

PATENT SPECIFICATION

(11) 1 480 622

1 480 622

- (21) Application No. 41867/74 (22) Filed 26 Sept. 1974
 (31) Convention Application No. 405507 (32) Filed 11 Oct. 1973 in
 (33) United States of America (US)
 (44) Complete Specification published 20 July 1977
 (51) INT CL² G03C 1/66
 (52) Index at acceptance
 G2C 1D3D 1G1 1G5 C1A



(54) PHOTOGRAPHIC METHOD FOR PRINTING PARTICLE PATTERN WITH IMPROVED ADHERENCE

(71) We, RCA CORPORATION a corporation organized under the laws of the State of Delaware, United States of America, of 30 Rockefeller Plaza, City and State of New York, 10020, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates in general to a photographic method for printing a pattern of particulate material upon a surface of a support by applying to said surface a coating mixture comprised of a water-soluble polymer which is crosslinkable into insoluble form by actinic radiation in the presence of hexavalent chromium ions, a water-soluble dichromate photosensitizer for said polymer and said particulate material, exposing said coating to a pattern of said actinic radiation until exposed portions of said coating are rendered insoluble, and flushing said exposed coating with an aqueous solvent to remove soluble portions of said coating while retaining insoluble portions of said coating in place.

A commercial color television picture tube of the apertured-mask type is a cathode-ray tube which includes a screen structure comprised of a multiplicity of red-emitting, green-emitting, and blue-emitting phosphor elements upon the inner surface of the viewing window of the tube. Usually, these phosphor elements are arranged in groups of threes or triads in a regular pattern, each triad having a red-emitting element, a green-emitting element, and a blue-emitting element. An apertured mask (also called shadow mask), positioned in the panel in closely spaced relation with the phosphor elements, aids in selectively exciting the phosphor elements.

In order to make a television picture with suitable resolution and color purity, the viewing screen must be comprised of a very large number of phosphor screen elements of relatively small and uniform sizes which are accurately positioned with respect to one another. In one process for printing the phosphor screen

elements, the inner surface of the viewing window is coated with a mixture comprised of phosphor particles, a polyvinyl alcohol and a water-soluble dichromate sensitizer, such as ammonium dichromate, for the alcohol. Actinic radiation is projected from a small area light source in a so-called "lighthouse" through the apertured mask onto the coating. The mask functions as a photographic negative (of positive) to transmit a pattern of radiation which produces, in the coating, regions of relatively greater solubility than other regions of lesser solubility. The exposed coating is developed by flushing with an aqueous solvent, until the unexposed and substantially unexposed portions of coating are removed leaving the insoluble exposed portions, which are a particle pattern of phosphor elements, adhered to the supporting surface.

The development of the particle pattern is one of the critical steps in the process because the exposed regions of the coating may lack sufficient adherence to the supporting surface and therefore may be washed away. Excessive light exposure cannot be used as an aid to adherence, because as exposure is increased the insoluble portions grow in size and become too large. Consequently, one phosphor element might overlap another phosphor element. Since the phosphor element size is limited by a particular screen design, it is important that the proper exposure be provided to produce phosphor elements of the desired size as well as to have adequate adherence to the supporting surface.

It has been found in accordance with the invention, that the addition of small amounts of water soluble vanadates, for example ammonium metavanadate or sodium metavanadate, added to the prior dichromate-sensitized polyvinyl-alcohol coating mixture increases the adherence of the exposed portions of the coating to the supporting surface during development. At the same time, an enhancement of the photosensitivity of the coating is observed. This combination of desirable characteristics was not anticipated because, in general, enhanced photosensitivity which allows a reduced exposure time usually results

50

55

60

65

70

75

80

85

90

95

(16)

in a loss of adherence. Generally, the invention may be used to print patterns of particulate material.

One example of the invention is described as follows:

Prepare a coating composition of the following formulation:

292 grams green-emitting, copper-activated zinc-cadmium sulfide phosphor particles,

233 grams 10-weight-percent aqueous solution of polyvinyl alcohol having an average molecular weight of about 170,000 to 220,000,

13 grams 35-weight-percent aqueous dispersion of an acrylic polymer, such as a Rhoplex AC-73, marketed by Rohm and Haas Chemical Company, Philadelphia, Penna.,

14 grams 10-weight-percent aqueous solution of ammonium dichromate,

46 grams 0.5-weight-percent aqueous solution of ammonium vanadate NH_4VO_3 ,

402 grams deionized water.

The coating composition is carefully mixed and the viscosity adjusted to be in the range of about 20 to 50 centipoises. The pH is about 6.4. The formulation is then flow coated upon the inner surface of the faceplate of a 25-inch rectangular color television picture tube and dried. The apertured mask for the faceplate is then inserted in the mounts provided therefor and the faceplate assembly positioned upon a lighthouse platform. Ultraviolet light from the small area light source in the lighthouse is projected through the mask which permits a pattern of light to fall incident upon and expose the coating for about 6 minutes. The faceplate panel is then removed from the lighthouse and the mask removed from the faceplate panel. The exposed coating is developed by flushing with water to remove the unexposed and substantially unexposed and soluble portions of the coating, while retaining the exposed and insoluble portions of the coating in place.

The invention may be used to print any particle pattern (pattern of particulate material) upon any supporting surface. The particles may be luminescent or nonluminescent, may be light-absorbing, may be any body color in reflected light, and may have special properties such as being magnetic, or ferroelectric, or dielectric.

The invention may be used particularly to print viewing-screen structures for cathode-ray tube, electroluminescent devices and other displays. Dot screen and line screen structures are examples. By "viewing screen structure" is meant any component part of a viewing screen for a display device, for example, a luminescent layer, or a light-absorbing layer for a cathode-ray tube target; or an alpha numeric pattern for an electroluminescent display; or an informational pattern for an advertising or safety display. Where the particles are luminescent, they may emit in any

portion of the spectrum as a result of any form of excitation.

The example above is the use of the invention to produce a screen structure (the green-emitting field) for a color television picture tube by the slurry process. Many suitable coating formulations adaptable for the invention as applied to the slurry process are described in U.S. patent No. 3,269,838. In general, however, the coating formulation used in the invention comprises (1) a water-soluble polymer which is crosslinkable into insoluble form by actinic radiation in the presence of hexavalent chromium ions, (2) a soluble dichromate photosensitizer for the polymer, (3) a water-soluble vanadate, and (4) particles of the pattern material.

The polymer may be an organic colloid, such as gelatin or fish glue, but is preferably a polyvinyl alcohol having a molecular weight greater than about 120,000. The polymer must be "dichromatizable"; that is, capable of being rendered photosensitive by dichromate ions, particularly by hexavalent chromium ions, so that actinic radiation can render the polymer insoluble.

The photosensitizer is a source of hexavalent chromium ions and may be any water-soluble dichromate such as sodium dichromate, potassium dichromate, or ammonium dichromate. The photosensitizer may be present in amounts of about 2 to 10 weight percent of the weight of water-soluble polymer present. Concentrations of dichromate higher than 10 weight percent have little added effect. Although the photosensitivity speed is higher with 10-weight-percent dichromate present, lower concentrations often are used in practice because improved adherence is realized.

The screen-structure material may be, for example, luminescent particles, particles of inert material, or particles of light-absorbing material, which is to be photo-deposited as a screen structure. The coating may, if desired, include a nondichromatizable resin such as an acrylic copolymer, which is not rendered photosensitive by dichromate ions but may otherwise affect the properties of the coating.

The vanadate may be any water-soluble vanadate, for example sodium metavanadate NaVO_3 , potassium metavanadate KVO_3 , or ammonium metavanadate NH_4VO_3 . The vanadate may be present in amounts of about 0.1 to 4.0 weight percent of the weight of water-soluble dichromatizable polymer present. Enhancement of sensitization with as low as 0.1 percent concentration is noticeable; however typical concentrations are about 1.0 weight percent vanadate. Higher concentrations up to about 4.0 weight percent vanadate also display the characteristics of improved adherence and enhanced photosensitivity, but appear to have about the same effect as compositions containing about 1 to 2 weight percent vanadate.

The coating is exposed to a pattern of actinic radiation. Any actinic radiation such as visible light rays, ultraviolet light rays, or cathode rays may be used. Equipment for exposing the coating is described in the art. A significant quality of the exposure is that, although coating portions may be insolubilized by the actinic radiation, nevertheless the insoluble coating portions may not adhere sufficiently to the supporting surface to remain in place through the development step. Adherence may be evaluated in a quantitative manner by using the segment exposure method. By this method, different segments of a coated glass panel are exposed, to a dot pattern of light for different amounts of time for example, from 3 to 10 minutes in one-minute increments and then developed with water. After developing, the panel segments are examined and the phosphor-dot diameters microscopically measured to determine the minimum exposure time needed for the dots to just adhere or for the loss of only a few dots. An adherence number is determined. This is defined as the ratio of the maximum exposure time to yield the required dot diameter to the minimum exposure time for which the phosphor dots barely adhere. For example, if the required dot diameter is obtained by an eight-minute exposure and dots are lost below a 5-minute exposure, then the adherence number is 8/5 or 1.6. The greater the adherence number the better.

The results of five adherence tests with the mixed dichromate and vanadate sensitizers and with only a dichromate sensitizer are tabulated in the TABLE below showing the effects on the adherence number as well as the reduction in exposure time for the required dot diameters. The tests were run by the segment-exposure method described above, using the formulations shown in the example, except

that the concentration of ammonium dichromate sensitizer, the selection of the vanadate, the concentration of the vanadate, and the exposure time were provided as indicated in the TABLE. All of the other parameters in the process, such as application cycle, screen weight, lighthouse intensity, lighthouse collimator size, method of developing, drying temperatures, etc. were essentially identical in each group. A direct comparison cannot be made by adherence number between test groups 1, 2, 3 etc., because the test conditions for the groups were not necessarily identical.

A vanadate has been used by itself as a sensitizer for polyvinyl alcohol, as described for example in Netherlands Patent Application 69-07022 (U.K. Specification No. 1270159). However, it has been found that a vanadate sensitizer by itself imparts very poor adherence to the exposed film. This is illustrated in test 6A in the TABLE below where the polyvinyl alcohol was sensitized solely with about 6.5-weight-percent ammonium metavanadate. Even with a long exposure time (24 minutes), the adherence was very poor, being rated much less than 1.0; that is, many dot losses occurred even with a 24-minute exposure. However, when the same polyvinyl alcohol formulation was sensitized solely with 8-weight-percent ammonium dichromate in test 6B, the adherence number rose to 1.6.

The beneficial effect of the vanadate addition does not appear to be sensitive to the pH of the slurry. The maximum pH range evaluated was about 6.4 to 8.5. The Example given above appears as test 5B in the TABLE where the adherence number is 2.2. A comparable formulation without ammonium vanadate present yielded an adherence number of 1.6, as shown by test 5A.

TABLE

Group and Test No.	Weight % Ammonium Dichromate	Weight % NH_4VO_3 or NaVO_3	Exposure Time for Desired Dot Size (Minutes)	Adherence No.
1A	10	—	9-1/2	1.5
1B	10	1.0 NH_4VO_3	8-1/2	2.0
2A	5	—	16	1.7
2B	5	0.5 NH_4VO_3	8	2.2
2C	5	0.25 NH_4VO_3	11	2.2
3A	10	—	5-1/2	1.2
3B	10	1.0 NaVO_3	4-1/2	1.8
4A	9	—	12-1/2	2.2
4B	9	1.0 NaVO_3	9	2.5
4C	9	4.0 NaVO_3	8-1/2	2.4
5A	6	—	7	1.6
5B	6	1.0 NH_4VO_3	6	2.2
6A	0	6.5 NH_4VO_3	24	<1.0
6B	8	—	13	1.6



1,480,622

WHAT WE CLAIM IS:—

1. A photographic method for forming a pattern of particulate material upon a surface of a support by applying to said surface a coating mixture comprised of a water-soluble polymer which is crosslinkable into insoluble form by actinic radiation in the presence of hexavalent chromium ions, a water-soluble dichromate photosensitizer for said polymer, a water-soluble vanadate and said particulate material, exposing said coating to a pattern of said actinic radiation until exposed portions of said coating are rendered insoluble, and flushing said exposed coating with an aqueous solvent to remove soluble portions of said coating while retaining insoluble portions of said coating in place.
2. The method in accordance with Claim 1, wherein said soluble vanadate is at least one of sodium meta - vanadate, potassium meta - vanadate and ammonium meta - vanadate.
3. The method in accordance with Claim 2, wherein said soluble vanadate is present in said coating mixture in concentrations of 0.1 to 4.0 weight percent of the weight of said water-soluble polymer.

4. The method in accordance with Claim 1, wherein said dichromate photosensitizer is at least one of sodium dichromate, potassium dichromate and ammonium dichromate.

5. The method in accordance with Claim 1, wherein said water-soluble polymer is a polyvinyl alcohol.

6. The method in accordance with Claim 1, wherein said support is the faceplate of a cathode ray tube envelope.

7. A method of forming a particle pattern substantially as hereinbefore described using any herein indicated coating mixture containing a vanadate and a source of hexavalent chromate ions.

8. A method according to any preceding Claim used for forming a phosphor pattern on a viewing screen structure.

9. A viewing screen structure having a particle pattern formed thereon by a method according to Claim 8.

T. I. M. SMITH,
Chartered Patent Agent,
50 Curzon Street,
London, W1Y 8EU.
Agent for the Applicant.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1977
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.