June 25, 1946. L. R. KOLLER 2,402,900

LIQUID SETTLING PROCESS

Filed Jan. 15, 1944

Fig. 1.

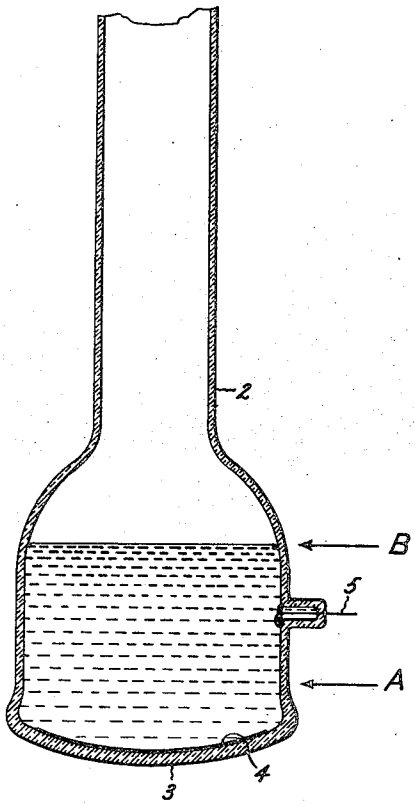
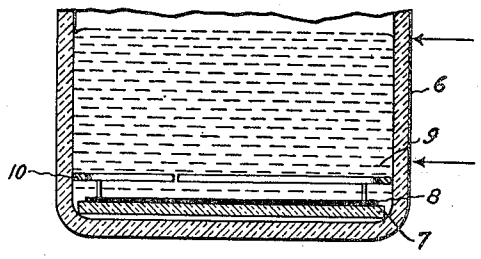


Fig. 2.



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LIQUID SETTLING PROCESS

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5 Claims. (Cl. 117—34)

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The present invention relates to the production of thin films or coatings on a support or base member. In particular, my invention relates to the production of thin coatings of phosphors, or other mineral material, in a condition of homogeneity and freedom from imperfections.

In accordance with my invention the deposition of the finely divided mineral material upon a desired supporting surface is carried out by the settling or subsidence of suspended material in a non-aqueous medium which contains a suitable bonding agent in solution. When the desired coating has been formed, its cohesiveness is increased by the addition to the suspending liquid of an agent which reduces or destroys the solvency of such liquid for the dissolved bonding agent, and causes the deposited coating to become immune to the disturbing effect of movement of the liquid above it. Hence, the coating and liquid can readily be separated from one another.

Heretofore coatings of phosphors have been made by suspending finely divided material in water or an aqueous solution.

One of the advantages of the present process which employs a non-aqueous medium is its suitableness for the production of coatings of materials which are soluble in water.

Another advantage consists in the increased facility with which the non-aqueous liquid medium can be separated from the coating after the coating has been rendered cohesive.

While my invention is generally applicable to the production of thin coatings from powders of mineral materials having per se little cohesiveness, it will be explained with particular reference to formation of cathode ray screens from mineral materials which become luminescent or darkened in response to cathode ray excitation.

The accompanying drawing shows in Fig. 1 a cathode ray bulb in a partially fabricated state, as illustrative of one class of devices for the manufacture of which my invention is applicable; and Fig. 2 illustrates the application of the invention to the production of coatings on loose plates.

Fig. 1 illustrates an elongated bulb 2, which in this case has a slightly curved end wall 3 upon which it is desired to affix a coating 4 of material which will fluoresce or otherwise respond to an impinging beam of cathode rays in the completed device. It is immaterial in so far as the practice of the present process is concerned whether the supporting surface is flat or departs somewhat from a flat or plane surface. The electrodes and

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associated electrode parts of such device have not been shown in order to simplify the drawing. They may be of conventional construction. The single sealed-in conductor 5 which is shown makes contact to an electrode (not shown) which in a later stage of manufacture is deposited as a film adjacent the end wall with its cathode-ray responsive screen 4.

A coating, such as indicated at 4 upon the internal surface of the end wall 3, may consist of a phosphor, as for example zinc silicate, or may consist of a water-soluble, so-called "dark trace" material, such as an alkali halide, for example, or caesium or potassium chloride. Any desired mineral material suitable for a desired purpose may be applied in thin layers by the practice of the present process.

When water, or an aqueous solution, is chosen as the suspending medium, the deposition of water-soluble materials such as the alkali halides obviously is excluded. Even when the chosen mineral product is insoluble in water, considerable difficulty is experienced in the removal of the aqueous medium from the settlings as they are disturbed by the flow of the liquid medium when the supernatant liquid is removed mechanically by decantation, syphoning, or otherwise.

As heretofore indicated, improved results are obtained by suspending the powdered mineral material in a non-aqueous liquid having dissolved therein a minor amount of a resin-like bonding agent. For example, the liquid suspending medium may consist of amyl acetate having dissolved therein nitrocellulose within a range of about 0.1 to 0.7% by weight. The amount of nitrocellulose may be varied considerably without detriment. In place of amyl acetate, various other liquids in which nitrocellulose is soluble may be used.

The nitrocellulose-amyl acetate solution containing the suspended powder is carefully introduced into the container 2 up to an approximate level indicated by the arrow A. When a desired thin layer of powder 4 has been deposited by settling, gravitationally from the suspending liquid which is in excess as indicated, a solvency-modifying agent, such as benzene, C_6H_6, is introduced, for example, up to the level indicated by the arrow B, that is, in excess of the original liquid. The benzene should be introduced in such manner that the deposited coating remains undisturbed, for example, by being introduced through a tube having peripheral or distributed fine orifices. As nitrocellulose is much less soluble in the result-

ing liquid mixture, the deposited coating 4 is toughened.

The supernatant liquid may be removed from the toughened coating by pouring, syphoning, or otherwise, with little likelihood of disturbing the coating to a harmful extent. The remaining residue of liquid wetting the coating is removed by evaporation. The bulb then is ready for the next fabrication operation, one of the operations which may include the wetting of the dried coating with sodium or potassium silicate solution. The coated bulb may be baked at a sufficiently high temperature, preferably in the presence of air, to remove the residue of nitrocellulose associated with the phosphor or other coating material.

My invention is not restricted in its practice to a choice of the particular solvent and particular resin type of bonding agent which has been chosen in the above example. In place of cellulose nitrate and various other forms of cellulose esters, may be employed, for example, cellulose acetate, cellulose butyrate, or a mixed ester, such as cellulose acetate butyrate. Other compounds of cellulose such as ethyl cellulose may be employed.

Various solvents other than amyl acetate may be employed, for example, butyl acetate, nitro propane, or methyl ethyl ketone may be used in place of the amyl acetate. The precipitating reagent may be ethyl alcohol. When ethyl cellulose is employed as the bonding agent the solvent may consist of toluene or a mixture of ethyl alcohol and butyl alcohol. The precipitating agent in this case may consist of gasoline.

Bonding agents other than cellulose compounds may be employed as, for example, methyl methacrylate. In this case the solvent may consist of a suitable ester as butyl acetate or a suitable ketone such as methyl ethyl ketone or acetonylacetone. The precipitating agent may be ethyl alcohol. Shellac also may be used as a bonding agent dissolved in ethyl alcohol. In this case water may be the precipitating agent. Methyl silicone may be employed as the bonding agent, the solvent in this case consisting of benzol. Acetone may be employed as a precipitating agent for rendering the methyl silicone insoluble.

The carrying-out of the present process is not restricted to a bulb or container in which a deposited coating is desired for use. In Fig. 2 is shown a receptacle 6, in part broken away, near the bottom of which is located a plate 7 upon which a coating 8 is deposited from a suspension in a solution containing a bonding agent as above described. The depth of the suspension 9 is indicated by the lower arrow. A solvency modifier then is introduced up to the level indicated by the upper arrow. The liquid is removed by decantation or otherwise, the plate being held in position by an expansible holder 10 if the liquid is poured from the plate 7, or the plate 7 may be removed from the liquid. The plate 7, with its coating 8, finally is dried and further treated as desired.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of applying a coating of fluorescent material on a supporting surface which consists in suspending such material in a finely divided state in a non-aqueous liquid containing less than about one per cent of a cellulose ester dissolved therein, causing a desired amount of said suspended matter to deposit gravitationally from the suspending liquid upon a chosen supporting surface, adding to said liquid a second liquid which is miscible with said first liquid but is non-solvent for said cellulose ester thereby reducing the solvency of said liquid for said cellulose ester, and increasing the cohesiveness of the deposit formed on said surface, removing said liquid from the deposited material, and heat-treating said deposit.

2. The method of applying a coating of cathode ray responsive material upon a foundation surface which consists in suspending said material in a finely divided state in a solution of nitrocellulose in amyl acetate, causing a desired amount of said suspended matter to be deposited by subsidence upon a chosen foundation surface, adding benzene to said solution while maintaining said coating undisturbed thereby toughening said coating, and removing said liquid.

3. The method of applying a coating of finely divided phosphor on the inner surface of a portion of the wall of a cathode ray tube envelope which consists in introducing into said envelope a suspension of the desired phosphor in a finely divided state in an organic liquid containing in solution a resin-like bonding agent, gravitationally setting said phosphor as a coating upon the chosen wall surface, adding a precipitating liquid which is miscible in said solvent and is a non-solvent for said bonding agent, pouring supernatant liquid from said coating and removing the remaining residue of said liquid by evaporation.

4. The steps in the method of applying a fluorescent coating on a foundation surface by causing the desired material in a finely divided state to subside from a solution of a cellulose ester bonding agent in an organic solvent which consist in toughening a coating thus produced by mixing with said solution a liquid material which is a non-solvent for said bonding agent and pouring the resulting liquid mixture from said coating.

5. The method of forming coatings of fluorescent materials on supporting surfaces which consists in suspending such material in a finely divided state in a body of non-aqueous liquid having a resin-like bonding material dissolved therein, causing a desired amount of suspended material to be deposited by subsidence from said liquid body as a coating upon a chosen supporting surface, mixing the supernatant liquid with a second liquid which is miscible with said non-aqueous liquid and is non-solvent for said bonding material, thereby increasing the cohesiveness of said coating, mechanically separating said liquid from said coating and drying said coating by evaporation.

LEWIS R. KOLLER.