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COLOR OSCILLOGRAPH RECORDING PAPER

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ABSTRACT OF THE DISCLOSURE

Multicolor oscillograph recording material having on a support a hardened green sensitive silver halide emulsion layer of low blue sensitivity containing a diffusion-fast color former yielding a magenta image on development with an aromatic p-amino developing agent, a hardened gelatin interlayer, a hardened middle layer of silver halide emulsion containing a cyan color former, a hardened gelatin interlayer, a hardened upper layer of red sensitive silver halide emulsion of low blue sensitivity containing a yellow color former, and a hardened gelatin surface layer.

This invention relates to color oscillograph recording paper and, more particularly, to three-color photosensitive recording paper having utility for recording oscillograph traces in seven or more hues.

Photosensitive papers adapted for light recording, for example, oscillograph recording, 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 same 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, improve efficiency of inspection in changing conditions of operation and hence are 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 are also desired.

In the Carl E. Johnson and Dewey M. Dumers U.S. patent application Ser. No. 462,063, filed June 7, 1965 is described two-color photosensitive recording paper having utility for recording oscillograph traces in three or more colors. While the two-color photosensitive recording paper described and claimed therein represents a considerable advance in the art, the advantages emanating from a three-color paper having improved trace separation and readout are readily apparent. These advantages will be magnified if the three-color recording paper can be processed by handling procedures which approximate those employed with conventional black and white oscillograph papers and will provide completely acceptable visual discrimination results even though the silver in the dye images is not bleached out.

An object of this invention, therefore, is to provide a new recording paper 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 of this invention is to provide a three-color recording paper 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 invention contemplates a photographic material comprising a flexible support, preferably paper, bearing on at least one surface thereof (a) an undercoating comprising a silver chlorobromide emulsion layer of low blue sensitivity, optically sensitized to green and containing a magneta color former; (b) a gelatin separation layer comprising a hardened gelatin layer; (c) a middle coating comprising a light-sensitive silver bromoiodide emulsion of high blue sensitivity without containing an optical sensitizing dye but containing a cyan color former; (d) a hardened gelatin separation layer; (e) an outer coating comprising a silver halide sensitive emulsion layer of low blue sensitivity, pan-sensitized and containing a yellow color former; and (f) a hardened gelatin surface layer. The middle emulsion layer has a higher sensitivity to blue light than the other two silver halide emulsion layers when compared at 460 to 480 mu.

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 or part roll of a recording 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 may be entirely exposed before its removal from the oscillographic recorder and its subsequent development by conventional means.

The photographic silver halide emulsions which can be advantageously employed in the recording papers of this invention are the type customarily employed in the art and include such well-known types as silver chloride, silver chlorobromide, silver bromide and silver bromoiodide emulsions.

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 a chemical compound which is capable of reacting with the oxidation product of an aromatic amino developing agent, preferably one of the p-phenylenediamine series, e.g., 4-N,N,-diethylamino aniline, 4-N,N-di-(β-hydroxyethyl)-aminoaniline to form visible dye images of the quinoneimine, indoaniline, azomethine of phenazine (azine) series. These color formers which are fast to diffusion are well known and are illustrated by the compounds described in U.S. Patents 2,500,487; 2,547,307; 2,829,975 and others. These color formers fast to diffusion are further illustrated by 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 - acetaminophenyl)-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 millimols of color former to about 2 to 20 grams of silver halide.

The invention contemplates the use of one or more sensitizing dyes capable of sensitizing in any desired region of the spectra. It is preferred that the dyes employed should be nonmigratory 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 cyanine, cyazine, merocyanine, styryl and related sensitizing dyes.

In addition to the foregoing, one or more of a large number of substances which have been proposed as being effective in retarding or preventing fog when such entities are incorporated in light-sensitive silver halide emulsions may be employed in the instant invention. These photographic adjuncts are commonly referred to as antifoggants or stabilizers, and, typically, may be a compound which has a mercapto function as the reactive group in its molecular structure.

Additionally, certain other adjuvants normally incorporated into silver halide photographic emulsions, such as, for example, wetting agents, etc., 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.) normally specified for the processing of photographic materials. Compounds which have been used for hardening of gelatin and gelatin emulsion layers include formaldehyde, triacryl formal hydroxyaldehydes, glyoxal and its derivatives, as well as mixtures of such aliphatic aldehydes with an aromatic hydroxy compound such as phenol, or resorcyclic aldehyde. Other conventional hardeners also applicable include alum, chromalum, chromium acetate and the like.

As stated, the inner-, middle- and outer-coatings of emulsion are coated with a thin hardened, hydrophilic colloid layer of gelatin. These colloid layers are alkali permeable. Hardening of these layers may be effected by use of the conventional hardeners set forth above.

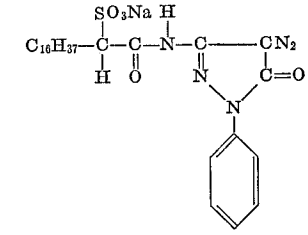
Suitable supports for the novel silver halide emulsions and elements of this invention include the flexible supports used in the prior art for light writing and oscillographic recording elements. In general, the supports will be a photographic grade of paper that has a fair degree of opacity of which unsized, flexible paper is preferred. In this regard, 55 g./m.^{2} document paper (100% rag) without baryta coat or other surface is especially preferred. However, there can be used any opaque, 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 sensitizing dye for the green portion of the spectrum (1/2000 solution) 0.1 gram of an antifoggant, e.g., a tetrahydropyranthioether; 30 cc. of a wetting agent comprising a 10% solution of an ammonium salt of a sulfate ester

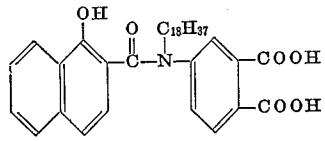
of an alkyl phenoxypolyoxyethylene ethanol; 1.2 grams of a hardener, preferably triacrylformal; and 15 grams of a magenta color former having the formula:



500 cc. of water was added to the above ingredients so as to adjust same to a proper viscosity for coating on 55 gram document paper (100% rag). This emulsion coating was applied in a thickness corresponding to a metallic silver coating weight of from 0.5 to 0.8 gram silver/square meter of coated area.

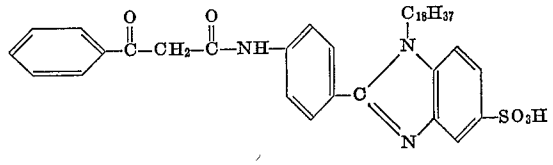
In the same operation but at a different coating station, a 3.5 percent by weight gelatin surface solution containing the above-described wetting agent and 18 cc./kg. of 10 percent formaldehyde solution was added.

In a second coating operation, to 1000 grams of a high speed bromoiodide emulsion was added 0.1 gram of an antifoggant; 30 cc. of a wetting agent used as a 10 percent solution of an ammonium salt of a sulfate ester of an alkyl phenoxypolyoxyethylene ethanol; 1.2 grams of a hardener preferably triacrylformal; and 15 grams of a cyan color former having the formula:



1000 cc. of water was added to the above ingredients so as to adjust same to a proper viscosity and the so-adjusted emulsion was coated on top of the surface layer covering the magenta layer to a coating thickness corresponding to a silver coating weight of 0.5 to 0.8 gram of metallic silver per square meter. As in the preceding steps, a 3.5 percent by weight gelatin solution was applied in the same operation.

In a third coating operation, to 1000 grams of the same low blue sensitive chlorobromide emulsion was added 120 cc. of a sensitizing dye for the red region; 0.1 gram of an antifoggant; 30 cc. of a wetting agent used as a 10 percent solution of an ammonium salt of a sulfate ester of an alkyl phenoxypolyoxyethylene ethanol; 1.2 grams of a hardener, preferably triacrylformal; and 15 grams of a yellow color former having the formula:



Sufficient water was added to the above ingredients so as to adjust same to a proper viscosity and the so-adjusted emulsion was coated on top of the gelatin layer above the cyan layer to a coating thickness corresponding to a silver coating weight of from 0.5 to 0.8 gram of metallic silver per square meter of over-coated area.

In the same operation but at another coating station there was applied a 3.5 percent by weight gelatin solution containing the above described wetting agent and a hardening agent.

Galvanometer identification:	Filter	Transmission	Absorption
A	Red	640–700 μm	Blue green.
B	Green	520	Red and blue.
C	Blue	430	Green and red.
D	Yellow	580 thru 700	Blue.
E	Magenta	455 and 700	Green.
F	Cyan	480	Red.
G	0.1 Neutral density	400–700	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 commercially available automatic oscillogram processor and processed at a rate of about 4 feet/minute for a contact time of about 30 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.
2	Color developer.
3	Fixer.
4	Fixer.

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

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:	
Hypo (sodium thiosulfate, anhydrous)	130.0
Water, up to 1 liter.	

The resulting processed paper showed the following distinct and separate traces.

Galvanometer identification:	Trace
A	Yellow.
B	Magenta.
C	Cyan.
D	Red.
E	Green.
F	Blue.
G	Black.

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 temperatures. Thus, the above filters were selected for use with a white light source. For practical use with an oscillograph using a UV or tungsten light source. Non-limiting examples of the filters which may be suitably employed are as follows.

Color trace:	Filter type (Wrattan numbers)
Magenta	56, 57, 58, 61, 74.
Cyan	47, 47B, 48, 48B, 49, 49B.
Blue	44A, 44.
Red	12, 15, 16.
Yellow	29, 25, 70.
Green	32, 34.
Black	Neutral density.

EXAMPLE II

A recording paper was prepared and exposed in a manner similar to that of Example I except that the resulting exposed recording paper was processed as follows:

In a first step the exposed material was contacted with the color developer utilized in Example I, above. The contact time was adjusted to 60 seconds and at a temperature of 100° F. The thus-treated material was subsequently treated to a short stop treatment employing a 2.5% by weight solution of $NaHSO_3$ for 30 seconds at 100° F.

In a third step the material was bleached employing a bleach of the following composition:

Potassium ferricyanide	g— 50
Potassium ferrocyanide	g— 5
Sodium bromide	g— 15
Disodium phosphate	g— 11
Citric acid	g— 8
Formaldehyde	ml— 15

with sufficient amounts of water up to about 1 liter. The material was bleached for 30 seconds at a temperature of 100° F.

Upon termination of the bleaching step the exposed and processed material was fixed employing the fixer of Example I for 60 seconds at 100° F.

In a final step the material was washed at a temperature of 100° F. for a period of 60 seconds.

Upon comparison of the two developing processes, it is evident that the bleaching of the image silver somewhat improves color purity, especially in the red and yellow images produced. Advantageously, however, for recognition as discreet and readily discernable traces, the unbleached traces, e.g., as produced in Example I, are extremely satisfactory.

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 material for the improved recording of oscillograph traces which comprises a flexible support bearing on at least one surface thereof, in the following order, (a) a hardened undercoat comprising a green sensitive silver halide emulsion layer of low blue sensitivity and containing a color former fast to diffusion capable of forming a magenta image upon developing with an aromatic p-amino developing agent, (b) a hardened gelatin intersurface layer, (c) a hardened middle coat comprising a gelatin silver halide emulsion containing a color former capable of forming a cyan image upon reacting with the oxidation products of an aromatic p-amino developing agent, (d) a hardened gelatin intersurface layer; (e) a hardened outer coat comprising a red sensitive silver halide emulsion layer of low blue sensitivity containing a color former for the yellow image, and (f) an outer surface comprising a hardened gelatin layer.

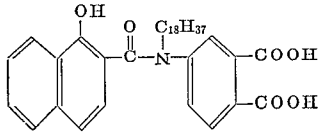
2. The paper of claim **1** in which the middle emulsion layer has a higher sensitivity to blue light than the two other silver halide emulsion layers when compared at 460 to 480 mu.

3. The material of claim **1** in which the three silver halide emulsion layers are coated to a silver halide coating

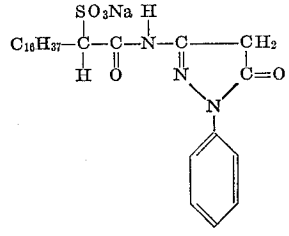
weight corresponding from about 0.5 to 0.8 gram of silver per square meter.

4. The material of claim 1 in which the hardener is triacrylformal.

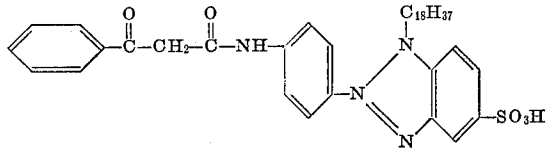
5. The material of claim 1 in which the cyan color former has the formula:



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



7. The material of claim 1 in which the yellow color former has the formula:



8. A process of forming a multicolored image which comprises exposing with a plurality of selectively filtered colored lights, a multicolor recording material for the improved recording of oscillograph traces which comprises a flexible support bearing on at least one surface thereof, in the following order, (a) a hardened undercoat comprising a green sensitive silver halide emulsion layer of low blue sensitivity and containing a color former fast to diffusion capable of forming a magenta image upon developing with an aromatic p-amino developing agent, (b) a hardened gelatin intersurface layer, (c) a hardened gelatin silver halide emulsion layer of high blue sensitivity and containing a color former capable of forming a cyan image upon reacting with the oxidation products of an aromatic p-amino developing agent, (d) a hardened gelatin intersurface layer, (e) a hardened outer coat comprising a red sensitive silver halide emulsion layer of blue sensitivity containing a color former for the yellow image, and (f) an outer surface comprising a hardened gelatin layer, developing the imagewise exposed recording material with a developer solution comprising an aromatic p-amino developing agent, fixing the color developed material, and drying the same without bleaching and washing the processed material.

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96—74

Disclaimer

3,490,904.—*Carl E. Johnson* and *Dewey M. Dumers,* Binghamton, N.Y. COLOR OSCILLOGRAPH RECORDING PAPER. Patent dated Jan. 20, 1970. Disclaimer filed Sept. 30, 1982, by the assignee, *Eastman Kodak Co.*

Hereby enters this disclaimer to all claims of said patent.

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