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L. CHALKLEY

3,071,464

PHOTOGRAPHIC PROCESS

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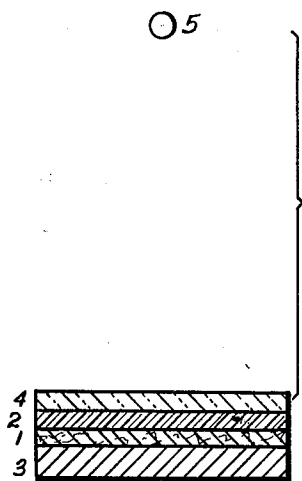


Fig. 1

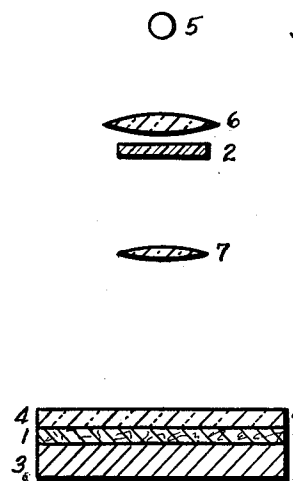


Fig. 2

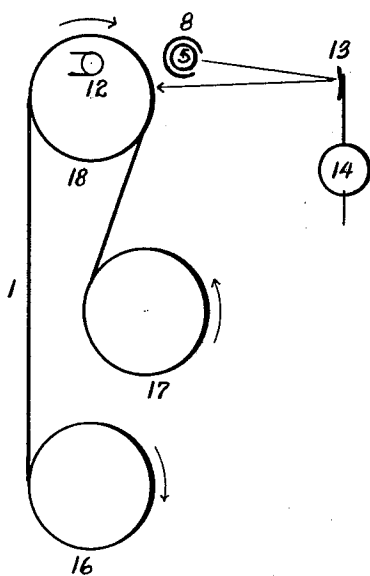


Fig. 3

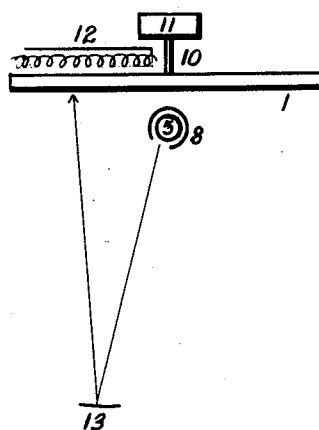


Fig. 4

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1

3,071,464

PHOTOGRAPHIC PROCESS

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12 Claims. (Cl. 96—27)

This invention relates to a photographic process, and more particularly to one in which the photosensitive material is activated by heat during the photographic exposure.

Photographic methods have many advantages for the duplication of documents, recording of data and storage of information. The operations of development and fixing associated with photographic methods are disadvantages, and various devices have been introduced to reduce the burden of these operations.

From the standpoint of convenience the ideal process would be one in which neither development nor fixing would be required. This goal is approached by the direct printing out processes in which the image is completely formed by the action of light alone without need for supplementary development of any sort to bring out the image.

However, printing out processes have their own limitations. They require more exposure to produce an image than a good developing out process. Therefore, printing speed may become a problem and it is desirable to use as fast printing material as possible. Also the unexposed portions of a print that has not been developed or fixed retain their sensitivity and are further printed when exposed to actinic radiation with the result that the print becomes fogged when examined, copied or otherwise used in an illuminated place. The effect of fogging can be materially reduced by the use of printing out photographic materials that are sensitive only to ultraviolet radiation, because prints made upon them can be examined or copied by visible light, and even projected upon a screen, without fogging. However, few visible light sources are completely free of ultraviolet, and some, such as fluorescent lamps, are relatively rich in ultraviolet. Therefore fogging remains more or less of a problem, especially with printing out materials having the greatest printing speed.

The present invention provides another means for reducing the fogging of prints upon printing out materials that have not been fixed, while retaining maximum printing speed. It utilizes printing out materials that have a high temperature coefficient of photochemical reaction. Exposure is made upon these materials while they are heated to bring out their maximum printing speed. The prints are cooled to room temperature, at which the printing speed is less than one tenth of that of the hot material. Thus fogging during examination or other use of the print is reduced to less than one tenth of the rate shown by ordinary materials of comparable printing speed. The process may be applied to photographic materials effectively sensitive only to ultraviolet, and thus afford an extension of the fogging reduction provided by such materials as described above. However, the process is not limited to ultraviolet sensitive materials.

In known photographic processes the image produced by exposure of a hot photographic film or paper is very little stronger than the image produced by the same exposure upon the same material when it is cold. Thus an increase of 100° centigrade in the temperature of a silver bromide photographic plate no more than doubles its printing speed.

In the present process printing is carried out upon heated printing-out materials which when hot have over ten times their printing speed at room temperature. The print is then cooled to room temperature, thereby reducing the sensitivity of the print so that the unexposed por-

2

tions will not fog in ordinary use, and thus partial fixing is effected without chemical processing.

The process is useful for copying documents, for duplicating purposes such as printing from a stencil, for recording mirror galvanometer traces, for other recording instruments such as barographs, pyrometers, etc. The process has the advantages that it is fast, requires no chemical processing by either gasses or liquids, prints out the full image instantaneously without physical or chemical development. Other unique advantages will appear from the following discussion.

Heat has been used in other photographic processes. Thus heat may be employed to develop or to accelerate the development of an image after the photographic material has been exposed. With some materials, such as photosensitive glass, heat alone develops the image. The heat development processes differ from the present process in that they require development by heat treatment after exposure in order to produce an image, while in the present process the image appears fully formed during exposure and without any delay for development. Also the heat development process destroys the photosensitivity of the original material so that the developed print cannot be printed on again, whereas in the present process the heating during exposure does not impair the sensitivity of the unexposed portions of the photographic surface. The cooling after printing effects fixing for ordinary use. On reheating the material becomes sensitive again and previously unexposed portions of the surface can then be printed upon. This characteristic of the new process makes it useful for serial recording of information, as on a ledger sheet. The entries already printed upon a sheet may be examined, scanned, photographed or otherwise used, and at any time additional entries may be printed upon the sheet by re-heating it again for the duration of the new exposure. And this process may be repeated.

Heat also has been used alone to produce photographic images, as when a waxed paper is exposed to a radiant heat pattern of sufficient intensity to melt the wax where the heat is applied but leave the wax unmelted where the heat is not applied. In contrast, the present process employs not only heat but visible and ultraviolet light to produce an image, the actual printing being done by the light alone upon the uniformly heated photographic surface. The heat accelerates the action of the light but does not produce the image. Processes that print by heat alone are essentially low resolution processes. In the waxed paper process the melted wax tends to diffuse or run and thus to reduce definition. Basically all radiant heat printing processes are limited in resolution by the long wave length of the radiation itself. On the other hand, the present process, which prints by visible or ultraviolet light, is inherently a high resolution process which can yield microscopically sharp images and be used for the microfilm storage of information. Also the waxed paper radiant heat process is an extremely high contrast process useful only for black and white work, whereas the process of this specification can print half tones and give a full range of gradation.

In the present invention high temperature coefficient printing-out materials are used. By a high temperature coefficient printing-out material is meant a photosensitive product that prints out a fully formed image without chemical or physical development, and that shows at least a ten fold increase in printing speed produced by an increase in temperature of 100° C., the printing speed being reduced again when the temperature is lowered. Examples of such materials are given below.

High Temperature Coefficient Printing Material No. 1

In a ball mill heated to 50° C. is placed 1 liter of 10% aqueous gelatin solution also at 50° and 100 g. of

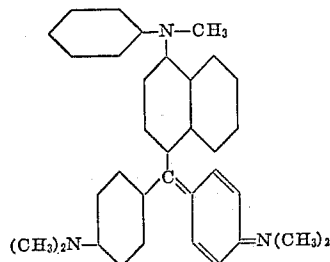
3

salicylal- β -naphthylamine. The mixture is ground to a homogeneous emulsion and coated onto paper, film or glass plates, which are then dried. The finished material is light yellow and on long exposure at room temperature to strong blue, violet or ultraviolet light prints out a red image. Heating the material to 80° increases the printing speed to incandescent lamp light more than ten times. The increased printing speed is lost when the material is cooled. This material should be printed by strong light and cooled immediately after printing. It is useful for the temporary storage of information and proof prints. The photographic image fades in a few weeks on storage in the dark at room temperature, or in a few seconds at 135° C., the original yellow color being restored. The faded surface may be printed upon again, and the process repeated a large number of times.

High Temperature Coefficient Printing Material No. 2

A solution of 2 g. of bis-(4-dimethylaminophenyl)-(4-N-methyl-anilinonaphthyl-1)-acetonitrile, the preparation of which is described below, in 100 ml. of dimethylformamide is applied to 20 pound filter paper which is dried in a stream of dry air at 50°. On exposure to wave lengths shorter than 3700 Å. at room temperature the paper prints extremely slowly a violet image which is permanent and does not fade on storage. At 150° C. the printing speed to an S4 lamp is increased over ten times.

Preparation of bis-(4-dimethylaminophenyl)-(4-N-methyl-anilinonaphthyl-1)-acetonitrile.—To a solution of 5 g. of C. I. Basic Blue 8, Colour Index No. 42563 having the formula

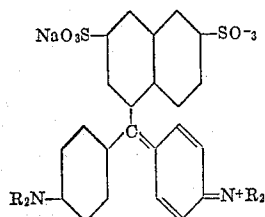


in 125 ml. of water is added at room temperature a solution of 2 g. of sodium cyanide in 25 ml. of water, and the mixture allowed to stand for 1 hour. The voluminous precipitate is then collected on a filter, washed with water and air dried. The product is purified by repeated solution in 6 times its weight of dimethylformamide and reprecipitation with water.

High Temperature Coefficient Printing Material No. 3

One gram of Naphthalene Green V cyanide, the preparation of which is described below, is dissolved at 75° C. in a mixture of 3.2 ml. of normal sodium carbonate solution and 35 ml. of water, and the solution cooled and made up with water to a total volume of 75 ml. Filter paper (20 pound basis weight) is wet by dipping in this solution and air dried. The paper prints a green permanent image on exposure to ultraviolet light. When heated to 130° C. the printing speed to an S4 lamp is over 20 times as great as at room temperature.

Preparation of Naphthalene Green V Cyanide.—To a solution of 100 g. of Pontacyl Green NV Extra (E. I. du Pont de Nemours & Co. brand of Naphthalene Green V Colour Index No. 44025 having the formula



4

where R is chosen from the group consisting of $-\text{CH}_3$ and $-\text{C}_2\text{H}_5$) in 500 ml. of water at 80° is added a solution of 28 g. of 97% sodium cyanide in 60 ml. of water and the mixture stirred well and allowed to cool to 25° by standing at room temperature for 12 hours. To the clear reaction solution is added 1200 ml. of a saturated aqueous solution of sodium chloride, and the mixture allowed to stand over night. The upper clear aqueous layer is then decanted from the heavy viscous material that has precipitated on the bottom and walls of the reaction flask or vessel. The decanted solution is discarded. The viscous precipitate is washed with 50 ml. of saturated sodium chloride solution, which also is discarded. The precipitate is then dissolved at room temperature by stirring with 200 ml. of fresh water, and the solution filtered. To the filtrate is added 175 ml. of normal hydrochloric acid, and the mixture allowed to stand at 25° C. for 48 hours or until crystallization, which sometimes is slow to start, has taken place. The crystalline precipitate is collected on a filter, washed with 50 ml. of ice water, and dried in a vacuum desiccator over sulfuric acid. The crude Naphthalene Green V cyanide is purified by recrystallization from 200 times its weight of water.

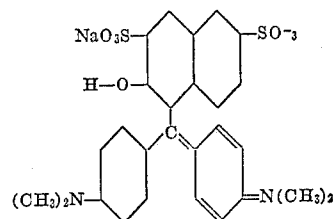
High Temperature Coefficient Printing Material No. 4

One gram of Naphthalene Green V cyanide, the preparation of which has been described above, is dissolved at 75° C. in a mixture of 3.2 ml. of normal sodium carbonate and 32 ml. of water. This solution is then mixed with 35 ml. of a 10% aqueous solution of gelatin also heated to 75° C., the temperature lowered to 40° C. and the solution coated onto glass plates using 1 ml. of solution to cover 2 square inches of surface. The dried film is transparent and produces images with very high optical resolution.

High Temperature Coefficient Printing Material No. 5

One gram of Wool Green S cyanide is dissolved in 50 ml. of boiling water to which is added 1.68 ml. of normal sodium hydroxide solution. The resulting clear solution is cooled to 25°, and 20 pound weight filter paper wet by dipping in the solution and air dried. Exposure of the sensitized paper to ultraviolet light prints a green image. The printing speed to an S4 lamp at 130° C. is more than 15 times the speed at 25° C.

Preparation of Wool Green S Cyanide.—To a solution of 25 g. of Kiton Green S. Conc., the Ciba Company brand of Colour Index No. 44090 having the formula,



in 125 ml. of water at 70° C. is added a solution of 6.5 g. of 97% sodium cyanide in 25 ml. of water. The flask containing the resulting solution is closed and heated at 85° C. for 1 hour, during which time the deep blue color fades. The solution then is cooled to 25° C. and filtered from a little precipitate, which is discarded. To the filtrate is added an equal volume of saturated sodium chloride solution, and the mixture allowed to stand over night. The resulting precipitate is collected on a filter, washed with saturated sodium chloride solution and dried in an oven at 100° C. The dry product is dissolved in 135 ml. of warm water. To this solution is added 4 ml. of concentrated hydrochloric acid. The mixture is cooled to 0° C. and held at this temperature for 4 days, or until crystallization takes place. The precipitate is collected on a filter, washed with 20 ml. of ice water, and dried in a vacuum desiccator over sulfuric acid.

5

In addition to the above, other high temperature coefficient photosensitive materials, may be employed.

The photographic process may be carried out conveniently by the methods shown in the drawings. FIGURE 1 illustrates a means for making a contact print. FIGURE 2 shows a method for making a print by projection. FIGURE 3 shows an application of the process to a strip chart recorder. FIGURE 4 shows its use in a disc chart recorder.

In FIGURE 1, 3 is the metallic top of a hot plate capable of being heated to 80–140° C. by steam or electricity. Upon the heated surface is placed the high temperature coefficient photographic material 1, and over this the master copy 2 to be printed. If this copy is on a flexible material, such as paper, tracing cloth or film, it is covered by a glass plate 4 to hold the master copy 2 in close contact with the photographic material 1. If the master copy 2 has a rigid form, such as a glass plate or metallic stencil, the glass plate 4 may be omitted. Printing is carried out by radiation from the lamp 5. If the plate 4 is used it must, of course, be transparent to the effective radiation from the lamp, 5. After printing the photographic material 1 is removed from the hot plate. Contact with atmosphere at room temperature immediately cools and fixes the print.

In printing by projection as illustrated in FIGURE 2, the high temperature coefficient photographic material 1 is placed on the hot plate 3, and if the photographic material is flexible paper or film, covered with the glass plate 4. Light from the lamp 5, condensed by lens 6, passes through the master copy 2 the image of which is focused by lens 7 upon the heated photosensitive material 1.

In FIGURE 3 the unexposed high temperature coefficient photographic paper or film 1 is in the form of a strip which is stored on a roller 16. From 16 the photosensitive strip 1 unwinds to run over a metallic roller 18 that is heated internally by an electric heating element 12 to a surface temperature of 80° to 180° C. The photographic paper or film 1 is heated by contact with the surface of the hot roller 18 while exposed to the image of the point source lamp 5, formed by the concave mirror 13 on a galvanometer of which 14 represents the coil. From the hot roller 18, the film or paper 1 passes to the take-up roller 17 which is at room temperature. The lamp 5 is housed in a light shield 8 to prevent direct radiation from the lamp 5 reaching the heated sensitive material 1 on the roller 18.

FIGURE 4 is a view from above of a disc chart recorder using the process. Here the high temperature coefficient photographic material is in the form of a stiff paper disc 1 that holds its shape when mounted on the clockwork shaft 10 rotated by a clock mechanism 11. The sensing instrument, which may be a galvanometer as in the apparatus of FIGURE 3, or an aneroid barometer, or a pressure gauge, or other, is equipped with a concave mirror 13 which focuses an image of the point source lamp 5 upon the moving photosensitive chart 1. The radial strip of chart along which the light beam travels is heated from the rear by radiation from a length of electric heating element 12. As the chart 1 is rotated by the clock 11, the portion simultaneously heated by the element 12 and exposed to the focused beam from the lamp 5, passes out of range of the heat radiated by the heating element 12 and is cooled and thereby reduced in sensitivity by contact with the atmosphere at room temperature. If the disc chart 1 is coated with the high temperature coefficient printing material No. 1, described above, the arrangement of FIGURE 4 is useful for batch processing in kilns, autoclaves, and the like, where the batch cycle spans several days because the image printed on this phototropic sensitive material fades with time and the same chart may be used continuously over and over again without confusing the traces from different batches. Yet successive traces will indicate immediately any deviation in processing from batch to batch.

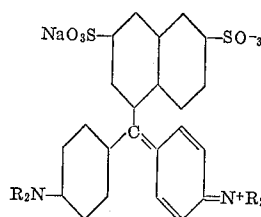
6

It will be seen that in the process as exemplified by each of the illustrations the high temperature coefficient photographic material is heated to an elevated temperature, preferably from 70–160° C., at the moment of exposure, and then cooled immediately after exposure to reduce the sensitivity of the photographic material and thus fix the image. Heating prior to exposure is not necessary, and any that may take place is incidental to the mechanical operations necessary for providing a heated photographic material at the moment of exposure. After exposure the print is cooled as rapidly as is mechanically practicable. No heat is needed to develop or fix the image, and heating after exposure is undesirable and to be avoided.

It will be apparent that there are many other means for heating the high temperature coefficient photographic material during exposure, such as by radiation from a heat lamp, or by a blast of hot air, or by preheating a glass plate coated with the high temperature coefficient film and exposing the film immediately after removal from the heat. Also there are other applications and ways in which the process may be carried out that will be apparent to those skilled in the art.

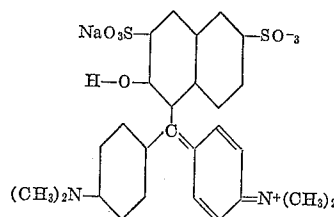
I claim:

1. The photographic process comprising the steps of raising the temperature of a high temperature coefficient printing-out composition containing a naphthalene derivative chosen from the group consisting of the cyanide of a diphenyl-naphthyl-methane dye and salicylal- β -naphthylamine coated onto a supporting surface to above 60° C. and below the melting point of the said naphthalene derivative, and exposing said coated surface to light while maintained within said temperature range to effect the formation of a visible image.
2. The process of claim 1 wherein said naphthalene derivative is salicylal- β -naphthylamine.
3. The process of claim 1 wherein said naphthalene derivative is the cyanide of a diphenyl-naphthyl-methane dye.
4. The process of claim 1 wherein said naphthalene derivative is bis-(4-dimethylaminophenyl)-(4-N-methylanilino)naphthyl-1)-acetonitrile.
5. The process of claim 1 wherein said naphthalene derivative is the cyanide of Naphthalene Green V, Colour Index No. 44025 of formula



where R is chosen from the group consisting of $-\text{CH}_3$ and $-\text{C}_2\text{H}_5$.

6. The process of claim 1 wherein said naphthalene derivative is the cyanide of the dye Wool Green S, Colour Index No. 44090 of formula



7. The photographic process comprising the steps of raising the temperature of a high temperature coefficient printing-out composition containing a naphthalene derivative chosen from the group consisting of the cyanide of a diphenyl-naphthyl-methane dye and salicylal- β -naphthylamine coated onto a supporting surface to above 60° C.

7

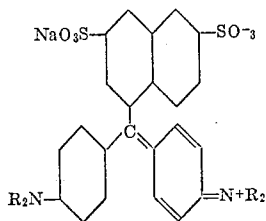
and below the melting point of the said naphthalene derivative, exposing said coated surface to light while maintained within said temperature range to effect the formation of a visible image, and cooling the printed coated surface below 40° C.

8. The process of claim 7 wherein said naphthalene derivative is salicylal- β -naphthylamine.

9. The process of claim 7 wherein said naphthalene derivative is the cyanide of a diphenyl-naphthyl-methane dye.

10. The process of claim 7 wherein said naphthalene derivative is bis-(4-dimethylaminophenyl)-(4-N-methylanilinophenyl-1)-acetonitrile.

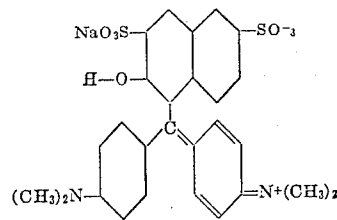
11. The process of claim 7 wherein said naphthalene derivative is the cyanide of the dye Naphthalene Green V, Colour Index No. 44025 of formula



8

where R is chosen from the group consisting of $-\text{CH}_3$ and $-\text{C}_2\text{H}_5$.

12. The process of claim 7 wherein said naphthalene derivative is the cyanide of the dye Wool Green S, Colour Index No. 44090 of formula



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