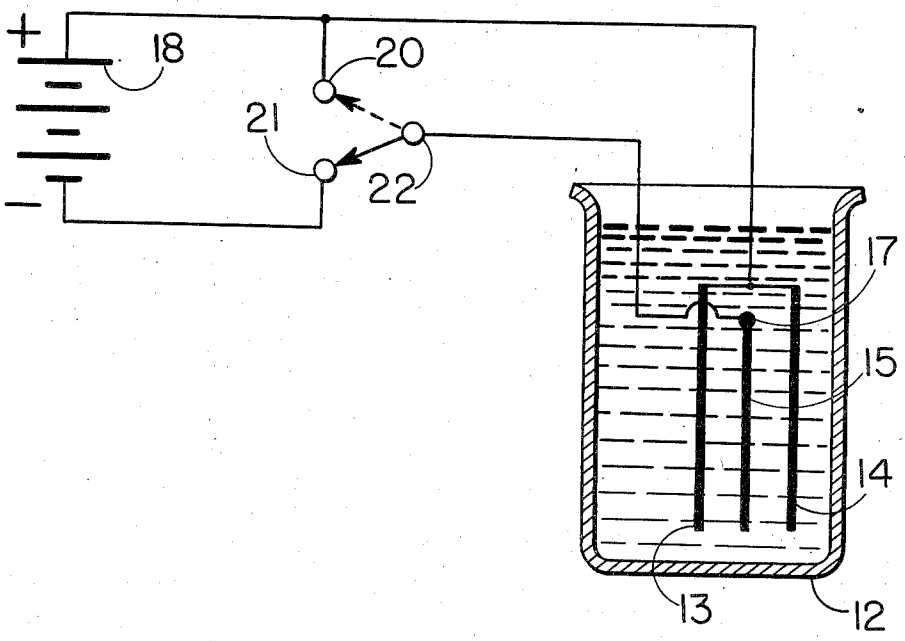
March 11, 1958 J. H. HUNTER ET AL 2,826,538

METAL BLACKENING PROCESS

Filed May 3, 1955



INVENTORS

James H. Hunter

Leo K. Kosowsky

BY George W. Crowley

ATTORNEY

United States Patent Office 2,826,538
Patented Mar. 11, 1958

2,826,538

METAL BLACKENING PROCESS

James H. Hunter, Redding Ridge, and Leo K. Kosowsky, Bridgeport, Conn., assignors to Columbia Broadcasting System, Inc., Danvers, Mass., a corporation of New York

Application May 3, 1955, Serial No. 505,762

4 Claims. (Cl. 204—24)

This invention relates in general to a process for blackening metal and in particular to the blackening of aperture masks for color television picture tubes.

In color television picture tubes, as they are presently known and used, beam separation is accomplished by an aperture mask. This mask is usually a curved metallic member perforated over its surface by a large number of circular apertures. The mask is located adjacent a phosphor screen composed of myriads of dots symmetrically arranged in groups of three primary color generators. Three electron guns are provided in the neck of the tube and the aperture mask serves to restrict the impingement of the beam from each gun to only phosphors of a given color-generating type.

To obtain resolution of the degree necessary to good color pictures, the dots of phosphor must be made extremely small. Diameters of as little as 17 or 18 thousandths of an inch are common in color picture tubes. The diameters of the mask apertures are correspondingly small to provide beam separation and excitation of only the desired phosphor dots.

The apertures in the mask being so limited in size cause a large portion of the electron beams from the guns to strike the mask itself rather than passing through to the phosphors. A loss in brightness of picture occurs as a result of this, but it is still possible to present a satisfactory color picture using electron beams of high intensity. A second trouble, which is of greater concern than the first, is the heating of the mask which ensues under the heavy electron bombardment. Such heating with accompanying expansion of the mask causes misregistry of apertures in the mask and phosphor dots on the screen and loss of a true picture. The fact that the electron beams are run at such high intensities to compensate for brightness lost by the mask blocking portions of the beam aggravates the mask-heating problem.

Recognition of the problem has led to several attempted solutions. The idea of blackening the mask to improve its radiating and general heat-handling capacities arose immediately. Early efforts were made to blacken the mask with graphite. Other attempts were made to plate a metal over the mask and blacken that metal. With the exception of one process which is still being investigated, the proposed methods have been unsatisfactory. These reasons are many, but the more important objections have been:

(1) The process was too expensive.

(2) The blackening material did not adhere to the mask under operating conditions.

(3) Results could not be consistently duplicated.

(4) The blackening did not leave a dull surface.

(5) The surface was not sufficiently black.

(6) The mask material was weakened by the process.

The present invention has as its primary object the provision of a metal blackening process which is applicable to any metal object.

Another object is to provide a process which is particularly useful in blackening aperture masks for color picture tubes.

Still another object is to provide a blackening process which avoids the above-listed disadvantages of known processes.

A further object is to provide a process for blackening color picture tube aperture masks which produces a dull black finish that adds strength to the mask.

A still further object is to provide a blackening process which does not clog or otherwise change the apertures of a color picture tube mask.

In general, the invention consists in a process for forming a dull black adherent coating on any platable metal, the process being of singular value in the manufacture of aperture masks for color television picture tubes. The process is carried out by thoroughly cleaning the member to be plated. Then the member is plated with chromium in such a manner as to build up separate layers of chrome thereon. Following this, periodic plating and oxidizing of the plated surface in repetitive cycles takes place to achieve a black chrome oxide which is firmly bonded by subsequent plating of chrome. For a better understanding of the present invention together with other objects, features and advantages, reference should be made to the following description which should be read in connection with the accompanying drawing, the single figure of which is a perspective view, partly schematic, of a preferred form of apparatus which may be used with advantage in carrying out an important feature of the invention.

Referring to the drawing, there is shown a lead-lined tank 12 which contains a suitable chrome plating solution, which may be, for example, chromic acid and sulphuric acid, the chromic acid being of a strength of 33 to 55 ounces per gallon and the sulphuric acid being of a strength of 0.3 to 0.5 ounces per gallon. The temperature of the bath should be about 125° F. and the Baumé between 21–28½.

Within tank 12 and immersed in the bath are suitable electrodes 13 and 14 which may be of lead combined with a small amount of antimony. At a point midway between electrode 13 and 14, member 15 which is to be blackened is suspended. Electrodes 13 and 14 may with advantage be made of a number of segments in order that they may be changed in size to present surface areas comparable to that of the object being plated and oxidized. In the present example, member 15 is actually an aperture mask for a color television picture tube which is flat and will be formed into a spherical shape after blackening.

In this simple case of a flat object, electrodes 13 and 14 are most easily formed of strips suspended from a bar. If the blackening were to be done after the mask is formed into a spherical shape, the electrodes 13 and 14 would be similarly curved to maintain approximately equal spacing from both sides of the mask to the nearer electrode.

Connected to member 15 are a series of electrical contacts 17 which may be clips or other suitable devices for establishing contact. To avoid maldistribution of plating or undesirable localized heating effects, contacts 17 are disposed symmetrically about member 15. A source of direct voltage 18 having a no-load voltage of about 8 volts is provided. The positive terminal of voltage source 18 is connected to a contact 20 of a switch, thence directly to electrodes 13 and 14. The negative terminal of voltage source 18 is connected to contact 21 of the switch, and contact 22 of the switch is connected to contacts 17 which are distributed about the periphery of member 15.

In carrying out the process of the present invention, member 15 is first thoroughly cleaned. It is degreased,

for example, by an alkaline soak, dipped in cyanide at about 150° F., water rinsed, dipped in mild etching solution for about 15 seconds, water rinsed, dipped in a 10% muriatic acid solution and water rinsed.

Member 15 is then placed in the bath as shown in the drawing, with the switch so positioned that member 15 is cathodic relative to electrodes 13 and 14. Plating of member 15 continues for approximately one minute, then member 15 is removed. Two additional one-minute plating applications are performed in the same manner to build up three separate chrome layers.

Following the three plating steps, member 15 is once more placed in the bath. Plating in the manner described above is permitted for 10 seconds. Then the switch is thrown to connect contacts 20 and 22 and to break the connection between contacts 21 and 22. This removes external voltage and literally shorts electrodes 13 and 14 to member 15 externally of the bath. This short-circuited condition continues for 10 seconds. The entire plating-shorting cycle is then repeated for a total of 5 minutes. In other words, plating is done for 10 seconds, then short-circuiting is done for 10 seconds over a 5 minute period.

During the 10 second short-circuiting periods, oxidation of the layer plated on member 15 immediately previous to the shorting occurs. The chrome oxide so formed is black in color and is bonded securely by the plating of the period following. Successive cycling continues to build up thin layers of chrome oxide which are succeedingly blacker until a color equilibrium is reached, usually at about 5 minutes.

The theory of operation of the blackening process is as follows. Member 15 being chrome plated and in a chromic acid solution with electrodes 13 and 14 being, for instance of lead results in the formation of a battery having a voltage of about 1¼ volts. Under short-circuited conditions, member 15 becomes anodic relative to electrodes 13 and 14. As such, member 15 is subjected to anodic polarization. The solution in which member 15 is immersed is a strongly oxidizing medium. Hence, each thin film of chrome plated on member 15 during the plating portions of the cycle becomes oxidized with the formation of black chromium oxide. Following plating periods cause trapping of the oxide film. Repetition of the cycle of plating and oxidizing builds up numerous layers of chrome oxide trapped by chromium and member 15 becomes progressively duller and darker.

In the particular application of this process to color picture tube aperture masks, numerous advantages result. The process is relatively inexpensive, the black film is strongly adherent, easily reproduced, and quickly applied. Also, the finished aperture mask is resistant to corrosion and heat, is chemically inert and non-magnetic. Most important, the mask is actually strengthened rather than weakened as in most blackening processes. Apertures of the mask are not reduced in diameter because the nature of the plating operation is such that chrome is deposited on the flat portions of the mask and not in the openings themselves.

The process is susceptible of considerable modification to suit other needs of dullness or blackness as when other types of object are to be blackened. The blackness is a function of the time cycle and the current density. To a lesser extent the temperature of the bath is also a factor. Specifically, the lower the current density, the blacker the coating and the less the adherence. Also, the lower the temperature of the bath, the darker the deposit and the less the adherence. If the cycle is varied for longer plating and shorter oxidizing periods, the blackness is less and, conversely, longer oxidizing with shorter plating periods will give a blacker coating.

Lead electrodes need not be used, other metals being suitable, but a material whose reaction products are insoluble is preferred to avoid contamination of the plating solution. Since the reaction products which are encountered are primarily sulphates, which are usually soluble, lead is preferred as an electrode material.

Other modifications of the process which are within the purview of the invention will suggest themselves to those skilled in the art. The invention should not be limited to the exact processes shown but only by the spirit and scope of the appended claims.

What is claimed is:

1. A method for blackening a chromium-plated metal which comprises the steps of immersing said metal in a chromium plating bath, immersing an electrode in said bath, applying external direct voltage to said metal and to said electrode to make said metal cathodic relative to said electrode for 8 to 10 seconds whereby said metal receives a thin film of plated chromium, removing said external voltage from said metal and electrically connecting said electrode directly to said metal externally of said bath for 8 to 10 seconds to oxidize said thin film of chromium, reapplying said external direct voltage to said metal and to said electrode to cause plating of a further film of chromium over said oxidized original film of chromium and oxidizing said further film by electrically disconnecting said external voltage from said metal and connecting said metal to said electrode externally of said bath.

2. A method for blackening chromium-plated aperture masks for color television picture tubes which includes the steps of immersing one of said aperture masks in a chromium plating bath, immersing in said bath a pair of electrodes, each having a surface area comparable to that of said aperture mask, said aperture mask being disposed substantially equidistant from each of said electrodes, connecting said electrodes together, applying external voltage to said aperture mask and to said electrodes to make said aperture mask cathodic relative to said electrodes for a sufficient length of time to plate a thin film of chromium on said aperture mask, disconnecting said external voltage from said aperture mask, externally electrically connecting said aperture mask to said electrodes to make said aperture mask the anode of a voltaic cell formed in said bath for a sufficient length of time to oxidize said chromium film, and cyclically repeating said chomium plating and oxidizing operations until said aperture mask becomes blackened to the desired degree.

3. A method for blackening aperture masks for color television picture tubes comprising the steps of immersing one of said aperture masks in a chromium plating bath, immersing in said bath a pair of electrodes, each having a surface area comparable to that of said aperture mask, said aperture mask being disposed substantially equidistant from each of said electrodes, connecting said electrodes together, applying external voltage to said aperture mask and to said electrodes to make said aperture mask cathodic relative to the said electrodes for a period of approximately 3 minutes whereby a coating of chromium is plated on said aperture mask, disconnecting said external voltage from said aperture mask, externally electrically connecting said aperture mask to said electrodes to make said aperture mask the anode of a voltaic cell formed in said bath for a period of from 8 to 10 seconds whereby the outer portion of said coating is oxidized and cyclically connecting said aperture mask in cathodic and anodic relationship to said electrodes, each said relationship being held for a period of 8 to 10 seconds until said aperture mask becomes blackened.

4. A method for blackening metal which comprises the steps of immersing said metal in a chromium plating bath, immersing an electrode in said bath, applying external voltage to said metal and to said electrode to make said metal cathodic relative to said electrode for a sufficient length of time to deposit a thin film of chromium on said metal, removing said external voltage from said

metal and electrically connecting said metal directly to said electrode externally of said bath to make said metal tend to be anodic relative to said electrode for a sufficient length of time to oxidize said film and cyclically repeating said plating and oxidizing operations a plurality of times until the metal has been blackened to a desired degree.

References Cited in the file of this patent

UNITED STATES PATENTS

1,975,239 Ungelenk et al. ---------- Oct. 2, 1934

2,078,014 Oplinger et al. ---------- Apr. 20, 1937
2,575,712 Jernstedt ---------- Nov. 20, 1951
2,678,299 Geese et al. ---------- May 11, 1954

FOREIGN PATENTS

603,910 Germany ---------- Sept. 20, 1934
1,088,657 France ---------- Mar. 9, 1955

OTHER REFERENCES

Electroplating Engineering Handbook, Reinhold Publishing Corp., New York (1955), page 573.