

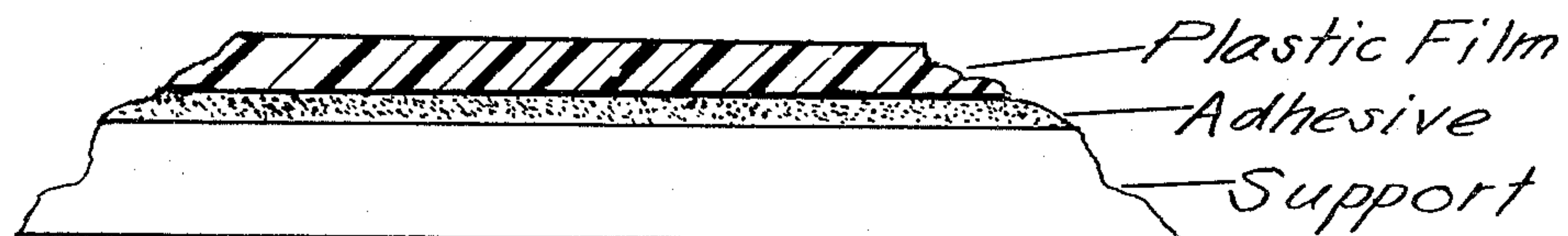
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S. C. SLIFKIN

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DIAZOTYPE DRY STRIP FILM

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INVENTOR  
*Sam Charles Slifkin*  
BY  
*Henry W. Coughlin and*  
*Leola J. Moller*  
ATTORNEYS

## UNITED STATES PATENT OFFICE

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## DIAZOTYPE DRY STRIP FILM

Sam Charles Slifkin, Binghamton, N. Y., assignor  
to General Aniline & Film Corporation, New  
York, N. Y., a corporation of Delaware

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This invention relates to light-sensitive diazotype layers. More particularly, it relates to such layers on a plastic strip film base.

In the photographic and reproduction fields it is often necessary to produce prints which can be transferred to a support which latter cannot itself be readily sensitized for photo reproduction purposes. For example, such a case would exist where it is desired to permanently affix a label notice or trade-mark design onto a metal surface of a machine. It has hitherto been possible to do this only by preparing a stock of designs in advance of their use. Such stock designs have been prepared by printing on metal plates suitable for mechanical or adhesive attachment to the surface of the machine or other surface where it is desired to display the design or by printing on stripping film or other type transfers also capable of being adhesively affixed to the desired surface. All of these known means for affixing or transferring a design to a selected surface are subject to problems of stocking the prepared designs. Any changes which have to be made or additions which have to be incorporated into the design introduce additional problems since new stocks have to be accumulated and the cost of old stocks, on the other hand, has to be absorbed.

It has now been discovered that a stripping film can be prepared containing a diazo photo sensitized layer by means of which the design of a trade-mark label, notice or the like can be conveniently reproduced from a master original. Such reproductions can be made immediately before use, thus the design can be kept up to date as corrections or additions can be made on the master original. If it becomes necessary to make major changes in the design only the master original need be replaced. The said master original can be made on any transparent or semi-transparent material such as tracing cloth, plastic film, transparentized paper, a stencil design or any similar material wherein the design is opaque to ultraviolet and other actinic light and the background is transmissive of such light.

The new strip film is prepared by affixing a plastic film to a non-absorbent or poorly absorbent support by means of a pressure sensitive adhesive. A composite film on support having the form pictured in the accompanying drawing results. This composite is then photo-sensitized

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on the plastic film side by a diazotype sensitizing solution. This is accomplished by the bead dip method of applying diazotype coatings to plastic film surfaces or by spraying or otherwise applying an excess of the sensitizing solution and doctoring off the excess with a doctor blade.

In the preferred bead dip method of coating, the composite strip film is drawn across a vessel containing the diazotype coating solution with the plastic film side of the composite in continuous contact with the meniscus of the coating solution. The coating solution will contain a solvent or plasticizer for the plastic film material. During the period of contact of the plastic film surface with the meniscus of the coating solution, this solvent or plasticizer will act on the film surface to produce a swelling or softening of the film. The film is thereby rendered susceptible to penetration and impregnation with the sensitizing components of the diazotype coating solution and is simultaneously impregnated with such components. The plastic film employed is preferably cellulose acetate although other cellulose ester films such as cellulose butyrate, cellulose propionate or mixtures of such cellulose esters may be used. Other types of plastic film such as cellulose ethers, such as cellulose ethyl ether, vinyl ethers and superpolyamides may be used also.

The particular solvent or plasticizer employed in the coating solution to aid the impregnation or penetration of the film surface by the light-sensitive components will depend upon the film material employed. Examples of typical volatile organic substances which function as swelling agents when used on the commonly known film materials listed above include ethyl alcohol, methyl alcohol, butanol, ethyl lactate, isopropanol, formic and acetic acids, acetone, diacetone alcohol, ethylmethyl ketone and methyl glycol. Softeners or plasticizers which may be used include tricresyl phosphate, tri-phenyl phosphate, tri-acetin and di-chlorhydrin.

The swelling medium or solvent for the plastic film may be employed singly, in combination with a known solvent such as water, benzene or toluene or it may be formed from a plurality of the swelling agents or solvents depending upon the nature of the plasticizer and the composition of the plastic film. Manifestly, there is no set rule for determining the proportions of the respective



ingredients of the swelling medium. However, I have found that a mixture of water and alcohol is particularly effective for this purpose and I prefer to use this mixture in a proportion of two to one by volume.

The adhesive which is used for affixing the plastic film to the non-absorbent base may be any pressure sensitive adhesive of the resin type such as rubber latex, polyvinyl alcohol, vinyl ether resins and polyisobutynol and the support or base material may be any non-absorbent or poorly absorbent material which is preferably sufficiently flexible to permit rolling and passage through a printing and developing machine of the type commonly used in exposing and developing diazotypes. Examples of such material are glassine paper, lacquered paper, cellophane, cellulose ester and cellulose ether and film base materials such as those given as examples for the sensitized film of the composite strip film.

In the coating solution which is used for sensitizing the strip film any combination of diazo and azo components which is suitable for the preparation of two-component diazotype layers and which will produce the shade desired for the final image may be employed. Diazo compounds which are suitable for such two-component diazotype layers are known to be those which are derived from 1,2 and 2,1-aminonaphthols, 1,4-aminonaphthols and aromatic p-diamines of the benzene series, particularly p-phenylene diamines which are N-mono or di-substituted on one of the amino groups. Examples of such diazo compounds which are commonly used in the production of diazotype images are the diazo derivatives of p-amino-N-methylaniline; p-amino-N-dimethylaniline; p-amino-N-ethylaniline, p-amino-N-diethylaniline, p-amino-N-hydroxyethyl aniline; p-amino-N-ethyl-N-hydroxyethyl aniline; 4-amino-2-methoxy-1-cyclohexyl aniline; 1-amino-4-(dibrom 2'6' benzyl)-aminobenzene; p-amino-N-diethyl-m-toluidine; 1-amino-3-methyl-4-ethylaminobenzene; 3-aminocarbazole; 1-amino-2-naphthol-4-sulfonic acid and 2-amino-1-hydroxy-3,6-naphthalene disulfonic acid.

As examples of suitable azo coupling components, there may be mentioned the sodium salt of 2-amino-8-naphthol-3,6-disulfonic acid, 2,3-dihydroxynaphthalene or its 6-sulfonic acid derivative,  $\beta$ -naphthol-3,6-disulfonic acid, 2,7-dihydroxynaphthalene, 1,7-amino-naphthol, 2-hydroxy-8-biguanide, 1-amino-8-naphthol-3,6-disulfonic acid, 1-naphthol-4-sulfonic acid, 1-naphthol-3,8-disulfonic acid, phloroglucinol, m-hydroxyphenyl-urea, acetoacetanilide, 7-hydroxy-1,2-naphthimidazole, 7-hydroxynaphthalene-1-biguanide and acetoacetyclohexyl-amide.

After the plastic film surface of the strip film composite has been sensitized with the diazotype coating solution, it is dried and stored for use. It may be used to apply a diazotype image to many types of surfaces such as the metal surfaces of machines mentioned above, glass, tile, wood, plaster, or anywhere that an adhesive-back strip film may be applied. In using it, the sensitized surface of the film is exposed to actinic light in the same manner as any diazotype surface under the picture or design to be reproduced. After so exposing the sensitized surface, the image is developed by treatment with ammonia fumes. The strip film containing the developed image of the design is then stripped off of its support and re-fastened to the desired surface by means of the adhesive remaining on the underside of the

stripped film. In another manner of using this diazotype sensitized strip film, the sensitized plastic film may be stripped from its support, applied to a sheet of metal, wood, or other such surface, and then exposed under the original of the desired pattern and developed by contacting the exposed surface with ammonia fumes. By this method, a dimensionally correct phototemplate may be made which can be subsequently stripped from the metal or wood surface when the necessary work has been completed.

The following examples are given as illustrative of typical coating solutions which may be employed for impregnating the cellulose acetate or other plastic surfaces of the strip film composite with a diazotype light-sensitized layer. It is understood that the invention is not in any way limited to the materials or proportions given in these examples. The proportions are by weight unless otherwise specified.

#### Example 1

A composite strip film comprising a cellulose acetate film adhesively affixed to a glassine support by means of a polyvinyl alcohol adhesive is drawn across the surface of a diazotype coating solution containing the following ingredients:

Water	-----cubic centimeters	100
Isopropanol	-----do	50
Formic acid	-----grams	3
Citric acid	-----do	3
Phosphoric acid	-----cubic centimeters	1
Phenylmethyl-pyrazolone	-----grams	1
ZnCl <sub>2</sub> salt of p-diazo-N-ethyl-N-hydroxy-ethyl aniline	-----grams	7

The surface of the cellulose acetate film is kept in contact with the meniscus of this solution by drawing the strip film across the surface of the coating solution in the form of a curve tangential to the surface of the coating solution. The coated film is then dried, exposed to light under an original design, and developed by drawing the film through an atmosphere of ammonia fumes. The thus treated film containing the developed image of the original is then stripped off the glassine support and fastened to a desired surface which may be paper, metal, glass or other like surface. The image of the design is reproduced in a red color.

#### Example 2

A strip film made by adhesively affixing a cellulose butyrate film to a glassine base by means of an adhesive polyisobutanol is sensitized on the exposed surface of the cellulose butyrate film by means of the following diazotype coating solution:

Water	-----cubic centimeters	100
Ethyl alcohol	-----do	50
Citric acid	-----grams	10
Thiourea	-----do	4
Formic acid	-----do	3
2,3-dihydroxynaphthalene	-----do	0.5
ZnCl <sub>2</sub> salt of 1-diazo-3-methyl-4-diethylaminobenzene	-----grams	7

This coating solution is sprayed onto the surface of the strip film which is then dried, exposed to light under an original design, and developed in the same manner as in the case of Example 1. The strip film containing the developed image is then stripped off the glassine support and re-fastened by means of the adhesive contained on the under-side of the cellulose butyrate film onto



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a metal surface. The azo dye image of the original design is developed in a deep blue shade.

### Example 3

A strip film composite made up by adhesively affixing a sheet of cellulose propionate film onto a glassine support by means of a vinylether resin adhesive is sensitized by the following diazotype coating solution.

Water	-----cubic centimeters	100
Ethyl alcohol	-----do	50
Citric acid	-----grams	10
Thiourea	-----do	4
Form acid	-----cubic centimeters	10
ZnCl <sub>2</sub>	-----grams	3
Phenylmethyl pyrazolone	-----do	0.5
ZnCl <sub>2</sub> of p-diazo-diethyl aniline	-----do	8

This coating solution is doctored onto the exposed surface of cellulose propionate film by means of a trough and doctor blade in accordance with the method generally employed in coating of diazotype papers. The film is then dried, exposed to actinic light under an original pattern and developed by contacting it with ammonia fumes in the same manner as in the case of Example 1. The image is developed in a red shade and the strip film bearing this image is stripped off of the glassine support and refastened to a metal base by means of the adhesive retained on the unsensitized side of the cellulose propionate film.

It is understood that any of the diazo compounds or azo components listed above, or any other diazo compounds or azo components known to the art for use in diazotype layers, may be substituted for the dye components employed in these examples, and that such other stabilizing agents as may be necessary for the production of a stable diazotype layer may be substituted for those specifically mentioned in the examples. Furthermore, any of the swelling agents, plasticizers, and solvents for the cellulose esters, cellulose ethers or other type of plastic film commonly used for that purpose may be used in place of the alcohols specifically mentioned in these examples to the extent that they are compatible in the light-sensitive solution and do not create interfering side reactions.

Since it is obvious that various changes may be made in the coating solution, the method of applying the coating solution to the carrier and in the production of the strip film carrier without departing from the nature and spirit of the invention, the invention is not limited to the specific

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details herein described, except as defined in the appended claims.

I claim:

1. A composition of matter comprising a plastic film of the class consisting of cellulose acetate, cellulose butyrate, and cellulose propionate, sensitized on one side with a diazotype layer containing a light-sensitive diazo compound of a p-phenylenediamine and an azo dye coupling component, said film being affixed on its other side to a glassine support by a pressure-sensitive adhesive of the class consisting of polyvinyl alcohol, polyisobutanol, and vinyl ether resin.

2. A composition of matter comprising a cellulose acetate plastic film sensitized on one side with a diazotype layer containing a light-sensitive diazo compound of a p-phenylenediamine and an azo dye coupling component, said film being affixed on its other side to a glassine support by polyvinyl alcohol adhesive.

3. A composition of matter comprising a cellulose butyrate plastic film sensitized on one side with a diazotype layer containing a light-sensitive diazo compound of a p-phenylenediamine and an azo dye coupling component, said film being affixed on its other side to a glassine support by polyisobutanol adhesive.

4. A composition of matter comprising a cellulose propionate plastic film sensitized on one side with a diazotype layer containing a light-sensitive diazo compound of a p-phenylenediamine and an azo dye coupling component, said film being affixed on its other side to a glassine support by vinyl ether resin adhesive.

SAM CHARLES SLIFKIN.

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