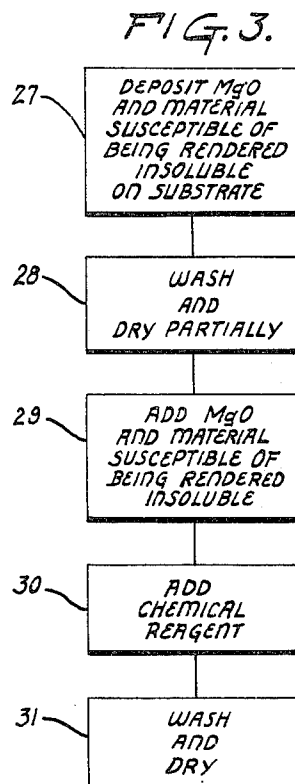
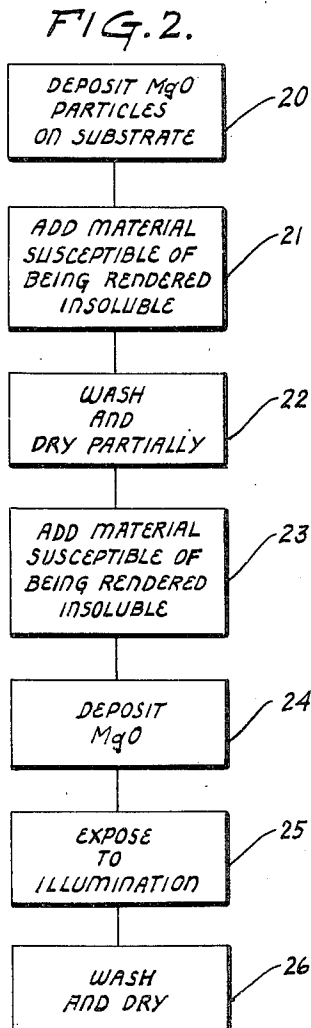
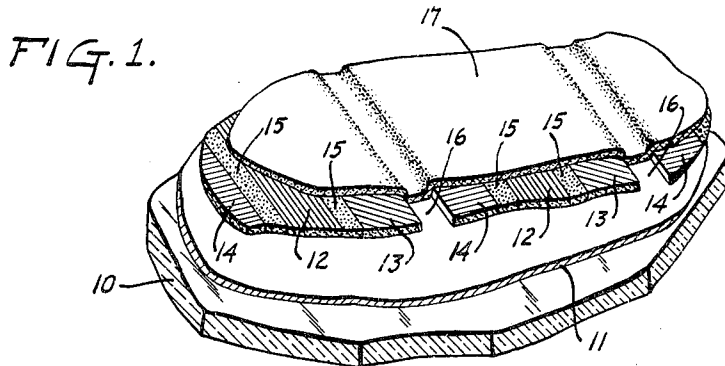


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METHOD OF DEPOSITING PARTICLES ON A CATHODE
RAY TUBE SCREEN STRUCTURE
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METHOD OF DEPOSITING PARTICLES ON A CATHODE RAY TUBE SCREEN STRUCTURE

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The present invention relates to improvements in the manufacture of cathode ray tube screen structures, and more particularly to improvements in the manufacture of cathode ray tube screen structures having surface portions which incorporate a material of high inherent secondary electron emissivity.

There exist various situations in which it is desired to form the electron beam interceptive surface of a cathode ray tube screen structure either partly or wholly of a material having high inherent secondary electron emissivity. For example, in the copending U. S. patent application of William E. Bradley and Meier Sadowsky, Serial No. 313,018, filed October 3, 1952 and assigned to the assignee of the present invention, there are shown and described a variety of cathode ray tube screen structures, different forms of which are useful for color television picture tubes, camera tubes and storage tubes, and each of which is characterized by having a beam interceptive surface whose principal constituent is a material of high inherent secondary electron emissivity, such as magnesium oxide, for example. In the aforementioned copending application it is disclosed that the effective secondary electron emissivity of such a screen surface is determined, to a great extent, by the nature of the underlying material. However, it has been found that other factors also have appreciable influence upon this effective secondary electron emissivity. Among the most important is the mode of formation of this surface portion, which in turn determines its structural details. The methods which have been used in the past for this purpose include deposition by spraying, by settling out of suspension, evaporation of the free metal followed by oxidation, and still others. With each of these prior art methods, it has been found that the resulting surface portion exhibits an effective secondary electron emissivity, under electron beam impingement, which differs appreciably for different regions of this surface material even though these different regions are ostensibly identical in their physical characteristics. Furthermore, it was found that the secondary electron emission yield—that is, the ratio of the number of secondary electrons emitted from a given surface portion to the number of primary electrons impinging upon the same surface portion—was less than had been expected on the basis of theoretical considerations. This discrepancy was especially noticeable for those surface portions whose effective secondary electron emissivity, as determined by the characteristics of the underlying material, was much higher than that of other portions of the screen structure.

Accordingly it is an object of the invention to provide a method of forming a layer of material on the previously formed portions of a cathode ray tube screen structure.

One of the methods by which secondary electron emissive surface layers have previously been formed on cathode ray tube screen structures involves the deposition thereon of the particles of secondary electron emissive material, dispersed in a substantial quantity of a photosensitive organic gel, the latter, at the time of deposition, being in its fluid, water soluble form. After this deposi-

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tion was carried out, the materials involved were exposed to illumination of sufficient duration and intensity to cause a layer of gel of the desired thickness to solidify and to become insoluble in water, trapping the secondary electron emissive particles either within the solidified layer or between this layer and the previously formed surface of the screen structure.

My improved method departs from the prior art procedure principally in that I carry out the deposition of at least the secondary electron emissive material not just once, but several times in succession. Preferably each deposition of secondary electron emissive material is accompanied by a deposition of the gel, but no exposure thereof is made until after the last deposition of secondary electron emissive material and gel. Instead, a treatment of the surface, such as by washing and partial drying is carried out between successive depositions. Why this particular procedure yields a surface with the aforementioned improved characteristics is not known with certainty. However, it is believed that the improvement may be due to the greater intimacy of contact between the surface of the previously formed screen portions and the electron emissive particles closest thereto which is achieved in this manner.

It is known that such particles, even though of a given uniform mesh size, have a variety of physical configurations. It is my belief that, during the washing operation which follows the initial deposition of the particles, most of these particles are flushed away since the accompanying gel, if any, has not yet been fixed by illumination, and therefore does not retain them in place. The only particles which do remain in place are those which have such a large ratio of contact surface area to weight that they will adhere to the underlying material even in the absence of solidified gel. This same phenomenon will occur after each successive deposition and wash-off prior to illumination. Consequently, after several repetitions, the concentration of particles with comparatively large contact surface areas will be much greater at the surface of the underlying material than it would have been if all of the particles originally deposited had been fixed in place by solidification of the gel after a single application. Thus there is produced enhanced intimacy of contact between the electron emissive material and the surface of the substrate on which it is formed. In any case, whether the foregoing is the true theoretical explanation or not, it remains a demonstrable fact that the electron emissive layer formed by the afore-described method possesses the desired properties of higher and more uniform electron emissivity. The important improvements which my method produces will be better appreciated from a consideration of the following detailed discussion in conjunction with the accompanying drawings wherein:

Figure 1 is an enlarged fragmentary view of a typical cathode ray tube screen for color television reproduction;

Figure 2 is a flow diagram outlining a method of fabricating the screen of Figure 1 in accordance with my invention; and

Figure 3 is a flow diagram outlining another method of fabricating the screen of Figure 1 in accordance with my invention.

The cathode ray tube screen structure illustrated in Figure 1 of the drawings, to which more particular reference may now be had, is similar in form to certain prior art structures, consisting of a glass substrate 10 which may be either the face plate of the cathode ray tube itself or else a separate glass plate supported within the tube envelope. Upon the electron beam confronting side of this glass substrate there is disposed a layer 11 of transparent conductive material such as stannic oxide, for example, for the purpose of maintaining equipotential conditions over one entire side of the screen

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structure. Upon the transparent conductive layer 11 there are disposed a plurality of parallel vertical phosphor strips, of which all those designated by reference numeral 12 are made of a fluorescent material emissive of red light in response to impingement by the electron beam of the cathode ray tube. Those strips designated by reference numeral 13 are made of a fluorescent material responsive to electron beam impingement to emit green light, while those designated by numeral 14 are similarly responsive to emit blue light. As shown in Figure 1, different ones of these phosphor strips are not contiguous. Instead, they are approximately equally spaced from each other, the spaces between red and green light emissive phosphor strips 12 and 13 and between blue and red light emissive phosphor strips 12 and 14 being filled with some material, such as unactivated willemite, which has approximately the same resistivity as the phosphor materials, and which does not emit light in response to electron beam impingement. The spaces 16 between green and blue light emissive phosphor strips 13 and 14, on the other hand, are left unfilled. Over the entire electron beam interceptive surface of this previously formed screen structure, including the phosphor strips, the unactivated willemite filler strips, and the exposed conductive coating portions 16, there is disposed a layer 17 of some material which has an inherently high secondary emission ratio at those potentials at which the screen structure of a cathode ray tube is conventionally operated. A variety of materials, such as magnesium oxide, silver, gold, tungsten and various other high atomic weight materials have this property. The glass substrate 10, conductive coating 11, phosphor strips and unactivated willemite strips may be formed in any conventional manner, as for example that described in the copending U. S. application of John W. Tiley, Serial No. 248,356, filed September 26, 1951 and assigned to the assignee of the present invention.

A preferred manner of forming, in accordance with my invention, the magnesium oxide surface layer 17 on the electron beam confronting surface of the previously formed portions of the screen structure is illustrated in the flow chart of Figure 2 to which more particular reference may now be had. The first step of this method, represented in Figure 2 by rectangle 20, involves the deposition of magnesium oxide particles on this beam confronting surface. This may be carried out in a variety of conventional ways, as for example by spraying the surface with a liquid suspension of such magnesium oxide particles. Alternatively these particles may be deposited by settling them out of a suspension, by evaporation, or by other conventional methods. In any case, if a liquid is involved in the deposition of the magnesium oxide particles, this liquid is preferably removed, as by decanting and drying, before the next step of the method is carried out. A suitable liquid medium, to be used in spraying or otherwise depositing the magnesium oxide, is denatured alcohol which is commercially available under the trade name "Solox". For spraying, a solution having equal volumes of magnesium oxide powder and alcohol is preferred, but these proportions are not critical. The next step, which is represented in Figure 2 by rectangle 21, involves the addition of a small quantity of an organic gel dissolved in a suitable liquid, preferably distilled water, to the magnesium oxide deposited in step 20. This gel may be any one of a variety of gelatinous substances, such as polyvinyl alcohol, for example, together with an activating agent which is preferably an alkali dichromate salt, such as ammonium dichromate, for example, the combination of dissolved gel and activating agent being a fluid or semi-fluid as long as it is not exposed to illumination, but solidifying upon exposure to such illumination and also becoming insoluble in water to the extent that it is no longer susceptible of being readily removed by the washing action of water. This addition of gel and activating agent is preferably carried

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out in darkened surroundings so as to avoid, for the time being, the aforementioned solidification of the gel. In the next step, represented in Figure 2 by rectangle 22, the screen structure is washed in distilled water, thereby removing most of the previously deposited gel, which is still water soluble at this stage, as well as most of the magnesium oxide. In fact, there are left deposited essentially only those of the magnesium oxide particles which have relatively large surface areas in contact with the underlying material compared to their weights. There is also left behind a small amount of gel and its activating agent which cling to the remaining magnesium oxide particles and, in some more or less random distribution, to certain exposed portions of the underlying material. The washing operation may be carried out by introducing a small quantity of water into the bulb while holding it with its screen in the lowermost position, swishing the water around once or twice and tilting the bulb so as to permit the water to run out through the open neck. This is followed by a drying operation which may be carried out by simply exposing the interior of the bulb to the surrounding atmosphere. Alternatively the drying process may be accelerated by subjecting the screen structure to moderate heating from some heat source, such as infra-red lamps or by directing a stream of warm air onto its surface. This is intended to remove substantially all traces of the water introduced during the washing step, but drying is stopped before appreciable desiccation of the remaining gel takes place. Since, as has been pointed out, drying occurs inherently during the interval between washing and the operation which follows drying, the drying step has been included with the washing step in the same rectangle 22 of the flow chart of Figure 2.

In the next step of the method, represented diagrammatically in Figure 2 by rectangle 23, another layer of gel and activating agent is formed on the interior surface of the previously formed portions of the screen structure. The material constituting this layer may be the same as that deposited in step 21. Alternatively it may be a different material having similar properties and preferably responsive to the same solidifying influences as the material added in step 21. In step 24, which follows, magnesium oxide is deposited on the gel layer formed in step 23. Because the material deposited in step 23 is in its fluid state, the magnesium oxide particles deposited in step 24 will penetrate into the gel layer and will distribute themselves within that layer in some more or less random fashion. The result of performing both steps 23 and 24 will be the formation of a layer of materials including the magnesium oxide particles dispersed in the gel. It is immaterial for the purposes of my invention which of these two steps is carried out first. The reason for showing them in the order of Figure 2 is that the gel determines the eventual thickness of the entire layer and, if it is deposited before the magnesium oxide, it can be inspected for uniformity and removed if defective without also having to discard the magnesium oxide particles. After the magnesium oxide particles have been deposited in the manner of step 24 and have had the opportunity to become dispersed throughout the layer of gel formed in step 23, the resultant structure is exposed to intense illumination from a source of light of a spectral composition to which the particular gel in use responds by solidifying. In the case of polyvinyl alcohol, a D.-C. arc lamp is very suitable as a source of illumination. Since it is particularly desired to solidify and to render insoluble those portions of the magnesium oxide-gel layer which are adjacent to the previously formed portions of the screen structure, the exposure to illumination takes place preferably through those previously formed portions or, in other words, through the face plate of the cathode ray tube. It is, of course, also feasible to illuminate the screen structure from its electron beam confronting side, but care must be taken in that case to provide a source

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of illumination sufficiently strong to penetrate the gel all the way down to where it contacts the previously formed portions of the screen structure. Furthermore, since solidification does not occur instantaneously, it is necessary to continue the illumination for a period of time sufficient so that all those portions which it is desired to harden have had an opportunity to do so. In a practical case, where it is desired to harden a layer of gel two or three mils thick, an exposure time of approximately five minutes will suffice.

The final step of the method, represented in Figure 2 by rectangle 26, consists of washing off the unsolidified portions of the gel, together with such magnesium oxide particles as may be contained therein, and drying the screen structure, this time until it is substantially completely dry.

An alternative method for forming the desired magnesium oxide surface layer in intimate contact with previously formed portions of the cathode ray tube screen structure is illustrated in Figure 3 of the drawings, to which more particular reference may now be had. This method begins with the same initial operations as the method of Figure 2 comprising, as did the latter, an initial step of depositing magnesium oxide and dissolved gel on the substrate constituted by the previously formed portions of the screen structure, followed by washing and partial drying of the resultant layer. In this alternative method the operations of depositing magnesium oxide and adding the gel can be carried out in the single step, which is diagrammatically designated in Figure 3 by rectangle 27 by preparing a suspension of magnesium oxide particles in the dissolved gel prior to its application to the substrate. The subsequent washing and partial drying operation is diagrammatically represented by rectangle 28. After drying has progressed to the point at which substantially all the water used in the washing operation has been removed, but before substantial desiccation of the gel takes place, more magnesium oxide and more gel are added, as shown in rectangle 29 of Figure 3. Instead of illuminating the resultant layer of gel and magnesium oxide, as was done in the method of Figure 2, there is now added a chemical reagent, such as, for example, minute silver particles, which also causes solidification and insolubilization of the gel, and resultant fixing in place of the magnesium oxide particles embedded therein. This step is represented in Figure 3 by rectangle 30. Again the concluding step of the method is that of washing the resultant structure to remove whatever gel remains soluble in water together with the loose magnesium oxide, followed by substantially complete drying prior to incorporation by conventional methods of the remaining structural elements of the cathode ray tube. This step is represented by rectangle 31 of Figure 3.

While each of the two specific processes described and illustrated in detail hereinbefore involves only a single repetition of the magnesium oxide deposition and wash-off step, it will be understood that this same step may be repeated any desired additional number of times depending only upon the requirements of intimacy of surface contact between the magnesium oxide layer and the underlying layers. In the manufacture of a screen structure such as that illustrated in Figure 1, which is suitable for use in a practical color television receiver tube, a single repetition of this step has been found to yield a surface which is emissive of secondary electrons in sufficient numbers and with sufficient uniformity.

While I have described my invention with reference to two specific embodiments, it will be understood that variations thereof will occur to those skilled in the art without departing from my inventive concept.

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For example, the use of a gel in conjunction with the particles to be deposited is not essential in all cases. The principal reason for providing this gel is that in its presence the total thickness of the particle layer is readily controllable merely by control of the depth to which the gel is allowed to solidify before wash off. Consequently good uniformity of particle layer thickness can readily be obtained by use of a gel. However, where such uniformity is not important or where it is preferred to achieve it by other means, the gel may be completely omitted.

Where a gel is desired, virtually any organic gel can be used. In particular, while it is preferred to use synthetic organic gels such as, for example, the aforementioned polyvinyl alcohol, for the sake of their high degree of uniformity and purity, natural organic gels free from contaminating impurities may also be used. Thus animal gelatines, animal glues, egg albumen, and the various natural gums, such as gum acacia, which are rendered water insoluble when exposed to light in the presence of a dichromate or other photosensitive catalyzing agent, are also suitable for the purposes of the invention.

It will also be apparent that not only magnesium oxide, but also finely divided particles of other secondary electron emissive materials such as those hereinbefore enumerated, may be deposited in the manner hereinbefore described. Furthermore, if it is desired to form a secondary electron emissive layer only on certain portions of the screen structure, selectively, then exposure to illumination or addition of a chemical reagent may be carried out selectively for those same portions only, so that they alone remain deposited after the final washing operation. In view of these and other possible variations, I desire the scope of the invention to be limited only by the appended claims.

I claim:

1. The method of forming a layer of secondary electron emissive material in intimate contact with a substrate constituted by the previously formed portions of a cathode ray tube screen structure, said method comprising the steps of depositing on the surface of said substrate particles of said material dispersed in a material which is water soluble at deposition and which is responsive to a stimulus to become insoluble, washing said surface with water to remove all but those of said particles which are in intimate contact with said surface, depositing on said surface additional particles of the same material, also dispersed in a fluid material which is water soluble at deposition and which is responsive to a stimulus to become insoluble, and subjecting said deposited material to said stimulus.

2. The method of claim 1 characterized in that said particles are of magnesium oxide.

3. The method of claim 1 further characterized in that the said stimulus to which said water soluble material is responsive and subjected is light.

4. The method of claim 1 further characterized in that the said stimulus is a chemical reagent.

5. The method of claim 1 further characterized in that said material which is water soluble at deposition is an organic gel activated with an alkali dichromate salt.

6. The method of claim 5 further characterized in that said organic gel is polyvinyl alcohol.

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