United States Patent

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[72] Inventors **Carl E. Johnson;**
Dewey M. Dumers, both of Binghamton, N.Y.

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[73] Assignee **GAF Corporation**
New York, N.Y.

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[54] **COLOR OSCILLOGRAPH RECORDING PAPER**
6 Claims, No Drawings

[52] **U.S. Cl.** **96/22,** 96/74
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[50] **Field of Search** ..... 96/48 QP, 22, 74

[56] **References Cited**

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Primary Examiner—Norman G. Torchin
Assistant Examiner—Mary F. Kelley
Attorneys—Walter C. Kehm, Samson B. Leavitt and George L. Tone

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ABSTRACT: Light-sensitive multicolor recording paper for oscillograph traces, having on a support, an undercoat of green-sensitive gelatin-silver bromoiodide emulsion in which the iodine amounts to 0.2–2.0 mol percent of the silver and containing a magenta color former, a gelatin interlayer, an overlying blue-sensitive gelatin-silver bromoiodide emulsion in which the iodine is 4–12 mol percent of the silver content and containing cyan color former, and a gelatin surface coating. By using yellow and magenta filters of different density for the exposing light and subjecting the material to color development, at least three different color traces can be produced.

COLOR OSCILLOGRAPH RECORDING PAPER

This invention relates, in general, to color oscillograph recording materials and, in particular, to photosensitive recording paper which finds immediate and practical utility for recording oscillograph traces in at least three colors.

Photosensitive papers adapted for light recording, for example, oscillograph recording, are known. Such materials are both of the printout type and the developing-out type. The printout type of material requires no development step and may or may not be fixed. Such materials are generally much slower than the materials used in developing-out processes and have poor image permanency. The developing-out type, as the name implies, requires that the exposed material be chemically developed, fixed and washed in order to provide a stable visible image on said material. It is this second type of printing material with which the present invention is concerned.

As light recording, e.g., oscillograph recording has increased in importance, there have evolved fields of use in which a multicolored recording is desirable. Wind tunnel and flight testing are examples of procedures where a plurality of colored traces is of considerable value. Idealized trace separation and readout of recorded data, of course, improves efficiency of inspection in changing conditions of operation and hence, is desired. Further, test results which can be recorded and visually observed in a relatively brief interval of time and using a simplified system of processing with a minimum number of solutions is also desired.

Accordingly, it is an object of this invention to provide a new recording material for use in oscillograph recording which has an extremely high sensitivity and will improve trace separation and readout.

Another object of this invention is to provide a simplified system of processing such papers for development employing a minimum number of solutions.

A further object of this invention resides in the provision of a color system which closely approximates the handling procedures used with conventional black and white oscillograph papers.

Still another object is a procedure which does not require a bleach step to remove image silver as required in conventional color systems.

Other objects and advantages of this invention will become further apparent from the following detailed description thereof.

In accordance with the above-defined objects, means have been devised for the accomplishment thereof which contemplate a photographic material comprising, (a) a flexible support bearing on at least one surface thereof, (b) an undercoat, (c) a separating layer comprising hardened gelatin, (d) an outer coating and, (e) a hardened gelatin surface layer.

The flexible support is usually "photographic paper" or "recording paper," which terms are used throughout the specification and claims to include photosensitive emulsions in any suitable support such as paper, film or other usable medium. It is preferred, however, to employ a paper such as 45–90 grams/square meter Document Paper (100 percent rag) without baryta coat or other surface or a paper similar thereto.

The undercoat layer comprises a silver bromoiodide emulsion which before optical sensitization has a low sensitivity to light having a wavelength of 480 microns and above. This undercoat layer has an iodide content of from about 0.2 to 2.0 mole percent, based on the amount of silver present in the emulsion. This undercoat is optically sensitized to the green region of the spectrum and contains a colorless color former, fast to diffusion, capable of reacting with the oxidation products of an aromatic p-amino developing agent to form a magenta dye image.

The outer coating comprises a silver bromoiodide emulsion layer having a high sensitivity to light in the 400–510 micron range when devoid of any optical sensitizing dye. The bromoiodide content of this outer layer ranges from about 4.0 to 12.0 mole percent based on the amount of silver present in the emulsion. This layer, further, contains a color former capable of forming a cyan dye image upon color development. For best results the sensitivity of the outer coating layer in the wavelength region of 480 to 500 microns should be at least two and one-half to three stops higher, (six to eight times faster) than the corresponding sensitivity of the undercoating layer.

The invention contemplates conventional photographic recording techniques in exposing the photosensitive emulsions to light in a oscillograph recorder. The recorder is necessarily provided with suitable colored filters in front of galvanometers used in conjunction therewith. The conventional photographic recording techniques, generally referred to as oscillography, involves the exposure of an entire roll of a record paper to the information to be recorded with subsequent and separate chemical development of the roll thus exposed. In this procedure a record roll of approximately 250–400 feet in length is entirely exposed before its removal from the oscillographic recorder and its subsequent development by conventional means.

In accordance with the invention, the color formers employed herein are those which are well known in the photographic art. The term "color former" is used throughout the specification and claims to define an essentially colorless compound fast to diffusion which is capable of reacting with the oxidation products of an aromatic p-amino developing agent, particularly of the N,N-disubstituted p-phenylenediamine series as exemplified by N,N-diethylamino aniline, hydroxyethyl)-aniline and the like, to produce dyes of the azomethine, quinoneimine, indoaniline and phenazine (azine) series. Such color formers are well known to persons skilled in the art and described in the patent literature, for instance in U.S. Pat. Nos. 2,500,487; 2,547,307; 2,829,975 and others. Illustrative of the color formers which are usable in accordance with this invention are compounds such as: 1-octadecyl-2-(2',1'-hydroxynaphthyl)-benzimidazole-5-sulfonic acid as a cyan color former; 1-(4'-phenoxy-3'sulphophenyl)-3-stearyl-5-pyrazole as a magenta color former; and 2-(4'-benzolyl-acetoaminophenyl)-1-octadecylbenzimidazole-5-sulfonic acid as a yellow color former. Generally speaking, the quantity of color former used per unit of silver halide is selected in such a way that sufficient density of the trace is achieved upon exposure and developing so as to provide proper readout. Specifically, it is recommended that the ratio of color former to silver halide per silver halide emulsion layer be about 10 millimole of color former to about 2 to 20 grams of silver halide.

The invention contemplates the use of a sensitizing dye capable of sensitizing in the green region of the spectrum. If desired, the blue sensitivity of the blue sensitive layer can be further increased by the use of a sensitizing dye for the blue. It is preferred that these dyes should be nonmigratory in the emulsion in which they are present so that the dyes cannot wander freely from layer to layer. Nonlimiting examples of sensitizing dyes usable herein are the various cyanine, carbocyanine, merocyanine, styryl and related sensitizing dyes which are well known to persons skilled in the art.

The emulsions may contain the usual coating finals such as those proposed to retard or prevent fog in light-sensitive silver halide emulsions. These compounds are commonly referred to as antifoggants or stabilizers and are, in many instances, heterocyclic compounds with a plurality of nitrogen atoms or with a mercapto group in their molecule.

Certain other adjuvants normally incorporated into silver halide photographic emulsions, such as wetting agents, may also be employed.

In accordance with this invention, it is contemplated to treat the aqueous gelatin dispersions and gelatin silver halide emulsions employed herein with a hardening agent in order to reduce the tendency of the layers to soften, melt or reticulate during processing, particularly at temperatures which are higher than the temperature of 68° F. (20° C.) previously specified for the processing of photographic materials. Com-

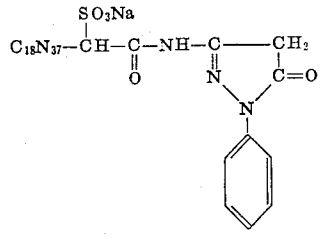
pounds which have been used for the hardening of gelatin and gelatin emulsion layers include formaldehyde, hydroxyaldehydes, glyoxal and its derivatives, triacrylformal, as well as mixtures of such aliphatic aldehydes with an aromatic hydroxy compound such as phenol, or resorcylic aldehyde. Other conventional hardeners also applicable include alum, chromalum, chromium acetate and the like.

Suitable supports for the novel silver halide emulsions and elements of this invention include the flexible supports used in the prior art for oscillographic recordings. These supports may be transparent but, in general, a photographic grade flexible paper is selected. In this regard, 55 g./m.^{2} of Document Paper (100 percent rag) without a baryta coating or other surface coating is especially preferred. However, there can be used any other flexible material suitable for coating with a photographic colloid silver halide emulsion.

The invention will be further illustrated by, but is not limited to, the following examples:

EXAMPLE I

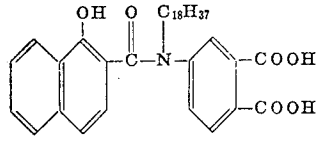
An improved recording paper was prepared by adding to 1,000 grams of a low blue sensitive bromoiodide emulsion containing 1.8 mole percent iodide the following ingredients: 165 cc. of a 1:2,000 solution containing a sensitizing dye for the green; 7 cc. of a 2 percent solution of a triazaindolzinc antifoggant; 60 cc. of a 10 percent solution of an ammonium salt of a sulfate ester of an alkyl phenoxypolyoxyethylene ethanol which serves as a coating aid; 25 cc. of a 6 percent solution of a triacrylformal hardener; 25 cc. of a 0.2 percent solution of a tetrazaindene restrainer and 20 grams of a magenta color former having the formula:



Thirty (30) grams of gelatin were added to the above ingredients along with 1,000 cc. of water so as to adjust it for the proper coating viscosity on 55 g./m.^{2} Document Paper (100 percent rag). This coating was applied to a thickness corresponding to a metallic silver coating weight of 0.4 gram per square meter.

In the same operation but at a different coating station, a 3.0 percent by weight gelatin surface solution containing the above wetting agent and 18 cc./kg. of a 10 percent formaldehyde solution was added.

In a second coating operation to 1,000 grams of a high speed bromoiodide emulsion were added 7 cc. of a 2 percent solution of a triazaindolzinc antifoggant; 45 cc. of a 10 percent solution of an ammonium salt of a sulfate ester of an alkyl phenoxypolyoxyethylene ethanol which serves as a coating aid; 30 cc. of a 6 percent solution of a triacrylformal hardener; and 20 grams of a cyan color former having the formula:



Forty (40) grams of gelatin were added to the above ingredients along with 1,000 cc. of water so as to adjust it for a proper coating viscosity. The so-adjusted emulsion was coated on top of the magenta layer to a coating thickness corresponding to a metallic silver coating weight of about 0.6 gram of silver per square meter.

In the same operation, but at a different coating station, 3.0 percent by weight of the above-described gelatin solution was applied.

The coated material with the two silver halide layers was exposed using a commercially available oscillograph (manufactured by the Midwestern Instruments Corp.) employing a tungsten light source (2,850° K.) under the following conditions:

Galvanometer identification	Filter	Transmission	Absorption
A	Yellow	580 through 700	Magenta.
B	Magenta	455 and 700	Cyan.
C	Yellow [1]	580 through 700	Deep purple.
D	Magenta [1]	455 and 700	Deep blue.
E	Yellow [1]	580 through 700	Dark magenta.

[1] Color correction.

The lamp voltage was set at 12 volts and paper travel rate was adjusted at 25 inches/second.

In order to expose the recording paper, signal generators were used to apply a sine wave of 20 cycles/second to each galvanometer and the amplitude was varied to give a trace deflection of from 1 to 4 inches.

The resulting exposed material was then placed in a standard automatic oscillogram processor as manufactured by Consolidated Electrodynamics Corp., and processed at a rate of about 6 feet/minute for a contact time of about 20 seconds in each tank. In such processor apparatus 4 tanks were utilized, each being maintained at a temperature of about 100° F., with the following tank arrangement as to contents:

Tank Number	Tank Contents	
1	Color Developer	(6 liters)
2	Color Developer	(4 liters)
3	Fixer	(4 liters)
4	Fixer	(4 liters)

The availability of two developer and two fixer tanks made it possible to extend the processing time and to extend the useful life of the processing solution.

In the foregoing the color developer and fixer utilized contained the following ingredients and in the following amounts:

COLOR DEVELOPER

Ingredient	Amount
Sodium pyrophosphate	1.0 gram
Sodium sulfite (anhydrous)	4.0 grams
Sodium carbonate (monohydrate)	60.0 grams
Potassium bromide	1.0 gram
4-N,N,-di (β-hydroxyethyl)-aminoaniline	7.5 grams
Water	up to 1 liter with pH adjusted to 10.6

FIXER

Ingredient	Amount

HYPO (sodium thiosulfate, anhydrous	130.0 grams
Water	up to 1 liter

The resulting processed paper showed five distinct and separate traces, namely, magenta, cyan, purple, deep blue and dark magenta. The magenta trace was produced by the light from galvanometer A which was fitted with the yellow filter. The cyan trace was produced by the light from galvanometer B which was fitted with the magenta filter. The purple trace was produced by the light from galvanometer C which was fitted with a yellow color-correction filter, the deep blue trace by the light from galvanometer D, which was fitted with a magenta filter and the dark magenta trace was produced by the light from galvanometer E which was fitted with a yellow color-correction filter.

It should be noted that in practice the filters selected to produce the various desired colored trace lines are determined by the speed of the sensitive material as related to the light source intensity and the color temperature. Thus, the above filters were selected for use with a tungsten light source. For practical use with an oscillograph using a UV light source, other filters may be needed especially to balance the so-called "white light" trace. Nonlimiting examples of the filters which may be suitably employed are as follows:

Color Trace	Filter Type
Magenta	Wratten Nos. 12, 15, 16, 56, 57, 58, 61, 74
Cyan	Wratten Nos. 32, 34, 47, 47B, 48, 48A, 49, 49B
Blue to purple magenta	From 10Y to 50Y and 10M to 50M

The processing technique employed offers several advantages. The availability of two developer and fixer tanks makes it possible to extend not only the developing time and fixing time but also the useful life of the processing solutions. The omission of the bleaching step results in color pictures which contain a warm tone silver deposit. The presence of the silver deposit makes it possible to reproduce the oscillograph recording on diazo-type materials.

Modifications of the invention will occur to persons skilled in the art. It is, therefore, not intended to be limited in the patent granted except as necessitated by the appended claims.

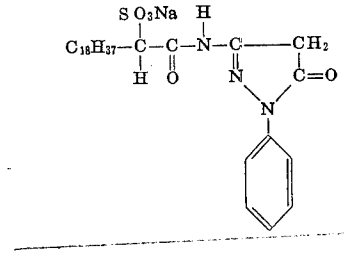
What is claimed is:

1. A multicolor recording paper for recording oscillograph traces in at least three colors which comprises (a) a flexible support bearing on at least one surface thereof, in the following order: (b) an undercoat of a hardened silver bromoiodide emulsion, having a low sensitivity to light having a wavelength of 480 microns and above, and being optically sensitized to the green and containing a color former capable of forming a magenta dye image upon color development, said emulsion having an iodide content ranging from 0.2 to 2.0 mole percent based on the amount of silver present, (c) a hardened gelatin intersurface layer, (d) a hardened silver bromoiodide outer emulsion coating which is blue sensitive in the wavelength region ranging from 400 to 510 microns and containing a color former capable of forming a cyan dye image upon color development, the iodide content of said upper emulsion ranging from 4.0 to 12 mole percent based on the amount of silver present, and (e) as an outer surface layer, a hardened gelatin layer.

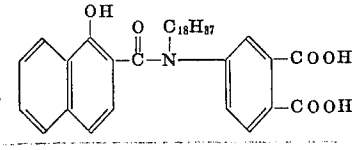
2. The paper of claim 1 in which the silver halide emulsion layers are coated to a silver coating weight of about 0.4 grams silver per square meter.

3. The paper of claim 1 in which the outercoat silver halide emulsion layer has a light sensitivity in the wavelength region from 480 to 500 microns region which is at least six times higher than that of the undercoat silver halide emulsion layer.

4. The paper of claim 1 in which the magenta color former has the formula:



5. The paper of claim 1 in which the cyan color former has the formula:



6. A process of forming a multicolored image which comprises exposing with a plurality of selectively filtered colored lights, a multicolor recording paper for recording oscillograph traces in at least three colors which comprises, (a) a flexible support bearing on at least one surface thereof in the following order: (b) a hardened silver bromoiodide emulsion, having a low sensitivity to light having a wavelength of 480 microns and above, and being optically sensitized to the green and containing a color former capable of forming a magenta dye image upon color development, said emulsion having an iodide content ranging from 0.2 to 2.0 mole percent based on the amount of silver present in the emulsion, (c) a hardened gelatin intersurface layer, (d) a hardened silver bromoiodide emulsion coating which is blue sensitive in the wavelength region ranging from 400 to 510 microns and containing a color former capable of forming a cyan dye image upon color development, the iodide content of said outer coated emulsion layer ranging from 4.0 to 12.0 mole percent based on the silver present, and (e) as an outer surface layer, a hardened gelatin layer, developing the imagewise exposed recording material with a color developer solution comprising an aromatic diamine developing agent and fixing the color developed material without bleaching and washing the processed material.