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3,336,596

MEDIUM FOR ELECTRON BEAM RECORDING

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FIG. 1

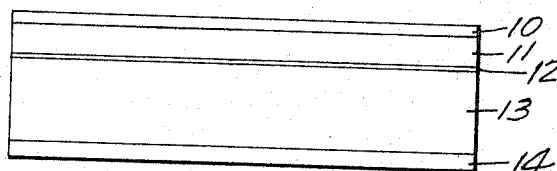


FIG. 2

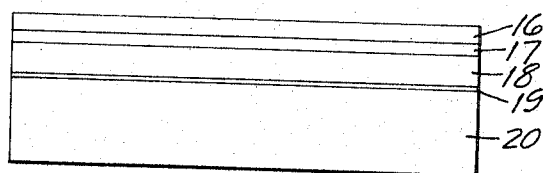
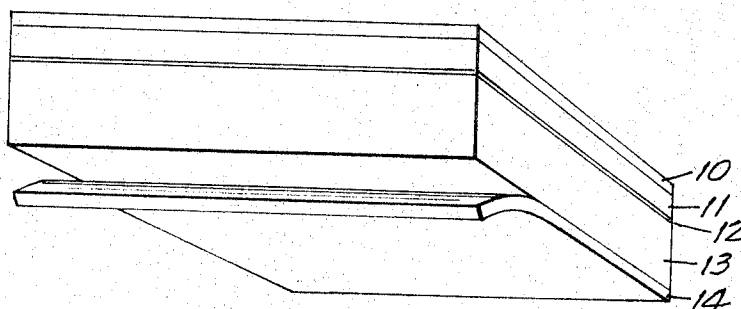


FIG. 3



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MEDIUM FOR ELECTRON BEAM RECORDING

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This invention relates to new and very useful information storage media and to methods for using the same.

More particularly, this invention relates to a class of sheet-like recording media in which electron beam modulation can be directly recorded and from which such recorded modulation can be directly read out by conventional optical projection (i.e. transmission) techniques.

The invention further relates to processes for using such media in which a conductive layer initially present in such medium is physically removed, as by peeling or the like.

Heretofore, the art has experienced great difficulty in recording directly upon or in one face of a recording medium the information associated with a modulated electron beam scanning such face. Factors which have militated against such direct recording procedures include the vacuum operating conditions, the limited capacity of electrons to penetrate recording materials, the deterioration of material due to radiation damage, and especially the charge build-up in material associated with direct electron exposure.

There has now been discovered a sheet-like electron beam recording medium and process for using same which enables one to record therein during a vacuum recording operation an image-like pattern (latent or visible) corresponding to variations in an electron beam modulated with information to be stored when such beam scans one face thereof. During such recording operation, the medium dissipates electrons, the dissipations occurring at such a rate as to maintain the inherent associated electrostatic charge potential build-up in and on the medium during recording at a level which is so low as not to affect appreciably (i.e. deleteriously) the scanning electron beam or the recording being formed thereby. During recording, the conducting layer can be grounded. After such recording operation and before readout by conventional optical transmission (e.g. projection) techniques, the resulting medium is processed so as to be either light absorptive in imaged areas (in the case of negative recordings) or light absorptive in unimaged areas (in the case of positive recordings).

A sheet-like storage medium of this invention employs as its information storage component an electron sensitive layer and as its charge dissipation component a removable, electrically conductive layer. Supporting these two layers together into an integral construction is an optically clear base support layer.

Accordingly, it is an object of the present invention to provide a sheet-like medium useful for direct electron beam recording and direct optical readout.

Another object is to provide a medium of the type indicated which employs an electron sensitive layer, a removable electrically conductive layer, and a base support layer.

Another object of this invention is to provide a sheet-like storage medium using, for instance, a layer of silver halide emulsion, which medium is adapted to directly record information associated with a modulated scanning electron beam.

Still another object of this invention is to provide an electron beam recording medium of the class indicated which is adapted to dissipate electrons during a recording operation at such a rate that there is substantially no effect upon the scanning modulated electron beam ac-

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complishing recording and no deleterious effects upon such medium.

A further object of this invention is to provide an electron beam recording medium of the class described which, after recording and subsequent processing has an image pattern formed therein and is non-light absorptive in unimaged areas in the case of positive recordings and clear in imaged areas in the case of negative recordings.

Another object of this invention is to provide an electron beam recording construction having therein a layer of material which is electrically conductive under vacuum environments and which is removable from such medium to leave substantially completely unaffected the remaining medium construction.

A still further object of this invention is to provide a method for directly recording under vacuum conditions the information associated with a modulated electron beam and for subsequently directly reading out such recorded information by direct optical projection (i.e. transmission) techniques.

One further object is to provide a method for removing what may be an optically opaque conductive layer from an electron beam recording medium by stripping so as to make such medium suitable after recording for readout by optical projection techniques.

Other and further objects of the present invention will become apparent to those skilled in the art from a reading of the present specification taken together with the drawings wherein:

FIGURE 1 is a vertical cross-sectional diagrammatic view of one embodiment of a medium construction of this invention wherein the conductive layer is located on the back face over the support layer;

FIGURE 2 is a view similar to FIGURE 1 but showing a second embodiment of a medium construction of this invention wherein the conductive layer is located on the front face over the electron sensitive layer; and

FIGURE 3 shows one manner in which a conductive layer employed in the embodiment of FIGURE 1 can be removed during processing following a recording operation.

The base support layer, the electron sensitive layer, and the conductive layer will now be described. Because electron beam recording operations are generally carried out under relatively high vacuum conditions, it is desirable though not necessary to use materials in the medium constructions of this invention which are vacuum stable. It is also desirable, though not necessary, in making medium constructions of this invention to employ materials which have minimal residual quantities of volatilizable gases, liquids and solids associated with them because such materials when released in vacuum during electron beam recording operations can interfere with the operation of the electron gun, especially its electron emission source, as those skilled in the art will readily appreciate.

As the base support layer there is employed an optically clear, dimensionally stable material having opposed parallel anchorable faces.

For purposes of this application, the term "optically clear" has reference to even and high (e.g. more than 50%) light transmission in the visible region of the spectrum.

The term "dimensionally stable" has reference to the fact that a material in a medium undergoes no appreciable changes in its dimensions under any of the (vacuum) recording, processing, storage and readout conditions to which such medium is to be subjected (i.e. such medium is not rendered inoperable by reason of dimensional changes in its support layer).

The term "anchorable faces" or simply "anchorable" has reference to the fact that the base support layer is capable of having other substances chemically or physico-

chemically fastened or bonded to either one or both faces thereof so as to form initially a composite, integral structure depending upon the layers used, and their positions in a given medium construction. Thus, such a base support layer may be subbed, primed or the like before being used in a medium construction of the invention.

As those skilled in the art will appreciate, it is necessary to employ as the base support a material which is capable of having other substances anchored to either one or both faces thereof. Preferred base support materials are film-forming organic polymers. A suitable thickness for a base support layer is from about 0.25 to 10 mils.

An especially preferred base support material is polyester film, such as that type technically known as polyethylene terephthalate film. Other suitable base support materials useful in the construction of sheet-like storage media of the present invention are polycarbonates, cellulose esters, polystyrenes and the like.

As the electron sensitive layer there is employed a composition capable of developing therein, following exposure thereof to excited electrons, internally changed regions corresponding to, or representative of, the excited electrons striking such regions. Such regions are detectable (observable) by means of the passage or transmission of light energy (i.e. energy having wavelengths of from about 200 to 700 millimicrons) therethrough because such light energy is selectively or differentially transmitted by such regions compared to the adjacent regions.

It will be appreciated that such regions are in an image-wise pattern of either a positive or negative character, depending upon recording conditions and nature of the particular electron sensitive material used as well as upon the processing applied.

The electron sensitive composition is further characterized by the fact that when in a layered form within a medium construction of this invention, even the inherent limited power of excited electrons (i.e. those derived from a modulated electron beam) is sufficient to enter such layer and effect the desired exposure thereof so as to produce an image-wise recording of these excited electrons. While there are many ways, as those skilled in the art will appreciate, to effect this result, it is achieved in the present invention by controlling the uniform distribution of electron sensitive elements in the electron sensitive composition in such a way as to make a layer of such composition in a medium construction as thin as practicable and yet achieve maximum change in the electron sensitive layer during the beam dwell time upon a given surface area of such medium.

For purposes of this invention it is generally convenient and satisfactory to employ an electron sensitive composi-

tion which when deposited in a layered form upon an inert surface to a thickness of about 2μ (microns) will develop an optical density of at least one when exposed to not more than 10^{13} electrons per square centimeter of layer surface area of suitable acceleration to penetrate substantially all of the electron sensitive layer.

The optical density D of an electron sensitive layer deposited in a medium construction of this invention is defined by the relation $D = \log O$ where O is the opacity.

If I_0 and I are the incident and transmitted intensities respectively the opacity is given by I_0/I . Optical clarity can be measured as the reciprocal of the opacity or I/I_0 .

It will be appreciated that the term "develop," "developing" or equivalent as used in this context may or may not involve subsequent chemical or physical processing following a recording operation so as to produce the desired changes in an electron beam exposed, electron sensitive composition.

The term "dwell time" as used in this application has reference to the average time as for instance in microseconds the spot diameter formed by a moving electron beam spends in an area equal to its own.

The term "element" as used in this application has reference to a functional component of the electron sensitive composition which may consist of a homogeneous mixture of chemical combination of one or more chemical entities.

In general, such electron sensitive compositions are well known to those skilled in the art. For convenience and reference purposes various classes of these imaging materials are summarized in the following Table I. In this table, the term "imaging process" has reference to the manner in which an image is formed by a physical or chemical change in a given medium construction. Exposure is generally prolonged until the image material has undergone a change sufficient to effect the desired recodation of information. The term "development" has reference to a particular chemical or physical process by which the change or alteration in image material created during exposure to electron radiation is detected and amplified. Development may (a) require a second, separate, and subsequent processing step following exposure, or (b) occur simultaneously with, or as a direct and dependent consequence of, exposure to electron radiation. The term "fixing" has reference to a process step subsequent to development which produces desensitization of areas in an image material to subsequent or further exposure to electron and photon radiation. Depending on the nature of the phenomena utilized, development and/or fixing may not be necessary, may be eliminated, or even may be accomplished simultaneously with one another.

TABLE I.—FUNCTIONAL DESCRIPTIONS OF IMAGING PROCESS STEPS WITH DIFFERENT IMAGING SYSTEMS

	I. Imaging Process	II. Development	III. Fix	IV. Process
1	Destroy a reactant.	Chemical reaction forming a visibly distinct product in non-exposed areas.	Not needed.	Diazo-Bruning, Ozalid. ¹
2	Photodecomposition producing gaseous products in a thermo-plastic film.	Heat to expand gas within softened film producing light scattering bubbles.	Exposure to uniform photon energy.	Vesicular Diazo. ²
3	Create a heat pattern (localized increase in temperature).	Heat sensitive physical or chemical change to produce a visibly distinct product.	Background is heat sensitive unless "fixed."	Thermography. ³
4	Create a pattern of a chemical reactant.	Transfer and chemical reaction to yield a visibly distinct product.	Not needed.	Sympathetic ink. ⁴
5	Generate acidic reactant.	Conversion of basic dye to acid form.	do.	Described herein below.
6	Producing structural re-arrangement.	Photochromatic (conversion of one chemical species to different chemical species).	do.	Photochromic micro-image (PCMI). ⁵
7	Free radical generation.	Synthesis of photon absorbing material.	Heat.	Wainer reaction. ⁶
8	Degradation of silver halide to free silver.	Chemical amplification of the exposed latent image.	Chemical removal of undeveloped silverhalide.	Photography. ⁷

¹ U.S. Patent Nos. 2,829,976; 2,807,545; 2,755,185; 2,774,669; 2,691,587.

² U.S. Patent No. 2,950,194.

³ U.S. Patent No. 2,740,896.

⁴ British Patent No. 844, 077; 844, 079; 844, 256; Niepce de St. Victor, *Photographic News* 2 (1859).

⁵ Y. Hirshberg J. Chem. Phys. 27, 758 (1957); South Africa Patent No. 61,861; French Patent No. 1,272,053; Belgium Patent No. 607,355; British Patent Nos. 887,958; 88,902; 883,803; U.S. Patent Nos. 3,090,687; 3, 038,812;

3,020,171; 2,953,454; 3,022,318.

⁶ U.S. Patent No. 3,042,515, R. H. Sprague and M. Roscow Photo Sci. and Eng. 8, 91 (1964); R. H. Sprague and It. L. Fitcher Ibid p. 95; U.S. Patent No. 3,102,029.

⁷ Gladkides "Photographic Chemistry," volumes 1 and 2 published by Fountain-Press (London, 1958); see especially pages 341-353 and 369-389.

The conventional diazo processes mentioned in Table I involves production of a colored azo dye. Exposure to excited electrons of a stabilized diazonium compound destroys its ability to react with a coupler and hence produce a dye. In the unexposed areas the dye-forming reaction occurs readily upon the addition of an alkaline material (ammonia vapor) if the diazo system already contains a coupler component or both an alkaline material and coupler.

In the so-called vesicular diazo process mentioned in Table I, exposure to excited electrons decomposes a diazonium salt dispersed in a thermoplastic binder. When the medium is subsequently heated, the nitrogen produced by the decomposition expands in the softened binder producing a vesicular, light scattering image in the exposed areas.

In Example 4 of Table I selective surface absorption or selective deposition can be used to create a differential chemical pattern of an imaging system component corresponding to that on the original graphic master. If the tinctorial power of the reaction product is high, or if the transferred material is a reaction catalyst, transfer of only very small amounts of material can provide a visible image. Thus, some degree of amplification may be possible.

For some time it has been known in the arts that upon exposure of highly halogenated polymers such as polyvinyl chloride or polyvinylidene chloride to excited electrons one obtains acidic reaction products generated in the polymer matrix, directly as a result of the irradiation. If in such a polymer matrix there is incorporated the basic form of an acid-sensitive dye such as one of the commonly known indicator dyes such as phenolphthalein, then, upon exposure and generation of the acid component in the matrix, a color change is produced in the irradiated areas.

Photochromic materials are well known in the photochemical art. Such materials, when exposed to excited electrons, undergo a structural rearrangement which results in the formation of a differently and usually more colored species, compared to the initial color. A wide variety of such compounds are included in the chemical class known as benzoinindolinopyranospiroane. The National Cash Register Company-developed photochromic imaging system utilizing this general technology for the recording of grain-free microimages can be employed in making the electron-sensitive layer in media of this invention.

The exposure to excited electrons of highly halogenated alkanes, such as carbon tetrabromide, bromoform, or chloroform produces a highly chemically reactive radical. When, for example, a substituted aromatic amine is incorporated in close proximity thereto, upon subsequent heating an image is formed. The literature discloses the Horizons, Incorporated has made practical utilization of this color forming reaction in preparation of electron-sensitive compositions. These compositions, when suitably layered in combination with fluorescent composition, can be used in electron-sensitive layers in media constructions of this invention.

Example 5 of Table I utilizes a dehydrohalogenation electron-sensitive system which employs a combination of two components: an acid sensitive indicator and a highly halogenated polymer. The acid sensitive indicator is capable of changing color at pH below about 7 when the highly halogenated polymer is capable of liberating an acid component. The halogenated polymer is normally solid and has a molecular weight of at least about 1,000 and further has at least 25% of labile halogen selected from the group consisting of chlorine and bromine. The indicator is generally homogeneously distributed throughout the halogenated polymeric binder, and is preferably dissolved therein. It may also be provided as a localized coating or be concentrated in the top surface of the polymeric binder in a particular medium construction.

Preferably the polymers are soluble in conventional organic solvents. Solubility, of course, 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 as the aliphatic acrylates (e.g. n-butyl acrylate, methyl acrylate, ethyl acrylate, methyl methacrylate, beta-chloroethyl acrylate, etc.), acrylonitrile, vinyl chloride, 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, fluorotrichloro ethylene, 1,1-difluoro - 2,2, - dichloroethylene, trichloroethylene, etc. copolymerized with vinyl or vinylidene chloride or bromide or with 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.

Although the halogenated polymers are desirably deposited from solution as a film on a surface, 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, antioxidants and other stabilizers may be added to improve good storage life.

Since the highly halogenated polymers serve as a relatively non-volatile source of hydrohalic acid, no other brominated or chlorinated compounds which liberate acid under electron beam exposure are required for electron beam imaging.

An electron sensitive composition for use in media of this invention can be prepared by mixing a minor amount of the acid sensitive indicator system with a solution of the highly halogenated polymer and backing. If a transparent imaging material is desired, it will be appreciated that many of the highly halogenated polymers are made more relatively light transmissive in the form of a thin film. For each equivalent weight of acid sensitive indicator from about 1 to about 1,000 acid equivalents of the halogenated polymer are employed, although the ratio of these ingredients varies with the particular indicator system, and its acid sensitivity, which is employed. Other additives, e.g. plasticizers, oxidizing agents, etc. may be incorporated into the actinic radiation sensitive coating (preferably such additives are chosen so as to not liberate acid under actinic radiation). Additional films or coating may be provided on the actinic radiation sensitive layer to protect it from abrasion, etc., provided they are relatively transmissive to the electron beam.

With electron sensitive compositions such as just described, a color change therein is generally observed immediately after exposure to excited electrons or shortly thereafter upon subsequent exposure to air thereby providing a visible imaging record in a layer of such a composition. In some instances, when the acid sensitive indicator is reversible, as with the acid-base indicator dyes, the image can be erased by heating the electron sensitive composition 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 electron sensitive composition. Erased electron sensitive compositions of this type can be re-used for recording with electron beams although subsequent depletion of the polymeric acid source eventually reduces the efficiency of recording.

It is sometimes convenient to leave the indicator out of a highly halogenated polymer film initially. Then after exposure of such film to actinic radiation, the liberated acid in the image (exposed) areas can be subsequently developed by contacting the exposed surface of the highly halogenated polymer with the acid sensitive indicator system. A separate development roller or bath may be

used for this post development step or a second medium construction incorporating or carrying the indicator can be physically brought into contact with the exposed surface of such medium. Such a post development procedure using an acid indicator containing film can be used to prepare multiple copies.

A simple standard test procedure to assist in the selection and definition of highly halogenated polymers and indicator systems useful in such media of this invention employs ultra-violet light. The procedure is to add to a film-forming halogenated polymer 5 milligrams of Congo Red A to 1.0 milliliter of a 20 weight percent solution of such 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 ultra-violet light source to provide about 0.08 watt per square centimeter of radiant energy of 2000 to 3000 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 suitable acid sensitive indicator by using a 20 weight percent solution of vinylidene chloride-acrylonitrile copolymer (90/10 mol ratio) and 5 milligrams of the acid sensitive indicator system, a strong color change after the ultraviolet exposure indicating a useful indicator for the electron beam recording media.

An especially preferred type of electron sensitive composition comprises silver halide emulsions.

As the photographic silver halide emulsion layer for use in the present invention, one can employ virtually any silver halide emulsion since such emulsions are generally sensitive to electron beams. However, it is greatly preferred for purposes of producing sheet-like storage media of the present invention to use emulsions which are particularly useful for electron beam recording. For the purpose of constructing media of this invention it is desirable to use fine grain emulsions, that is, emulsions having an average grain size less than about 0.5 micron.

In a given media construction the thickness of the silver halide emulsion is largely dependent upon the quantity of silver per unit of area which is to be used for recording. Typically, the layer of silver halide emulsion contains from about 5 to 50 milligrams of silver per square decimeter of surface area.

A preferred silver halide emulsion for use in medium constructions of this invention is one which has an average grain size of less than 0.5 micron and a silver-to-gel ratio of about 1:1.

It is sometimes convenient in fabricating medium constructions of the present invention to overcoat the electron sensitive layer with a top coat, particularly when such emulsion layer constitutes the uppermost or bottom-most exposed portion in a completed medium construction. As a top coating material one can employ a thin layer of gelatin, say, one less than about 0.5 micron in thickness. Such a layer does not interfere with the development of, for example, silver halide emulsion, following a recording operation and serves to protect the recording medium against accidental abrasion and dust particles during a recording operation as well as during subsequent storage following development.

In order to achieve a good anchoring between the base support layer or material and the particular silver halide emulsion, it is sometimes desirable to employ a very thin layer or layers of subbing material to the surface of the base support layer before the same is coated with an electron sensitive layer. Subbing compositions are known and understood to those skilled in the art. Conventional subbing agents for silver halide emulsions, for example, are listed in Glafkides' *Photographic Chemistry*, volume I, pages 467-469.

As the removable, electrically conductive layer in a medium construction of the invention there is employed a material which has a resistivity of not more than about 10^6 ohms per square (and preferably not more than about 10^3 ohms per square) as measured in vacuum of about 10^{-5} mm. Hg. As a practical matter in preferred medium constructions, the conductive layer is adhered to either the electron sensitive layer or to the base support layer.

Such removable electrically conductive layer further has the capacity to adhere to the base support layer or to the electron sensitive layer with a force which is sufficient to prevent separation of the removable electrically conductive layer from the remainder of a given medium construction during normal handling, processing, and storage conditions prior to and during a recording operation. However, this conductive layer further has the capacity to be removed from the remainder of a medium construction without appreciably affecting at the time of removal:

- (a) the optical clarity of the base support layer, and
- (b) the image quantity of information developed in the electron sensitive layer.

As a preferred class of removable electrically conductive layers used in medium constructions of this invention there is employed a conductive layer which has the capacity to adhere to the base support layer or to the electron sensitive layer, as the case may be, by a peel force in air of at least about 4 grams per inch width. For the purposes of this invention "peel force" is measured in the same manner as the 180° adhesion strength test described in A.S.T.M. test procedure number D-1000. It will be appreciated that such adherence or bonding may be achievable or achieved by the manner in which the conductive layer is formed and/or by the manner in which a given medium construction of this invention is manufactured, as is more particularly described below. Chemical physico-chemical and/or physical forces may be involved. However, this peel force for a group of more preferred removable electrically conductive layers is such that when a given medium of the invention incorporating such preferred conductive layer is placed in an aqueous liquid at a temperature of not over about 70° F., such conductive layer can be peeled from the remainder of such medium without affecting either the qualities (a) or (b) above indicated. The aqueous medium in such preferred layer serves to swell or otherwise favor separation from the remainder of a medium construction. Layers which are formed of compositions which swell in water and which at the same time are relatively inert towards the electron sensitive layer and the base support layer are used conveniently in such preferred class of removable conductive layers. In such layers removal can be effected by using very little and occasionally no physical force, as when the conductive layer swells in water or partially dissolves in water, to such an extent that it is completely lifted away from the adjoining or adjacent layers. Of course, there is no need for the conductive layer to be water swelled, or water soluble, because, for example, one can employ a non-aqueous liquid medium or even accomplish the stripping in air without liquid immersion. It is preferred to employ conductive layers which are stripped away when not more than about 5 or 10 weight percent of such a layers initial weight is lost, by dissolution when an entire medium construction is subjected to immersion in a liquid.

Another preferred type or class of removable electrically conductive layers comprises a composition consisting essentially of a dispersion of conductive particulate materials in an organic polymeric binder, such composition being formed into a stratum or layer which has the capacity to adhere to and be removable from the base support layer or the electron sensitive layer by the above-indicated minimum peel force and which further has a resistivity of not more than that above indicated.

Another preferred type or class of removable electrical-

ly conductive layers comprising a metallic foil or sheet which is electrically conductive and which has coated on one face thereof a pressure sensitive adhesive such that the peel and removal properties of the resulting composite layer construction satisfies the conditions above indicated for conductive layers usable in this invention.

Naturally, in all medium constructions of this invention the electron sensitive layer is so adhered to the associated base support layer as not to be separated therefrom at said time of removal of the conductive layer therefrom.

The desirability of incorporating a conductive layer into a recording medium of the invention comes about from the fact that the presence of an electrostatic charge during recording impairs sharpness, resolution and accurate positioning of the recorded image. The aforementioned electrostatic charge is built up in the electron sensitive layer or any other insulating layer placed in first order of electron impingement. This charge can adversely affect the performance of a recording medium.

In general, the conductive particulate materials dispersed in such organic polymeric binder have sizes and densities in any given medium construction, etc., dependent upon the electrical conductivity desired, medium thickness and other related physical characteristics desired in such construction. In general, the particles have sizes less than about 2 microns and the quantity of such particles loaded or dispersed in an organic polymeric binder is entirely dependent upon the degree of conductivity desired. Since conductivity is a matter which will vary widely from one type of particle to another, it is not convenient or practical to give generalized values as to the quantity or particles suitable for all medium constructions.

Suitable conductive particulate materials include conductive carbon particles, and metal particles of a metal such as copper, silver, aluminum, magnesium, or the like. Suitable organic polymeric binders used in the electrically conductive layer are dimensionally stable, film-forming materials.

Examples of organic polymeric binders which can be used in medium constructions of this invention and which can be removed only by mechanical stripping (peeling) procedures include the polyamide resins such as the soluble nylon types and the like.

Examples of organic polymeric binders which can be used in medium constructions of this invention and which can be removed by a combination of water swelling as well as mechanical peeling include polymethyl vinyl ether/maleic anhydride, polymethyl vinyl ether/maleic anhydride esters, styrene/maleic anhydride, poly alkyl vinyl ethers, such as poly vinyl ethyl ether, poly vinyl isobutyl ether, and copolymers thereof; and the like.

It will be appreciated that in some medium constructions of this invention the conductive layer can be substantially completely removed (e.g. stripped) from the remainder of such medium by mere water swelling provided, of course, the soak time or contact time of such medium construction with the swell water is continued for a sufficient time to effect such removal.

It will be appreciated that in a given medium construction of this invention, the total thickness of, and the interrelationship between layers thereon is such that, immediately after a recording operation, the charge in volts remaining E , the charge in coulombs remaining q , and the distance d between adjacent faces of said electron sensitive layer and said removable conductive layer is such that

$$E=kqd$$

where k is a proportionality constant. If E is too large, then there are the possibilities of (a) excessive arcing near the electron sensitive layer with the result that fogging of the recorded image can occur, (b) the recording modulated electron beam is deflected in adjacent areas so

that accurate positioning of the beam with respect to the medium is lost in recording, and (c) the medium is physically attracted by electrostatic forces to surrounding or adjoining surfaces to such an extent the medium becomes difficult to handle (i.e. transport) in the recording equipment.

Such layer interrelationship and medium total thickness considerations depend not only upon the nature of the starting materials but also upon the manner in which a particular medium construction is assembled, aside from recording, processing, and readout conditions.

Usually the layers are kept distinct one from the other in a medium construction. While adjoining layers need bear no special relationship to one another, it will be appreciated the electron sensitive layer should be so located with relationship to the exterior surface of a given medium construction so as to facilitate any necessary or desirable development of that layer following a recording operation. It is preferred to keep the electron sensitive layer as close as possible, consistent with the type of construction desired and with the materials of construction being used, to the conductive layer so as to keep d as small as possible in a given construction. Preferred medium constructions in general are flexible and thin so as to have total thicknesses of the same order of magnitude commonly associated with conventional photographic film and magnetic tapes so as to permit the use of transport mechanisms similar to those used in magnetic tape recorders and motion picture equipment.

In FIGURE 1 is shown one embodiment of a medium construction of the invention. This medium comprises a top coat layer 10 of gelatin or the like, an electron sensitive layer 11 comprising a silver halide emulsion or the like, a subbing layer 12 (adapted to fasten the layer 11 to the base support 13), a base support layer 13 of polyester film or the like, and a removable conductive layer 14 of nylon resin loaded with conductive carbon particles or the like.

In FIGURE 2 is shown another embodiment similar to FIGURE 1 but showing an alternative arrangement of layers of a medium construction of the invention. This medium comprises a removable conductive layer 16 of nylon resin loaded with conductive carbon particles or the like, a top coat layer 17 of gelatin or the like, an electron sensitive layer 18 comprising a silver halide emulsion or the like, a subbing layer 19 (adapted to fasten the layer 18 to the base support layer 20), and a base support layer 20 of polyester film or the like.

An especially preferred class of medium constructions within the teachings of the present invention are those capable of recording information in a high density manner, that is to say, capable of recording information at densities greater than about 10^5 bits of information per square centimeter of surface area.

When one prefers to have a medium construction within the scope of the present invention which has optimum electrical properties, then the removable conductive layer can be overcoated or placed on top of the electron sensitive layer in a medium construction where the other face of the electron sensitive layer is adhered to one face of a base support layer. On the other hand, when one desires to have a medium construction within the teachings of the present invention wherein the problems of achieving coating thickness and uniformity are generally minimized, then the removable conductive layer can be adhered to the base support layer in an arrangement where the electron sensitive layer is adhered to the other face of such base support layer.

Media constructions of this invention can be prepared by any convenient, conventional procedure. For example, to make a construction of FIGURE 1, one can begin with a preformed optically clear base support layer. Then one face of such layer can be subbed and coated in turn with a layer of electron sensitive composition or the base support can be purchased already subbed on one or both

sides. Finally, the removable conductive layer can be coated upon the opposed face of the base support layer. Conveniently, the various coatings can be applied as solutions or slurries of composition in a volatile liquid using knife, roll, or similar coating procedures. After application, a coating may be dried before another layer is coated.

Electron sensitive compositions do not constitute in themselves any part of this invention but rather are known to the art, no detailed explanation or description of such treatments is considered necessary or desirable herein beyond that already given above in reference to Table I.

To use a medium construction of this invention, one exposes same to a modulated, electron beam under vacuum conditions making sure that the conductive layer is grounded during such beam exposure. As the techniques of electron beam recording are well worked out and form no part of this invention, no detail explanation thereof is given herein. However, for illustrative purposes, it is noted that a typical conventional electron beam recording operation may utilize an electron beam characterized by having a beam diameter of from about 1 to 25 microns, a voltage of from about 10 to 30 kv., a current flow of from about 10^{-8} to 10^{-6} amps and adapted to scan a target area at a rate such that the dwell time is from about 10^{-8} to 10^{-5} seconds. Vacuum pressures commonly range from about 10^{-6} to 10^{-3} torr.

A medium construction of this invention is positioned in the target area and can be either stationary or moving during beam exposure, depending upon equipment considerations, media sensitivity, nature of information being recorded, and the like.

As described above, the conductive layer is separated from a medium construction by any convenient, conventional, stripping procedure.

Instead of using a silver halide emulsion as the electron sensitive layer, one can employ another type of electron sensitive composition in place thereof, such as each of those listed in Table I above. Such other electron sensitive composition is then deposited in layered form in a medium construction as just described in the foregoing example. Then when the resulting medium is used for electron beam recording and thereafter processed to remove the conductive backing before read out, faithful reproduction of recorded information is similarly achieved on readout.

After a recording operation an exposed medium construction is removed from the vacuum chamber wherein recording is accomplished, such medium is processed to remove its conductive layer and accomplish any necessary or desirable chemical or physical treatment of the electron sensitive layer, as, for example, to develop a latent image when this layer is a silver halide emulsion. As such chemical or physical treatment is a characteristic associated with the particular type of electron sensitive composition employed in any given medium construction, and as such chemical and physical treatment involves procedures well known to those of ordinary skill in the art and form no part of the present invention, they are not described in detail herein.

One manner in which a removable conductive backing layer may be stripped away is illustrated by FIGURE 3. Here is shown a removable conductive layer 14 being peeled away from base support layer 13.

After processing in which the conductive layer is removed by stripping, the resulting medium can be read out by any convenient, conventional procedure. For example, the optical projection method of readout can be accomplished by placing the medium in a conventional photographic projection system and projecting it on a white surface.

The invention is further illustrated by reference to the following specific examples. In these examples, the word "parts" has reference to parts by weight unless otherwise stated.

(a) *Removable conductive layer: Formulation and application*

The following dispersion is formulated:

Nylon resin -----	parts--	60
Ethanol -----	do--	272
Water -----	do--	68
Conductive carbon black -----	do--	24
A surface active agent, Triton X-100 -----	drops--	2

The nylon resin (type Zytel 61 from E. I. du Pont de Nemours and Company in Wilmington, Del.) is mixed with the ethanol and water in a reactor flask fitted with a mechanical stirrer and reflux condenser. The mixture is heated under reflux on a steam bath for one (1) hour until all the resin dissolves.

To a standard quart ball mill jar containing one-half inch steel balls is added the conductive carbon black (type Vulcan XC-72 from the Cabot Corporation of Boston, Mass.) and the surface active agent (type Triton X-100 from Rohm & Haas Corporation of Philadelphia, Pa.).

The ball mill jar is placed on the mill for one hour, the nylon resin solution is then added and the mixture is returned to the mill for sixteen (16) hours.

This dispersion is then coated on the unsubbed side of a flexible optically clear base support of polyethylene terephthalate (available as type A, 500 gauge, Mylar from E. I. du Pont de Nemours and Company in Wilmington, Del.) which is provided with a subbing layer to make aqueous coatings adhere to it on the opposite side. This substratum is prepared according to the teachings of British Patent No. 552,085 (1943).

The carbon black dispersion is coated on the unsubbed face using a flat-bed knife coater with an orifice setting of 0.0025 inch and dried in an oven at 200° F. for ten (10) minutes. The dried coating thickness is about 0.0003 inch and the electrical resistance is about 25,000 ohms per square.

(b) *Electron sensitive layer*

A silver halide emulsion is prepared according to the principles described in Glafkides' Photographic Chemistry, volume I, pages 341-353 and pages 369-389. The resulting emulsion contains 3.5% silver, a silver-to-gelatin ratio of 1:1 and a mol ratio between silver bromide and silver chloride of 12 to 88.

The emulsion is coated on a sample of the non-dispersion coated but subbed side of the polyester film on a photographic film coating machine equipped with an extrusion applicator. The coated emulsion layer after coating is approximately 2.5 microns thick and contains approximately 25 milligrams of silver per square decimeter.

The emulsion preparation, coating and subsequent steps are carried out under red photographic type illumination only.

The emulsion is supercoated with a protective gelatin layer of about 0.5 micron thickness. This layer is prepared as described in Glafkides Photographic Chemistry, volume I, paragraph 359, pages 386 and 387. This film construction is now slit into film strips of 16 millimeter width and perforated.

(c) *Use of medium construction*

The medium is now used for exposure by electron beam as follows:

The medium is mounted into a 16 millimeter motor driven sprocket drive tape transport mechanism and guided under an electron beam in a vacuum chamber under a vacuum of about 5×10^{-4} mm. Hg. The axis of rotation of the sprocket is parallel to the direction of the deflection of the electron beam so that the plane of

film movement is effectively perpendicular to the direction of deflection. Film or tape speed is about 9 inches per second.

A conventional television-type deflection is used to deflect the electron beam. The horizontal deflection is accomplished by driving the deflection coil on the electron gun with a 15,750 cycles per second sawtooth current. The sawtooth has a scan period of about 53.5 microseconds and a retrace period of about 10 microseconds. The resultant horizontal deflection of the electron beam is set for about 1 centimeter width at the surface of the medium.

The electron beam is about 10 microns in diameter at the surface of the medium and has an acceleration of about 15 kilovolts. The beam current is intensity modulated by applying a modulating voltage at the gun grid. The intensity modulation of the beam corresponds to the information to be recorded. The peak beam current during such modulation is about 0.1 microampere.

The medium and electron gun are mounted in a vacuum chamber held at about 5×10^{-4} mm. Hg pressure.

The recording takes place by simultaneously moving the film or tape and deflecting, and modulating the electron beam so that a scanned line-like latent image pattern of the information results.

After recording and removal from the vacuum chamber, the exposed medium is immersed in neutral water for about 15 seconds after which the conductive coating is manually peeled away from the remainder of the medium construction. Stripping force is estimated to be less than one gram per inch width. There is substantially no effect upon the optical properties of the base support layer or upon the quality of the recorded information in the electron sensitive layer.

Next, the resulting medium is developed in a developer of the following composition for one minute at 68° F.:

Water	cc	500
p-Methylaminophenol sulfate	gms	2.2
Sodium sulfite	gms	96.0
Hydroquinone	gms	8.8
Sodium carbonate, monohydrate	gms	56.0
Potassium bromide	gms	5.0
Add cold water to make 1.0 liter.		

An equivalent developer is commercially available as Kodak D-19 developer, manufactured by Eastman Kodak Company. After development, the media is rinsed in water at about 68° F. for thirty (30) seconds and transferred to a fixing bath at about 68° F. for about two (2) minutes. Composition of the fixing bath is as follows:

Water (125° F. at time of mixing)	cc	640
Sodium thiosulfate (hypo)		240.0
Sodium sulfite (desiccated)	gms	15.0
Acetic acid (28% pure)	cc	18.0
Boric acid, crystals	gms	7.5
Potassium alum (aluminum potassium sulfate)	gms	15.0
Add cold water to make 1.0 liter.		

An equivalent fixer is commercially available as Kodak fixer for films, plates, and papers as manufactured by Eastman Kodak Company.

After fixing, the medium is washed in water at about 68° F. for about five (5) minutes. The medium is then removed and allowed to dry.

For retrieval (readout) of the recorded information the film medium is positioned in a 16 millimeter movie projector and projected against a white surface.

Faithful reproduction of recorded information is achieved.

EXAMPLE 2

The same procedures and coating formulations are followed as in Example 1 except that the removable electri-

cally conductive layer and the electron sensitive layer are coated on a different base support layer. The base support layer employed is cellulose triacetate film which is optically clear and has a thickness of about 5 mils (commercially available from Eastman Kodak Company). This base support is subbed on one side to receive the silver halide emulsion according to procedures described in P. Glafkides' Photographic Chemistry, volume I, page 469 and is processed in the same manner. When the medium is subjected to a recording operation and then processed both according to the teachings of Example 1, part c, it is observed that a peel force equivalent to about 3 grams is necessary to separate the conductive backing from the remainder of the medium construction.

EXAMPLE 3

Using the same base support member coated with the silver halide emulsion as in Example 1, conductive dispersion is prepared in the following manner:

	Parts
Polymethyl vinyl ether/maleic anhydride	10
Isobutyl alcohol	90

The methyl vinyl ether/maleic anhydride 1:1 copolymer designated as MVE/MA (commercially available as type Gantrez AN from General Aniline and Film Corporation), is added slowly to the isobutyl alcohol in a reactor flask fitted with a mechanical stirrer and a reflux condenser. The mixture is heated with agitation under reflux for fourteen (14) hours until a clear solution results. The acid number is found to be about 130 at the completion of this reaction producing approximately a 15% solution in isobutyl alcohol of the half isobutyl ester of MVE/MA.

This solution is used as follows:

	Parts
15% half isobutyl ester solution (above)	1720
Conductive carbon black	125
Glycerine	27
Surface active agent	1

The 15% half isobutyl ester of MVE/MA solution is added to a gallon can together with the glycerine and surface active agent (type Triton X-100, Rohm & Haas). While mixing the solution with a type Eppenbach Homomixer manufactured by Gifford Wood Company in Hudson, N.Y., the carbon black is added (type Vulcan XC-72, a product of Cabot Corp.). Upon completion of this addition the dispersion is allowed to mix an additional 15 minutes. Finally, an additional 780 grams of isobutyl alcohol is blended in bringing the pigment-to-binder ratio to 1:2.

This dispersion is then coated on the base support on the face opposite the electron sensitive emulsion by the conventional knife over flat bed method and air dried.

The medium is recorded in the manner of Example 1, part c and the removal of the conductive layer effected in the following manner:

The medium is immersed in neutral solution of water for 10 seconds allowing manual peeling of the conductive layer from the remainder of the medium while still in the water. Peel force is equivalent to less than one gram per inch width. Some subbing action is desirable to facilitate separation.

EXAMPLE 4

To provide electron beam recording media having a strippable conductive layer, the following procedure is employed:

To a 5 mil polyethylene terephthalate (polyester) film backing of photographic grade in optical properties, hav-

ing one face subbed to receive silver halide emulsions and the other face coated with a low release coating similar to that described in U.S. Patent No. 2,532,011 is laminated to the face opposite to the subbed face a pressure-sensitized adhesive coated aluminum foil. The aluminum foil pressure-sensitive stock roll consists of a crude-rubber adhesive coating the formulation of which is described in Handbook of Adhesives, I. Skeist, Reinhold Publishing Corporation, New York, pages 586-592 and a backing of a 0.0005 inch thick hard roll aluminum sheet stock (type 1145-H19, Alcon aluminum foil, Aluminum Company of America). The stock roll has a low release silicone polymer coated paper liner, available as Type GATX, from the Riegel Paper Co., Chicago, Ill. The low-release side of the paper liner is wound against the pressure-sensitive adhesive coated face of the aluminum foil to reduce unwind tension.

The laminated construction described above is then coated on the subbed surface of the polyester film with a silver halide emulsion made as indicated in Example 1 to produce a dry coating thickness of about 2.5 microns. The manner with which the photographic layer is applied to this construction is described in Example 1 above. After slitting and perforating the stock roll of laminated foil and photographic film, rolls of 16 millimeter width film are obtained which are suitable for recording by means of the electron beam apparatus in the manner described in Example 1.

The recorded or sensitized film is then removed under darkroom conditions from the vacuum chamber of the electron beam apparatus and stripped free of the conductive aluminum layer. The recorded or sensitized film is then developed in a developer solution for about two minutes at about 68° F., employing processing solutions described in Example 1.

After fixing, the film is washed in water at about 68° F. for about five minutes. The imaged film is then allowed to dry resulting in an optically projectable photographic film.

EXAMPLE 5

To provide electron beam recording media having a strippable conductive layer, the following procedure is employed:

To a 5 mil polyethylene terephthalate (polyester) backing of photographic grade transparency which is subbed on one face and coated on the other face with a low release coating, is laminated to the side opposite to the subbed side conductive pressure-sensitive adhesive coated aluminized polyester film construction. The latter construction is prepared as follows:

To 84 grams of 30% solids pressure sensitive crude-rubber type formulation are added 75 grams of conductive silver powder, available as Grade V-9 (E. I. du Pont de Nemours, Inc.) and 20 grams of heptane. Typical pressure-sensitive adhesives useful in constructing media of this invention are described in Handbook of Adhesives, I. Skeist, Reinhold Publishing Corporation, New York, pages 586-592. The above mixture is stirred until a uniform dispersion is achieved. The dispersion is then knife coated at a 4 mil setting of the knife orifice onto the aluminized surface of a 1 mil polyethylene terephthalate (polyester) film. The aluminized surface, provided by the vapor-coating process, is about 1000 Å. thick on the 1 mil thick polyester film and has a resistance of about 0.8 ohm per square. The backside of such aluminized film is also coated with a low-release silicone polymer coating to reduce unwind tension of the pressure-sensitive adhesive coated stock roll. The low-release coating similar to that described in U.S. Patent No. 2,532,011. The adhesive coated construction is dried at 150° F. for 4 minutes.

The laminated construction consisting of said subbed

5 mil transparent polyester film with the conductive adhesive coated aluminized 1 mil film adhered to the backside is then coated under darkroom conditions on the subbed surface with a photographic emulsion according to the teachings of Example 1. The electron sensitive layer after drying is about 2.5 microns in thickness and after slitting and perforating the resulting construction provides an electron beam recording medium.

The resultant recording medium is suitable for recording in the electron beam recording apparatus. After recording in the vacuum in the manner described in Example 1, the sensitized medium is removed from the vacuum chamber and under darkroom conditions stripped from the conductive adhesive coated layer. The exposed sensitized layer is then developed in the manner and process described in Example 1. The resultant imaged film is then suitable for optical projection of the recorded information.

We claim:

1. A sheet-like storage medium adapted to
 - (a) develop therein an image pattern corresponding to information associated with a modulated electron beam when such a beam scans one face thereof during a recording operation,
 - (b) dissipate electrons during such an electron beam scanning operation, said dissipation being at a rate sufficient to maintain the electrostatic potential associated therewith in said medium at a level which substantially does not adversely affect the recorded image,
 - (c) be processed after such recording operation and before readout by conventional optical transmission techniques so that the imaged areas selectively modulate transmitted light,
2. said medium comprising in combination
 - (a') an optically clear, dimensionally stable, base support layer having opposed parallel anchorable faces,
 - (b') an electron sensitive layer composed of an electron sensitive composition which, when deposited in a layered form upon an inert surface is characterized by having the chemical capacity to develop an optical density of at least one when exposed to not more than 10^{14} electrons per square centimeter of layer surface area, said electrons accelerated to penetrate substantially all of this sensitive layer,
 - (c') an electrically conductive layer characterized by
 - (1) being positioned either over said electron sensitive layer or over said base support layer, and
 - (2) having the capacity to be removed with physical force from the remainder of said medium without appreciably affecting at time of removal:
 - (a'') the optical clarity of the base support layer, and
 - (b'') the image quality of information developed in said electron sensitive layer.
3. The medium of claim 1 wherein said conductive layer is separated from the remainder of said medium by peeling using a peel force of at least about 4 grams per inch width.
4. The medium of claim 1 wherein said conductive layer is positioned on that face of said base support layer opposed to that on which said electron sensitive layer is positioned.
5. The medium of claim 1 wherein said base support layer is a polyester film.
6. The medium of claim 1 wherein said base support layer is a cellulose ester film.
7. The medium of claim 1 wherein said electron sensitive layer is a silver halide emulsion.
8. The medium of claim 1 wherein said conductive layer has a resistivity of not more than about 10^6 ohms per square in a vacuum of about 10^{-5} mm. Hg.
9. The medium of claim 1 wherein said conductive

layer consists essentially of an organic polymeric binder having conductive particulate material homogeneously distributed therewithin, said layer being adhered to one face of said medium by a peel force in air of at least about 4 grams per inch width.

9. The medium of claim 1 wherein said conductive layer comprises a pressure sensitive adhesive coated conductive metal foil.

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References Cited

UNITED STATES PATENTS

2,664,043	12/1953	Dalton	346—135 X
3,185,995	7/1965	Dickens	346—1
3,196,011	7/1965	Gunther et al.	96—1

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,336,596

August 15, 1967

Richard F. Dubbe 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 65, for "charges" read -- changes --;
column 4, line 16, for "folowing" read -- following --; column
5, line 42, for "includes" read -- included --; column 6,
line 5, for "Vinyldiene" read -- Vinylidene --; line 72, for
"image" read -- imaged --; column 14, line 66, for "subbing"
read -- slubbing --; column 16, line 5, for "'eachings" read --
teachings --.

Signed and sealed this 8th day of October 1968.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents