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ELECTRON BEAM RECORDING MEDIUM WITH AMINO-AZO INDICATOR AND HALOGENATED POLYMER COATING

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The present invention relates to media for recording intelligence, particularly for the recording of intelligence by means of an electron beam, and to the process in which such media are used.

Cathode ray tubes with phosphor screens having a visible response essentially instantaneous with electron beam impingement have been commonly used for transducing transmitted intelligence in electrical form into a visual form. However, the image on the phosphor screens of such tubes is transistory and cannot be stored for any length of time without auxiliary means for providing a permanent record. Numerous efforts have been directed to recording permanently the transitory images on cathode ray tubes by various electronic and optional photographic methods. Special tube faces have been suggested to permit the use of electrostatic development of special papers passed continuously over the tube face, but these tube constructions frequently have produced records with poor resolution due to various forms of distortion associated with the system. The recording of a light image on a medium containing an acid-base type indicator dye and a halogenated compound which produces hydrochloric acid under the influence of light, has been described in the literature. However, applicant has found that such media, when placed under vacuum conditions for direct electron beam impingement, tend to lose volatile reactants, e.g. the relatively low molecular weight halogenated compounds.

It is an object of this invention to provide an electron beam recording medium which can be used under vacuum conditions and which can be activated with direct electron beam impingement.

It is another object of this invention to provide an electron beam recording media which can provide relatively stable storage of intelligence over an extended period of time.

Still another object of this invention is to provide a recording medium for reliable and efficient recording of images formed by an electron beam.

Yet another object of this invention is to provide a process for transducing electrical information into a visual record.

A further object of this invention is to provide means for recording facsimile or electrical intelligence.

Other objects and advantages will be apparent from the following description.

In accordance with this invention the above and other objects are realized by providing a recording media which comprises a substrate, preferably an electrically conductive substrate, on which is superimposed a layer containing an oil soluble amino azo indicator dye in basic form and a highly halogenated polymeric binder. Although the indicator is generally homogeneously disposed throughout the halogenated polymeric binder, and is preferably dissolved therein, it may also be provided as a localized coating on or in the top surface of the polymeric binder.

The oil soluble amino azo indicator dyes change color at a pH of from about 7, preferably in the pH range of 2 to 4, and have relatively low volatility, e.g. a boiling point above about 90° C. at atmospheric pressure. These indicators become quinoid in the presence of acid and are characterized by their good sensitivity and, in the case of

Congo red A, ability to form very stable images. The oil soluble amino azo indicators have been found to be outstanding, since the presence of sufficient water solubilizing groups (e.g. acyl groups and their salts) to adversely affect oil solubility tends to reduce the electron beam sensitivity of the film. Solubility of the indicator in the highly halogenated polymeric binder normally permits optimum results with a minimum concentration of indicator.

The highly halogenated polymers which liberate hydrogen halide upon electron beam bombardment should be normally solid and of sufficiently high molecular weight to prevent their volatilization (i.e. above 1000 preferably above 10,000 number average molecular weight), the film forming, and contain, in addition to hydrogen, from about 25 to about 73 weight percent of labile chlorine or bromine. For ease of coating the electrically conductive substrate the polymers desirably are soluble in conventional organic solvents such as tetrahydrofuran, acetone, 2-butanone, methyl ethyl ketone, etc., although other solvent systems can be used for the more difficultly soluble polymers such as polyvinyl chloride and polyvinylidene chlorine. Solubility can be adjusted to some extent by employing copolymers, a balance being achieved between halogen content and copolymer solubility. Vinylidene chloride copolymers with such monomers the aliphatic acrylates (e.g. n-butyl acrylate, methyl acrylate, ethyl acrylate, hexyl acrylate, methyl methacrylate, beta-chloroethyl acrylate, etc.), acrylonitrile, vinyl choride, vinyl acetate, vinyl butyrate, etc, are preferred highly halogenated polymer systems. Ethylenically unsaturated monomers with a high halogen content, such as 1,1,3,3,3-pentachloropropene-1, fluorotrichloroethylene, 1,1-difluoro-2,2-dichloroethylene, trichloroethylene, etc. copolymerized with vinyl or vinylidene chloride or bromide or with the aliphatic acrylates can also be employed. Halogenated aromatic polymers are considerably less effective than the halogenated aliphatic polymers, although the copolymerization of a suitable halogenated aliphatic monomer with an aromatic monomer (e.g. styrene, vinyl toluene, vinyl carbazole, etc.) selected for its solubility characteristics is suitable. With the preferred vinylidene chloride polymers the chlorine concentration ranges from about 25 to about 73 percent, preferably from about 40 to about 70 percent by weight. With the vinyl chloride polymers the chlorine concentration ranges from about 35 to 55 percent, preferably from about 20 to about 55 percent by weight of the polymer. Although the halogenated polymers are desirably deposited from solution as a film on the electrically conductive substrate, they may also be deposited from a latex or intimate dispersion. With those polymers which tend to decompose slowly in the presence of ordinary light and atmospheric oxygen, anti-oxidants and other stabilizers may be added to improve good storage life.

Since the highly halogenated polymer serves as a relatively non-volatile source of hydrohalic acid, no other brominated or chlorinated compounds which liberate acid under electron beam exposure are required in the film. In fact, the monomeric or non-polymeric halogenated compounds are undesirable not only because of their higher volatility in vacuum but also because of their frequently encountered sensitivity to moisture, air oxidation and photodecomposition under visible light and their adverse effect on the physical properties of the film, such as by dilution of the polymeric vehicle. Materials which are highly sensitive to visible light, e.g., silver halide, zinc oxide, etc., are also undesirable, since the media construction should be essentially stable to visible light. Slight fading of certain indicators upon extended exposure to visible light is unobjectionable. Non-polymeric sources of hydrogen halide and materials sensitive to visible light are therefore excluded from the sheet.

The media of this invention may be prepared by mixing a minor amount of the acid sensitive amino azo indicator dye with a solution of the highly halogenated polymer and coating the resulting admixture as a thin film, i.e., usually from 1 micron to several mils, preferably from about 2 to about 15 microns, onto the electrically conductive substrate. Aluminum foil, metal coated plastic, conductive papers, etc., can be used for the electrically conductive substrate. If a transparency is desired or if it is desired to view the image through the backing, a thin, light transmissive aluminum vapor coated plastic (e.g., polyethylene terephthalate) or a conductive glass (e.g., Nesa glass) substrate may be used in conjunction with a light transmissive, electron beam sensitive coating. Many of the highly halogenated polymers may be made even more relatively light transmissive in the form of a thin film. For each equivalent weight of acid sensitive amino azo indicator from about 1 to about 1000 acid equivalents of the halogenated polymer are employed, although the ratio of these ingredients varies with the particular indicator dye, and its acid sensitivity, which is employed. Other additives, e.g., plasticizers, oxidizing agents, etc., may be incorporated into the electron beam sensitive coating, provided they do not serve to liberate acid under the electron beam. Additional films or coatings may be provided on the electron beam sensitive layer to protect it from abrasion, etc., provided they are relatively transmissive to the electron beam.

With the media described above a color change is generally observed in the sensitive coating immediately upon electron beam impingement or shortly thereafter upon exposure to air, thereby providing a visible record. In some instance the image can be erased by heating the media to about 100° C. to 150° C. for approximately 30 seconds, the color change being probably due to the volatilization of the acid and an increase in effective pH of the media. Erased media of this type can be reused for electron beam recording, although subsequent depletion of the polymeric acid source eventually reduced the efficiency of the recording.

It is also within the scope of this invention to impinge the electron beam on a media comprising the highly halogenated polymer film on an electrically conductive substrate, leaving the amino azo dye out of the polymer film. After the exposure to the electron beam, the liberated acid in the imaged areas can be subsequently developed by contacting the exposed surface with an amino azo indicator dye. A separate development roller or bath may be used for this post development step, or a second film construction incorporating or carrying the indicator dye can be brought into contact with the exposed surface of the media. One advantage of a post development using an indicator-containing film is the ability to prepare multiple copies.

If the electron sensitive layer can be supported on and contiguous with an electrically conductive roll or plate during beam exposure, the electrically conductive substrate of the recording media can be eliminated as an integral part of the media construction. However, good electrical contact between the electron sensitive layer and a conductive backing, normally maintained at ground potential, is best achieved with an integral or unitary media construction including an electrically conductive layer contiguous with the electron beam sensitive layer.

Although the foregoing description has been directed to electron beam recording, the media described are also sensitive to other forms of relatively high energy irradiation which causes the liberation of hydrohalic acid from the highly halogenated polymer, and alpha, beta and gamma radiation as well as X-rays and ion particles and ultraviolet light below 3,000 angstroms may also be employed at appropriate energy levels.

Since ultraviolet light below 3,000 angstroms is similar to an electron beam in its effect on the recording media of this invention, a simple standard test procedure has been developed to assist in the selection and definition of the preferred highly halogenated polymers and amino azo indicator dyes for use in the electron beam sensitive layers of the media. The suitability of a film forming halogenated polymer is determined by adding 5 milligrams of Congo red A to 1.0 milliliter of a 20 weight percent solution of the polymer in a suitable solvent, such as tetrahydrofuran. This solution is then knife coated onto a cellulose acetate, polyethylene terephthalate or glass backing to provide a dry film of 0.1 mil thickness. A sample of this dry film is placed at a sufficient distance from an ultraviolet light source to provide about 0.08 watt per square centimeter of radiant energy of 2,000 to 3,000 angstroms wavelength. The sample is irradiated for a period from 2 to 30 seconds. Generation of a blue color indicates a halogenated polymer containing "labile" halogen useful in the electron beam recording media of this invention. The same standard test procedure is modified for selection of a particularly suitable acid sensitive amino azo indicator dye by using a 20 weight percent solution of vinylidene chloride acrylonitrile copolymer (90/10 mol ratio) and 5 milligrams of the acid sensitive indicator dye, a strong color change being desired after the ultraviolet exposure.

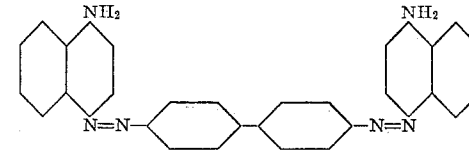
The following examples will serve to illustrate the recording media and processes of this invention.

Example 1

To 4 ml. of a 20% (by weight) solution of vinylidene chloride/n-butyl acrylate copolymer (90/10 mol ratio, approximately 60% chlorine) in tetrahydrofuran, was added 10 mg. of Congo red A dye (unsulfonated Congo red prepared from tetrazotized benzidine and 1-naphthyl amine) and 4 drops of cyclohexanone. This solution was used to prepare a film of 0.1 mil dry thickness when it was knife coated onto 3 mil aluminum vapor coated polyethylene terephthalate film.

An electron beam recording made with a scanning rate of 60 fields/sec., 10 kv., 5 microampere beam current, 10 micron spot size and 50 microsecond/scan line (262.5 lines/field) produced a direct print out blue image on an orange background. The individual scan lines were distinctly visible under a microscope. The change in optical density between background and image was about 0.5 optical density units.

Congo red A has the following structure:



Example 2

To 4 ml. of a 20% (by weight) tetrahydrofuran solution of a polymer of vinylidene chloride/n-butyl acrylate (92/8 mole ratio, approximately 62% chlorine) was added 20 mg. of Congo red A dye and 4 drops of cyclohexanone. This solution was used to prepare a film of 0.1 mil dry thickness by knife coating onto 3 mil aluminum vapor coated polyethylene terephthalate film. When it was recorded as above a similar image was obtained having an optical density difference of 0.6 between background and image.

Example 3

Films prepared and recorded as above using 20% tetrahydrofuran solutions of vinyl chloride/vinyl acetate copolymer (43% by weight chlorine); vinylidene chloride/acrylonitrile copolymer (54% chlorine); vinylidene chloride/acrylonitrile copolymer (67% chlorine); tosylated polyvinyl alcohol; chlorinated polypropylene; copolymers of vinylidene chloride with any of methyl acrylate, β-chloroethyl acrylate, vinyl chloride, vinyl acetate or vinyl butyrate, into each of which 1–20 mg. of Congo red A

dye were added (per 200 mg. polymer) yielded direct print out images. The optical density difference between image and background varied depending on the specific polymer and the amount of dye used. However, the films all gave differences lying in the range of 0.1–0.3 optical density units.

Example 4

To 4 ml. of a 20% (by weight) solution of a polymer of vinylidene chloride/n-butyl acrylate (90:10 mole ratio; approximately 60% chlorine) in tetrahydrofuran was added 20 mg. of 4-phenylazodiphenyl amine and 4 drops of cyclohexane. This solution was used to prepare a film of 0.1 mil dry thickness when it was knife coated onto 3 mil aluminum vapor coated Mylar film.

An electron beam recording made with a scanning rate of 60 fields/sec., 10 kv., 5 microampere beam current, 10 micron beam spot and 50 microsecond/scan line showed a direct print out, brown image on a pale yellow background. The individual scan lines were distinctly visible under a microscope. The change in optical density between image and background was about 0.5 optical density units.

Example 5

Using a vinylidene chloride/n-butyl acrylate copolymer (about 60% chlorine) and the same procedure for coating and recording as outlined above in Example 1 the following amino azo dyes were tested:

Dye	Color Change	Optical Density Chg.
(a) p-(4-aminoaphthylazo)-phenyl mercuric acetate.	Yellow to brown.	0.5
(b) 4-(p-dimethylamino-benzeneazo)-phenyl mercuric acetate.	Yellow to tan.	0.3

Example 6

A recording medium having outstanding characteristics was prepared by adding 0.030 g. of Congo red A to 3.5 ml. of a solution of 5.00 g. of a copolymer of 87% vinyl chloride and 13% vinyl acetate dissolved and diluted to 100 ml. with methylethyl ketone. To this solution was added 1.5 ml. of methylethyl ketone, 4.0 ml. of n-amyl acetate and 1.0 ml. of 1,1,2,2-tetrachloroethane (these last two solvents are added to decrease the evaporation rate and to obtain unblushed coatings). The resulting clear red solution was then dip coated onto aluminum foil at a rate of 43 ft. per second. The coated foil was pulled vertically into a 1½ inch diameter tube where it was allowed to dry. Solution 1.25 to 5.00 g. per 100 ml. solvent gave dry coating thickness of 3 to 5 microns. The dried, coated foil was then evaluated for sensitivity using an electron gun having an unmodulated, non-sweep beam from about 2,000 to 15,000 volts and beam currents up to about 50 microamperes. The spot size was about 0.50 mm.^{2}. A sensitivity of about 0.1 microampere-second/mm.^{2} was obtained. This corresponds to a recording sensitivity of about 4 megacycles per second.

Media using other concentrations of polymer and Congo red A were prepared and successfully tested for electron beam sensitivity.

The n-amyl acetate and tetrachloroethane added to eliminate blushing of coatings may be replaced by other materials such as cyclohexane or dimethyl Cellosolve.

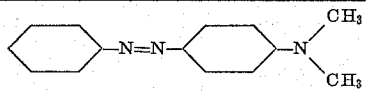
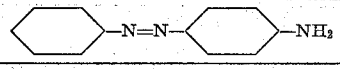
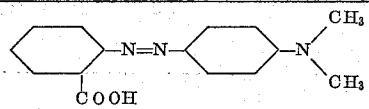
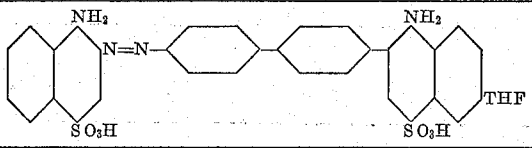
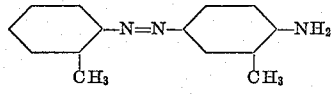
In general, those acid sensitive amino azo indicators with a marking energy of below 10 microampere-seconds/mm.^{2}, preferably below 0.3 microampere-second/mm.^{2}, are superior for the recording sheets of this invention.

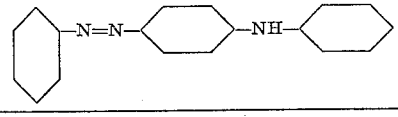
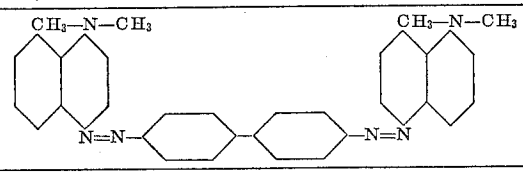
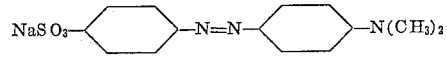
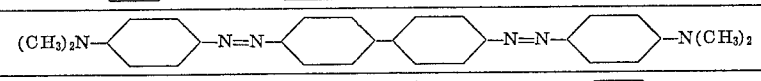
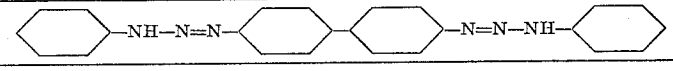
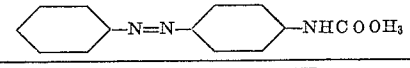
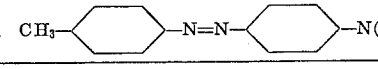
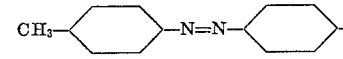
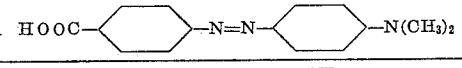
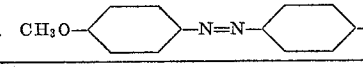
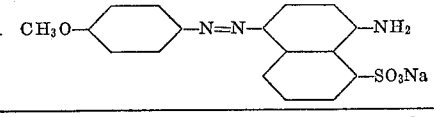
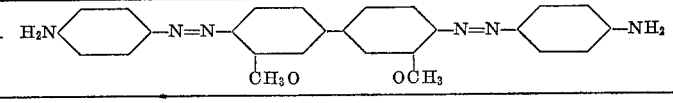
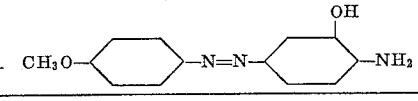
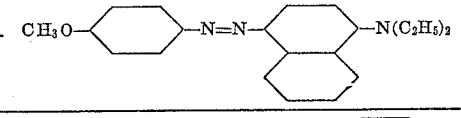
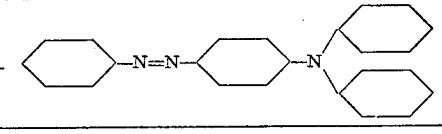
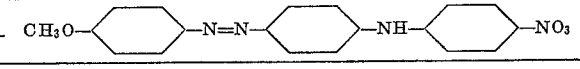
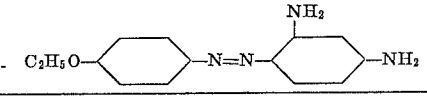
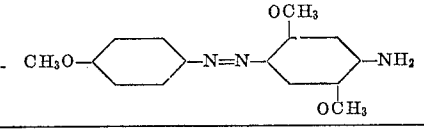
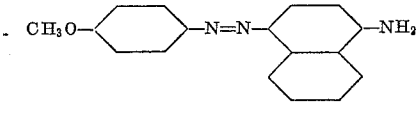
Example 7

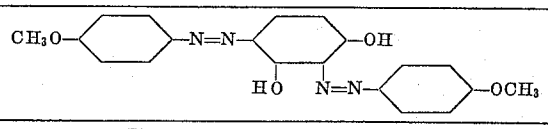
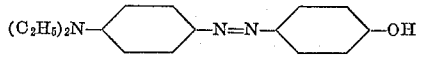
An admixture of a halogenated copolymer (87 mol percent vinyl chloride and 13 mol percent vinyl acetate) and methyl yellow (1 part dye to 10 parts by weight of copolymer) was coated onto a metal substrate to provide a dry film thickness of 0.1 mil. Methyl yellow changes color in a pH range of about 2.8–4.4. During an electron beam exposure of 1 field (60 fields per second) at television scanning rate (30 frames per second), a red image was formed on the yellow background.

In the examples of Table I the highly halogenated binder was a copolymer of 88 mol percent vinyl chloride and 12 mol percent vinyl acetate, the weight ratio of indicator to binder being about 1 to 5.

TABLE I.—AMINO AZO DYES IN ELECTRON SENSITIVE MEDIA

Example	Indicator	Energy to Mark (microamperes, sec., at 2,000 volts)	Color Response
A		0.2	Red on yellow.
B		.03	Do.
C	 (Methyl Red)	.2	Do.
D		10	Blue on red, poor solubility.
E		.2	Blue, on red excellent stability.
F		1	Red on yellow.

Example	Indicator	Energy to Mark (microamperes, sec., at 2,000 volts)	Color Response
G		.2	Do.
H		1	Blue on red.
I		5	Red to yellow.
J		2	Orange on yellow.
K		3	Do.
L		6	Tan on yellow.
M		.2	Red on yellow.
N		.03	Purple on yellow.
O		1	Red to yellow.
P		.03	Purple on orange.
Q		.2	Blue on purple.
R		.03	Blue on red.
S		.03	Brown on tan.
T		40	Orange on yellow.
U		.02	Purple on yellow.
V		.33	Do.
W		.2	Brown on tan.
X		.2	Pale yellow on tan.
Y		.2	Purple on yellow, excellent stability.

Example	Indicator	Energy to Mark (microamperes, sec., at 2,000 volts)	Color Response
Z.....		.2	Red on tan.
ZZ.....		.2	Yellow on tan.

Various other embodiments of the present invention will be apparent to those skilled in the art without departing from the scope thereof.

The following is claimed:

1. A recording medium which comprises an electrically conductive metallic substrate and, superimposed thereon, a layer which is essentially insensitive to visible light, which is stable under vacuum conditions used in electron beam recording and which comprises an acid-sensitive oil soluble amino azo indicator in basic form and capable of changing color at a pH below about 7 and, as the sole remaining constituent capable of liberating hydrogen halide under exposure to an electron beam, a normally solid, highly halogenated polymer having a molecular weight of at least about 1000 and having at least 25 weight percent of labile halogen selected from the group consisting of chlorine and bromine.

2. The recording medium of claim **1** in which said film has from about 1 to about 1000 acid equivalents of said halogenated polymer per equivalent of acid sensitive indicator.

3. The recording medium of claim **1** in which said acid sensitive indicator is Congo red A.

4. The recording medium of claim **1** in which said highly halogenated polymer is a copolymer of vinylidene chloride and an aliphatic acrylate.

5. The recording medium of claim **1** in which said highly halogenated polymer is a copolymer of vinyl chloride and vinyl acetate.

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UNITED STATES PATENT OFFICE

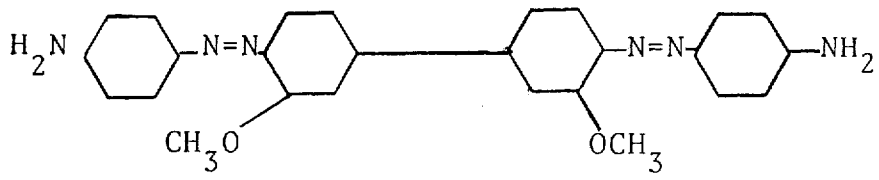
CERTIFICATE OF CORRECTION

Patent No. 3,370,981 February 27, 1968

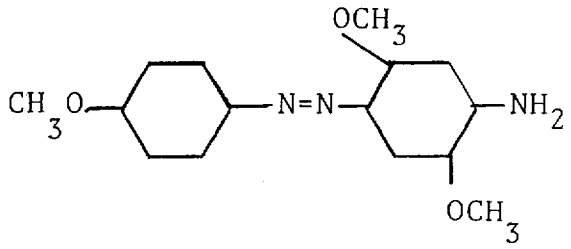
William O. Ney, Jr., et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 13, "the film" should read -- be film --. Columns 5, 6, 7, 8, 9 and 10, TABLE I, in the sub-heading, line 2 thereof, "microamperes," each occurrence, should read -- microamperes- --. Columns 7 and 8, same Table I, opposite Example "R", the indicator formula should appear as shown below:



same Table I, opposite Example "X", the formula should appear as shown below:



Signed and sealed this 11th day of November 1969.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents