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## METHOD OF MANUFACTURING A LAYER CONSISTING OF NONCONDUCTING PULVERULENT MATERIALS ON CURVED SURFACES

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2 Claims

### ABSTRACT OF THE DISCLOSURE

The invention relates to a method of manufacturing a layer of nonconducting pulverulent materials on bent surfaces by electrophoretic deposition from a dispersion in an apolar medium. Particularly the invention relates to such a method of manufacturing luminescent screens on concave surfaces of fibre-optical plates.

Luminescent screens having a high resolution of up to 120 lines/mm. have been manufactured up till now by sedimentation of suspensions of fine luminescent materials. For the required quality this process is very time-consuming and sensitive to perturbations while a considerable number of rejects occurs. The process can only be performed satisfactorily on flat glass surfaces.

The above-mentioned concave luminescent screens may be used on fibre-optical plates for improving the optical properties and for coupling television cameras. However, serious drawbacks were found during manufacture of such luminescent screens. The sedimentation on the concave surface does not lead to a layer of uniform thickness but more material is accumulated in the low central part than at the edges. In addition the special glass commonly used for fibre-optical plates is attacked by the water from the dispersion of luminescent materials so that it cannot be used again when a sedimentation process has failed. The high number of rejects to be expected is unacceptable with a view to the high cost price of the fibre-optical plates.

An object of the present invention is to provide a method in which the luminescent screen is provided by electrophoretic process in an apolar medium.

The electrophoretic deposition of materials consisting of fine particles from a polar medium is generally known. By adsorption of ions of an electrolyte dissociated in the polar solvent the particles are charged and may be transported in an electrical field. However, difficulties occur when selecting materials whose particle size is larger than that which provides a colloidal solution, that is to say, more than approximately 1  $\mu$ m. Particularly the adhesion to the glass surface is insufficient and cloud formation and irregularities occur in the layer during the drying process.

Electrophoresis in apolar solvents has been described in the United Kingdom patent application 26,827/70 in the name of the applicant. This application states the condition that a controlled and stable charge of the particles must have taken place, which charge is stronger than the natural charge by means of contact potential differences and similar mechanisms. Such a charge of particles is effected by dissociative adsorption of surface-active, ion-forming materials which are soluble in oil and which comprise bivalent or multivalent ions, while this charge is intensified and stabilized preferably by given macromolecular materials having side chains.

However, these dispersions do not lead to adhesive layers on the above-mentioned concave, polished fibre-

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optical surfaces. The layers obtained from these dispersions vary already when they are taken from the dispersion and during the subsequent drying process.

According to the invention it has been found that satisfactorily adhesive layers can be obtained on bent surfaces under given circumstances.

The method according to the invention is characterized in that the dispersion comprises surface-active, ion-forming materials which dissociate yielding bivalent or multivalent ions, and in addition a macromolecular addition consisting of vinyltoluene-vinyl-acetate polymers, while the method is performed at a field strength of more than  $10^4$  v. cm.<sup>-1</sup>. The extra steps taken for the method according to the invention relate to the possibility of using much higher field strengths during electrophoresis in apolar solvents than in polar solvents in which breakdown soon occurs due to their high own conductivity. The use of higher field strengths as occur in the method according to the invention makes it possible to obtain a denser packing and hence a better adhesion. This effect is enhanced by the choice of the special macromolecular addition which results in cross-linking and hardening after the deposition under the influence of the high electrical field. Furthermore an adhesion gradient is obtained so that the layer can be polished very satisfactorily.

The addition may be fired at 300° C. without damaging the luminescent material, at which temperature the luminescent materials must be fired after deposition.

The luminescent screens obtained on bent surfaces exhibit a high resolution up to 120 lines/mm. The layer has a uniform thickness. As compared with the above-mentioned sedimentation method, the method according to the invention has the advantage that the fibre-optical element can be re-used for an unlimited number of times when the manufacture of the layer has failed because solvents are used which do not attack the glass. In addition this method has the advantage that it can be performed within several minutes, whereas the sedimentation method requires more than 10 hours.

In order that the invention may be readily carried into effect it will now be described by way of an example.

### EXAMPLE

The manufacture of a uniform rigidly adhering luminescent screen of approximately 1.5 mg./cm.<sup>-2</sup> on a bent fibre-optical element was performed in the following manner:

The fibre-optical element was provided with a conducting layer. Transparent tin oxide layers or vapor-deposited aluminum layers may be used, but alternatively organic materials which can be removed later on by means of evaporation may be used with an addition of an electrolyte.

A small cell was placed with the aid of a rubber seal on the fibre-optical element thus prepared which cell had an adjustable convex counter electrode at a distance of 10 mm. and which contained the suspension. The convex electrode may be adjusted in such a manner that a uniform layer thickness is obtained on the concave substrate. The suspension was prepared in advance.

The following mixture:

- 1 g. ZnCdS
- 3 ml. of a 33% solution of "Pliolite VRAC," a toluene-vinylacetate copolymer in a molar ratio of between approximately 85/15 and 70/30 having a low molecular weight,
- 0.01 g. Ca-dialkylsalicylate,
- 0.01 g. Ca-alkylsulphosuccinate, in which alkyl represents propyl or higher hydrocarbon radicals, was dispersed

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in 50 mls. of toluene and subsequently diluted with 200-400 mls. of isoparaffin, preferably iso-octane.

The size of the cell and the dilution of the suspension were matched in such a manner that together with the cell filling also the deposited quantity of the luminescent material was fixed.

After a direct voltage of 25 kv. was applied the layer was deposited within 5 seconds at a current of from 20-25  $\mu$ a. The voltage was maintained to the cell for approximately 10 further minutes for the purpose of hardening the layer. A minimum residual current flowed during this period. After careful removal of the solvent and moderate drying the luminescent screen was available for further processing, for example, for polishing.

What is claimed is:

1. In the method of manufacturing a layer consisting of electrically nonconducting pulverulent materials on a curved surface by electrophoretic deposition, the improve-

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ment which comprises employing a dispersion of the pulverulent materials in an apolar medium containing in addition a surface active ionic material, capable upon dissociating of yielding bivalent or multivalent ions, and a toluene-vinyl acetate copolymer and carrying out the method at a field strength of more than  $10^4$  v.cm.<sup>-1</sup>.

2. The method of claim 1 wherein the pulverulent material is a luminescent material and a luminescent screen is formed.

#### References Cited

#### UNITED STATES PATENTS

2,898,279	8/1959	Metcalfe et al. ....	204-181
2,947,677	8/1960	Blickwedel .....	204-181
3,020,224	2/1962	Blank et al. ....	204-181
3,459,651	8/1969	Weininger et al. ....	204-181

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