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PHOTOGRAPHIC PRODUCT CONTAINING A STRIPPABLE MASK

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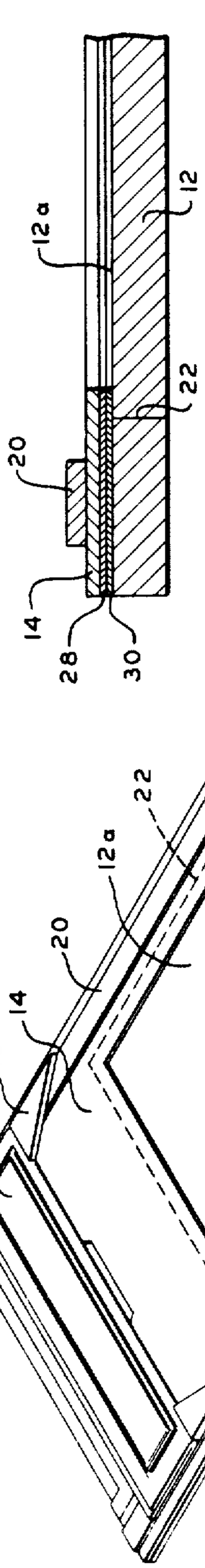

FIG. 2

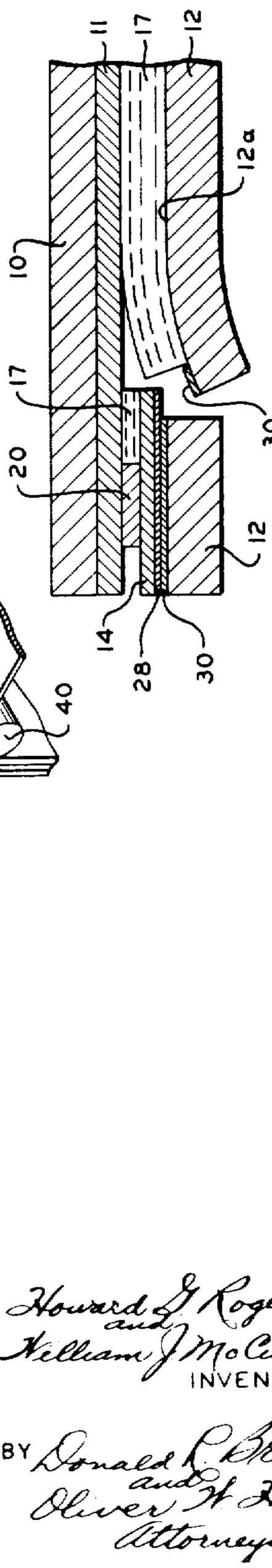

FIG. 3

FIG. 1

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PHOTOGRAPHIC PRODUCT CONTAINING A STRIPPABLE MASK

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5 Claims. (Cl. 95—88)

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This invention relates to photography and more particularly to improvements in photographic products of the type adaptable for the production therewith of a positive image under the selective control of the development of a negative image.

A principal object of the present invention is to provide means for framing the positive image which are an improvement over the means shown in the copending application of Edwin H. Land, Serial No. 641,809, filed January 17, 1946 (now Patent No. 2,612,450, issued September 30, 1952).

Another object of the invention is to provide such framing means in the form of a mask which is capable of being readily separated from the image-carrying layer and of confining excess spread liquid between the frame and the photosensitive layer containing the developed negative image.

Still other objects of the invention are to provide such a framing means that is cheap to manufacture, that can be applied to the image-carrying layer in a simple manner, and that can be rolled up without separating from this layer.

These and other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the product possessing the features, properties and the relation of components which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawing wherein:

Figure 1 is an isometric diagrammatic view of one preferred form of the invention during the use thereof, with parts cut away for clarity of illustration;

Fig. 2 is a diagrammatic exaggerated enlarged sectional view taken along the line 2—2 of Fig. 1; and

Fig. 3 is a diagrammatic exaggerated enlarged sectional view similar to Fig. 2 wherein the operation of removing the processed positive image is shown.

In general, the present invention relates to improved framing means for a positive image-carrying layer adapted to be brought into superposed relation with an exposed silver halide photosensitive layer and processed by spreading therebetween a viscous liquid capable of developing a latent negative image in the photosensitive

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layer and forming a positive image thereof on the surface of the image-carrying layer. In one preferred form of the invention, this framing means comprises a thin paper mask or frame which has a cut out portion defining an image area on the surface of the image-carrying layer. This frame is temporarily bonded to the surface of the image-carrying layer during the manufacture thereof. This bond is preferably created by the use of a double layer of incompatible plastics between the thin paper mask and the image-carrying layer, the two plastics having a greater affinity for their adjacent sheets than they have for each other. Their affinity for each other, however, is sufficient to hold the mask on the image-carrying layer during handling, storage and use thereof. In one preferred form of the invention the frame is thinner than the desired thickness of the layer of spread liquid and additional spacer means may be provided on top of the frame for predeterminedly separating the image-carrying and photosensitive layers.

The product of the present invention also preferably includes a container releasably holding the processing liquid and a trap for trapping excess spread liquid. The container and trap are preferably assembled as a part of the image-carrying layer, being placed on top of the frame. Thus the liquid is released, spread and trapped between the photosensitive layer on the one hand and the frame and image area of the image-carrying layer on the other.

Referring now to Fig. 1 there is shown an isometric, diagrammatic view of one preferred form of the invention with portions thereof cut away for clarity of illustration. In this figure, 10 represents a photosensitive layer having its photosensitive surface extending upwardly. An image-carrying layer 12 is shown with a positive image area 12*a* on its upper surface. This area 12*a* is defined by a cut-away portion of a mask 14 secured to the surface of the image-carrying layer. Placed on top of the framing mask 14 is a container 16 having therein a processing liquid 17. This container extends transversely of the image-carrying layer and is capable of releasing its contained liquid for spreading across area 12*a*. Adjacent the opposite edge of area 12*a* is a trap comprising a pair of trapping members 18. Extending longitudinally of the image-carrying layer along the margins thereof is a pair of spacer strips 20 which, together with marginal portions of the mask 14, predeterminedly separate the photosensitive and image-carrying layers. In a preferred form of the invention, the image-car-

rying layer 12 is provided with a plurality of perforations 22 to permit tearing out of the image area portion 12*a*, and a hole 24 may also be provided for assisting in commencing such tearing. As can be seen the hole 24 is preferably positioned under the container 16 and a corresponding hole 26 is provided in the mask 14, this latter hole being somewhat larger than hole 24.

Referring now to Fig. 2 which is an exaggerated, diagrammatic, enlarged sectional view of the image-carrying layer of Fig. 1 taken along the line 2—2, there are shown in more detail certain aspects of the present invention. In Fig. 2, like numbers refer to like elements in the other figures. As can be seen from an examination of Fig. 2, there are two layers 28 and 30 between the mask 14 and the image-carrying layer 12. Layer 28 is preferably a plastic such as polyvinyl alcohol, while layer 30 is preferably a plastic such as ethyl cellulose. These two incompatible plastic layers adhere more strongly to their adjacent paper layers than they adhere to each other, although their adherence to each other is sufficient to hold the mask smoothly on the surface of the image-carrying layer during the manufacture, storage and use of the product.

In a preferred form of the invention the photosensitive layer 10 comprises a paper base upon which is coated a layer 11 (shown in Fig. 3) of a silver halide emulsion and preferably a gelatino silver iodo-bromide emulsion. The image-carrying layer 12 preferably comprises a sheet of baryta paper which has been treated as set forth in the following nonlimiting example:

Example 1

A sheet of single-weight baryta paper is run through a bath containing by weight 11 grams of cadmium acetate, .37 gram of lead acetate and 11 grams of zinc nitrate per 100 cc. of water, the sheet being in contact with the bath for about 10 seconds.

Solution A is prepared by adding 60 grams of cadmium acetate, 2 grams of lead acetate and 60 grams of zinc nitrate to 200 cc. of water. Solution B is prepared by adding 28 grams of sodium sulfide and 300 grams of silica aerogel to 2800 cc. of water. Solution C is prepared by adding 160 cc. of solution A to 500 cc. of solution B and thoroughly mixing. The resulting mixture is then applied to the surface of the previously coated baryta paper by dipping the sheet into a bath of the mix and removing the excess mix from the sheet, as it leaves the bath, by means of a soft rubber buffing roll which rotates in a direction opposite to the direction of travel of the sheet. Thereafter the sheet is coated with a .05% water solution of gelatin to provide a surface to which the mask adheres well. Alternatively, the sheet may be coated with a solution containing about .5 gram of cellulose acetate in 100 cc. of a mixture of 2 parts of ethyl acetate and 1 part of methanol.

The mask 14 preferably comprises .0017 inch thick tissue paper on which layers 28 and 30 are coated as set forth in the following non-limiting example:

Example 2

Layer 28 is applied by passing the sheet through a water solution of the plastic, such as a 10% water solution of polyvinyl alcohol and removing the excess by means of a doctor blade and roller, the resulting coating being thick enough to give a shiny smooth surface to the mask. After drying the polyvinyl alcohol coat, layer 30 is similarly applied by use of a solution containing 80 grams of ethyl cellulose, 13 cc. of diethyl phthalate, 320 cc. of toluene and 80 cc. of denatured alcohol. In a preferred form of the invention, about 3.24 cc. per square foot of polyvinyl alcohol solution and about 7.54 cc. per square foot of ethyl cellulose solution are applied to the tissue paper. The ethyl cellulose coating, together with the polyvinyl alcohol coating, increases the thickness of the tissue paper to about .0025 to .003 inch. Other organic solvents such, for example, as isopropyl acetate may be used.

The coated tissue paper, after drying, is next cut to the shape shown in Fig. 1, the image area portion and the hole 26 being stamped out by a suitable die. Thereafter the mask is bonded to the previously prepared baryta paper, the ethyl cellulose coating of the mask being next to the baryta surface. This bonding may be accomplished, for example, by passing the two sheets between a pair of 4-inch steel rolls under an 18 pound load and having surface temperatures of between 250° and 300° F. With such temperatures and pressures the paper speed may be about 9 inches per minute.

In still another method of preparing and adhering the mask, the steps set forth in the following nonlimiting example are followed:

Example 3

The mask, comprising a .0015 inch thick calendered condenser tissue paper is coated in a polyvinyl alcohol bath of the type set forth in Example 2. Then an ethyl cellulose coating is applied from a bath containing 500 cc. of isopropyl alcohol, 60 grams of ethyl cellulose and 12 grams of triphenyl phosphate. After the mask has been cut to shape it is secured to the image-carrying layer by placing the two sheets between platens, the platen adjacent the mask being heated to about 320° F. The platens are then squeezed together under a one ton pressure for less than ½ second.

The edge spacer strips 20 are then applied to the mask prepared in accordance with Example 1 or 2, these spacer strips 20 preferably comprising kraft paper, or cellophane, about .001 to .0015 inch thick and having a suitable pressure sensitive adhesive such as a blend of unvulcanized rubber and a tack-producing resin. The strips preferably raise the total thickness of strips and mask, at the marginal portions of the image-carrying layer, to about .004 inch. The containers are formed of a paper-backed metal foil having an alkali-inert inner coating of polyvinyl butyral and a strip of ethyl cellulose along the sealed edge as described in the copending application of Edwin H. Land, Serial No. 652,612, filed March 7, 1946 (now Patent No. 2,634,886, issued April 14, 1953).

The transversely tapered trapping members 18 are preferably made of a semi-crepe paper tape about .15 inch thick secured to the mask by means of a suitable adhesive.

The container is preferably secured to the image-carrying layer by means of a strip of an adhesive, for example, polyvinyl butyral, applied to the bottom of the leading edge thereof. The leading edge is then flattened and sealed to the image-carrying layer by pressing downwardly with a heated narrow iron, for example.

In one preferred form of the invention, the photosensitive layer 10 comprises a suitable paper base upon which is coated a "fast" gelatino silver iodobromide photosensitive emulsion. For

use with such an emulsion and an image-carrying layer as prepared in Example 1, a preferred liquid composition includes the following ingredients in the relative proportions given below:

Example 4

	Grams
Water	1860
Sodium carboxymethyl cellulose	93
Sodium sulfite	78
Sodium hydroxide	74.6
Sodium thiosulfate	14.5
Citric acid	38.5
Hydroquinone	52.0
Chlorobenzotriazole	1.5

In the use of the novel product described above, the photosensitive emulsion 11 of the photosensitive layer 10 is suitably exposed in the camera, the two layers 10—12 constituting the preferred product of the invention being suitably disposed within the camera so that they may be advanced past a processing means in the camera with the exposed area of the photosensitive layer in coincident superposed relation to the positive image area 12*a* of the image-carrying layer. In a preferred type of camera the processing means comprises a pair of pressure rolls indicated at 40 in Fig. 1. As the two layers 10—12 pass between these rolls, the container 16 is positioned therebetween and the liquid 17 is forced therefrom by the increased hydraulic pressure created by the rolls 40. Continued movement of the two layers causes the released liquid to be spread in a uniform thin layer between the two outer layers 10—12, the thickness of the spread layer of liquid being determined by the thickness of the spacer strips 20 and mask 14 (including coatings 28 and 30). This layer of spread processing liquid 17 is shown in Fig. 3, it being seen that the thickness of the spread layer of liquid 17 adjacent area 12*a* is about equal to the total thickness of the spacer 20 and the composite mask 14. Liquid spread beyond the end of area 12*a* is trapped due to the separation of the pressure rolls, with consequent decrease in hydraulic pressure on the liquid, by the trapping members 18. Motion of the product is then preferably stopped and the composite lamination is maintained in the dark for about 1 minute. A door provided in the camera may then be opened and the positive image area 12*a* can be removed from the lamination by inserting a fingernail through hole 24 (shown in Fig. 1) and tearing the image-carrying layer along perforations 22. Since the mask 14 is cut away at 26 in the neighborhood of hole 24, the stripping of the image-carrying layer from the mask at the same time is facilitated. As can be seen from Fig. 3, that portion of the ethyl cellulose layer 30 on the image area 12*a* is stripped away from its adjacent polyvinyl alcohol layer 28. The portion of ethyl cellulose 30 adhering to image area 12*a* thus forms a border for the positive image formed in or under layer 17 of the processing liquid. It should also be noted that the portions of liquid 17 spread between the mask 14 and the photosensitive layer 10 are trapped between these layers when image area 12*a* is removed.

It should be pointed out, in connection with the diagrammatic representation of Fig 3, that the layer of spread liquid quickly dries out, during and after the processing to form a film of about .0002 inch thick. Thus, when the time occurs for the image area 12*a* to be torn out the film 17 formed by the spread liquid is considerably thinner than shown, although it is usually not completely dry within a minute of spreading. The latter portion of the drying is accomplished by evaporation of the water from the surface thereof exposed as a result of removal of area 12*a*.

When the product, prepared as set forth in accordance with Examples 1 and 2, is processed by spreading the liquid between the photosensitive and image-carrying layers, the developer develops exposed silver halide grains and the sodium thiosulfate, concurrently with the development, forms soluble silver complexes with unexposed silver halide grains. These complexes migrate to the image-carrying layer where they are converted to a positive image comprising silver, the sulfide slowly released from the surface of the image-carrying layer forming silver sulfide specks around which large silver grains are formed. The cadmium acetate and zinc nitrate are slowly released to lower the alkalinity of the liquid to a point where oxidation of the excess developer does not occur. Meanwhile, the sodium carboxymethyl cellulose is forming a dimensionally stable film which adheres to the surface of the image-carrying layer. The above-described reactions (with the exception of the lowering of the pH) are completed in about 1 minute and the positive image area is then separated from the lamination comprising the photosensitive and image-carrying layers. As explained above, this separation is preferably accomplished by opening the door, inserting a fingernail through hole 24 and tearing the image-carrying layer along lines 22, thus revealing the final stable positive image.

While preferred forms of the invention have been described above, numerous other modifications thereof are possible without departing from the scope thereof. For example, the mask 14 (plus layers 28 and 30) may be made thicker than the .0025 to .003 inch mentioned above. In this case, the spacing strips may be eliminated since the mask will give sufficient thickness to allow for proper spread of the liquid.

With either of the above modifications of the invention, the top surface of the mask (and the spacing strip 20) may be coated with a water-soluble adhesive to increase the adhesion of the mask to the emulsion layer 11. Such an adhesive may comprise gum arabic coated from a water solution thereof on to that side of the mask opposite to coatings 28 and 30.

In addition to the above modifications, the containers and traps of the present invention may be secured to the photosensitive rather than the image-carrying layer. Also, the spacing strips 20 may be eliminated in several other preferred forms of the invention. In one of these forms, the mask thickness (including layers 28 and 30) is about the thickness desired for the layer of spread liquid. In another preferred form, the mask thickness is as described previously and one of the pressure rolls 40 of the camera has thickened shoulder portions engaging the margins of the lamination formed by the pressure rolls. Such shoulders may have a radius greater, by about .001 to .002 inch, than the other part of the roll, depending upon the thickness of the mask and the desired thickness of spread liquid. Equally, numerous other processing liquids may be employed with numerous types of photosensitive materials and image-carrying layers of the type described, for example, in the copending application of Edwin H. Land, Serial No. 729,578, filed February 19, 1947.

When a "slow" silver bromide or silver chloride emulsion is used, the image-carrying layer 12 may comprise a sheet of plain baryta paper to which the mask of Example 2 or 3 is laminated as described therein. With such a photosensitive layer and image-carrying layer, the liquid of Example 4 may be used, preferably without the chlorobenzotriazole.

The liquid in the container may carry only a part of the processing reagents and others may be included in solid form in the sheets. For example, the developer may be included in the photosensitive emulsion.

Since certain changes may be made in the above product without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. An elongated composite sheetlike photographic product comprising an elongated image-receiving layer for use in a photographic transfer process as image-receptive material for receiving a transfer image and having at least one image area portion on one surface thereof adapted to receive a transfer image, an elongated mask sheet, provided with at least one aperture, superposed on and secured to said surface of said image-receiving layer and overlying border portions of each said image area portion in a position to provide the border for a transfer print formed on said image area portion, each said aperture being slightly smaller in area than said image area portion and being registered with said image area portion so that the edges of the aperture are positioned to lie within the edges of said image area portion, and two layers of adhesive interposed between said mask sheet and said surface of said image-receiving layer and bonding said mask sheet and said image-receiving layer together and providing a strippable adhesive bond, a first of said adhesive layers covering the surface of said mask sheet which is closest to said image-receiving layer when said image-receiving layer and said mask sheets are in superposed relation, the second of said layers of adhesive covering the surface of said first layer of adhesive which is furthest removed from said mask sheet, said two layers of adhesive extending substantially coextensively of said surface of said mask sheet and of each other and said two layers of adhesive having a readily cleavable line of demarcation therebetween, said first layer of adhesive having a greater affinity for said mask sheet than it has for said second layer of adhesive and the second layer of adhesive having a greater affinity for said image-receiving layer than it has for said first-named adhesive layer.

2. A photographic product comprising an elongated flexible image-receiving sheet material for use in a photographic transfer process as image-receptive material for receiving a transfer image, an elongated flexible sheet in superposed relation to a surface of said image-receiving sheet and providing a mask over portions of said image-receiving sheet, said mask having at least one aperture therein which defines a picture area on said image-receiving sheet when said mask is superposed thereon, and two layers of adhesive interposed between said mask and said surface of said image-receiving sheet and bonding said mask and image-receiving sheet together, one layer of adhesive comprising a coating of polyvinyl alcohol covering the surface of said mask which is closest to the image-receiving sheet when the image-receiving sheet and the mask are in superposed relation and a second layer of adhesive comprising a coating of ethyl cellulose covering the surface of said layer of polyvinyl alcohol which is furthest removed from said mask, said layer of ethyl cellulose being adhered to said surface of said image-receiving sheet.

3. The product of claim 1 wherein said two bonding layers comprise incompatible materials.

4. The product of claim 1 wherein one of said two bonding layers comprises a water-soluble plastic and the other bonding layer comprises a water-insoluble plastic, at least one of said plastics being thermoplastic.

5. In a photographic product of the character defined in claim 2, an image-receiving sheet which comprises baryta paper and a mask which comprises paper.

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Certificate of Correction

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Howard G. Rogers et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 3, line 56, for ".05%" read *0.5%*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 18th day of May, A. D. 1954.

[SEAL]

ARTHUR W. CROCKER,
Assistant Commissioner of Patents.

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