

Oct. 14, 1969

NOBORU MASUDA

3,472,687

TRANSPARENT ELECTROSTATIC RECORDING MEDIUM

Filed March 24, 1965

2 Sheets-Sheet 1

FIG. 1

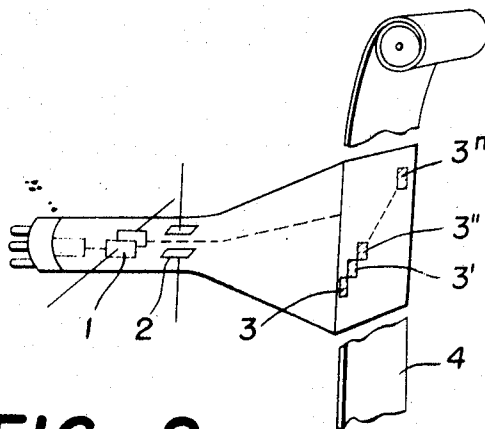
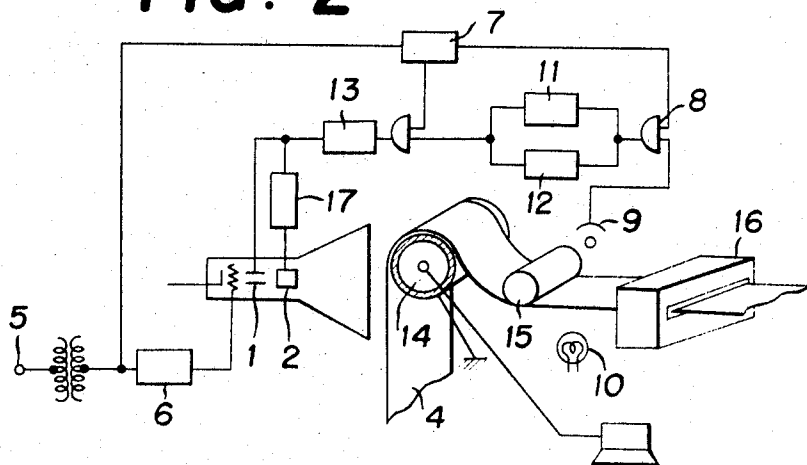


FIG. 2



Noboru Masuda

INVENTOR

BY *George A. Angrove*
Attorney

Oct. 14, 1969

NOBORU MASUDA

3,472,687

TRANSPARENT ELECTROSTATIC RECORDING MEDIUM

Filed March 24, 1965

2 Sheets-Sheet 1

FIG. 5

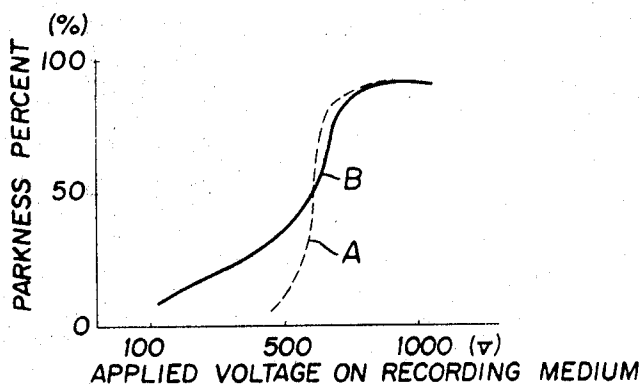


FIG. 3

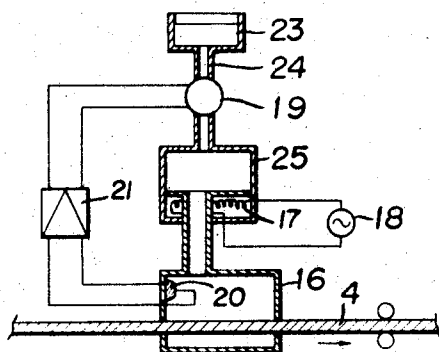
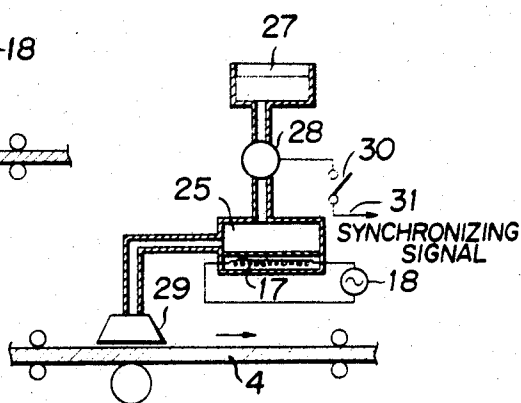


FIG. 4



Noboru Masuda
INVENTOR

BY *George P. Caporale*
Attorney

1

3,472,687

TRANSPARENT ELECTROSTATIC
RECORDING MEDIUM

Noboru Masuda, Tokyo, Japan, assignor to Denki Onkyo Co., Ltd., Tokyo, Japan, a corporation of Japan
Filed Mar. 24, 1965, Ser. No. 442,302
Int. Cl. H05b 33/28; H01b 1/00; B44d 1/00
U.S. Cl. 117-211 1 Claim

ABSTRACT OF THE DISCLOSURE

A transparent recording medium for electrostatic recording comprising a transparent layer of synthetic resin, an electrolyte coated on one surface of said transparent layer and a surface active agent applied on the other surface of said transparent layer.

This invention relates to systems of processing information and more particularly to a system of processing information adapted for use in combination with teleprinters utilizing perforated papers.

In computers and the like a mechanical means has been used wherein sheets of paper, in the form of tapes serving as an intermediate recording medium, are perforated. In other types of recording, electrostatic recording sheets, or sheets of paper coated with an insulator have been used but each of these has various defects. The principal defect of the mechanical perforated system is its low perforating speed because of the mechanical method so that it is impossible to attain high speed transmission and reception of information suitable for presently used transmission lines. On the other hand, in the system utilizing sheets of paper coated with an artificial resin as the information processing medium it is difficult to provide the required high ratio between signal and noise so that its operation is not satisfactory because a reflected light beam is utilized in this system.

This invention contemplates providing an information processing system characterized in that a code tube is positioned in contact with a single layer of a transparent synthetic resin or with a small gap therebetween, an electron beam travelling through a zone of reduced pressure inside said code tube is focused on a code plate located on the front surface of the code tube so as to charge static electricity on the single layer of synthetic resin, and, an opaque substance having a polarity opposite to said static electricity is caused to adhere on said single layer to vary the degree of transmission of light so as to act as a memory or storage and then to reproduce the information.

While the specification concludes with claims particularly pointing out and distinctly claiming the subject matter which I regard as my invention, it is believed that the invention will be best understood from the following description taken in connection with the accompanying drawings, in which:

FIG. 1 is an enlarged perspective view, partly in section, of a code tube constructed according to this invention;

FIG. 2 is a block diagram, partly in perspective, of the information processing system embodying this invention;

FIGS. 3 and 4 show diagrams to explain the fixing device utilized in this invention; and

FIG. 5 is a plot of an electrostatic recording characteristic curve.

Referring now to FIG. 1 of the accompanying drawing there is shown an enlarged view of a code tube embodying this invention comprising a pair of horizontal deflecting plates 1 adapted to create a required electric

2

field to cause an electron beam to deflect and focus on code electrodes 3 located on a code plate at the surface of the tube. There is also provided a pair of vertical deflecting plates 2 which operate in the same manner as the horizontal deflecting plates 1. It is to be understood that the magnitude of the potentials applied to these deflecting plates are suitably adjusted by external circuits, not shown, depending upon the running speed of a recording medium 4. The code electrodes 3 are made of an electrostatic conductor such as a conductive metal, a resinous substance or an electric conductive glass. Each of the electrodes is insulated by an electric insulator. Although not limited thereto, glass is a preferable material. If required, a fluorescent material is applied onto the surface insulator of an electrically insulated material, so as to produce fluorescence when the electron beam impinges upon portions other than the electrode plates so as to determine whether the electron beam is suitably impinging upon the respective code electrodes or not. The electrode may take a form of a tube provided with a suitable slit to control the flow of the electron beam, said tube being provided with a plurality of stylus electrodes embedded in its surface. The recording medium 4 comprises a single layer of a synthetic resin such as polyethylene, polypropylene, polystyrene, polyvinyl chloride and the like. One of the inorganic electrolytes, i.e. potassium carbonate, sodium chloride, boric acid, potassium chloride, chlorous acid, potassium bicarbonate, potassium hydroxide, calcium hydroxide, barium chloride, aluminum hydroxide and the like, or one of the organic electrolytes, i.e. phenol formaldehyde resin, cresol formaldehyde resin, resorcinol, metaphenylene; diamine, polymethacrylic acid, protein, gelatin, amalanth-dye, Eosine G, polymethylene imine, dichloroethylamine, phenol carboxylic acid, acetoacetic acid, acetylene dicarboxylic acid, ethyl malonic acid, acetaldehyde sulphonic acid, acenaphthalene sulphonic acid, polyacrylic acid, linoleic acid, palmitic acid, aspartic acid and the like, or a mixture thereof is dissolved in water or an organic solvent and the solution is applied onto the recording surface of the recording medium prior to recording and the opposite surface of the recording medium is provided with a thin coating of less than few microns thickness consisting of a transparent conductive high molecular substance, for example, a surface active agent such as glycerin, a certain type of complex compound, especially a compound produced by chelate combining a resin and a metallic substance, or a semiconductive material such as a silicon resin, especially those having a resistivity of less than 10^{14} ohms/cm., or a substance having π bond and of relatively low resistivity.

While the above described recording medium is disclosed in Japanese patent application No. 50,956 of 1962, it was found that the same function can be provided by having the record supporting medium made of a polyethylene having a small number of double bonds into which approximately from 0.1% to 0.005% of a surface active agent or activator has been incorporated at the time of moulding the film.

In order to aid in understanding the principle of this invention, the following must be considered, however it should be understood that the invention is by no means limited to such particular arrangement and that this invention is based on the discovery that static electricity is collected on an electric insulator of a thickness of about 100μ by mixing or pre-treatment operation. The reason of improving collection of the static electricity by pretreatment can be considered as attributable to the following two considerations.

First, as is well known in the art, although a synthetic resin insulator becomes charged with electricity by fric-

tion or contact it is possible to reduce such a charge to zero or substantially zero by neutralizing it with a pre-treating liquid prior to recording. By this treatment better result can be expected than the case wherein a high AC voltage is applied before recording. More particularly, in recording mediums having superior recording voltage viz recording density characteristic, it is usually difficult to eliminate noise due to the charge created by the initial friction, and, because of the low saturation limit of the medium, so that uniform recording can not be expected owing to the effect of the initial noise. Prior electrostatic recording sheets consisting of papers coated with polyethylene and the like have such recording density viz voltage characteristic as shown in FIG. 5 so that it is a relatively easy matter to remove the initial noise and such prior recording sheets are quite different from the inventive system wherein static electricity is collected only by the corona discharge in air. By this reason the recording system of this invention requires pretreatment.

Second, it has been thought that non-polar substances do not undergo any polarization so that they are not charged with electricity by friction. However practically all substances are charged with electricity. This is because impurities that adhered to the surface of the substance cause the surface to be active and that such substance can produce latent recorded images only in the presence of surrounding medium or air. The insulating property merely serves to retain the electric charge collected and does not contribute to better collection thereof. Japanese patent applications Nos. 12,292/52, 42,889/52 and 42,890/52 disclose test results showing that electrolytic substances give better result. According to one feature of this invention the surface of the recording medium is coated with an electrolyte. Test results show that such coating of electrolyte gives better results than recording mediums having powders of impurity adhering thereon.

Powdery material is unsuitable because the particles are too large to provide resolution. For example, it is known that materials belonging to the stearic acid series have good charge collecting properties. It has also been found that these materials treated with radio isotope also have good charge collecting property.

By these reasons it is believed that static electricity is well collected but a good record can be produced even when the synthetic resin is not insulative by extending the above described considerations.

If one considers that neither the powder method nor radio isotope method provide resolution, incorporation of a substance of such character in molecular state in the synthetic resin would not decrease resolution but rather result in a good record. While it is expected that it is very difficult to uniformly incorporate such an electrolytic material into a substantially oily synthetic resin it was found that so-called surface active agents are effective as such an additive.

The following is an example of the method of preparing the recording medium of this invention.

A surface active agent was dissolved in alcohol and mixed with polyethylene pellets. Then the pellets were dried at a temperature of 100° C. to cause the electrolyte to adhere on the pellets. Since the resultant pellets are uniformly coated with said electrolyte or surface active agent when they are molded in a film molding machine, a recording medium of uniformly mixed composition can be produced. Results of extensive tests made on these recording mediums show that certain agents give good result.

When one or more such agents are added to a polyethylene base, in the ratio of 0.08-0.1 part of the former and 100 parts of the latter, good results were obtained. By experiment it was found that compounds of the non-ionic series, polyoxyethylene castor oil ether, polyoxyethylene lauric acid ether series having a value of 3 to 14 of hydrophile-lyophile balance are especially suitable for

the surface active agent. The surface resistance of the recording sheet is approximately 1×10^8 - 1×10^{15} ohms/cm. and has no relation with the recording density. This means that the substance incorporated into the high molecular insulating substance functions just like an impurity so that the interior of the insulating material is charged with the electricity of the ions but the electric charge, when the material is considered as a whole, is zero. If a positive charge is applied from the outside to the substance which has had incorporated therein a surface active agent the negative ions will lose their ionic property by being acted on by the positive charge so that they will be exchange in the form of atoms or molecules. In other words, when considered as a whole, it can be considered that a positive charge adheres on to the recording medium. This is obvious from the fact that when a positive potential is applied a positive charge adheres to the substance and the incorporation of the surface active agent greatly improves the collection of the electrostatic charge.

The interstices between particles incorporated in the resin act as void type streamer so that thickness between voids is very thin. "Void type streamer" is directed to the phenomenon that the surface active agent particles incorporated into the film resin function as if they were airways or void spaces in the recording medium. Void discharge is very abruptly produced, and electron avalanche is seen. By this reason better results or obtainable than the case where a sheet coated with polyethylene is used as the recording medium.

Referring now to FIG. 2 which diagrammatically illustrates an information treating system embodying this invention, an input circuit 5 thereof may be connected to any type of information source such as a computer, transmission line and the like. Picture signals received by the input circuit 5 are amplified to the desired level by means of an amplifier 6 for recording informations. A portion of the received signal is also supplied to a circuit 7 including a synchronous segregating circuit and error word detecting circuit. Usually the circuit 7 may comprise a known circuit such as a parity check circuit but preferably may be an AND gate or an inhibit circuit. The synchronous segregating circuit may be of start and stop type or of a type utilizing a digital synchronizing circuit. In any case it is combined with a parity check circuit but preferably may be an AND gate or an inhibit circuit. The synchronous segregating circuit may be of start and stop type or of a type utilizing a digital synchronizing circuit. In any case it is combined with a parity check circuit so that when an error word is produced it will immediately send an inhibit signal to an inhibit gate while at the same time send a signal to a synchronous shaping circuit 13. These circuits are constructed by convention elements such as transistors and electronic tubes in such a manner that upon generation of an error word the electrical bias applied to a deflecting circuit is increased or decreased to swing the electron beam to the outside of the tube surface. A pair of synchronous pulse generating circuits 11 and 12 are provided to generate synchronize pulses in the form of signals which correspond in any time series. The frequency of these pulses are slightly modified by applying a suitable bias voltage. These circuits are also constructed such that they are controlled from the outside to oscillate in synchronism. The phase relation between pulse generating circuits 11 and 12 is such that when the circuit 11 starts to oscillate from 0 phase the circuit will start to oscillate from π phase so that when pulses generated by these circuits are combined and shaped, a continuous rectangular wave will be formed. These circuits may be formed by a conventional multi-vibrator circuit or a Hartley circuit. The outputs from the pulse generating circuits 11 and 12 are combined by a circuit 13 which is coupled to the synchronous segregating circuit 7 via an AND gate and operates to vary the bias potential of the code tube to swing out the electron beam upon re-

5

6

ceival of an inhibit signal. Thus, presence of error words or miss-operation in the circuit will cause the electron beam to swing to the outside of the code electrodes of the code plate. Each photoelectric tube or photosemiconductor element 9 is provided for each column, it being understood that said tube or element 9 being positioned at right angles to the direction of running of the recording medium in the transversal system. The light rays emanated from a light source 10 are intercepted by information or dark spots recorded on the recording medium passing in front of the photoelectric tube 9 so as to detect the spacing or pitch between recorded information. In front of and in parallel with the electrodes on the code tube is disposed a rotary electrode 14. The recording medium 4 is moved between the code tube and the rotary electrode 14 so that its rear surface or the surface coated with a conductive material closely engages the peripheral surface of the rotary electrode. A drum 15 is provided to apply a light opaque substances onto the latent images corresponding to information which is electrostatically recorded on the recording medium. Usually, the magnet brush method may be used which is common in the electronic photography art. It is desirable to make as low as possible the surface resistance of the magnet brush because too high surface resistance results in the difficulty of adhesion of the toner or results in the so-called fog thus greatly impairing information. It is preferable to utilize the drum 15 to apply a magnet and rubber incorporated with a conductive substance for the purpose of decreasing resistivity or apply conductive paint to rubber. When metallic magnets are employed it is preferable to cement them to a shaft by means of an electrically conductive adhesive. A mixture comprising iron powder (carrier) and a toner (resin and pigment) in the ratio of about 100:5 is magnetically applied on the magnetic structure constructed as above so that it will rub with a slight pressure of the surface of the recording medium. One example of the toner used herein was prepared by a method which comprises dissolving 100 parts of chlorinated rubber, 5 parts of rosin, 5 parts of dystuff and 75 parts of carbon black in trifluorethylene by means of a ball mill or rolls, milling the mixture for about 8 hours, drying by a suitable method, and then pulverizing. Good results were obtained when the mixture was pulverized by using a jet or an ejection technique. The particle size varies around a size of about 5 microns. This example is only an illustration and good results can be expected where a non-soluble resin and a soluble resin are mixed at a proper ratio and are then dispersed and the proportion between the resin and the solvent utilized for fixing is properly selected. In this example, acetone was utilized as the solvent and the toner comprised chlorinated rubber, i.e. the non-soluble resin, and rosin, i.e. the soluble resin. The same consideration can be applied to coloring agent, thus the pigment corresponds to the non-soluble substance and the dyestuff to the soluble substance.

By suitably combining these materials desired effects can be substantially provided. Developed recording medium 4 is then introduced into a fixing tank 16 containing acetone, for instance. Where the recording medium is made of polyethylene, an exterior heater is provided for the tank to maintain the temperature inside the tank within a range of from 60° to 70° C. This temperature can be readily maintained by using a suitable temperature responsive element and a relay, not shown.

FIG. 3 illustrates a diagrammatic representation of a fixing device adapted to fuse and solidify a colored resinous material which has been caused to adhere electrostatically on to the recording medium made of an artificial resin. A solvent contained in a reservoir 23 is supplied into an evaporating tank 25 through a pipe 24 under the control of an electromagnetic valve 19. The tank 25 is provided with an electric heater 17 energized from a commercial source 18 to heat the tank 25 at a

temperature higher than the evaporation temperature of the solvent. The toner electrostatically adheres onto the surface of the recording medium and is adapted to be fused and solidified by the action of the vapor of the solvent at a suitable temperature of course depending upon the type of the recording medium used, and the type of the solvent. It is necessary to maintain at a proper value the ratio of the vaporized solvent and the air contained in the tank 25. Usually a combination comprising an element 20 sensitive to the organic solvent and a suitable electric circuit 21 is used to suitably control the electromagnetic valve 19 to maintain said ratio. Usually the element 20 sensitive to the organic solvent utilizes the adsorption property of the solvent, flexibility, and contact resistance of electric conductive minute particles. Generally, the electrically conductive particles are dispersed in a resinous material so that when the resinous material absorbs the organic solvent it will swell to increase the contact resistance of the conductive particles. The variation in the resistance value causes variation in the current flow which is amplified to operate the electromagnetic valve 19. When the solvent is evaporated from the resinous material it will contract to decrease the contact resistance of the individual conductive particles, thus decreasing the resistance of the element 20. Where acetone is used as the solvent it is preferable to make the resinous material by using a mixture comprising chlorinated rubber and styrene in the ratio of about 3:1. Generally this mixture is required to have good solvent adsorption as well as evaporation properties. Although carbon black is suitable as the electrically conductive material, powders of aluminum and lead also have good solvent adsorption property and may be used if desired. Selection of these materials are determined by considering such factors as the running speed of the recording medium 4, the temperature condition in the tank 16, the location of the sensitive element 20 in the fixing tank 16, and the like factors.

FIG. 4 illustrates a modification of FIG. 3. The solvent contained in a reservoir 27 is supplied to an evaporating tank 25 via an electromagnetic valve 28 which is controlled by a start-stop signal supplied from a switch 30, which in turn is electrically connected to a starting circuit 31 via a conductor 31. The vapor of the solvent generated in the evaporation tank 25 is ejected under pressure onto the surface of the moving recording medium 4 through a narrow slit 29.

The operation of this invention is as follows: Referring again to FIG. 2, when any information signals for example, five unit signals for teletypewriter are received from the input circuit 5, the synchronizing signal will be separated from a series of information signals by the operation of the synchronous segregating circuit 7. Concurrently therewith this segregating circuit checks whether the received signals correspond to signals at the transmitting terminal in the ratio of 1:1, or not. Inasmuch as various means of parity check are well known in the art, it is believed unnecessary to describe it in detail. It should be understood, however, that upon occurrence of an error word the circuit 7 will act to vary the deflection current so as to send out deflection pulses which are substantially larger or smaller than the normal deflection current thus swinging out the electrode beam not to impinge upon any of the electrodes 3, 3', 3''... embedded in the surface of the code tube (FIG. 1). Received information signals are deflected and scanned to repeat on and off operations at positions corresponding to the weight of the codes. The control grids are so controlled that a large quantity of the electron beam is caused to impinge upon the code electrodes 3, 3', 3'', 3'''... 3ⁿ at required positions. In this way, electrostatic latent images are produced on the surface of the recording medium 4 made of a transparent synthetic resin and passing through a gap defined between the code electrodes and the back or supporting electrode 14. As-

suming now that the running speed of the recording medium 4 is denoted by VO and the deflection speed by V, then by making $VO=V$, black spots will be formed transversally of the recording medium. Of course it is necessary to adjust the deflection currents so that the electron beam may properly impinge upon the code electrodes 3, 3', 3'' . . . Since the supporting electrode 14 is rotated synchronously with the running speed of the recording medium 4 there is no slip between them, so that the latent images of the information thus produced can be satisfactory reproduced without any accompanying noise caused by the restraining electric field of the synthetic resin. After developing the latent images, the recording medium 4 is neutralized and is then removed from the supporting electrode. However, the recording medium 4 made of a synthetic resin has larger elongation under a mechanical tension than ordinary papers, spacings or pitches between adjacent informations may be different from the desired value, thus causing undesirable error in time series between codes, which is of course detrimental to the processing of the information. The circuits 8, 9, 10, 11 and 12 shown in FIG. 2 serve to control this pitch which operate as follows: Light rays emanated from lamp 10 and arrive at photoelectric tube 9 after passing through the transparent recording medium 4. When it is assumed that information is recorded on this recording medium and that the medium is running at a constant speed, the intensity of light rays arriving at the photoelectric tube will be varied accordingly thus producing electric signals having values corresponding to the intensity of impinging light rays. If these elements were installed at a position corresponding to a single unit, such an arrangement can not provide accurate indication of the pitch of information because there is the case where no signal is recorded depending upon the nature of the received information. To eliminate this difficulty if synchronizing signals are recorded on the sides of the recording medium or a plurality of elements are provided corresponding to all codes, there would be at least one recorded unit among five units. In other words, it becomes possible to detect the pitch of the recorded information. Corresponding synchronous signal pulse waves obtained in this manner are applied to AND gate 8 where they are compared with the signal coming from the detector circuit 7. The compared signals are applied to oscillator circuit 11 or 12. When the oscillator 11 is set to start oscillation from 0 phase, the oscillator 12 should be set to start to oscillate from π phase. The signal applied to these oscillators 11 and 12 is the difference between the control signal supplied from the circuit 7 and the signal corresponding to the elongation of the recording medium 4 which are compared by the AND gate 8. Usually, since the elongation of the synthetic resin comprising the recording medium is smaller than the time interval of the synchronizing signals, the oscillators 11 and 12 are constructed to oscillate near the center of said two signals. As these oscillators operate in response to the mean value of variations in the elongation of the recording medium, the variation in the width of the pulse will produce a signal corresponding to said elongation.

This signal of varying width is then applied to an integrator to produce a variable DC basis voltage which is applied to the oscillator 11 or 12 to vary the frequency thereof corresponding to said variable bias voltage. The signal is then converted into a deflecting voltage of a saw teeth wave form so as to correct the elongation of the recording medium, thus assuring recording at a proper pitch. Instead of gradually deflecting the electron beam by the on-off control of the control grids of the code tube, the on-off signals may be used to directly control the deflection voltage, or it may be possible to cause a constant electron beam to impinge upon the code electrodes 3, 3', 3'' . . . 3ⁿ while a constant potential is applied to the control grids of the code tube. The latent

images produced in the manner above described adhere by the electrostatic force alone and in order to permanently fix these latent images, the recording medium 4 is passed through the fixing tank 16. This tank is usually maintained at approximately 60° C. to dissolve and fix the toner which is adhering on the recording medium by the electrostatic force. In the recording system utilizing a recording medium made of a transparent synthetic resin it is not possible to use the thermal fixing method as in the electronic photography. More particularly, the medium which can record information in this manner is generally made of a thermoplastic resin, the amount of heat absorption is greatly different at portions where colored substance is adhering and portions where the colored substance is not present. As a result the portions of the medium where information is recorded undergo great change under the influence of heat and hence are impractical.

The photo-read out method which is now widely used in teletypewriter can be readily applied to read out the recording medium. When the photo read out method is used for the conventional system of utilizing papers perforated with circular perforation, the building up portions of the read out pulses are slightly inclined owing to the circular perforations whereas according to this invention the information is recorded as square black spots so as to produce rapidly building up pulses. Further in accordance with this invention, it is not necessary to use a circuit for converting series signals into parallel signals but instead it is possible to record series signals as a parallel record by mere control of the deflecting current of the code tube. In addition, according to this invention information can be readily and economically processed at a high speed because of the absence of mechanical operation. Utilization of a transparent synthetic resin as the recording medium results in an improved information processing system with low signal to noise ratio with regard to the transmission of light rays through the medium.

While above this invention has been described as embodied in a information recording system, it will be obvious that this invention can also be applied to a recording device for the conventional facsimile transmission. In this case the recording stylus of the recording device is provided in multiple to record the received facsimile. Thus, excellent transparent duplicated images can be produced which may be satisfactorily used as motherplate of the diazo type copier. The transparent recording medium of this invention can be used in the same manner as silver chloride photographic films which are presently used in facsimile receivers.

I claim:

1. A transparent recording medium for electrostatic recording comprising:

a transparent layer of synthetic resin selected from the group consisting of polyethylene, polypropylene, polystyrene and polyvinyl chloride,

an electrolyte coated on one surface of said transparent layer selected from the group consisting of potassium carbonate, sodium chloride, boric acid, potassium chloride, chlorous acid, potassium bicarbonate, potassium hydroxide, calcium hydroxide, barium chloride, aluminum hydroxide, phenol formaldehyde resin, cresol formaldehyde resin, resorcinol, metaphenylene diamine, polymethacrylic acid, protein, gelatin, amalanth dye, polymethylene imine, dichlorodiethylamine, phenol carboxylic acid, acetoacetic acid, acetylene dicarboxylic acid, ethyl malonic acid, acetaldehyde sulphonic acid, acenaphthalene sulphonic acid, polyacrylic acid, linoleic acid, palmitic acid and aspartic acid, and

a surface active agent applied on the other surface of said transparent layer selected from the group con-

sisting of glycerin and silicone resin of a resistivity
of lower than 10¹⁴ ohms/cm.

References Cited

UNITED STATES PATENTS

3,072,543	1/1963	Lubow	346—135
3,193,907	7/1965	Fyler	346—74

3,308,473	3/1967	Sawazaki	346—74
3,212,931	10/1965	Kubota	346—74

BERNARD KONICK, Primary Examiner
L. J. SCHROEDER, Assistant Examiner

U.S. Cl. X.R.

117—63, 68, 223; 346—74, 135