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[54] **METHOD FOR APPLYING ORGANIC POLYMERIC COATING COMPOSITION TO FERROUS-METAL SURFACES**

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[51] **Int. Cl.²** **B32B 3/10;** B05D 3/02

[58] **Field of Search** ..... 117/99, 161 UE, 132 C, 117/33.5 C, 33.5 CM; 96/36.1; 313/402; 427/247, 388; 428/137

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[57] **ABSTRACT**

A method for reducing the sizes of apertures in a ferrous-metal mask including the steps of coating the mask with a water-based-coating composition containing a polyvinyl alcohol polymeric material which is water-insolubilized when ferrous or ferric ions are present, and a water-soluble passivator for ferrous-metal surfaces, such as sodium nitrite, and then drying the coating. Inclusion of a passivator in the coating composition reduces or eliminates the formation of localized coating discontinuities, usually comet shaped, in the coating.

3 Claims, No Drawings

METHOD FOR APPLYING ORGANIC POLYMERIC COATING COMPOSITION TO FERROUS-METAL SURFACES

BACKGROUND AND SUMMARY OF THE INVENTION

This invention relates to a method for coating a ferrous-metal surface in the presence of oxygen and water with a composition containing an insolubilizable organic polymeric material.

In some manufacturing processes, it is desirable to coat a ferrous-metal surface with a polymeric coating from a water-based composition. For example, one process for preparing an image-screen structure for a color television picture tube includes coating a ferrous-metal (cold-rolled steel) apertured mask with a polyvinyl alcohol composition to temporarily reduce the aperture sizes. The surface of the mask may have a black oxide layer formed thereon. Such a process is referred to as a meniscus closure process and is described, for example, in my patent applications Ser. Nos. 211,475, (now abandoned) and 211,476 (now U.S. Pat. No. 3,811,926 issued May 21, 1974,) both filed Dec. 23, 1971. In such a process, a meniscus or membrane is produced across each mask aperture, and then the meniscus is broken and the remaining coating material is consolidated into a coating of the desired thickness on the aperture walls.

In using this or similar processes, defects appear on the ferrous-metal surface which are called "comets" because they are usually comet shaped. A comet includes a "head" or module of polymeric material that is tinted and is much less soluble or dispersible in warm water than the polymeric material in the initial coating composition. An attached "tail" usually extends from the head in the direction of flow of the coating material during the coating step. The tail is a thinner-than-normal coating.

Prior to coating, the mask surface may be cleaned so that, upon examination, the surface is smooth and essentially free of particles and obstructions. Filtration of the coating composition just prior to coating removes all nodules and particles from the coating composition which could produce comets. Nevertheless, even with such extraordinary precautions, comets appear in the final coating causing unwanted variations in the thickness of the coating and in the amount of closure of the apertures.

The term "ferrous-metal," as used herein, refers to a class of metal compositions which contain iron as a major constituent and exhibit corrosion or rusting when exposed to water and oxygen. Cold-rolled steel and chromium-iron alloys containing up to 10 weight percent chromium and the balance iron are exemplary of ferrous materials.

It has been found that the number of comets produced during the coating of a ferrous-metal surface with a water-based coating composition is materially reduced or completely eliminated by including in the coating composition a passivator or inhibitor for ferrous-metal surfaces. Known passivators are water-soluble sources of anions selected from the group consisting of nitrite, chromate, molybdate, tungstate, benzoate, cinnamate and phosphate. The preferred passivators are nitrites, particularly sodium nitrite, which is preferably present in concentrations of about 0.05 to 0.10 weight percent of the coating composition. Generally, the passivator may be present in concentrations of about 0.01 to 0.50 weight percent of the coating composition.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The invention will now be described with respect to a particular method for temporarily reducing the mask-aperture sizes in a meniscus closure process for making a viewing-screen structure for a cathode-ray tube. However, the invention may be used and advantages achieved wherever a water-based coating composition containing an insolubilizable polymeric material is coated on a ferrous-metal surface.

Prepare a coating composition containing the following constituents in about the indicated proportions by weight:

3.84 percent Polyvinyl alcohol (Vinol 540)
0.375 percent Wetting/dispersing agent (Gafac LO-529)
0.625 percent Coloring agent (orange R dye)
0.05 percent Passivator (sodium nitrite)
11.39 percent High-boiling liquid (ethylene glycol)
83.72 percent Low-boiling liquid (water)

It has been found desirable to stock the coating composition at near neutral pH without the passivator included. Just prior to use, the passivator is added to the coating composition, the pH of the coating composition is adjusted to about 7.3 to 7.5 with sodium hydroxide, and the viscosity of the coating composition is adjusted with the addition of water to a viscosity of about 35 centipoises at 28°C.

A dome-shaped ferrous-metal apertured mask is now coated on the convex surface thereof with the coating composition. One method of applying the coating composition is described in my above-cited patent application, Ser. No. 211,476, and need not be repeated in detail here. In this method, the mask is rotated about an axis tilted upward from the horizontal and normal to the surface in the central portion of the mask. A stream of a liquid-coating composition is projected into an upward trajectory and into contact with the convex surface of the rotating mask substantially at the top of its trajectory. After about one rotation of the mask, the stream is removed, and the rate of rotation is increased to cause excess liquid to fly off the mask by centrifugal force. The retained liquid coats the convex surface and also produces a meniscus membrane that closes each aperture.

The central portions of the meniscuses or membranes are then opened to form temporary apertures smaller than the final-sized apertures of the mask. One method of opening the membranes is described in my above-cited patent application Ser. No. 211,475, and need not be repeated in detail here. In this method, the coated apertured mask is first heated at a slower rate to a lower temperature until the thickness of the membrane across each aperture is reduced to a thin meniscus. The coated mask is further heated at a faster rate and to a higher temperature until the membrane ruptures and the residual material is consolidated into a coating of the desired thickness on the walls of the apertures. The surfaces of the wall coatings define the smaller temporary apertures.

The use of a passivator in the novel method provides a substantially uniformly thick coating over the surface of the mask that is free of comets. Similar coating compositions which do not contain a passivator generally

produce comets on the mask surface. Similar coatings that do not contain a passivator, particularly those that contain chloride ions, produce coatings which have many more comets therein. It is believed that the uniformity of the coating thickness and the freedom from comets produced by the novel method provide more uniform films and membranes resulting in a greater uniformity in the size of the temporary apertures that are produced. By incorporating a passivator in the coating composition, extraordinary process steps of precleaning and/or prepassivating the mask prior to coating are eliminated, and also the additional equipments necessary to carry out these procedures are eliminated. There is no elapsed time between passivation and coating during which further damage can occur to the mask surface.

An image-screen structure may then be produced using the mask with the smaller temporary apertures as a temporary master. The mask with the temporary apertures may be used to deposit the phosphor elements of an image-screen structure by methods such as described, for example, in U.S. Pat. No. 3,406,068 to H. B. Law. The mask with the temporary apertures may also be used to deposit a light-absorbing matrix, such as the process described for example in U.S. Pat. No. 3,558,310 to E. E. Mayaud.

GENERAL CONSIDERATIONS

A study of the source and causes of comets was conducted. Close examination of the comet head reveals in many cases a rough pit in the ferrous metal surface, or a granular growth of red iron oxide. In other cases, no apparent defect in the ferrous metal surface is visible under about 40 power magnification. Special cleaning procedures with strong caustic, ultrasonics, sandblasting, and/or liquid honing failed to remove the defect sites and often worsened the situation.

It is believed that there is electrolytic cell action between two or more of (a) the ferrous metal of the mask, (b) the black oxide layer normally formed in the surface of the mask, (c) local contaminant and oxide areas on the mask surface, and (d) local metal defects. The presence of an electrolyte (the water-based coating composition) provides the required additional ingredient to generate red hydrated ferric oxide and hydrogen ions at the comet sites. Some probable chemical reactions are:

$$2Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2 \text{ and}$$

$$4Fe(OH)_2 + 2H_2O + O_2 \rightarrow 4Fe(OH)_3$$

Ferric oxide can be shown to insolubilize polyvinyl alcohol in deliberate seeding experiments. Thus, the generated ferric compounds, which are sources of ferric and ferrous oxides, could produce a comet head or nodule of insolubilized polymeric material. The reduced pH can be shown to reduce the viscosity of the coating composition in the pH range involved. Reduction of pH, as from the generation of hydrogen ions at the local sites, can produce the comet tails. Comet tails can also be produced by a blockage of flow of the coating composition by the comet head.

Experimentally a number of observations support the above model. First, the polymeric material may be eliminated as a source of comets by coating a glass plate of similar shape and noting that no color-shifted water-insoluble comet heads are produced on the glass plate. Second, the structure of the comet tail, which produces reduced closure of the mask apertures, and increased clarity, and reduced light dispersion of the coating, may be simulated through a reduction of the pH of the coating to about 6 or lower. When the coating composition has a pH greater than 7.5, the temporary apertures have a smaller hole for greater closure and have a film structure of greater light dispersion qualities. Third, comets may be artificially generated by seeding with particles of ferric oxide, ferric chloride, or any of a number of the polarizing salts which are acidic in solution. Fourth, mechanical disturbances to the black iron oxide surface layer provide sites for comets. This may be observed from probe marks, dispense nozzle marks, and deliberate marks on the metal surface made with a pin at very low contact pressures.

The preferred passivators are inorganic oxidizing agents having the ability to react slowly with the iron of the ferrous metal in direct contact but reducing actively under cathodic currents. Nitrites, chromates, tungstates, and molybdates all fall within this category. The tungstates and molybdates require the presence of oxygen to function properly. Since the normal situation for coating in the novel method is in air and there are relatively large surface areas through which oxygen can be introduced into the system, there are few circumstances where molybdates and tungstates cannot be used. Chromates must be carefully controlled when used with the polyvinyl alcohol system because they may cause premature polymerization of the polyvinyl alcohol at certain pH levels and because glycol, if it is present, may be spontaneously oxidized and result in a pH drop which degrades the coating characteristics of the composition. A detailed discussion of passivators for ferrous metal surfaces appears in H. H. Uhlig "Corrosion and Corrosion Control" 2nd Edition, John Wiley & Sons, New York, N.Y. 1971.

Nitrites, particularly sodium and potassium nitrites, in concentrations of 0.05 to 0.1 weight percent of the coating composition produce a significant reduction of the number of comets produced. It is believed that the nitrite with or without dissolved oxygen in the coating composition breaks down under the influence of the galvanic action at defect sites to provide passivation at the site thus limiting the comet-producing action. Effective passivation of most defects takes place within one minute or less, sufficiently rapidly to prevent or greatly limit the number of comets formed. As little as 0.01 weight percent nitrite may be used. Up to 0.50 weight percent nitrite may be used in the coating composition. However, it is considered that the excess over 0.10 percent is unnecessary.

Instead of polyvinyl alcohol, one may use any other polymeric material which is insolubilizable by the presence of heavy metal ions such as ferrous or ferric ions, or by the rise in the pH of the coating composition. The polyvinyl alcohol preferably has an average molecular weight of about 80,000 to 200,000 and is present in the coating composition in concentrations of about 2 to 6 weight percent.

In the coating composition, compatible liquid vehicles such as methyl alcohol, ethyl alcohol, propyl alcohol or butyl alcohol may be substituted in part for water. The mono-alcohols may be substituted in part for water in the formulation to hasten drying. The polyalcohols may be substituted in part for water at various ratios to vary the action at higher temperatures and to provide desired properties at these higher temperatures. Since alcohols are more expensive than water and may create fire hazards, they are not generally used. Other high-boiling liquids may be substituted for

ethylene glycol in the preferred composition. Suitable high-boiling liquids include glycerin, glycol, and triethylene glycol. Other short chain hydroxylated vehicles may also be substituted.

I claim:

1. A method for reducing the sizes of apertures in a ferrous metal mask comprising the steps of coating said mask with a water-based composition consisting essentially of a polyvinyl alcohol polymeric material and 0.01 to 0.50 weight percent of the coating composition of a water-soluble passivator for ferrous-metal surfaces, and then drying said coating.

2. The method defined in claim **1** wherein said passivator is a water-soluble source of anions selected from the group consisting of nitrite, chromate, molybdate, tungstate, benzoate, cinnamate, and phosphate.

3. The method defined in claim **1** wherein said passivator is an alkali nitrite comprising 0.05 to 0.10 weight percent of said composition.

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