Sept. 29, 1953 W. J. McCUNE, JR 2,653,530

COMPOSITE PHOTOGRAPHIC PRINT-RECEIVING SHEET

Filed Nov. 13, 1951

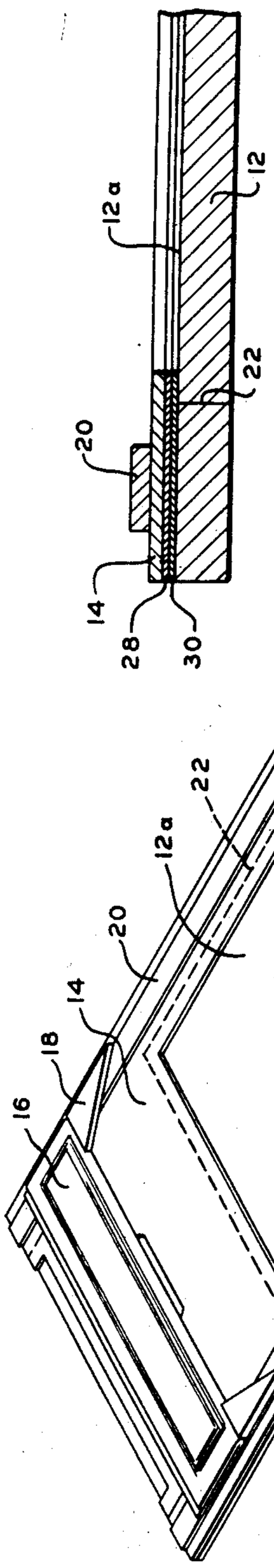

FIG. 2

FIG. 1

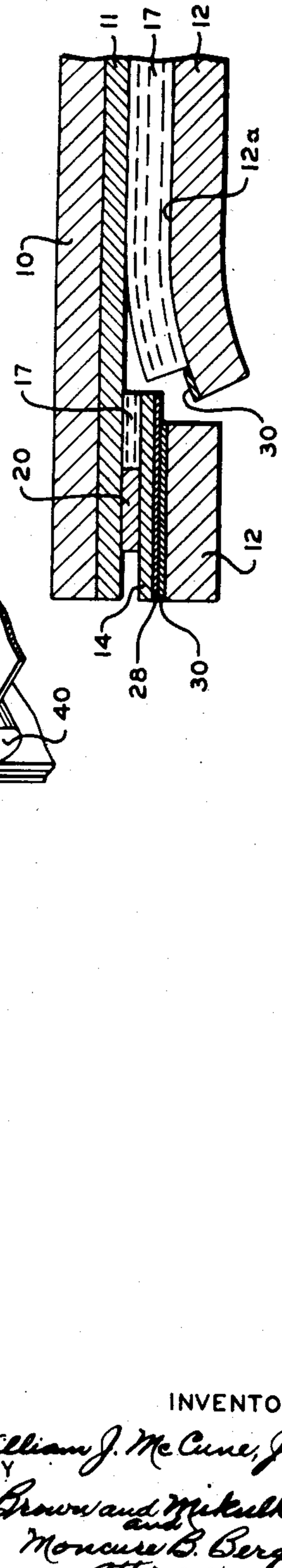

FIG. 3

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COMPOSITE PHOTOGRAPHIC PRINT-RECEIVING SHEET

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6 Claims. (Cl. 95—88)

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This invention relates to photographic products and more particularly to improved print-receiving elements adapted to have prints formed thereon by transfer.

This application is a continuation-in-part of my application Serial No. 116,385, filed September 17, 1949, for Composite Photographic Print-Receiving Sheet, now abandoned.

One object of the present invention is to provide a novel composite print-receiving sheet for use in the performance of transfer processes, said sheet giving a finished framed print at the completion of the process.

Another object of the present invention is to provide a novel composite print-receiving sheet of the above type which includes, as part of the composite structure thereof, all of the reagents, including the liquid, for performing the transfer process.

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 an improved composite print-receiving sheet for having transfer prints formed thereon. In one preferred form the composite sheet comprises a suitable image-carrying layer on which there is mounted a framing means in the form of a thin paper mask having an aperture therein for defining an image-receiving area on the image-carrying layer. A section of the image-carrying layer, including this image-receiving area, is detachable from the remainder of the image-receiving layer and is also strippable from the mask.

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The mask serves to confine the image formed on the image-carrying layer to the image-receiving area so that when the detachable section is removed it provides a finished print in which the image is bounded by a decorative border.

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

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-carrying 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 iodobromide 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 0.5% 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 nonlimiting 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.

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 in the preceding examples the mask 14 has been shown as strippably secured to the image-carrying layer 12 by the use of two layers of incompatible plastics which provide a strippable bond, it will be appreciated that other bonding means or structures may be employed. For example, the mask may be coated on one surface with a layer of a single material possessing adhesive properties and having a greater affinity for the material of the mask than for the material of the receiving sheet. In this regard, a water-soap solution may be utilized, for example a 5 to 40% water-soap solution made of Ivory soap. Alternatively, the mask may be coated with a thin layer of a fatty substance or soap which is insoluble in water and then may be covered after drying with a layer of hardened gelatin or collodion. In regard to soap, or soap and hardened gelatin, reference is made to "Photography, Theory and Practice" by L. P. Clerc, second edition, Pitman Publishing Corp., New York, New York, page 159, footnote 3, and also to the copending application of Edwin H. Land, Serial No. 708,007, filed November 6, 1946, for Photographic Product and Process (now Patent No. 2,647,055, issued July 28, 1953) and Patent No. 2,563,342, issued to Edwin H. Land on August 7, 1951, for Photographic Product and Process. Additionally, the mask surface to be adhered to the image-carrying layer may be coated with gelatin to which has been added an appropriate amount of glycerin whereby to suitably control the bond strength of the gelatin, as is well understood by the art. In lieu of these practices, the mask may be coated with a suitable pressure-bondable rubber cement. These and other procedures for forming a strippable bond between the mask and the image-carrying layer are employable in carrying out the invention. A mask coated with any of the just-described stripping layers is intended to be adhered to the image-carrying layer in the manner described in Example 2 hereof by passing the finished mask and the receiving sheet layer between pressure rolls.

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 onto 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. As a new product, a composite print-receiving sheet comprising, in combination, an image-receiving layer, a masking layer superposed on and secured to said image-receiving layer and having an aperture therein which leaves an area of said image-receiving layer uncovered for receiving an image by transfer, said image-receiving layer being strippable from said masking layer and being provided with perforations which extend at least partially therethrough and which are located in surrounding relation to said uncovered area at positions outside of the marginal edges of said uncovered area whereby to provide a detachable section which includes the uncovered area and a border surrounding said area, said masking layer overlying said perforations to cover the same, and a rupturable container mounted on said masking layer adjacent one edge of said uncovered area, said container carrying a processing liquid which is spreadable from said container over said uncovered area, the liquid in the container being sufficient in amount to cover said uncovered area, said sheet containing photographic reagents, including a silver halide developer, so located that the release of the liquid from the container over the uncovered area of the image-receiving layer places said reagents in condition to form a transfer print of a latent image contained in a silver halide emulsion superposed on said uncovered area.

2. As a new product, a composite print-receiving sheet comprising, in combination, an image-receiving layer, a masking layer superposed on and secured to said image-receiving layer and having an aperture therein which leaves an area of said image-receiving layer uncovered for receiving an image by transfer, said image-receiving layer being strippable from said masking layer and being provided with perforations which extend at least partially therethrough and which are located in surrounding relation to said uncovered area at positions outside of the marginal edges of said uncovered area whereby to provide a detachable section which includes the uncovered area and a border surrounding said area, said image-receiving layer having an aperture adjacent the perforations to facilitate manual detachment of said detachable section along the perforations, said masking layer overlying said perforations to cover the same, and a rupturable container mounted on said masking layer adjacent one edge of said uncovered area, said container carrying a processing liquid which is spreadable from said container over said uncovered area, the liquid in the container being sufficient in amount to cover said uncovered area, said sheet containing photographic reagents, including a silver halide developer, so located that the release of the liquid from the container over the uncovered area of the image-receiving layer places said reagents in condition to form a transfer print of a latent image contained in a silver halide emulsion superposed on said uncovered area.

3. As a new product, a composite print-receiving sheet comprising, in combination, an image-receiving layer, a masking layer superposed on and secured to said image-receiving layer and having an aperture therein which leaves an area of said image-receiving layer uncovered for receiving an image by transfer, said image-receiving layer being strippable from said masking layer and being provided with perforations which extend at least partially therethrough and which are located in surrounding relation to said uncovered area at positions outside of the marginal edges of said uncovered area whereby to provide a detachable section which includes the uncovered area and a border surrounding said area, said masking layer overlying said perforations to cover the same, and a rupturable container mounted on said masking layer adjacent one edge of said uncovered area, said container carrying a processing liquid which is spreadable from said container over said uncovered area, and trapping means mounted on the masking layer adjacent the edge of said uncovered area opposite the container, said trapping means being adapted to confine liquid from the container which spreads beyond said uncovered area, the liquid in the container being sufficient in amount to cover said uncovered area, said sheet containing photographic reagents, including a silver halide developer, so located that the release of the liquid from the container over the uncovered area of the image-receiving layer places said reagents in condition to form a transfer print of a latent image contained in a silver halide emulsion superposed on said uncovered area.

4. The product of claim 1 wherein the reagents include a silver halide solvent in addition to the silver halide developer.

5. The product of claim 4 wherein the silver

halide developer and the silver halide solvent are contained in solution in the liquid in the container.

6. A photographic product comprising an elongated, flexible, composite image-receiving sheet material for use in a photographic transfer process as image-receptive material for receiving a transfer image and comprising an image-receiving layer, a masking layer superposed on and secured to a surface of said image-receiving layer and providing a mask over portions of said image-receiving layer, said masking layer having at least one aperture therein which defines a picture area by leaving an area on said image-receiving layer uncovered for receiving an image by transfer, said image-receiving layer being strippable from said masking layer and being provided with perforations which extend at least partially therethrough and which are located in adjacent relation to each said uncovered area at positions outside of marginal edges of said uncovered area whereby to provide a detachable

section which includes said uncovered area and a border surrounding the area, said masking layer overlying said perforations to cover the same, and a rupturable container mounted on said masking layer adjacent one edge of each said uncovered area, said container carrying a processing liquid which is spreadable from said container over said uncovered area, the liquid in the container being sufficient in amount to cover said uncovered area, said product containing photographic reagents, including a silver halide developer, so located that the release of the liquid from the container over an uncovered area of the image-receiving layer places said reagents in condition to form a transfer print of a latent image contained in a silver halide emulsion superposed on said uncovered area.

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No references cited.