preferred for the supports. Such flexible sheet supports can be formed from any of the natural or synthetic polymers, either in the form of a film thereof or a paper prepared from fibers of such polymers with suitable binders. Suitable examples include the synthetic polymers, such as the condensation polymers, e.g., the polyamides and polyesters; the addition polymers, e.g., polyvinylpyrrolidone, polyvinyl alcohol, and the various acetal esters and ethers thereof; and other polymers and copolymers well known in the polymer art. Another convenient source of the preferred flexible sheet supports is found in the natural and modified natural polymers, more particularly those based on cellulose, including the cellulose esters,

cellulose ethers, mixed ether-esters, regenerated cellulose, cellulose itself, for instance, in the form of shaped objects of cellulose pulp, linters, and fibers, i.e., the well-known papers and the like.

The necessary 1,2-aromatic dialdehyde complementary color-forming component of the copying elements useful in the present new copying process, as stated above, can be brought into the necessary operative association with the sheet support by any of the techniques well known in the coating and impregnating arts. In the case of films of polymers which are not easily penetrated by the aromatic 1,2-dialdehyde or solutions thereof, for instance, a preformed sheet of a condensation polymer such as polyhexamethylenedipamide, the 1,2-aromatic dialdehyde in solution in a suitable solvent at the desired concentration, and, if desired, in combination with a suitable protective binder which is preferably adherent to the substrate, e.g., ethyl cellulose, can be topcoated on the polyhexamethylene-adipamide film and the solvent allowed to evaporate. There is thus obtained a polyhexamethylenedipamide base with a layer of the desired thickness of the aromatic 1,2-dialdehyde protected by the ethyl cellulose binder.

If it is desired to obtain a deep image, i.e., where the colored copy positive penetrates the support sheet, a convenient method is to dissolve the polymeric material forming the flexible sheet support in a suitable solvent and to add thereto the required amount of the aromatic 1,2-dialdehyde to give the desired concentration of the desired thickness and then to cast the solution by conventional film-casting techniques and allow the solvent to evaporate, whereby there is obtained a sheet support carrying uniformly dispersed therethrough the desired aromatic 1,2-dialdehyde complementary color-forming reactant. In those instances where the sheet support being used is absorbent of, or easily penetrated by, suitable solvents for the aromatic 1,2-dialdehydes, e.g., in the case of most of the conventionally available paper stock, it is necessary only to dip the paper stock in a solution of the aromatic 1,2-dialdehyde at the desired concentration and allow the solution to impregnate and be absorbed by the paper support. Upon evaporation of the solvent, the aromatic 1,2-dialdehyde will again be substantially uniformly and homogeneously distributed throughout the thickness of the paper. The resultant color positive image obtained from such an impregnated paper will likewise be deep in that it will be formed throughout the thickness of the paper. It should be noted that in a direct positive process such as that described, the visible image is formed from the aromatic 1,2-dialdehyde that has not been acted upon by the light. Thus if clean, white backgrounds are to be obtained, it is essential that all the aldehyde in the exposed areas be destroyed. Since paper fibers scatter or absorb a large portion of the actinic light, longer exposures are required when the paper support itself is impregnated with the sensitive mixture.

As to the operable aromatic 1,2-dialdehydes, o-phthalaldehyde itself is the most preferred since it is the most readily available. The aromatic 1,2-dialdehydes need not be of this simple structure but may, however, carry one or more functional or non-functional substituents, for instance, 4-nitro-1,2-phthalaldehyde, 3-carboxy-4-methoxy-5-methyl-1,2-phthalaldehyde, i.e., gladiolic acid, 4-hydroxy-1,2-phthalaldehyde, 4-bromo-1,2-phthalaldehyde, 4-bromo-5-hydroxy-1,2-phthalaldehyde, 4,5-dimethyl-1,2-phthalaldehyde, 3-carboxy-4,5-dimethoxy-1,2-phthalaldehyde, 3-carboxy-4-methyl-5-methoxy-6-hydroxy-1,2-phthalaldehyde, naphthalene-2,3-dialdehyde, and the like.

As to the new copy elements of the present invention which are likewise useful in the new copying process of the invention, these elements comprise a support, an aromatic 1,2-dialdehyde, dispersed in a transparent binder which can be the support, and optionally a sensitizing agent. The support materials and binders for these new

elements can be of the types just previously described in the generic sense for the copying process. The same applies to the operable aromatic 1,2-dialdehydes. The optional sensitizing agents include benzophenone, benzoin, anthraquinone-2-sulfonic acid, phenanthraquinone, acriflavine/stannous chloride, azobis(cyclohexanecarbonitrile), and the like. The primary effect of the sensitizer appears to be to absorb radiation in a spectral region where the phthalaldehyde itself has low absorbance and gives an excited or activated species that is capable of reacting with the aldehyde or of transferring energy to it.

As stated in the foregoing, the development of the color image in the unexposed areas, i.e., the areas corresponding to the dark areas in the original being copied, is effected by reaction with an ammonium salt. This development step can be effected in two separate steps or in a single step. Thus, the ammonium salt may be provided by simply fuming with ammonia and then with acid whereby the salt is formed in the layer or by simply spraying the layer with an aqueous ammonium salt solution. While the development can be effected by these fuming or liquid spraying operations, for obvious reasons of convenience it is preferred that the necessary ammonium salt be provided through thermally activatable precursors thereto present in an auxiliary developer or transfer sheet or in some circumstances as integral components of the light-sensitive copy sheet. Suitable developers include ammonium salts, such as ammonium chloride, ammonium acetate, ammonium bicarbonate, ammonium sulfite, diammonium phosphate, ammonium fluoride, ammonium bromide, ammonium bichromate, ammonium carbonate, ammonium chromate, ammonium citrate, ammonium formate, ammonium molybdate, ammonium nitrate, ammonium oxalate, ammonium phosphate (monobasic), ammonium stearate, ammonium sulfate, and ammonium thiocyanate.

In addition to the ammonium salts listed above, urea and acetamide act as thermal developers at higher temperatures (170–200° C.).

The color image can be developed by applying to the exposed copy sheet a developer sheet comprising a suitable support having in operative association therewith the requisite ammonium salt developer. Such developer sheets are easily prepared by impregnating paper with an aqueous solution of the ammonium salt and drying. The developer sheet is simply put in intimate contact with the exposed copy sheet and the two sheets are heated to the development temperature while maintaining said contact. Developing temperature will lie in the 90–180° C. range and developing time in the 1–20 second range. Using these techniques with the ammonium salts having relatively low dissociation temperatures, such as the acetate, propionate, sulfite, bicarbonate, and the like, the decomposition of the ammonium salt will result in the substantially conjoint transfer from the separate developer sheet to the exposed copy sheet of both ammonia and the acid, whereby the color image will be developed in the exposed copy sheet.

On the other hand, using the separate developer sheet technique and the ammonium salts of higher dissociation temperature, migration from the developer sheet is slow and the unreacted aromatic 1,2-dialdehyde in the unexposed areas of the copy sheet will exhibit sufficient vapor pressure to migrate to the developer sheet. Under these conditions of thermal development, the components necessary to give the color image, i.e., the unreacted aromatic 1,2-dialdehyde in the unexposed areas and the ammonium salt in the developer sheet will only come together in the developer sheet, whereby the developed color image will appear not in the copy sheet but rather in the developer sheet. Ammonium salts of higher dissociation temperature suitable for this transfer technique include: ammonium sulfate, ammonium nitrate, ammonium chloride, and ammonium bromide. It should be noted that as the developing temperature is increased,

there is more and more transfer of the dissociable ammonium salt to the copy sheet, so that the image appears both on the copy and developer sheet. Some of the ammonium salts, e.g., ammonium molybdate, show very slight tendency to migrate to the copy sheet. Thus as illustrated in Example V, it is possible to obtain more than one copy from the copy sheet. Accordingly, such techniques are preferred in those instances where more than one copy of the original is desired. Obviously for such multicopy techniques, it is preferred that not only the separate developer sheet approach be used, preferably involving the ammonium or substituted ammonium salts of the higher dissociation temperatures, but also that the aromatic 1,2-dialdehyde components present in the copy sheet be one of the higher boiling aromatic 1,2-dialdehydes.

As illustrated in Example IV, it is possible to include the ammonium salt developer layer on the same support with the aromatic 1,2-dialdehyde layer if the element structure is arranged to prevent premature contact of the reactive components. In Example IV this is achieved by having the materials in separate layers and applying the second layer from a solvent which does not soften or attack the first layer. It is also possible to utilize ammonium salt precursors that in themselves do not react with the aromatic 1,2-dialdehydes, but that decompose on thermal treatment to give ammonia or an ammonium salt. Such a composition comprises urea or urea and citric acid with the aromatic 1,2-dialdehydes. However, for best storage stability it is generally preferred to have the aldehyde and developer on separate supports.

In the following examples which are submitted to illustrate further the present invention but not to limit it, the parts given are by weight. The reflection densities referred to were obtained on a Welch "Densicon" densitometer as discussed in Rev. of Sci. Inst., 19, 827 (1948), using a reflection densitometer attachment, from which the scanning light beam is projected onto the work surface at a 45° angle of incidence and diffusely reflected therefrom vertically into the receiver lens of the instrument through a field stop onto the cathode of the photo tube.

EXAMPLE I

A solution containing about one part o-phthalaldehyde, about five parts medium viscosity, completely hydrolyzed polyvinyl alcohol, and 94 parts water was coated as a thin layer on filter paper and dried under subdued light. A strip of this coated paper was exposed stepwise (1–16 minutes) under a photographic line negative in a vacuum printing frame to the light from an RS sunlamp at a distance of eight inches. There was no visible change. The exposed strip was sprayed with a dilute aqueous solution of ammonium acetate. The coated paper turned a fairly uniform gray except in the 16-minute step, where the portions exposed to light were a lighter gray color. A second strip of the coated paper was exposed under black paper letters to light from two 15-watt mercury vapor germicidal lamps (2537 Å. radiation) for 1–16 minutes and then sprayed with aqueous ammonium acetate solution as before. Clear, visible images were obtained in those areas exposed four minutes and greater. With the four minute exposure the image (the shielded portions) was gray-black on a lighter gray background. With the 16 minute exposure the image was gray-black on a faint gray background.

EXAMPLE II

By procedures similar to those described at page 641 of "Organic Syntheses, Coll. vol. III," John Wiley, New York, 1955, for the oxidation of o-nitrotoluene to o-nitrobenzal diacetate, 4-nitro-1,2-dimethylbenzene was oxidized to 4-nitro-1,2-di(benzal diacetate), a white solid, M.P. 122–124° C. This compound was refluxed with an ethanol, hydrochloric acid, water solution essentially as given in the reference for hydrolysis of the o-nitrobenzal

diacetate to o-nitrobenzaldehyde. The resultant clear, yellow solution was neutralized with sodium bicarbonate and extracted four times with equal volumes of methylene dichloride. The extracts were combined, dried over anhydrous sodium sulfate, and concentrated to a yellow oil containing crude 4-nitro-1,2-phthalaldehyde by evaporation of the methylene chloride. The yellow oil was taken up in methanol and this solution was used to impregnate strips of filter paper. An impregnated strip was fumed over concentrated ammonium hydroxide for two minutes and then over acetic acid for two minutes, resulting in the formation of a deep brown-black stain in the treated area. Another impregnated strip was exposed under a positive transparency for 5–15 minutes to light from a 450-watt quartz mercury arc at a distance of ten inches. There was no visible change. The exposed strip was fumed as above, thereby developing an image of the text in the transparency. In the areas exposed for five minutes, the image was brown-black on a dark gray background; in those exposed for 15 minutes, the background had faded to a yellow-gray color.

EXAMPLE III

A standard barium sulfate/gelatin-coated photographic paper stock was overcoated with an aqueous solution of a medium viscosity, completely hydrolyzed polyvinyl alcohol to give a polyvinyl alcohol coating weight of about 50 mg./dm.². When this coating was dry, a topcoating of a solution of eight parts of o-phthalaldehyde and six parts of citric acid in 3000 parts of a 10% solution of ethyl cellulose in 80/20 (by volume) toluene/ethanol was applied to give an o-phthalaldehyde coating weight of 5 mg./dm.². The dry, coated paper was white and glossy. A developer paper (type "A") was prepared by impregnating 16-pound bond paper with a solution of 85 parts water, 15 parts ammonium acetate, and four parts glycerol, squeegeeing the paper on a flat surface to remove excess solution, and drying. A positive transparency was prepared by sticking black paper letters to a sheet of cellophane. Strips of the o-phthalaldehyde coated paper were exposed under this position to light from a 450-watt quartz mercury arc for 30 seconds at a distance of 10 inches and were then pressed against the "A" developer paper for 10 seconds at 130–135° C. A sharp blue-black image of the text in the transparency was obtained on a white background in the exposed sheet. The reflection density of the dark portion of the image (the unexposed areas) was 1.32–1.42, while the reflection density of the exposed background was 0.06–0.09. These measurements were made with white light using the reflection density attachment of a Welch "Densicon" densitometer. Using shorter exposures with additional samples of the coated paper, the background density was greater since not all of the o-phthalaldehyde was deactivated. Images were easily visible with exposures of five to ten seconds. A two-minute exposure under a single 15-watt germicidal lamp at a distance of ½ inch followed by thermal development against the "A" paper as above gave a blue-black image on a very light gray background.

EXAMPLE IV

A solution of 50 parts of a 15% aqueous solution of ammonium acetate, one part of glycerol, and 50 parts of a 10% aqueous solution of medium viscosity, completely hydrolyzed polyvinyl alcohol was coated onto barium sulfate/gelatin coated photographic paper stock to give an ammonium acetate coating weight of ca. 150 mg./dm.². When this coating was dry, a top-coating of a solution of 1.5 parts of o-phthalaldehyde, one part of citric acid, 25 parts of ethanol, and 150 parts of a 10% solution of ethyl cellulose in an 80/20 (by volume) mixture of toluene/ethanol was applied to give an o-phthalaldehyde coating weight of 20 mg./dm.². The coating, when dry, had a faint brown tint. It could be blackened merely by pressing onto a hot surface at 120–140° C. for ten seconds. When

the coating was exposed to the light from a 450-watt quartz mercury arc at a distance of ten inches under a positive transparency, a direct positive image was obtained in the exposed sheet merely by pressing on a hot surface at 120° C. for ten seconds. An image was visible with light exposures as short as seven seconds, but the background was gray. With exposures of two minutes or longer, the background was essentially colorless.

EXAMPLE V

Barium sulfate/gelatin coated photographic paper stock was coated by means of a doctor knife with an aqueous 10% solution of medium viscosity, completely hydrolyzed polyvinyl alcohol to give a polyvinyl alcohol coating weight of about 150 mg./dm.². When this coating was dry, a topcoating of a solution of eight parts of o-phthalaldehyde in 3000 parts of a 10% solution of ethyl cellulose in 80/20 (by volume) toluene/ethanol was applied to give an o-phthalaldehyde coating weight of 50 mg./dm.². After drying, the coated paper was white and glossy. A developer paper (type "B") was prepared by treating bond paper with a solution of 20 parts of ammonium molybdate and 25 parts of urea in 100 parts of water as described in Example III. A strip of the o-phthalaldehyde coated paper was exposed under a positive transparency to the light from a 450-watt quartz mercury arc for 30 seconds and then pressed against the molybdate-treated paper at 140° C. for ten seconds. A laterally reversed, brownish purple transfer image was thereby produced on the developer paper. The exposed o-phthalaldehyde layer was then pressed against a second sheet of the developer paper under the same conditions and a second transfer image obtained. The density of the second transfer image was lower than the first, but the image was still perfectly legible. There was only a very faint gray image visible on the exposed o-phthalaldehyde layer after the two transfers.

EXAMPLE VI

As in Example V photographic paper stock was coated with a solution of 20 parts of o-phthalaldehyde, five parts of citric acid, and ten parts of benzophenone in 3000 parts of a 10% solution of ethyl cellulose in 80/20 (by volume) toluene/ethanol to give an o-phthalaldehyde coating weight of about 13 mg./dm.². The coated sheet was exposed at a distance of ten inches for four minutes under a continuous-tone transparency to the light from the 450-watt quartz mercury arc. The exposed coating was then developed by pressing against a sheet of impregnated developer paper "A" of Example III for ten seconds at 125° C. A pleasing continuous-tone print of the transparency was thereby obtained in the exposed sheet.

EXAMPLE VII

A solution of five parts of o-phthalaldehyde and five parts of benzophenone in 400 parts of ethanol was applied to plain two-mil cellophane to give an o-phthalaldehyde coating weight of ca. 17 mg./dm.². A developer paper was prepared as described in Example III by impregnating onionskin paper with a solution of five parts of ammonium chloride in 50 parts of water. A sheet of the coated cellophane was exposed for ten minutes under a positive transparency of a lens test chart to the light from a 450-watt quartz mercury arc at a distance of ten inches. The exposed sheet was then pressed against the ammonium chloride treated developer at 170–180° C. for ten seconds. A dark purple positive image faithfully duplicating all details of the original was thereby obtained in the exposed sheet. The transmission density of the darkened portion was 0.75, while the exposed, i.e., the clear areas, exhibited a density of 0.02.

EXAMPLE VIII

A solution of six parts of o-phthalaldehyde, 100 parts of ethanol, and 600 parts of a 10% solution of ethyl

cellulose in 80/20 (by volume) toluene/ethanol was coated onto polyvinyl alcohol subbed cellulose acetate film base to give an o-phthalaldehyde coating weight of about 20 mg./dm.². Exposure for 5 to 10 minutes under a positive transparency to the light from a 450-watt quartz mercury arc lamp followed by fuming over ammonium hydroxide and then over acetic acid, as in Example II, gave a blue-black image of the text in the transparency. With exposures of 160 seconds or longer, the background was essentially clear.

EXAMPLE IX

A solution of three parts of o-phthalaldehyde and one part of citric acid in 150 parts of an aqueous 10% solution of medium viscosity, completely hydrolyzed polyvinyl alcohol was applied to barium sulfate/gelatin coated photographic paper stock to give an o-phthalaldehyde coating weight of about 100 mg./dm.². After drying, the

Developing Papers

A solution of 96 parts of water and four parts of glycerol was mixed with 15 parts of an ammonium salt as listed in the table below and the solution used to impregnate bond paper as described in Example III.

Test Procedure

A strip of the developer paper was placed in contact with a strip of Coating A (above) and the combination pressed on a hot plate at 100° C. for ten seconds. The procedure was repeated with additional strip combinations at 120°, 140°, and 160° C. The same procedure was followed with Coating B. The reflection densities of both the coating and the developer paper were then obtained on the Welch "Densicron" densitometer. The results are shown in the table below.

REFLECTION DENSITIES OF COATINGS (C) AND DEVELOPER PAPERS (DP)

Developing temp., ° C.	100				120				140				160			
	A		B		A		B		A		B		A		B	
	C	DP	C	DP	C	DP	C	DP	C	DP	C	DP	C	DP	C	DP
Ammonium salt in developer paper																
Acetate.....	0.97	0.18	0.99	0.15	1.15	0.16	1.55	0.17	1.07	0.18	1.36	0.13	S	S	1.29	0.14
Aluminum sulfate.....	0.07	0.10	0.08	0.12	0.06	0.11	0.07	0.13	0.07	0.11	0.07	0.11	S	S	S	S
Bicarbonate.....	0.92	0.16	1.59	0.15	0.78	0.31	1.24	0.17	0.60	0.27	0.95	0.17	0.58	0.23	0.86	0.16
Bichromate.....	0.09	C	0.09	C	0.17	C	0.20	C	0.24	C	0.34	C	S	S	S	S
Bisulfate.....	0.07	0.11	0.07	0.11	0.09	0.12	0.07	0.11	0.07	0.11	S	S	S	S	S	S
Bromide.....	0.13	0.71	0.08	0.67	0.15	0.80	0.10	0.82	0.16	0.87	0.12	0.82	0.27	0.55	0.26	0.52
Carbonate.....	1.04	0.17	1.75	0.12	0.88	0.21	1.23	0.11	0.66	0.30	1.06	0.13	0.50	0.29	0.96	0.12
Chloride.....	0.08	0.71	0.08	0.65	0.12	0.95	0.14	0.83	0.18	0.86	0.17	0.79	0.33	0.72	0.43	0.55
Chromate.....	1.08	C	1.42	C	1.07	C	1.42	C	0.97	C	1.30	C	0.73	C	S	S
Citrate.....	0.15	0.61	0.25	0.54	0.27	0.64	0.38	0.64	0.31	0.52	0.42	0.32	0.54	0.37	0.72	0.44
Fluoride.....	0.80	0.12	0.92	0.10	1.02	0.15	1.51	0.12	1.10	0.15	1.50	0.13	1.32	0.14	1.61	0.12
Nitrate.....	0.09	0.53	0.07	0.54	0.13	0.76	0.11	0.58	0.16	0.90	0.21	0.86	0.29	0.92	0.52	0.63
Oxalate.....	0.70	0.30	0.49	0.19	0.68	0.50	0.83	0.35	0.50	0.50	0.78	0.36	0.50	0.43	0.67	0.39
Persulfate.....	0.07	0.11	0.07	0.11	0.07	0.12	0.07	0.11	0.06	0.11	S	S	S	S	S	S
Phosphate (mono).....	0.07	0.26	0.06	0.11	0.09	0.32	0.11	0.17	0.13	0.23	0.21	0.20	0.16	0.29	S	S
Phosphate (di).....	0.49	0.18	0.59	0.12	0.87	0.17	1.23	0.11	0.98	0.18	1.44	0.11	0.71	0.20	1.24	0.15
Stearate.....	0.14	0.35	0.12	0.28	0.26	0.59	0.27	0.57	S	S	0.31	0.41	0.27	0.33	S	S
Sulfate.....	0.09	0.50	0.14	0.47	0.17	0.78	0.27	0.63	0.22	0.50	0.33	0.38	S	S	0.48	0.30
Sulfite.....	0.88	0.11	1.13	0.10	1.15	0.10	1.84	0.10	1.32	0.13	1.80	0.11	1.35	0.18	1.55	0.11
Thiocyanate.....	0.14	0.58	0.11	0.50	0.38	0.76	0.32	0.59	0.56	0.88	0.65	0.85	0.77	0.71	0.84	0.55

S=coating and developer paper stuck together.

C=developer paper so dark from chemical used that transfer image was not visible.

coated stock had a very faint grayish tint, presumably caused by the action of the o-phthalaldehyde with gelatin of the paper. This coating was stored for five months open to the air at room temperature in darkness or under yellow lights. There was no noticeable change in color of the coating. A sheet of the aged, coated stock was exposed for four minutes under a positive transparency at a distance of ten inches to the light from a 450-watt quartz mercury arc lamp. The exposed strip was pressed against a sheet of impregnated developer paper "A" of Example III at 140-145° C. for 10 seconds. A deep black image on a very faint brown background was thereby obtained. The reflection density of the image (i.e., the unexposed areas) was 1.68; while the reflection density of the background was 0.12.

EXAMPLE X

Coating A

A solution of eight parts of o-phthalaldehyde in 3000 parts of a 10% solution of ethyl cellulose in an 80/20 (by volume) toluene/ethanol mixture was applied to polyvinyl alcohol-coated photographic paper stock as described in Example III to give an o-phthalaldehyde coating weight of about 5 mg./dm.².

Coating B

To the coating solution as prepared for Coating A was added eight parts of citric acid and the coating carried out in the same manner to give an o-phthalaldehyde coating weight of about 5 mg./dm.².

An advantage of this invention is that it provides a simple and dependable process for reproducing images. Another advantage is that the process is quite versatile and can be used for producing sensitive facsimile images and in copying of all kinds of records. A further advantage is that the process is simple and does not require the use of expensive materials or reproduction apparatus. A still further advantage is that the processes are quite rapid and produce excellent images.

I claim:

1. A process which comprises (1) exposing to actinic radiation, imagewise, a photosensitive element comprising a sheet support carrying a stratum of an aromatic dialdehyde containing 1-2 benzene rings and having the two aldehyde groups attached to adjoining aromatic ring carbon atoms and (2) developing the exposed element by treating it with an ammonium salt until a visible image forms in the unexposed areas.

2. A process as defined in claim 1 wherein the ammonium salt is formed in situ.

3. A process as defined in claim 1 wherein the ammonium salt is a non-oxidizing, non-acidic salt.

4. A process as defined in claim 1 wherein said aldehyde is o-phthalaldehyde.

5. A process as defined in claim 1 wherein said ammonium salt is ammonium acetate.

6. A process as defined in claim 1 wherein the aromatic dialdehyde is present in an amount of at least 0.25 milligram up to 100 milligrams per square decimeter of said support.

11

7. A process as defined in claim 1 wherein the development is carried out at an elevated temperature of 90° C. to 200° C.

8. A process as defined in claim 1 wherein the required ammonium salt is supplied from a layer different from the layer containing the aromatic dialdehyde by heating the layers while they are superposed in contact.

9. A process as defined in claim 8 wherein the two layers are on separate supports.

10. A photosensitive element comprising a solid layer of an organic polymeric binder transparent to actinic radiation and being free from groups that react with an aromatic 1,2-dialdehyde, there being present at least 0.25 milligram and up to 100 milligrams per square decimeter of said layer of an unreacted aromatic dialdehyde containing 1-2 benzene rings and having the two aldehyde groups directly attached to adjoining aromatic ring carbon atoms.

11. A photosensitive element according to claim 10 additionally containing in the layer a sensitizing agent

12

selected from the group consisting of benzophenone, benzoin, anthraquinone-2-sulfonic acid, acriflavine/stannous chloride and azobis(cyclohexanecarbonitrile).

12. A photosensitive element according to claim 10 wherein said layer is carried by a flexible transparent support.

References Cited in the file of this patent

UNITED STATES PATENTS

2,681,277 Morrison June 15, 1954

OTHER REFERENCES

Shonberg et al.: "Dimerization of O-Phthalaldehyde," Jour. Am. Chem. Soc., vol. 77, pages 5755-6, 1955.

Seekles: Rec. Trav. Chim., 43, 95-102 (1924), as reported in Chem. Ab., vol. 18, page 2145.

Analytical Chemistry, vol. 26, No. 7, page 1118, 1954. (Copy in Div. 59.)