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[54] **ELECTROGRAPHIC TAPE RECORDING MEDIUM**

[75] Inventors: **Klaus Brill**, Korntal; **Wolfgang Grothe**, Stuttgart, both of Germany

[73] Assignee: **Robert Bosch GmbH**, Stuttgart, Germany

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[52] **U.S. Cl.** .... **346/76 R**, 346/135, 346/74 R, 346/74 ES, 117/215

[51] **Int. Cl.** **B41m 5/18**

[58] **Field of Search** 346/135, 76, 74; 117/222, 117/215, 217

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Primary Examiner—Richard B. Wilkinson
Assistant Examiner—Vit W. Miska
Attorney, Agent, or Firm—Flynn & Frishauf

[57] **ABSTRACT**

A layer of a metallic oxide having a heat of formation less than that of aluminum oxide is provided between the paper or synthetic flexible carrier and an aluminum film having a square resistance of about 2.5 ohms. Electric current flows between a stylus and the aluminum layer, but the effect of the current is merely to initiate an aluminothermic reaction between the aluminum and the oxide which, however, is sharply limited to the path of the stylus over the medium as the stylus or the medium is moved, leaving a clearly visible trace.

4 Claims, 2 Drawing Figures

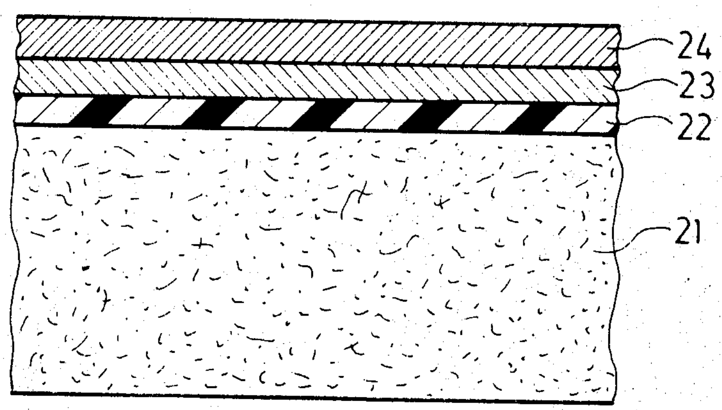


Fig. 1

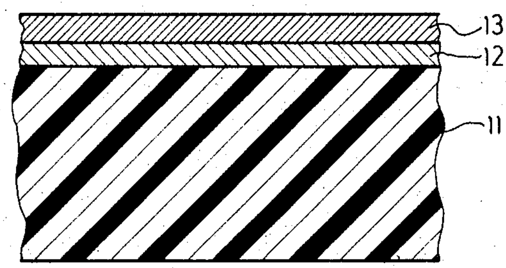
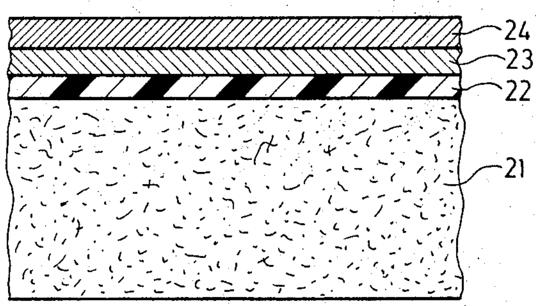


Fig. 2



ELECTROGRAPHIC TAPE RECORDING MEDIUM

This invention relates to a recording medium for graphic recording devices using a tape of insulating material as a carrier and having a covering layer composed essentially of aluminum.

The recording process utilizing known graphic recording media of this type uses a writing stylus through which an electric current flows into or out of the aluminum. The current flow under the point of the stylus melts the metal layer by means of the Joule heat produced. The layer coalesces there, the electrical contact is broken, and an arc is formed. The arc burns the layer out up to a certain spot size and then extinguishes. This process is repetitive if the paper or the stylus is advanced and a new contact is produced. The writing trace is thus formed by a series of discrete burnouts.

All the energy necessary for burning out aluminum in these graphic recording media has been provided by the electric arc. In the entire region of the arc plasma very high temperatures are reached. In consequence, the layer material vaporizes and is ionized in the plasma. By convection and under the influence of the electric field, a transfer of material takes place so that scales of aluminum oxide are formed on the stylus. These scales lead to interruption of the flow of current and thus also of the writing trace. For this reason, high writing voltages and stylus application pressures are necessary. The high mechanical and thermal stressing of the stylus leads to indications of wear of the stylus point as well as to so-called trails on the paper, which are weakly visible traces that arise even though neither a flow of current nor an arc was present. The causes of these "trails" are still unknown.

A further disadvantage of the known graphic recording media, even those with aluminum base, lies in the relatively high corrosion of the metal layer. Especially when resin coated paper is used as the carrier layer, solvent residues from the resin layer as well as materials containing acid or alkali groups which are likely to rub off the surface of pigment grains, come into contact with the metal layer, where they promote the corrosion of the metal. That means that the durability of the cover layer cannot yet be regarded or designated as satisfactory in many cases involving known graphic recording media.

A further disadvantage of the known graphic recording media is the polarity dependence of the quality of the traces produced. With the known graphic recording media, sharply bounded traces are obtained if the stylus has negative polarity. That leads, however, to relatively frequent gaps because in that case aluminum oxide is readily formed on the stylus, so that a higher application pressure is needed. For that reason, the stylus is generally connected to the positive pole of the voltage source in spite of the fact that the trace is not so sharply defined in that case. It is possible to reduce the application pressure in that fashion, however, because with positive polarity aluminum oxide no longer forms to the same extent at the stylus point.

It is the object of the present invention to improve the quality and the safety in operation of graphic recording media. In particular, it is an object to avoid or mitigate the formation of oxide layers or scale at the stylus point, so that the recording device can be operated with low application pressure, thus largely avoiding wear of its mechanically stressed parts. In addition, it is desirable for the quality of the inscribed traces to be, so far as possible, independent of polarity, so that this too is an object of the invention. Finally, it is an object of the invention to provide a graphic recording medium of high corrosion resistance and thereby to provide a medium of increased durability.

SUBJECT MATTER OF THE PRESENT INVENTION

Briefly, instead of supplying all the energy for the formation of the trace through the arc that is formed, a large proportion of the necessary energy is stored in the writing layer of the medium itself, in the form of latent chemical energy. This is accomplished by providing a layer of an oxide having a lower heat of formation less negative than that of aluminum oxide in between the carrier layer and the aluminum covering. Heat of formation is generally expressed with reference to 1 gram-atom of oxygen, so that the value for Al_2O_3 is minus 133 kilocalories per gram-atom of oxygen.

The graphic recording process involved in the application of the recording medium of the invention may be described as follows. The electric current flowing between the stylus point and the aluminum covering layer, by warming the layer and producing an arc sets off an exothermic reaction which delivers most of the necessary energy for producing the trace. This exothermic reaction is a so-called aluminothermic reaction. When manganese oxide, Mn_3O_4, is used for the intermediate layer, the reaction may be written as follows:

$$8\ Al + 3\ Mn_3O_4 \rightarrow 4\ Al_2O_3 + 9\ Mn + \Delta H = 607\ kcal.$$

THe amount of energy liberated depends upon the total amount of conversion as well as upon the stage or state of oxidation in which the metal in question (in this case manganese) is provided.

By inspection of the energy balance, it is evident that the energy liberated by the reaction with manganese oxide, Mn_3O_4, is by itself sufficient to vaporize an aluminum coating having a square resistance of 2.5 ohms, which corresponds to a mass distribution of 10 $\mu g/cm^2$. The fact that the place at which the formation of the trace takes place has been shifted from the arc plasma into the layer itself is doubtless responsible for the good quality of the traces obtained with the graphic recording medium of this invention. In this fashion, a local limitation or confinement of the reaction is reached that leads to very sharp traces. It has moreover been found that no polarity effect or influence is to be distinguished in the use of the graphic recording medium of the invention. The writing sensitivity of the layer is thus practically independent of the polarity of the stylus.

It furthermore appears that the intermediate metal oxide layer has the important effect of blocking the diffusion of the corrosive groups originating in the carrier layer, which tend to corrode the aluminum covering layer. In this manner the useful life of the aluminum layer of the graphic recording medium of the invention is substantially increased. It was determined by comparative corrosion tests that in the case of the aluminum layer of the new graphic recording medium, no attack of the aluminum layer was yet recognizable when the aluminum layers of recording media of previously used types already showed clearly visible corrosion effects.

In principle, all oxides having a heat of formation number with reference to 1 gram-atom of oxygen, that is smaller than that of aluminum oxide can be used for the middle layer of the recording medium. For the present purposes, however, certain aspects must be taken into account which come into play in connection with the production of the layers or in connection with the process of trace formation. In the first place, it is important that the oxide layer should be capable of being applied to the carrier layer in the simplest possible way. Next, the oxide layer serving as an intermediate layer should have no electric conductivity, for otherwise, because of the fact that the overall conductivity is composed of the partial conductivities of the adjoining materials and that the area resistance of the layer should amount to 2.5 ohms, the aluminum cover layer would have to be so thin as to become transparent. That is undesirable, since in that case the traces would not be clearly recognizable, especially in transmitted light.

Taking account, therefore, of these various aspects, it is particularly advantageous for the oxide layer to consist of one or more oxides of at least one of the following metals: manganese, chromium, iron, cobalt, nickel, tin.

The oxide layers can be applied to the carrier by known methods, as for example, direct vapor deposition, reactive vapor deposition, vapor deposition of the metal and subsequent oxidation, chemical vapor deposition or chemical precipitation from solution.

The individual layers of the graphic recording medium should appropriately have the following thicknesses: The carrier layer should have a thickness from 5 to 500 microns (μm), preferably 10 to 100 μm; the metal oxide layer should have a thickness from 0.005 to 1 μm, preferably 0.01 to 0.5 μm, and the aluminum layer a thickness from 0.01 to 0.5 μm, preferably 0.02 to 0.1 μm.

Illustrative examples of the invention are further described with reference to the accompanying drawing, wherein:

FIG. 1 is a cross-section of a graphic recording medium using an uncoated layer of synthetic material as a carrier, and

FIG. 2 is a cross-section of a graphic recording medium using a resin coated paper carrier layer.

In FIG. 1 the carrier layer 11 consists of a synthetic material film having a thickness of 50 μm. On this carrier a manganese oxide layer 12 is applied. This is accomplished by so-called reactive vapor deposition, i.e., the carrier tape 11 is exposed to manganese vapor in the presence of steam in a vapor deposition apparatus, so that manganese oxide, essentially Mn_3O_4 is formed. The thickness of this manganese oxide layer amounts to about 0.1 μm. In a further operation, an aluminum layer of about 0.07 μm is laid down on this manganese oxide layer in a second vapor deposition apparatus.

In FIG. 2 the carrier tape consists of a paper sheet 21 provided with a resin coating 22. Both together have a thickness of about 80 μm. On the resin layer 22, a manganese oxide layer 23 of about 0.08 μm thickness is vapor deposited in the same way as described above and thereon also likewise an aluminum layer 24 of the same thickness.

It is also possible to carry out vapor deposition of the oxide layer and of the aluminum layer one after the other in the same vapor deposition equipment, if a suitably constructed vapor deposition apparatus is available.

A comparison of the graphic recording media of the present invention illustrated in FIGS. 1 and 2 and described just above, with known recording media of the kind previously mentioned, provides the following comparative values:

For a particular standardized trace width and trace quality, a writing voltage from 30 to 35 volts was necessary in the case of the previously known recording media, whereas the same trace width and the same trace quality was already obtained with a writing voltage of 20 volts in the case of the recording medium of the present invention. With a stylus application pressure of 35 mp (milliponds) excellent traces could still be produced on the graphic recording medium of the invention, and actually also independent of whether the stylus was polarized negatively or positively with respect to the medium. For the previously known graphic recording media, on the other hand, with the same application pressure and negative stylus polarity, no more writing trace was visible and with positive stylus polarity, only an erratic writing trace with gaps could be obtained.

The improved corrosion resistance and the resulting layer durability of the graphic recording medium of the invention compared to the previously known recording media has already been mentioned above.

Although the invention has been described with reference to particular illustrative embodiments, it is to be understood that modifications and variations may be made within the inventive concept without departing from the spirit of the invention.

We claim:

1. A recording medium for graphic recording devices comprising:

a flexible tape of insulating material serving as a carrier layer;

a covering layer consisting essentially of aluminum;

an intermediate layer between said carrier layer and said covering layer composed of one or more oxides of at least one metal selected from the group consisting of manganese, chromium, iron, cobalt, nickel and tin, said oxide or oxides having a heat of combination less negative than aluminum oxide,

said intermediate and covering layers being mechanically supported on said tape.

2. A recording medium as defined in claim 1 in which said intermediate layer is composed essentially of one or more oxides of manganese.

3. A recording medium as defined in claim 1 in which said intermediate layer has a thickness between 0.005 and 1 micron and said covering layer has a thickness between 0.01 and 0.5 micron.

4. A recording medium as defined in claim 3 in which said intermediate layer has a thickness between 0.01 and 0.5 micron and said covering layer has a thickness of between 0.02 and 0.1 micron.

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