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COLOR OSCILLOGRAPH RECORDING PAPER

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U.S. Cl. 96—22 11 Claims

ABSTRACT OF THE DISCLOSURE

Multicolor recording paper for recording oscillograph traces in at least three colors comprising, on the flexible support, a hardened silver chlorobromide emulsion, sensitized to green light and containing a magenta color former, a hardened gelatin interlayer, a hardened silver bromoiodide emulsion having high blue sensitivity and containing a cyan color former, and an outer hardened gelatin surface layer.

This invention relates to color oscillograph recording materials and, more particularly, to photosensitive recording paper having utility for recording oscillograph traces in at least three colors.

Photosensitive papers adapted for light recording, for example, oscillograph, recordings, are known. Such materials are both of the print-out type and the developing-out type. The print-out 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 multi-colored 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.

An object of this invention, therefore, is to provide a new recording material for use in oscillograph recording which 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. Another object of this invention is to provide 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, as well as advantages emanating from this invention will become apparent from a reading of the following description.

The above objects are accomplished in accordance with the present invention which contemplates a photographic material comprising a flexible support bearing on at least one surface thereof (a) an undercoat comprising a silver chlorobromide emulsion layer having a low blue sensitivity, being practically insensitive to light having a wave length of 460 microns and above before optical sensitization, being sensitized to the green region of the spectrum

and containing 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; (b) a separating layer comprising a hardened gelatin layer; (c) an outer coating comprising a silver bromoiodide emulsion layer having a high sensitivity to the blue light without containing an optical sensitizing dye, but containing a color former capable of forming a cyan dye image upon color development; and (d) a hardened gelatin surface layer.

The terms "photographic paper" and "recording paper" are used throughout the specification and claims to include photosensitive emulsions disposed 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% rag) without baryta coat or other surface or a paper similar thereto.

Briefly, the invention contemplates conventional photographic recording techniques in exposing the photosensitive emulsions to light in an 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, N,N-di-(β-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 United States Patents 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′-benzolylacetaminophenyl)-1-octadecyl-benzimidazole-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 millimols 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 non-migratory in the emulsion in which they are present so that the dyes cannot wander freely from layer to layer. Non-limiting 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.

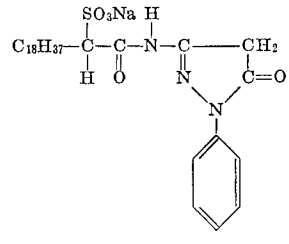
In accordance with this invention, it is contemplated to treat the aqueous gelatin dispersions and gelatin silver halide emulsions employed herein with a hardening agent in order to reduce the tendency of the layers to soften, melt or reticulate during processing, particularly at temperatures which are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

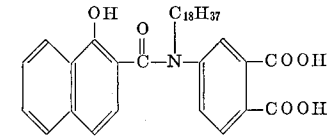
An improved recording paper was prepared by adding to 1000 grams of a low blue sensitive chlorobromide emulsion the following ingredients: 120 cc. of a 1:2000 solution containing a sensitizing dye for the green; 0.5 gram of an antifoggant; 30 cc. of a 10% solution of an ammonium salt of a sulfate ester of an alkyl phenoxypolyoxyethylene ethanol which serves as a coating aid; 1.2 grams of a triacrylformal hardener; and 15 grams of a magenta color former having the formula:



500 cc. of water was added to the above emulsions so as to adjust it for the proper coating viscosity on 55 gram Document Paper (100% rag). This coating was applied to a thickness corresponding to a metallic silver coating weight of 0.4 to 0.5 gram per square meter.

In the same operation but at a different coating station, a 3.5 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 1000 grams of a high speed bromoiodide emulsion was added 0.5 gram of an antifoggant; 30 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; 1.2 grams of a triacrylformal hardener; and 15 grams of a cyan color former having the formula:



1000 cc. of water was added to the above emulsion 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 0.7 to 0.8 gram of silver per square meter.

In the same operation, but at a different coating station, 3.5 percent by weight of the above-described gelatin solution was applied.

The 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 under the following conditions:

Galvanometer Identification	Filter	Transmission	Absorption
A	Yellow	580 through 700	Blue.
B	Magenta	455 and 700	Green.
C	Pale Magenta Color Correction.	455 and 700	Predominantly Green.
D	None		

The lamp voltage was set at 12 volts and paper travel rate was adjusted at 2.5 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 4 feet/minute. 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 No.:	Tank contents
1	Color developer.
2	Do.
3	Fixer.
4	Do.

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, grams
Sodium pyrophosphate	1.0
Sodium sulfite (anhydrous)	4.0
Sodium carbonate (monohydrate)	60.0
Potassium bromide	1.0
4-N,N-di(β-hydroxyethyl)-aminoaniline	7.5

Water up to 1 liter with pH adjusted to 10.6.

Fixer

Ingredient:	Amount, grams
HYPO (sodium thiosulfate, anhydrous	130.0

Water up to 1 liter.

The resulting processed paper showed four distinct and separate traces, namely, cyan, magenta, deep blue and purple. 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 deep blue trace was produced by the light from gal-

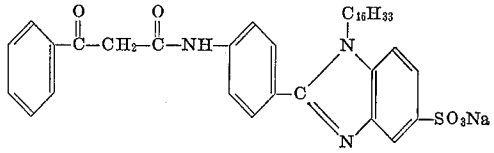
vanometer C which was fitted with the pale magenta color-correction filter and the purple trace by the light from galvanometer D, which was not fitted with a filter.

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, 47B, 48, 49.
Blue to bluish magenta -----	Neutral density or pale magenta color correction or pale yellow color correction filters.

EXAMPLE 2

A recording paper was prepared in a manner similar to that of Example 1 except for changes in the color formers employed. Thus, the paper was prepared by adding to 1000 grams of a low blue sensitive chlorobromide emulsion the following ingredients: 120 cc. of a sensitizing dye for the green, $\frac{1}{2000}$; 0.5 gram of an antifoggant; 30 cc. of a 10% solution of the ammonium salt of a sulfate ester of an alkyl phenoxypolyoxyethylene ethanol which serves as a wetting agent; 1.2 grams of triacrylformal hardener; and 10 grams of the magenta color former employed in Example 1, and 5 grams of a yellow color former having the formula:



About 500 cc. of water was added to adjust the emulsion to the proper viscosity for coating on 55 gram Document Paper to a coating weight corresponding to about 0.4 to 0.5 gram of silver/square meter.

In the same operation, a 3.5 percent by weight gelatin surface solution containing a wetting agent and 18 cc./kg. of a 10% formaldehyde solution was added to form a surface coating.

In a second operation, a layer was coated prepared from a high-speed bromoiodide emulsion containing 0.5 gram of an antifoggant; 30 cc. of the above wetting agent solution; 1.2 grams of a formaldehyde hardener and 10 grams of the cyan color former employed in Example 1 and 5 grams of the yellow color former employed in Example 1.

Similar to the procedure of Example 1, a 3.5% by weight solution of gelatin and formaldehyde hardener was applied as a surface coating.

The resulting recording paper was exposed and processed in the apparatus employed in Example 1 with the following results being obtained:

The light from galvanometer A which was filtered with the yellow filter produced a red trace; the light from galvanometer B fitted with the magenta filter produced a green trace. Unfiltered light was found to produce a substantially neutral gray trace.

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 diazotype 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 flexible support bearing on at least one surface thereof in the following order: (a) a hardened silver chlorobromide emulsion substantially insensitive to light of a wave length of 460 microns and above, being optically sensitized to the green and containing a color former capable of forming a magenta dye image upon color development, (b) a hardened gelatin intersurface layer, (c) a hardened silver bromoiodide emulsion coating having blue sensitivity and containing a color former capable of forming a cyan dye image upon color development, and (d) as an outer surface layer a hardened gelatin layer, each of said emulsion layers being coated to a silver coating weight of 0.4 to 0.8 gram silver per square meter.

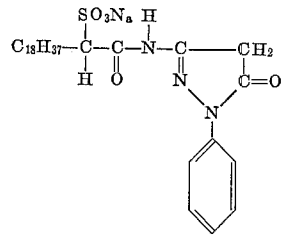
2. A recording paper according to claim **1** wherein the lower silver chlorobromide emulsion layer contains a mixture of a magenta and a yellow color former.

3. The paper of claim **1** in which the upper silver bromoiodide emulsion layer contains a color former for the cyan image and a color former for the yellow image.

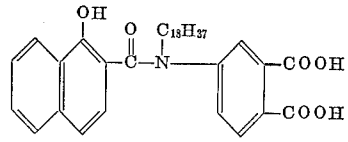
4. The paper of claim **1** in which the lower silver emulsion layer is coated to a silver coating weight of from about 0.4 to 0.5 gram silver per square meter, and the outer emulsion layer is coated to a silver coating weight of from about 0.7 to 0.8 gram silver per square meter.

5. The paper of claim **1** in which the silver halide emulsion layer is hardened with triacrylformal.

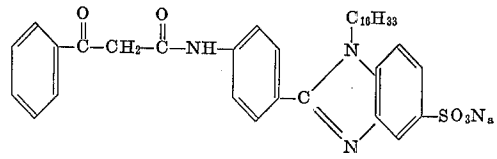
6. The paper of claim **1** in which the magenta color former has the formula:



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



8. The paper of claim **1** in which both the lower silver chlorobromide and the upper bromoiodide emulsion layers contain a yellow color former having the formula:



9. The paper of claim **6** in which said magenta color former is mixed with a yellow color former.

10. The paper of claim **7** in which said cyan color former is mixed with a yellow color former.

11. The 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 flexible support bearing on at least one surface thereof in the following order: (a) a hardened silver chlorobromide emulsion substantially insensitive to light of a wave length of 460 microns and above, being optically sensitized to the green and containing a color former capable of forming a magenta dye image upon color development, (b) a hardened gelatin intersurface layer, (c) a hardened silver bromoiodide emulsion coating having blue sensitivity and containing a color former capable of forming a cyan dye image upon color development, and (d) as an outer surface layer a hardened gelatin layer, each of said emulsion layers being coated to a silver coating weight of 0.4 to 0.8 gram silver per square meter, developing the imagewise exposed recording material with a developer solution comprising an aromatic amino developing agent and fixing the color developed material without bleaching the processed material.

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U.S. Cl. X.R.

96—74

Disclaimer

3,499,758.—*Carl E. Johnson* and *Dewey M. Dumers,* Binghamton, N.Y. COLOR OSCILLOGRAPH RECORDING PAPER. Patent dated Mar. 10, 1970. Disclaimer filed Sept. 30, 1982, by the assignee, *Eastman Kodak Co.*

Hereby enters this disclaimer to all claims of said patent.

[*Official Gazette March 22, 1983.*]