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P. F. VARADI ETAL

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ELECTRON EMISSIVE TAPES AND METHOD OF MAKING

Filed Jan. 3, 1961

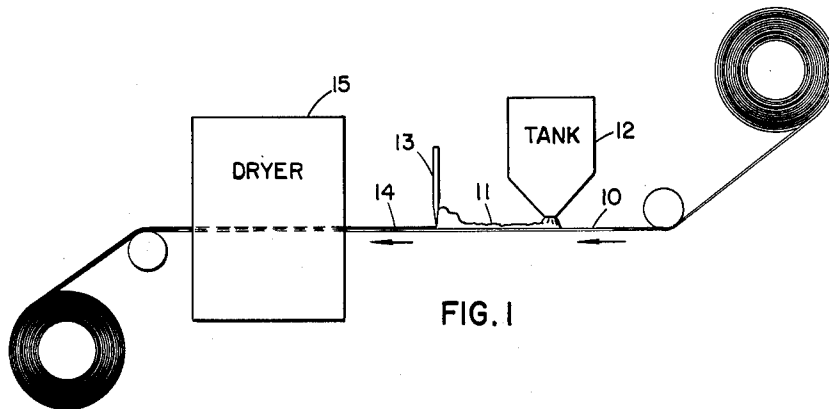


FIG. 1

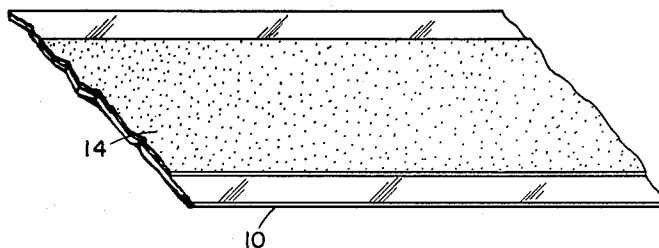


FIG. 2

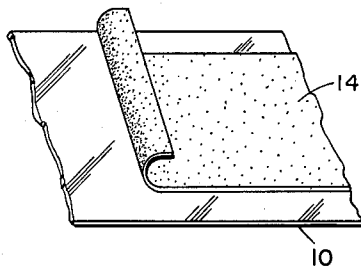


FIG. 3

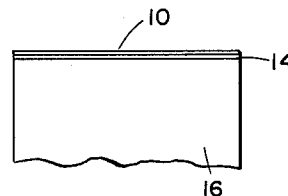


FIG. 4

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ELECTRON EMISSIVE TAPES AND METHOD
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1 Claim. (Cl. 161-167)

This invention relates to improvements in cathodes for
electron tubes and has particular reference to novel cath-
ode structures of the type embodying a metal base upon
a surface of which is applied a layer of electron emissive
material, and to a novel method of making such cathodes.

Oxide coated cathodes have been prepared by dragging,
spraying, painting or cataphoretically depositing upon
a metal base a layer of selected material capable of
copious emission of electrons when subjected to heat.
The spray technique probably has been most commonly
used, although the other methods are well known.

All of the foregoing methods are subject to serious
problems. For example, it has been found to be extremely
difficult to maintain uniform coating density and thick-
ness, and to reproduce a succession of batches or lots of
cathodes having identical physical, chemical and electrical
characteristics. Other problems arise also, where it be-
comes necessary to prepare such cathodes with extremely
accurate dimensions.

In order to overcome the difficulties in the manufacture
of cathodes by such prior art methods, prefabricated films
have been made comprising a mixture of alkaline-earth
carbonates such as barium, strontium, and calcium car-
bonates in a conventional nitrocellulose binder, which
film is applied to the cathode surface by utilizing a suit-
able solvent to obtain the desired adhesion. Such a film
has been improved upon by the present invention which
has as a primary objective the provision of a film which
may be readily affixed to a surface of practically any
shape by applying only relatively light pressure.

Another object is to provide a film or tape which will
comprise, as a binder for the electron emissive carbonates,
a material which will be substantially completely elimi-
nated before or during exhaust of an electron tube in
which the invention is utilized.

Another object is to provide a film of the above char-
acter which may be stored indefinitely, prior to affixing
to a cathode base, without deterioration.

A further object is the provision of a film of the above
character which is uniform in density and thickness, which
is self supporting with reasonable mechanical properties,
which has a low plastic content, and which has good ad-
hesion to the base metal before and after pumping of an
electron tube having a cathode utilizing the film.

Other objects and advantages of the invention will be-
come apparent from the following description taken in
connection with the accompanying drawings, wherein

FIG. 1 is a schematic view illustrating a method of
making an electron emissive tape in accordance with this
invention;

FIG. 2 is a fragmentary perspective view of a section
of tape made in accordance with this invention;

FIG. 3 illustrates one method of removing the emissive
film from the carrier film; and

FIG. 4 shows a film applied to a cathode base.

In coated cathodes of the prior art which employ nitro-
cellulose as a binder for the electron emissive material,
the nitro-cellulose decomposes to nitrous fumes, water
and CO, which are pumped out during the subsequent
breakdown of the cathode. The primary product is car-
bon and tar which can be observed during the early stages
of the breakdown process as a dark discoloration on the

surface of the cathode structure. Such carbon residue
may cause other evaporation products to be deposited in
the electron tube, which might cause subsequent troubles
in the operation of the tubes, particularly of high volt-
age tubes.

Another important disadvantage of using nitrocellulose
as a binder in such a film is that in order to form a
mechanically strong and self supporting film the ratio of
nitrocellulose to filling material is relatively high. Fur-
thermore, the nitrocellulose film becomes brittle and
hardens slightly during aging or under the influence of
light. This affects the storing properties of the prepared
film.

The extent of polymerization of the methacrylate is not
of importance so long as the polymers have sufficient ad-
hesive or binding properties and are also capable of sub-
stantially completely volatilizing without leaving residue
when subjected to heat during normal electron tube pro-
cessing.

Polymethacrylates have been found to be most suitable
for use as binders in films of this type. In the case of
polymethacrylates, a chain scission reaction takes place
when they are subjected to heat. This chain scission re-
sults in the depolymerization of the plastic forming their
monomeric esters, which are gaseous products at tube
processing temperatures. Thus, when using polymeth-
acrylates as binders for the emissive materials in films of
this character, during the breakdown of the cathodes the
polymethacrylate binders leave as gaseous products, with
little or no solid organic residues remaining in the coat-
ings.

Other film-forming polymers have been found to be
unsatisfactory. Cellulose nitrate, commonly used in
spraying techniques, leaves a residue of carbon; poly-
ethylene, polystyrene, polyvinyl acetate and polyacrylate
all leave various undesirable non-volatile residues. Some
of these materials discolor and become brittle when ex-
posed to sunlight, some have poor molding qualities,
some are altered physically by aging, and some have a
relatively low modulus of elasticity.

Polymethacrylates, however, have good molding quali-
ties, a relatively high modulus of elasticity, are not af-
fected by sunlight or aging, and are substantially com-
pletely volatile. The following Table A shows the de-
polymerization behavior, the brittle point of the polymers,
and the boiling points of the monomer esters of the resins:

Table A

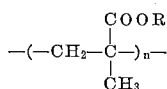
Polymer	Percent Depolymer- ization, 100 min. heating at 250° C. in vacuum	Brittle Point, ° C.	Boiling Point of the Monomer, ° C.
Polymethyl methacrylate.....	11	91	100
Polyethyl methacrylate.....	13.5	50	117
Poly-n-propyl methacrylate.....	23.5	37	141
Poly-iso-propyl methacrylate.....	15.5	-----	127
Poly-n-butyl-methacrylate.....	50	17	163
Poly-iso-butyl-methacrylate.....	19	-----	155
Poly-n-amyl methacrylate.....	31	3	-----

A measure of relative rates of monomer production
from the selected polymethacrylates was obtained by
measuring the yield of monomer produced by heating the
polymethacrylates in vacuum at 250° C. for about 100
minutes. From Table A it is apparent that poly-n-butyl
methacrylate gives the highest yield of monomer. It also
decomposes the fastest and at higher temperature com-
pletely to its monomer. The boiling points of the differ-
ent monomers are also shown in Table A. All the mon-
omers, as well as n-butyl methacrylate, are fluids at room
temperature and their boiling points are all below the

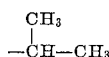
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regular bake temperature of an electron tube. Therefore, products of the poly-n-butyl methacrylate binder leave the electron tube completely during its oven bake, while residues from nitrocellulose binders remain. Poly-n-butyl methacrylate, furthermore, is elastomeric at room temperature.

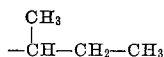
The chemical identity of the polymer is represented by the formula



where R is equal to the type of radical (alkyl group) in the monomer segment of the polymer chain as, for example, poly-n-butyl methacrylate where R is equal to $\text{---CH}_2\text{---}(\text{CH}_2)_2\text{---CH}_3$, polymethyl methacrylate where R equals ---CH_3 , polyethyl methacrylate where R equals $\text{---CH}_2\text{---CH}_3$, poly-n-propyl methacrylate where R equals $\text{---CH}_2\text{---CH}_2\text{---CH}_3$, poly-iso-propyl methacrylate where R equals



poly-iso-butyl methacrylate where R equals



or poly-n-amyl methacrylate where R equals



Other beneficial qualities of poly-n-butyl methacrylate, particularly, which make it advisable for use as a binder for the emissive materials in a tape or film of the desired character are its good adherence, good aging properties (it will not become brittle at room or lower temperatures), and small quantities are needed in comparison with the amount of filling material used. In fact, the film composition may contain only about six percent of binder.

A plasticizer is also used to give the film a softening effect without affecting other properties of the film. It is important here that the plasticizer, similarly to the resin, should completely evaporate or decompose, during the processing of the electron tube, without leaving any harmful residue. In accordance with this invention, the compounds known as sucrose-acetate-isobutyrate, dibutyl-phthalate and diethyl-oxalate may be used successfully with poly-n-butyl methacrylate. They decompose completely, have an excellent softening effect upon the resin, and do not affect the film's mechanical properties.

The film or tape is prepared by the techniques which are known and which comprise a "wet lamination"; that is, a mixture containing the filling material, the binder, the plasticizer and the solvent is spread upon a carrier film and subsequently dried.

The carrier film may be any selected material such as paper, Mylar, polyethylene or other flexible sheet material to which the mixture will adhere. Polyethylene is the most suitable for many reasons, being flexible, smooth, strong, capable of being made in very thin sheets, clean, and capable of being easily separated from the layer of dried mixture.

The solvent is preferably acetone, but amylacetate or ethylacetate may be used.

It is particularly pointed out that the term "emissive compound" is used herein to include any carbonates which are known to produce copious supplies of electrons when heated. For example, barium-strontium-calcium carbonates may be used in substantially any form, and any one of the three may be combined with only one or both of the others in any desired combination. Likewise, the term is intended to include the use of electron emissive carbonates in combination with selected amounts of metals such as nickel or tungsten in powdered form which provide the resultant cathode film with increased electrical conductivity, and with metals such as zirconium, titanium

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and tungsten which are included as activators. One example of an "emissive compound" is a mixture of 70% of nickel powder, 29% of carbonate, and 1% of zirconium hydride.

In preparing the mixture, it must be compounded so as to provide the required density of emissive carbonates. One film may be produced wherein the mixture is a film forming product containing about 6% by weight of poly-n-butyl methacrylate, 90% by weight of the emissive compound, and about 4% weight plasticizer. This composition is ball milled, using acetone as a solvent, and then spread evenly upon a sheet of polyethylene.

Referring to FIG. 1, polyethylene carrier film 10 is preferably provided in roll form as shown. The film forming mixture 11 is deposited upon a surface of the film 10 from a supply source such as tank 12. Then as the film is moved in the direction indicated by the arrows, the deposited mixture will be smoothed and made uniformly thick by means such as blade 13 which may be adjustable perpendicularly to the surface of the film so as to provide the layer of the mixture with controlled thickness such as, for example, from 30-50 microns.

After the film is coated with the uniformly thick layer 14, it is then dried in any suitable manner such as in dryer 15, whereupon the film forming material becomes self-supporting and removably attached to the carrier film. The laminated film may then be stored in rolls or sheets for subsequent use.

It is found that one such film can easily be provided having a thickness of 40 microns plus or minus 2½ microns, with the density of 1.8 g./cm.³. After breakdown of a tube embodying this cathode film the density was found to be 1.4 g./cm.³ and the surface roughness of the film was less than 2 microns.

A desired advantage of the poly-n-butyl methacrylate type of emissive tape or film, when compared with the nitrocellulose type, is in the variety of ways in which it may be applied to the surface of a cathode base. The film can be applied to the cathode surface by first separating it from the carrier film and using it as an entirely self-supporting film. As shown in FIG. 3, it can be easily peeled from the carrier film 10. It was also found, particularly in the case of cathodes 16 formed of nickel (FIG. 4), that it is possible to apply the film 14 directly to the cathode before separating it from the carrier 10. The carrier 10 may subsequently be easily removed from the cathode 16 after the emissive film 14 is sealed thereto.

The self-supporting emissive film 14 can be applied with cold or warm printing upon the cathode surface because of the good molding properties of the plastic material used in the preparation of the film. This printing of the film onto a cathode surface has been found to provide an efficient seal when merely relatively light pressure is applied to the film. A preferable technique includes removal of the film from the carrier, punching out from the film a piece having the desired shape, applying the punched-out piece to the area of the cathode to be coated, and applying relatively light pressure upon the film whereupon an efficient seal will be made. Such printing can be done cold in the case of matrix cathodes. In the case of nickel cathodes having extremely smooth surfaces, the printing is accomplished efficiently when the cathode is heated to about 100° C.

An important advantage is that only relatively low pressure is required to print a cathode with such a film. It has been found that such printing can be accomplished by applying a pressure of only about 10 kg./cm.². This can be done by use of a piece of soft rubber or any other soft plastic material. No special tooling is required.

Another satisfactory method for printing cathodes with an emissive tape or film embodies the use of a suitable solvent to form the bond between the film and the nickel cathode base. However, in such cases separation of the film from its carrier in advance is not necessary because after the formation of the bond between the nickel base

and the film, the carrier is released automatically from the film.

The presently described film has the advantage that both aliphatic and aromatic solvents can be used for bonding. When using nitrocellulose type films, suitable solvents are very limited in number. We have found that xylene, methyl-cellosolve-acetate and cyclohexanol are good solvents for our purpose.

It was further found that a printed cathode produced as described herein, has a very smooth surface, the roughness being less than 2 microns in comparison with standard sprayed cathodes wherein roughness of 5-15 microns occurs.

Electron tubes have been made and processed embodying nickel base cathodes having polished surfaces on which the emissive film was printed by the warm printing method described. Other cathodes of this type were printed cold with xylene as the bonding solvent. Both types of tubes were processed in conventional production pumping units and it was found that the breakdown pressures were usually lower in tubes having cathodes with printed films than in tubes having cathodes with sprayed coatings. It is believed that this is achieved due to the fact that the poly-n-butyl methacrylate binder breaks down to its monomer and is pumped away during the oven bake of the tube. After processing, tubes with printed cathodes of the previously described type were found to contain little or no evidence of undesirable residue. Furthermore, the electron emission and other characteristics of printed cathodes of the type described compare favorably in all respects with cathodes formed in accordance with other known prior art methods.

It is to be understood that modifications and changes in the structure and methods shown and described may be made by those skilled in the art without departing from the spirit of the invention as expressed in the accompanying claim.

We claim:

A transfer tape comprising a carrier and an electron emissive film removably connected thereto for transfer to an electron tube cathode and which has been formed and attached to the said carrier by thinly spreading thereon and drying a mixture containing about 6 percent by weight of poly-n-butyl methacrylate as a binder material capable of completely volatilizing without leaving residue when subjected to heat during normal electron tube processing, about 90 percent by weight of electron emissive compound substantially uniformly distributed throughout the binder material in an amount dependent upon the density desired of the resultant film and about 4 percent by weight of a plasticizer capable of completely volatilizing when subjected to heat during normal electron tube processing.

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