

[54] **PHOTOGRAPHIC TRANSFER MATERIALS**

3,210,187 10/1965 Thommes 96/83
3,314,793 4/1967 Kennard et al. 96/83

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[30] **Foreign Application Priority Data**

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[58] **Field of Search** **96/83, 87 R, 67**

[57] **ABSTRACT**

Photographic transfer materials are described incorporating adhesive substratum layers which are used in order to transfer the photosensitive layer from the transfer layer to another surface. An intermediate substratum layer comprising a polyamide soluble in a mixture of an alcohol and water is used. The photosensitive layer is preferably based on a water-soluble colloid or polymeric material.

[56] **References Cited**

UNITED STATES PATENTS

2,710,820 6/1955 Hilborn et al. 96/83

8 Claims, No Drawings

PHOTOGRAPHIC TRANSFER MATERIALS

This invention relates to photographic resist transfer materials of the kind incorporating adhesive substratum layers, which are used in order to transfer the photosensitive layer from the transfer layer to another surface, either prior to or after formation of an image.

In the preparation of screen printing stencils, for instance, it is common practice to employ photographic transfer materials to produce the master stencil image. Such a transfer material consists for example of a sheet of film support coated with a thin substratum of rubber, on top of which there is a photosensitive colloid layer. In use, the material is exposed to light through a master positive transparency in contact with the film support side of the transfer material and it is then processed to form a negative stencil image in the photosensitive colloid layer. The negative stencil image is held by the substratum layer, which itself remains adhered to the film support. While the colloid layer incorporating the stencil image is still wet, it is pressed against a stretched fabric such as nylon or silk or metal gauze and then allowed to dry and thus harden. The primary film support is then stripped away, leaving the hardened colloid stencil adhering to the screen fabric, thus providing a printing screen from which multiple prints can be taken. When the primary film support is removed from the dried stencil, it usually carries with it a layer of substratum in the open areas of the stencil, while in the solid areas the substratum remains on the stencil.

This type of material and the method of producing screens is described in detail in British Pat. Specification No. 665649. Commercial products of this type are known, such materials relying on a photosensitized gelatine layer for forming the stencil image and the substratum layer containing a natural or synthetic rubber. It must be appreciated that the substratum layer has to perform in several modes during the manufacture and use of the material. It must provide adequate dry adhesion for the unprocessed photosensitive layer. The exposed and hardened areas of the photosensitive layer must also be firmly adhered to the film support by the substratum layer during the process of washing and removal of the unexposed areas of the image. Finally, the substratum layer must allow the dried stencil layer to be released from the film support after it has been adhered to the receiving surface, e.g., a stretched screen fabric.

It has already been mentioned above that when using gelatine as the colloid for the photosensitive layer, it is found that a good substratum layer can be formed of a thin film of natural or synthetic rubber. Both dry and wet adhesion of the gelatine layer are adequate for the production of the stencil image. If, however, attempts are made to substitute other colloids or resins for the photosensitive layer, especially the synthetic types such as polyvinyl alcohol or hydroxy-alkyl cellulose, then it is no longer possible to use rubber for the substratum layer. While the rubber substratum usually gives adequate dry adhesion to the photosensitive layer, it completely fails to provide adequate wet adhesion during the processing of the stencil image. In this respect, great difficulty has been experienced in finding materials to serve as substratum layers and also to meet all the requirements when employing synthetic colloid photosensitive layers. An object of this invention, therefore,

is to provide a material or class of materials which enable all these requirements to be met.

According to the invention, a photographic transfer material consisting of a primary support and an image-forming photosensitive layer comprising a water-soluble colloid or polymer is provided, having an intermediate substratum layer which comprises a polyamide which is soluble in a mixture of an alcohol and water.

Suitable substratum layers are, for example, those based on polyamides which have first been methylolated and then etherified. These are commonly obtained by treatment of a linear polyamide with formaldehyde and alcohols.

In order to obtain good wet adhesion of the photosensitive colloid or polymer layer during the processing of the relief or stencil image, the soluble polyamide substratum layer must be sufficiently hydrophilic in character. This property is indicated by the preferential solubility of the polyamide in a solvent-mixture which contains water, together with an organic solvent. This does not mean that the preferred polyamide is only soluble in a solvent mixture containing water, but at the same time in order for a polyamide to be suitable it should show distinctly good solubility in a solvent system in which water is present. Soluble polyamide resins which are inherently hydrophobic in nature will tolerate very little water in the coating solvent and such polymers used alone are not suitable for the invention.

The relief or stencil-forming photosensitive layer is preferably one based on a water-soluble colloid for polymeric material, for instance, gelatine, polyvinyl alcohol, hydroxyethyl cellulose, polyacrylamide or polyvinyl pyrrolidone.

The photosensitive system can be such that, after imagewise exposure and suitable processing, an insoluble crosslinked image is retained on the support, while the non-image areas are removed by washing in a suitable solvent or solvent mixture, usually water.

One well-known photosensitive system is that consisting of a water-soluble colloid sensitized with a dichromate salt. Exposure to short wavelength light causes the colloid to be insolubilized, the unexposed areas then being removed by washing. In place of a dichromate sensitizer, it is possible to use ferric salts coupled with a peroxide free-radical-producing agent, e.g., as described in British Pat. Specifications Nos. 665649 and 883811. Other photo-crosslinking sensitizers well-known in the art which can be used are the diazo resins and aromatic azides.

The polyamide substratum of the present invention is particularly suitable to use with the photo-polymerization process described in U. S. Pat. application Ser. No. 117138 filed on 19th Feb. 1971 in the joint names of myself and John Arthur Sperry. This process employs a water-soluble colloid as a carrier for an unsaturated monomeric compound. Photo-polymerization of the monomer is effected by the aid of leuco sulphuric esters of indigo and thioindigo dyes and the carrier layer is thereby insolubilized by imagewise exposure to light.

Yet another well-known photo relief system which can be employed with the polyamide substratum is that based on a silver halide gelatine emulsion in which a tanning developer is used to insolubilize the gelatine surrounding the exposed silver halide.

Preferably, the supports on which are applied the polyamide substratum, together with the photosensitive layer, are sheet materials which are flexible and trans-

parent, such as plastics foils or films of cellulose esters, polyesters or copolymers of polyvinyl chloride and acetate. Such transparent films allow image-wise exposure to be effected through the support side of the photographic material. If, however, the photosensitive layer is of limited thickness, for example not more than 10 microns and preferably between 3 and 10 microns, it is possible to use opaque supports such as metal or paper and expose the material from the top side.

It will be appreciated by those experienced in the photomechanical art that, while transfer materials based on polyamide-subbed film supports according to this invention are particularly useful for the production of screen printing stencils, they can also be employed, in modified form if necessary, for the production of images which can optionally be transferred to supports other than screen fabrics, e.g., paper or metal surfaces, to serve as either etching resists or visible indicia or for other purposes. The above details and the examples given below are intended to illustrate rather than delimit the possible applications of materials based on polyamide substratum layers in accordance with the invention.

The transfer materials can, if so desired, alternatively be employed for the production of images in which the photosensitive layer is not transferred from the primary support. While the polyamide substratum provides an anchor layer which allows subsequent release of the photosensitive layer, the adhesion of the layer to the primary support is sometimes sufficient for certain applications where the image is required on the original support.

In the following Examples, amounts are given in parts by weight.

EXAMPLE 1

A sheet of polyester film, e.g. the du Pont product known as "Mylar" (Trademark), was coated with the following solution:

Ultramid IC*	1
Methanol	33
Methylene chloride	33
n-Propanol	33

This coating was applied using a wire-wound doctor bar, the wire diameter being 0.005. After drying the substratum layer, the following photosensitive layer was applied:

Water	15
Gelatine	4
Ferric ammonium oxalate	1
Glycerol lactate	0.5
Irgalite** Blue GLS	0.25

The photosensitive layer was coated to give a dry weight of approximately 20 g/sq.m.

The resultant film was exposed with the support side in contact with a line positive for 4 minutes at 2ft from two 125-watt mercury vapour lamps. After exposure, the gelatine coating was treated in a hardening solution, consisting of "2-volume" hydrogen peroxide. The film was then washed in warm water to remove the unexposed areas of gelatine, while the stencil of hardened gelatine was retained firmly adhering to the substrated film. The stencil was then pressed into contact with a stretched nylon fabric and allowed to dry. When dried, the primary support film was stripped away, leaving the gelatine stencil firmly adhering to the nylon fabric, thus providing a master for screen printing.

EXAMPLE 2

The same procedure was adopted as in Example 1, with the following exceptions:

The substratum layer consisted of the following solution:

Elvamide 8063***	1
Methanol	90
Ethyl cellosolve	10

The photosensitive layer consisted of the following sensitized gelatine solution:

Gelatine, 15% solution	20
Irgalite** Blue GLS	0.5
N,N-Methylenebisacrylamide	0.2
Acrylamide	2.0
Anthrasol****Orange HR	0.2
Diethyleneglycol.	0.5

EXAMPLE 3

A sheet of "Mylar" polyester film was coated with the following substratum:

Elvamide 8063***	1
Methanol	90
Ethyl cellosolve	10

After drying, the following photosensitive emulsion was applied:

Polyvinyl alcohol, 12% solution (88% hydrolysed)	20
Acrylamide	2
N,N-Methylenebisacrylamide	0.2
Anthrasol**** Orange HR	0.5
Diethyleneglycol	0.5

After drying the material, it was exposed in contact with a positive transparency for 1 minute at 2ft. from two 125-watt mercury vapour lamps. The film was then washed in cold water to remove the unexposed portions of the image, leaving an insolubilized stencil firmly adhering to the substrated film. This could then be transferred to a piece of stretched nylon fabric in the manner described in Example 1.

EXAMPLE 4

A sheet of polyester film was coated with the following substratum:

Calaton CA*****	1
Methylene Chloride	60
Methanol	40

When dry, the subbed film was coated with the following sensitized solution:

Polyvinyl alcohol, 12% (88% Hydrolysed)	20
Ammonium dichromate	0.5
Irgalite** Blue GLS	0.2
Water	10

After drying the film was exposed with the support side in contact with a line positive for 1 minute at 2 ft. from a 125-watt mercury vapour lamp. The image was then processed by washing in cold water to remove the unexposed areas of the coating. The resulting stencil was pressed into contact with a piece of stretched polyester fabric and allowed to dry. The primary film support was then peeled away, leaving the stencil adhering to the screen fabric.

* Ultramid IC is an alcohol-soluble polyamide supplied by Badische Anilin & Soda Fabrik AG.

** Irgalite is the Registered Trademark for pigments supplied by Geigy (UK) Ltd.

*** Elvamide 8063 is a soluble polyamide supplied by du Pont (UK) Ltd.

**** Anthrasol is the Registered Trademark of Farbwerke Hoechst AG.

***** Calaton CA is a polyamide material obtainable from I.C.I. Ltd.

I claim:

1. An element useful as a photographic transfer material, which comprises in combination a primary support and an image-forming photosensitive layer composed of a water-soluble colloid or polymer, and an intermediate substratum layer composed of a linear methylolated and etherified polyamide which is soluble in a mixture of an alcohol and water.

2. An element useful as a photographic transfer material defined according to claim 1, wherein the methylolated polyamide ether is one obtained by treating a linear polyamide with formaldehyde and an alcohol.

3. An element useful as a photographic transfer material defined according to claim 1, wherein the water-soluble colloid or polymer is a member selected from the class consisting of gelatine, polyvinyl alcohol, hydroxyethyl cellulose, polyacrylamide and polyvinyl pyrrolidone.

4. An element useful as a photographic transfer ma-

terial defined according to claim 1, wherein the photosensitive layer is a water soluble colloid or polymer which forms an insoluble cross-linked image upon exposure, characterized by solvent-removable non-image areas.

5. An element useful as a photographic transfer material defined according to claim 1, wherein the primary support is a transparent flexible sheet of plastic material.

6. An element useful as a photographic transfer material defined according to claim 1, wherein the primary support is an opaque material.

7. An element useful as a photographic transfer material defined according to claim 6, wherein the photosensitive layer has a thickness of not more than 10 microns.

8. A photographic transfer material defined according to claim 1, wherein the intermediate substratum layer consists essentially of 1 part by weight of the polyamide which is soluble in water and alcohol is a methoxy methylated nylon polymer, 60 parts by weight of methylene chloride, and 40 parts by weight of methanol.

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