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2,398,056

PHOTOGRAPHIC DRY STRIPPING MATERIAL

Filed June 15, 1943

FIG. 1.

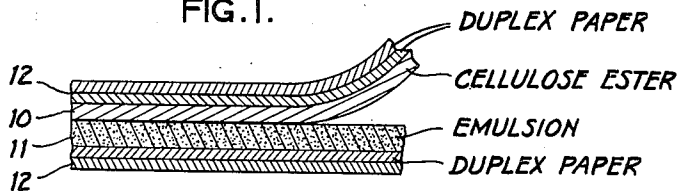


FIG. 2.

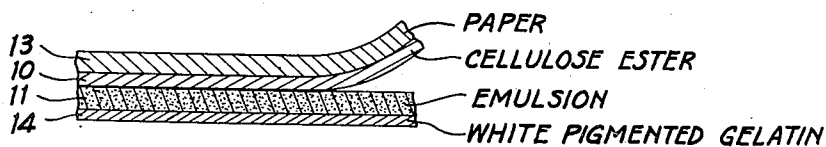


FIG. 3.

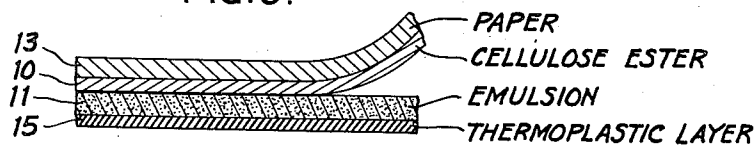


FIG. 4.

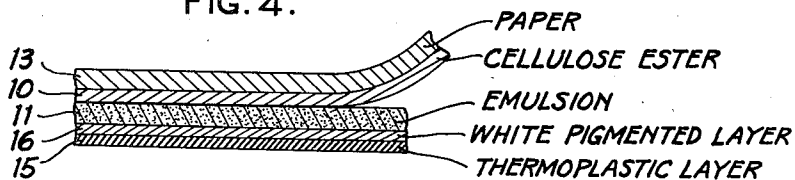
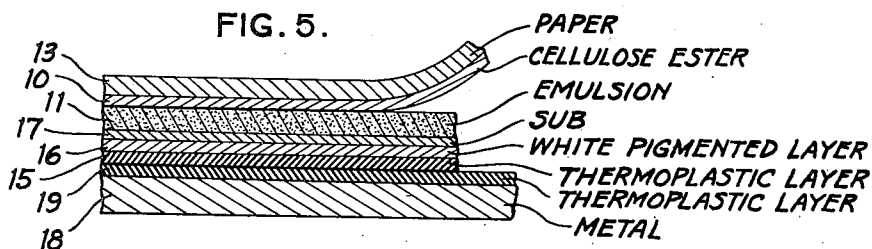


FIG. 5.



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PHOTOGRAPHIC DRY STRIPPING MATERIAL

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3 Claims. (Cl. 95—9)

This invention relates to photographic material and particularly to a stripping material which may be affixed to a rigid support.

Photographic stripping material is a photographic material in which one portion may be stripped from another portion before or after the formation of a photographic image in the sensitive layer of the material. Stripping may occur after the material has been wetted or may occur in the dry state. The present invention relates particularly to dry stripping photographic material.

The use of photographic stripping material in making templates or lay-outs on metal or other rigid material, for example in the automotive and aircraft industries, is now widely prevalent. The advantage of the use of a sensitive photographic material is that designs, such as mechanical drawings, may be copied rapidly onto the metal plate or other rigid support after it has been sensitized with the photographic material. Since it is not practical to sensitize large size metal sheets and transport them great distances, the use of a photographic stripping material affords a convenient method for sensitizing the plates at the place of use.

Sensitive photographic stripping material usually consists of a sensitive emulsion layer affixed, through a series of intermediate layers, to a temporary support. The sensitive layer is removed from the temporary support either before or after affixing it to the metal plate or other rigid material, and is then exposed and processed in contact with the rigid material. A stripping film of this general type is described in Nadeau U. S. patent application Serial No. 452,877, filed July 30, 1942, now U. S. Patent 2,326,058, granted August 3, 1943. Such material may be affixed to the metal plate by coating the metal plate with a lacquer, which is wetted with a solvent prior to lamination, and then pressing the emulsion side of the stripping film into contact with it. The disadvantage of this method of application is that the primer coated on the metal plate frequently contains ingredients which desensitize or otherwise adversely affect the properties of the sensitive photographic layer. The metal plate is frequently coated at some time long prior to the application of the stripping film and without a knowledge of the sensitometric properties of the photographic material. The sensitive layer is, therefore, frequently affected in an undesirable way by the material to which it is applied.

It is, therefore, an object of the present invention to provide a dry stripping film having a pro-

tecting layer coated over the emulsion layer. A further object is to provide a dry stripping film having a layer coated on the sensitive emulsion layer which will enable it to be affixed to a rigid support. Other objects will appear from the following description of my invention.

These objects are accomplished by applying to the sensitive emulsion layer of a stripping film, a layer of a material which will permit the emulsion layer to be affixed to a rigid support.

My invention contemplates the use of two types of emulsion overcoating layer. The emulsion may be overcoated with a thermoplastic adhesive layer which will allow heat bonding of the stripping film emulsion to the rigid support, or the emulsion layer may be overcoated with a white pigmented layer which may be overcoated with a white pigmented layer which may be caused to adhere to the rigid support. The pigmented layer may or may not be thermoplastic or it may be overcoated with a thermoplastic layer which will permit heat bonding of the emulsion layer to the rigid support.

In the accompanying drawing, Figs. 1, 2, 3 and 4 are sectional views of stripping material made according to my invention showing the temporary support partly removed. Fig. 5 is a sectional view of a stripping material made according to my invention showing the method of application of the material to a metal support.

The present method for the application of a sensitive stripping layer to a metal plate or other rigid support is to spray or coat the metal plate first with a priming coat and then with a white pigmented lacquer. The stripping film emulsion is then adhesively joined to the white pigmented lacquer coat. The white pigmented layer is used for the purpose of affording a high degree of contrast between the developed and undeveloped portions of the photographic layer so that the design is readily visible. According to my invention, one or both of these layers ordinarily applied to the metal plate are coated on the sensitive emulsion layer at the time of manufacture of the stripping material and the necessity for coating the metal plate, with its concomitant difficulties, is thereby avoided. It may, of course, be advisable to degrease or coat the metal or other rigid material before application of the stripping material to it, but otherwise no preliminary coating treatment is necessary when using the material of my invention.

I will now refer to various modifications of my invention with particular reference to the illustrations in the accompanying drawing.

A stripping film may be made by applying a

photographically opaque paper, such as a so-called duplex paper, having one side black and the other side white, to both sides of a sensitive stripping material. As shown in Fig. 1, a layer 10 of cellulose ester coated with a sensitive emulsion layer 11 would have applied to both sides of the duplex paper 12, preferably having the black side of the paper outermost. This material might be applied to a rigid support and the layer of cellulose ester 10 with its accompanying duplex paper stripped from the emulsion layer. This would leave a layer of duplex paper affixed to the emulsion layer with the white side adjacent the emulsion layer. Prior to stripping the temporary support from the emulsion layer, the metal could be handled in considerable amount of artificial light without fogging the emulsion and the duplex paper would also protect the emulsion from light after joining it to the metal plate but before the removal of the temporary support. Instead of duplex paper, any photographically opaque paper, either white or colored, can be used.

As shown in Fig. 2, the temporary support 10 of cellulose ester and the emulsion layer 11 are coated on a paper support 13. Over the emulsion layer 11 there is coated a white pigmented gelatin layer 14 and this white pigmented layer may be cemented to the metal plate or other rigid support using a liquid cement and the temporary support portion 10 and 13 removed as shown. In place of white pigmented gelatin, cellulose nitrate or other white pigmented lacquer may be used. The material of Fig. 2 may also be bonded to a metal plate having a thermoplastic layer on the metal, by heating the metal plate and bonding the emulsion overcoating to it.

Fig. 3 illustrates a modification of my invention in which a thermoplastic layer is applied over the sensitive emulsion layer. As shown therein, the cellulose ester support 10 coated with the emulsion layer 11 and backed with the paper support 13, has applied to the emulsion layer 11 a layer of a thermoplastic material 15. This layer may be a suitable heat bonding synthetic resin such as a polyvinyl acetate or polystyrene resin. A cellulose nitrate sub is preferably applied to the emulsion before coating the heat bonding layer. Upon heating this material sufficiently to cause softening, the film may be affixed to a metal plate or other rigid support and the temporary support removed as shown.

Fig. 4 illustrates a further modification of my invention in which the pigmented layer and the thermoplastic overcoating layer are combined. As shown therein the cellulose ester support 10 is coated with the usual emulsion layer 11 and backed with the paper support 13. A white pigmented layer 16 which may be a layer of gelatin, cellulose ester or synthetic resin containing a white pigment such as titanium oxide is coated on the emulsion layer 11. The white pigmented layer 16 is overcoated with the thermoplastic layer 15 of synthetic resin or other suitable heat bonding material.

A method of application of my material to a metal plate is illustrated in Fig. 5 of the drawing. As shown therein, the stripping material consisting of the cellulose ester support 10, emulsion layer 11 and paper temporary support 13 is coated with a subbing layer 17 of gelatin or other suitable material followed by the white pigmented layer 16 and the thermoplastic layer 15. Prior to application of this material to a metal plate 18, the metal plate is coated with a layer

19 of a thermoplastic material which may be similar to that of the thermoplastic layer 15 of the stripping film, in order to improve adhesion of the material to the metal plate. The metal plate is heated to produce tackiness of the layer 19 and the layer 15 may also be heated, and the layer 15 is then placed in contact with the layer 19 and the film rolled or pressed into contact with the metal plate so that the layers 15 and 19 are heat bonded. The layers 10 and 13 may then be stripped from the emulsion layer 11 leaving the sensitive material in contact with the metal plate and ready to receive a photographic image by exposure and development. As an alternative, the thermoplastic layer may be applied to the metal only, and the pigmented layer on the film bonded to it.

My invention will be further illustrated by reference to the following examples:

Example 1

A dry stripping film consisting of a paper base, a hydrolyzed cellulose acetate layer and a high contrast photographic emulsion layer such as that described in Nadeau U. S. Patent 2,326,058, is coated on the emulsion side with the following solution:

	Parts
Cellulose nitrate ($\frac{1}{2}$ second viscosity)-----	15
Polyvinyl acetate-----	5
Titanium oxide-----	25 to 40
Dibutyl phthalate-----	10
Ethyl alcohol-----	15
Acetone-----	95

In this formula the half second viscosity cellulose nitrate may be substituted by a more highly hydrolyzed nitrocellulose such as one having a viscosity of 2 to 5 seconds, a nitrogen content of about 11% and 30 to 100% soluble in ethyl alcohol. The polyvinyl acetate may be a material such as that sold by Rohm & Haas under the name V-6 Vinylite AYAA or a partly hydrolyzed polyvinyl acetate. In place of the titanium oxide pigment, zinc oxide may also be used. The solvents may vary greatly with higher proportions of either solvent mentioned or the addition of higher boiling solvents such as methyl Cellosolve, butyl acetate or any of the common lacquer solvents and diluents.

This layer is dried and is then overcoated with a heat bonding layer of the following composition:

	Parts
Polyvinyl acetate-----	10 to 15
Ethyl alcohol-----	50 to 70
Acetone-----	20 to 50

The polyvinyl acetate used in this layer may have the same composition as that employed in the pigmented layer first applied to the emulsion layer.

The outer layer of polyvinyl acetate has a "cold flow" at slightly elevated temperatures and it is, therefore, necessary to interleave the manufactured product with a wax tissue or to wax coat the reverse side of the finished paper to prevent adhesion of the polyvinyl acetate to it during storage.

In a modification of this material, a layer of nitrocellulose may be coated on the emulsion layer prior to application of the pigmented layer. This insures greater bonding of the subsequent layers to the emulsion after the stripping process.

A suitable solution for this purpose is the following:

	Parts
Cellulose nitrate.....	40
Methyl Cellosolve.....	10
Acetone.....	75 to 90

The nitrocellulose used in this layer is preferably one having a viscosity of 2 to 5 seconds, a nitrogen content of about 11% and being 30% to 100% soluble in ethyl alcohol.

When using this heat sealing product, it is necessary that the metal plate to which the seal is to be made be reasonably clean and dry. Although a good bond can be obtained by heat sealing the material directly to the metal plate, a more positive bond is obtained by dipping the clean plate in a very thin solution of polyvinyl acetate in alcohol. This also protects the developing solutions from rapid contamination by the raw metal plates and protects the metal plates from rusting and staining during the developing process. If a sufficiently heavy coat of polyvinyl acetate is made on the metal, the final thermoplastic layer may be omitted from the stripping material and heat bonding accomplished by the thermoplastic material in the pigmented layer.

Example 2

A sensitive stripping material consisting of a paper base, a hydrolyzed cellulose acetate layer and a photographic emulsion layer such as that described in Nadeau U. S. Patent 2,326,058 is coated on the emulsion side with a subbing layer having the following composition:

	Per cent
Cellulose nitrate.....	0.9
Methyl alcohol.....	99.1

The cellulose nitrate used in this layer preferably has a viscosity of 2 to 5 seconds, a nitrogen content of about 11% and is 30 to 100% soluble in ethyl alcohol.

This subbing layer is coated with a pigmented lacquer of the following composition:

	Per cent
Acetone.....	40.1
Ethyl alcohol.....	7.4
Butyl acetate.....	2.5
Cellulose nitrate (½ second viscosity).....	13.8
Tricresyl phosphate.....	9.3
Titanium oxide.....	26.9

A thermoplastic layer is then applied from the following solution:

	Per cent
Polyvinyl acetaldehyde acetal.....	12
Ethyl alcohol.....	88

The metal plate to which the material is to be bonded is preferably coated, for the reasons stated in Example 1, with a resin coating. This coating may be applied from a solution of the following composition:

	Per cent
Polyvinyl acetaldehyde acetal.....	9
Ethyl alcohol.....	60
Methyl Cellosolve.....	31

The thermoplastic material used in this coating is preferably a polyvinyl acetaldehyde acetal

such as one sold by Rohm & Haas Chemical Corporation under the trade name Alvar 7-70. The material is heat bonded to the metal plates by heating the metal to a temperature of about 240° F. for a sufficient length of time to render the resin plastic. It is then pressed into contact with the metal plate in any suitable way as by passing the material between rollers.

The thermoplastic material used in the method of my invention may consist of any suitable synthetic material such as polyvinyl acetate or an acetal resin such as polyvinyl acetaldehyde acetal or polyvinyl butyraldehyde acetal. The material must be water-resistant and should not be affected by the processing baths used in the development and fixing of the photographic material.

The pigment used in the pigmented layer of my film may consist of any suitable material such as titanium oxide or zinc oxide. Instead of white, colored pigments may be employed. The pigment may be in a separate layer or in the thermoplastic layer itself or may be incorporated in the sensitive emulsion layer.

I have referred to bonding my material onto a rigid support such as a metal plate. The metal plate may be iron, steel, brass, copper, aluminum or other metal. The film may also be heat bonded to other materials such as wood, Bakelite, or other synthetic resins, or cellulose esters. In certain cases, precautions should be taken to prevent softening or distortion of the material.

Reference has been made to the use of my invention in the preparation of templates and lay-outs on metal plates. In addition to its use on a metal plate where the plate is intended to be punched or cut in accordance with a design formed on the plate, the material may also be used for the preparation of designs or other indicia on rigid supports where the design is not intended to be used as a pattern.

It will be understood that the examples included herein are illustrative only and that my invention is to be taken as limited only by the scope of the appended claims.

I claim:

1. A photographic dry stripping film consisting, in order, of a paper temporary support, a stripping layer of a hydrolyzed cellulose acetate having an acetyl content of approximately 16-18%, a sensitive emulsion layer, a white pigmented layer and a thermoplastic layer.

2. A photographic dry stripping film consisting, in order, of a paper temporary support, a stripping layer of a hydrolyzed cellulose acetate having an acetyl content of approximately 16-18%, a sensitive emulsion layer, a white pigmented layer and a thermoplastic synthetic resin layer.

3. A photographic dry stripping film consisting, in order, of a paper temporary support, a stripping layer of a hydrolyzed cellulose acetate having an acetyl content of approximately 16-18%, a sensitive emulsion layer, a white pigmented cellulose ester layer and a thermoplastic polyvinyl resin layer.

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