

PATENT SPECIFICATION

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- (72) Inventors JOSEPH JOHN PIASCINSKI and
 ERNEST EDWIN DOERSCHUK



(54) A METHOD OF PRODUCING ETCH-RESISTANT STENCILS AND STENCILS PRODUCED THEREBY

(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 to a method for making an etch-resistant stencil on a metal work piece, particularly a metal sheet. The novel method may be used, for example, in etching an apertured mask for use in a color television picture tube.

The preparation of apertured masks by photoexposure and etching has been described previously; for example, in United States Patents Nos. 2,750,524, 3,199,430, 3,313,225 and 3,751,250. In a typical process, a thin metal sheet, such as of a cold-rolled steel or a copper-nickel alloy, is coated on both major surface thereof with a light-sensitive resist. The coatings are exposed to light images as by contact-printing exposure to render the exposed portions thereof less soluble in a particular solvent. The exposed coatings are developed to remove the more-soluble unexposed portions thereof, and then baked to render the retained, less-soluble, exposed portions etch resistant. Then, the sheet with the etch-resistant stencil thereon is selectively etched as desired, after which the stencils are removed from the sheet.

In prior methods, the light-sensitive resist is usually comprised of fish glue and an alkali-dichromate photosensitizer therefor. The resist is applied from an aqueous coating composition to the metal surface and then dried. In some prior methods, casein has been substituted for fish glue. Where casein has been substituted, the liquid coating composition has a pH of more than 7.0, usually about 9.0 to 10.0, in order to render the casein sufficiently soluble to deposit an adequate

amount of material to produce an etch-resistant stencil. Such high pH values reduce the photosensitivity of the resist and therefore require excessively long exposures for producing the stencil.

According to the present invention there is provided a method for producing an etch-resistant stencil upon a surface comprising applying to said surface a coating of a light-sensitive resist composition comprising an alkali metal or ammonium caseinate, an alkali metal or ammonium dichromate photosensitizer for said caseinate, and water and having a pH in the range from 5.8 to 7.0, drying said coating, exposing said coating to a light image, developing said exposed coating to remove unexposed portions thereof, and then baking said developed coating to render the remaining portions thereof etch-resistant. The coating composition may include also sodium borate (borax) to improve the solubility of the alkali metal or ammonium caseinate in water and to improve the developing properties of the coating.

A dichromate-sensitized alkali metal or ammonium caseinate layer produced from a liquid composition having a pH in the range of 5.8 to 7.0 exhibits higher photosensitivity and requires relatively short exposure times. The exposed layers may be developed with normal techniques to produce stencils with relatively high resolution. After the article is etched, the baked stencil may be removed easily with a caustic solution with little or no residue remaining.

In the drawing:

Figure 1 is a plan view of a metal sheet after etching according to the method of the invention, and

Figures 2 to 6 are sectional views through one portion of a metal sheet illustrating the steps of one embodiment of the method of the invention.

Figure 1 shows a plan view of an etched apertured mask blank 21 as it emerges from the etching machine. The mask blank 21

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(which is to be used in a color-television picture tube) is in a metal sheet 23 comprising a succession of such mask blanks 21a, 21 and 21b which are etched through at the margins 25 thereof except at convenient points (not indicated) sufficient to hold the mask blank 21 in place in the sheet 23. The mask blank 21 is comprised of an apertured central portion 27 defined by the broken line 28; and a skirt or peripheral portion 29 which is not apertured, although in some embodiments it may be etched partly through. This application is particularly concerned with the etch-resistant stencil used for etching the apertures in the apertured central portion 27. The apertures may be round and arranged in a hexagonal, diamond-shaped or other array. Or, the apertures may be rectangular slits arranged in vertical rows; for example, 6-mil by 30-mil slits on 30-mil centers. The apertures may be of other shapes and arrangements. In any of the embodiments, the aperture width may be uniform across the mask or may be graded in width or diameter from the center to the edge of the array as is known in the art.

The mask blank 21 is etched into a regular carbon or a low-carbon cold-rolled-steel sheet about 4 to 10 mils in thickness. The etching may also be conducted in sheets of other materials, such as invar alloy, or a copper-nickel alloy. The sheet 23 is passed through the various operations including cleaning the sheet, producing etch-resistant stencils on the sheet, etching the sheet to produce the apertures and to define the mask blanks, and then stripping the stencils from the sheet. Subsequently, the mask blanks 21 are torn from the sheet 23. The mask blanks 21 are then heat treated (annealed), roller leveled, formed on a press, and then blackened as is known in the art, to produce masks suitable for assembly into a color-television picture tube.

Figures 2 through 6 show a sequence of steps that may be used in making a round aperture in the central portion 27 of a hexagonal array of apertures in a 6-mil thick strip of low-carbon cold-rolled steel, as shown in Figure 1. The sheet 23 is coated on both major surfaces with a coating comprising an alkali metal or ammonium caseinate, an alkali metal or ammonium dichromate photosensitizer for the caseinate and water, and having a pH in the range from 5.8 to 7.0 and preferably in the range from 6.5 to 6.9, conveniently and preferably one of the coating compositions set forth below. The coatings are dried in air producing light-sensitive coatings 31 and 33 of dichromate-sensitized sodium caseinate, as shown in Figure 2. After the coatings have dried, the coated strip is positioned in a chase, such as is shown in U.S. Patent No. 3,751,250 between two light-opaque master patterns; one master pattern

face of the sheet 23, and the other master pattern 37 for the other coating 33 on the other major surface of the sheet 23, as shown in Figure 3. The light-opaque patterns may be of chromium or nickel metal coated on the inner surfaces of glass plates 39 and 41 respectively so that the patterns physically contact the coatings 31 and 33. The one master pattern 35 has a circular shape about 5 mils in outside diameter. The other master pattern 37 has a circular shape about 16 mils in diameter. Center lines of the one and the other master patterns are coincident, but may be offset from one another if desired.

As shown in Figure 3, the coatings 31 and 33 on the one and the other surfaces of the sheet 23 are now exposed to hardening radiation, as from a carbin-arc source, which radiation passes through the glass plates 39 and 41 and is incident on the coatings 31 and 33. The radiation insolubilizes the coatings 31 and 33 except where the one and the other master patterns 35 and 37 shadow the coatings. When the coatings are suitably exposed, the exposure is stopped, and the master patterns removed.

The coatings are now developed by flushing with water or other aqueous solvent to remove the unexposed, more-soluble, shadowed portions of the coatings 31 and 33. As shown in Figure 4, after development, the sheet 23 carries on its one surface a stencil comprising a coating 31 having a first circular opening 43 therein and, on its other major surface, a stencil comprising a coating 33 having a second circular opening 45 therein. The stencil coatings 31 and 33 with the openings 43 and 45 therein are now baked in air at about 275 to 325°C to develop etch resistance in the coatings.

The sheet 23 with the etch-resistant coatings thereon is now etched from both sides thereof in a single step to produce the desired aperture. Figures 5 and 6 show the stencil-coated sheet 23 at an early stage (Figure 5) when the etchant has dissolved a small amount of the surfaces of the sheet 23 in the uncoated areas thereof, and then at the end of etching (Figure 6). The etching is conducted in the usual manner employing a ferric-chloride hydrochloric-acid liquid etchant. Controlled amounts of chlorine gas are fed into the etchant to maintain its etching strength.

After the etching has been completed, the coated sheet 23 is washed with water to remove any residual etchant. Then, the etch-resistant coatings 31 and 33 on the one and the other surfaces if the sheet 23 are removed from the strip, by spraying thereon an aqueous solution of sodium hydroxide maintained at temperatures of about 50 to 80°C. After removing the stencil coatings, the sheet is washed in water and dried.

The following compositions in grams may be used in the foregoing method. Composi-

tion 1 is for a laboratory-sized batch, and composition 2 is for a pilot-manufacturing-sized batch. The properties given are for a freshly-mixed batch just prior to coating.

Coating Compositions		
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Sodium Caseinate	110.0	4157
Borax	12.0	441
Ammonium Dichromate	11.0	1030
Dispersing Agent	0.15	6
Bactericide	5.0	123
Water	to desired specific gravity	
Viscosity—cps @ 70°F (21.1°C)	11.5	7.5
Specific Gravity—@ 70°F (21.1°C)	1.032	1.030
pH	6.6	6.8

Mixing Composition 1

1. Dissolve the sodium caseinate in 800 ml. water at about 120°F (49°C) with rapid, high-shear stirring. One suitable sodium caseinate is "Ultra Supreme" (Trade Mark) sodium caseinate, code 03 grade, marketed by Erie Casein Co., Erie, Illinois.

2. Add the dispersing agent, such as "Triton" (Trade Mark) DF-18, to the sodium caseinate solution.

3. Dissolve the borax (hydrated sodium borate $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) in 100 ml. deionized water and heat the solution to about 90°C (194°F). Slowly add the hot borax solution to the sodium caseinate solution.

4. Dissolve the bactericide, such as phenol, in 100 ml. deionized water, and add this mixture to the sodium caseinate solution.

5. Dissolve the ammonium dichromate ($(\text{NH}_4)_2\text{Cr}_2\text{O}_7$) in 200 grams deionized water. Add this dichromate solution to the sodium caseinate solution.

40 Mixing Composition 2

1. Dissolve the borax in 4 liters of hot (about 80°C) deionized water. Add this borax solution to 32 liters of hot (about 80°C) deionized water.

2. Add the dispersing agent, such as "Sulframin" (Trade Mark) 4010, to the solution, and apply high-shear stirring to the solution for about two minutes.

3. Add the sodium caseinate to the borax solution with high shear stirring applied to form the sodium caseinate concentrate.

4. Add the bactericide to the sodium caseinate concentrate.

5. Cool the concentrate to about 20 to 23°C, and then add thereto a solution of the ammonium dichromate dissolved in 5 liters deionized water with stirring at slow speed.

6. Add deionized water to the concentrate to provide the desired specific gravity.

In the coating composition, several factors are important:

1. Any alkali metal or ammonium caseinate may be used. Sodium caseinate is preferred over potassium caseinate and ammonium caseinate because of its greater solubility in water and because of other characteristics. Alkali metal or ammonium caseinates, because of their greater solubility, can be exposed, developed and etched satisfactorily, while caseins, including caseins that are solubilized with alkali, cannot. It is preferred that the caseinate used shall have a high molecular weight, preferably above 250,000, in order to realize maximum photosensitivity in the dry coating. The caseinate comprises about 6 to 12 weight percent of the coating composition.

2. The pH of the coating composition must fall between 5.8 and 7.0, preferably between 6.5 and 6.9. The pH may not be lower than 5.8 or higher than 7.0, or the sensitivity of the coating will be inadequate. The specific gravity of the coating composition determines in part the thickness of the coating. The lower the specific gravity, the thinner the coating. Also, the higher the temperature in the coating chamber, the thinner the coating produced. Specific gravities of 1.028 to 1.032 produce suitable coatings between about 40 and 200 microinches thick.

3. Among sodium, potassium, and ammonium dichromate sensitizers, ammonium dichromate is preferred because it imparts greater sensitivity to the coatings. Also, ammonium dichromate has less of a tendency to crystallize out during the drying operation than the sodium and potassium dichromates. The exposure times of ammonium-dichromate-sensitized alkali-caseinate coatings are equivalent to that of ammonium-dichromate-sensitized fish-glue coatings. The sensitizer comprises about 5 to 30 weight percent of the alkali caseinate present.

4. The dispersing agent, which aids in producing the coating composition, may be selected from a large group of available dispersing agents. Some suitable dispersing agents are "Triton" (Trade Mark) DF-18 marketed by Rohm and Haas, Philadelphia, Pennsylvania, and "Sulframin" (Trade Mark) 4010 marketed by Witco Chemical Company, New York. The bactericide may be omitted if the coating composition is used within three days of the mixing of the alkali caseinate. Some suitable bactericides are phenol and "Dowicide" (Trade Mark) G-ST marketed by Dow Chemical Company, Midland, Michigan.

5. If, after the application of the coating composition, the temperature of the drying tunnel falls below 100°F (37.8°C), "specks" of ammonium dichromate may appear, causing serious mask-scan problems. A drying tunnel temperature of about 125°C (51.7°F) to 160°F (71.1°C) is recommended. The dry-

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ing oven should provide a temperature of about 90°C (194°F) at the top and bottom of the sensitized strip exiting the oven, as measured with a surface pyrometer.

6. The presence of borax (sodium borate decahydrate) in the coating permits faster and more satisfactory processing. Borax is a solubilizer for the alkali caseinates, especially for sodium caseinate. When borax is omitted, the alkali caseinate coating may be poorly developed. To overcome this problem, slower line speeds and higher developing temperatures may be necessary. This causes lower production rate. The optimum developing temperature is 100°F (37.8°C). The borax, when present, comprises about 0.5 to 1.5

of the weight of the alkali caseinate present in the coating composition.

7. Coating thicknesses on the metal sheet are an important parameter in mask manufacturing. If the resist is too thin, under 40 microinches, the etching will be nonuniform and cause mask defects. If the resist is too thick, over 200 microinches, the result will be longer exposure times, mechanical problems of abrasion sticking, pumpdown problems and poor mask uniformity. Typical thickness values of a coating containing sodium caseinate compared to one containing fish glue made from coating compositions having the same specific gravity (1.032) at 24°C (75°F) are:

	Sodium Caseinate	Fish Glue
At top of sheet	40 to 70 microinches	40 microinches
At 8" down from top	80 to 100 microinches	70 microinches
At 16" down from top	100 to 190 microinches	120 microinches

8. The preferred bake-in temperature for imparting etch resistance to a developed sodium caseinate coating must be in the range of 275°C to 325°C. Sodium-caseinate coatings baked at about 305°C (581°F) are most efficiently removed in the caustic wash after etching.

wherein said composition has a pH in the range of 6.5 to 6.9.

4. The method according to Claim 1 or 2, wherein said photosensitizer is ammonium dichromate.

5. The method according to Claim 1 or 2, wherein said caseinate is sodium caseinate.

6. A method for producing an etch-resistant stencil upon a surface, substantially as hereinbefore described.

7. A method of producing an apertured mask blank for a color-television picture tube substantially as described with reference to the drawing.

8. An etch-resistant stencil produced by the method claimed in any one of Claims 1 to 6.

9. An apertured mask blank for a color-television picture tube produced by the method of Claim 7.

WHAT WE CLAIM IS:—

1. A method for producing an etch-resistant stencil upon a surface comprising applying to said surface a coating of a light-sensitive resist composition comprising an alkali metal or ammonium caseinate, an alkali metal or ammonium dichromate photosensitizer for said caseinate, and water and having a pH in the range from 5.8 to 7.0, drying said coating, exposing said coating to a light image, developing said exposed coating to remove unexposed portions thereof, and then baking said developed coating to render the remaining portions thereof etch-resistant.

2. The method according to Claim 1, wherein said composition includes also sodium borate.

3. The method according to Claim 1,

A. A. THORNTON & CO.,
Chartered Patent Agents,
Northumberland House,
303/306 High Holborn,
London, W.C.1.



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ing oven should provide a temperature of about 90°C (194°F) at the top and bottom of the sensitized strip exiting the oven, as measured with a surface pyrometer.
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10 alkali caseinate coating may be poorly developed. To overcome this problem, slower line speeds and higher developing temperatures may be necessary. This causes lower production rate. The optimum developing
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40 of 275°C to 325°C. Sodium-caseinate coatings baked at about 305°C (581°F) are most efficiently removed in the caustic wash after etching.

WHAT WE CLAIM IS:—

45 1. A method for producing an etch-resistant stencil upon a surface comprising applying to said surface a coating of a light-sensitive resist composition comprising an alkali metal or ammonium caseinate, an alkali metal or
50 ammonium dichromate photosensitizer for said caseinate, and water and having a pH in the range from 5.8 to 7.0, drying said coating, exposing said coating to a light image, developing said exposed coating to remove
55 unexposed portions thereof, and then baking said developed coating to render the remaining portions thereof etch-resistant.

2. The method according to Claim 1, wherein said composition includes also sodium borate.

3. The method according to Claim 1,

wherein said composition has a pH in the range of 6.5 to 6.9.

4. The method according to Claim 1 or 2, wherein said photosensitizer is ammonium dichromate.

5. The method according to Claim 1 or 2, wherein said caseinate is sodium caseinate.

6. A method for producing an etch-resistant stencil upon a surface, substantially as hereinbefore described.

7. A method of producing an apertured mask blank for a color-television picture tube substantially as described with reference to the drawing.

8. An etch-resistant stencil produced by the method claimed in any one of Claims 1 to 6.

9. An apertured mask blank for a color-television picture tube produced by the method of Claim 7.

A. A. THORNTON & CO.,
Chartered Patent Agents,
Northumberland House,
303/306 High Holborn,
London, W.C.1.