

Jan. 29, 1946.

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2,393,583

COATING COMPOSITIONS FOR USE IN PREPARING PHOTO-TEMPLATES

Filed June 6, 1944

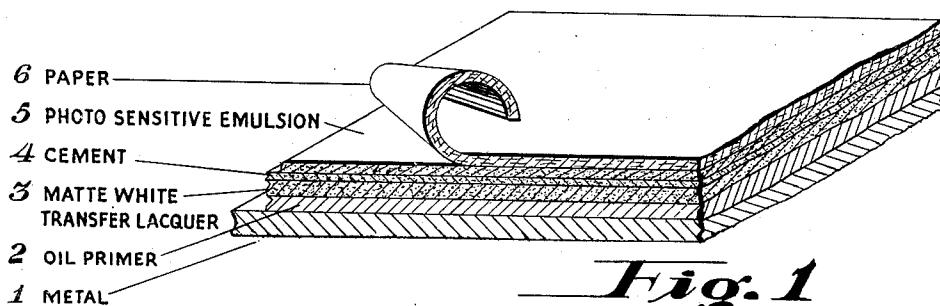


Fig. 1

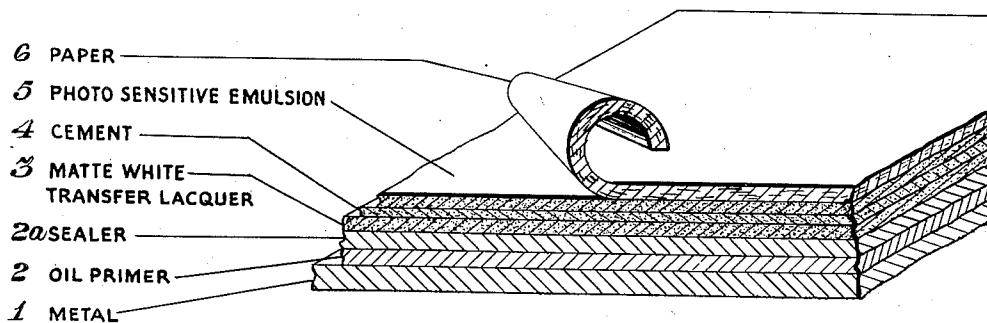


Fig. 2

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UNITED STATES PATENT OFFICE

2,393,583

COATING COMPOSITIONS FOR USE IN
PREPARING PHOTO-TEMPLATES

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Application June 6, 1944, Serial No. 538,928

9 Claims. (Cl. 95—8)

This invention relates to a coating system particularly adapted for the prevention of fogging of photo-sensitive films when they are applied over primers containing incompletely oxidized drying oils or other readily oxidizable materials, especially when used over a metal substrate in making templates.

These templates are usually made by transferring a photo-sensitive emulsion layer to a rigid base and are used largely in place of blueprints. The method of securing the emulsion to the metal is usually rather elaborate and consists essentially of applying one or more priming coats followed by a pyroxylin type lacquer. One method involves applying a coat of an opaque white primer by spraying to the metal base until a film of a .0008 to .0012 inch is obtained. The primer must then be thoroughly dried, after which two spray coats of a pyroxylin type white matte transfer lacquer are applied. The lacquer film is dried from one to four hours. The template is then taken to a dark room where a low solids content lacquer cement is applied to soften the transfer lacquer, after which an emulsion transfer paper is applied while the cement is still wet, the light sensitive emulsion side of the paper being in contact with the lacquer cement. The lamination is usually carried out between two resilient rolls under even pressure. After lamination the sensitive material is allowed to set overnight after which the paper backing is stripped off. The emulsion is then ready for exposure and development.

It has been found that if the panels made according to the above method are stored for a few days in the dark room before developing, an objectionable fogging of the emulsion is encountered. This fogging renders the template unsatisfactory because of much lessened contrast between the black lines and gray background which should preferably be pure white. It is highly desirable to obtain photo-template panels which will not fog when stored for several weeks.

While it is difficult to advance any theory with respect to the behavior of photo-sensitive salts, it appears at present that the above described fogging may be attributed to certain acid by-products of drying oil oxidation in the primer which have not been entirely driven off by baking or prolonged drying. It has been found that if the same primer should be baked in an oven between 200° and 300° F. or if it is permitted to dry four or five days before the lacquer is applied, no fogging occurs.

This invention therefore has as an object an improved coating system for use in photo-tem-

plate reproduction which reduces fogging. A further object is the production of a coating composition containing drying or semi-drying oils which do not darken or fog photo-sensitive emulsions in close proximity thereto. Another object of the invention is the production of a coating composition which, when applied between a paint containing an oil having drying properties and a photo-sensitive emulsion, will prevent darkening or fogging of the emulsion. A still further object is the provision of a photo-sensitive template which may be stored for a considerable time before development without fogging. Other objects will appear as the description of the invention proceeds.

These objects are accomplished by incorporating a basic material having a pH range between 7 and 12 in the primer coat containing the oil, or between the primer and the photosensitive emulsion. It may be incorporated in the primer containing the oil having drying properties or in the emulsion transfer lacquer applied over the primer. Another modification provides for introducing a separate sealer coat containing basic material having a pH range of 7 and 12 between the above mentioned primer and lacquer.

In the drawing, Figures 1 and 2 represent diagrammatic sections of a photo-template made according to the present invention. The parts are not drawn to scale. In both figures the metal base is shown as 1. Over this base is applied a primer 2 containing an oil having drying properties. In contact with the primer coat is a matte white transfer lacquer indicated as 3. Either of these two coats may contain a material having a pH between 7 and 12 as will be described more fully hereinafter. Figure 2 represents a modification of Figure 1 in that instead of, or in addition to, adding the basic material to coats 2 or 3, it is applied in a special sealer coat 2—a inserted between the primer and the transfer lacquer. The transfer lacquer 3 when dry is then softened with a low solids pyroxylin cement 4 and while still wet is laminated to a photo-sensitive transfer paper having a photo-sensitive emulsion 5 supported by a paper base 6. The paper 6 is subsequently stripped off. This leaves the photo-sensitive emulsion 5 attached to the template, which may be exposed and developed in any conventional manner.

The following examples illustrate suitable primers, sealers and lacquer compositions which may be used in the present invention, but it is to be understood that no limitation is placed thereon except as appears from the attached claims.

Example I.—Primer

	Parts by weight
Resin "A"-----	14.90
Petroleum solvent naphtha-----	34.60
Fibrous magnesium silicate-----	2.75
Titanium dioxide (anatase)-----	13.70
Talc-----	4.60
Silica-----	19.60
Portland cement-----	8.90
Litharge-----	.45
Lead-manganese resinate solution-----	.50
	100.00

The Portland cement used in the above example was pulverized to pass through #325 mesh screen.

Example II.—White primer

	Parts by weight
Resin "A"-----	14.90
Petroleum solvent naphtha-----	34.60
Fibrous magnesium silicate-----	2.75
Titanium dioxide-----	13.70
Talc-----	4.60
Silica-----	19.60
Calcium aluminate-----	8.90
Litharge-----	.45
Lead-manganese resinate solution-----	.50
	100.00

Resin "A" used in Examples I and II was formed from the following ingredients, using the proportions indicated, although other oils, alcohols and acids may be substituted:

	Parts by weight
Soya bean oil-----	44.43
Glycerine-----	16.70
Sodium hydroxide-----	.06
Water-----	.06
Phthalic anhydride-----	38.75
	100.00

In both of the above examples the pigments, extenders and basic materials are ground in the resin vehicle with sufficient solvent to obtain and maintain a satisfactory grinding consistency. Grinding may be carried out in a porcelain or buhrstone lined ball mill using porcelain balls or flint pebbles loaded to between 50% and 60% volume capacity of the mill and a batch:ball ratio of 1:2 by weight. A satisfactory dispersion is obtained as a rule between 30,000 to 45,000 cycles at a mill speed of about 1200 revolutions per hour. The charge may be thinned and handled as is customary in the art.

Example III.—Sealer coat

	Parts by weight
Zein-----	8.00
Ethyl alcohol (96%)-----	72.00
Water-----	19.35
Monoethanolamine-----	.65
	100.00

Example IV.—Sealer coat

	Parts by weight
Zein-----	8.00
Ethyl alcohol (96%)-----	72.00
Water-----	19.35
Triethanolamine-----	.65
	100.00

In the above two examples the zein is dissolved in the alcohol. The amine is dissolved in water separately, and is then added to the zein solution with mixing.

Example V.—Sealer coat

	Parts by weight
Zein-----	7.90
Ethyl alcohol-----	71.00
Water-----	19.72
Portland cement-----	1.38
	100.00

The zein is dissolved in the alcohol and the water added. The Portland cement is dispersed in the zein solution by grinding the mixture in a porcelain mill with pebbles. The zein used in the above three examples was "Mazein" sold by the Corn Products Refining Company. The Portland cement used in Example V is the same grade as used in Example I.

Example VI.—Sealer coat

	Parts by weight
Nitrocellulose 1/2 sec-----	3.2
Butyl acetate-----	44.0
Methyl ethyl ketone-----	43.8
Plasticizer-----	4.8
Toluol-----	3.2
Monoethanolamine-----	1.0
	100.0

The nitrocellulose is dissolved in the mixture of butyl acetate and methyl ethyl ketone. The plasticizer and toluol are mixed separately and then blended with the nitrocellulose solution. When the mixing is completed, the monoethanolamine is added. The plasticizer used in the above example was a castor oil modified glycol ester of sebacic acid. Other vegetable oil modified alkyd resin which act as plasticizers for nitrocellulose may be substituted in the formula.

Example VII.—White matte transfer lacquer

	Parts by weight
Plasticizer-----	12.0
Toluol-----	8.0
Titanium dioxide (anatase)-----	15.0
Basic calcium silicate-----	3.0
Methyl ethyl ketone-----	9.0
Nitrocellulose 1/2 sec-----	15.0
Butyl acetate-----	19.0
Methyl ethyl ketone-----	19.0
	100.0

The first portion of the above formula is ground in a porcelain ball mill using porcelain balls and a batch:ball ratio of 1:2 by weight for about 25,000 cycles at about 1200 revolutions per hour. The second portion, consisting of the nitrocellulose and solvent, is made up and blended with the first portion. The plasticizer may be that used in Example VI or its equivalent. The basic calcium silicate used in Example VII was prepared in accordance with U. S. Patent No. 2,263,606. Where desired, other prime pigments or extenders may be incorporated into the coating compositions herein disclosed, providing they do not interfere materially with the required pH.

While it is usually desirable that the color of the primer and that of the transfer lacquer be white and that the sealer be either white or

transparent, coating systems having any such color or shade that does not interfere with the photographic reproduction process fall within the scope of the present invention.

In general, it is advisable to maintain the acid number of the vehicle at the lowest possible value and this is usually accomplished by increasing the temperature or the period of heating, or by "blowing" the vehicle with an inert gas, or by catalytic decarboxylation of the organic acids. The allowable range of acid numbers will vary with the basic material used. Usually it is advisable to keep the acid number below 20.

While we prefer to grind the pigmented compositions in ball mills lined with porcelain or buhrstone, and using either porcelain balls or flint pebbles, any grinding procedures may be used which will result in satisfactory products.

In carrying out the invention the metal substrate is cleaned and all traces of grease and oil removed. A primer is then applied by any desired means and allowed to dry. The drying time may be about six to eighteen hours. Usually one coat is sufficient. A satisfactory primer may be one of those described in Examples I and II or one similar to "Preparakote" White manufactured by E. I. du Pont de Nemours & Company.

After the primer has dried, a white matte transfer lacquer is applied. This may be the composition given in Example VII or it may be "White matte transfer lacquer" sold under this name by the Eastman Kodak Company.

As a modification of the above procedure the alkaline material may be included in the coating system as a separate sealer coat between the primer and the white transfer lacquer. Any of the compositions disclosed in Examples III, IV, V, or VI may be applied in any conventional manner over the dried primer. Usually one coat of the sealer is sufficient, and those given dry in about 15 minutes.

When the sealer coat is dry, one or more coats of the white matte transfer lacquer is applied usually by spraying, although any means of obtaining a satisfactory uniform film may be used.

The metal panel bearing the coatings described above is now taken into the dark room and a cement is applied. Any transfer paper cement is suitable provided it adheres tenaciously to the transfer lacquer coat, dries quickly, and does not fog the photo-sensitive emulsion. The cement sold by the Eastman Kodak Company as No. 20806 for this purpose, has been found to be particularly satisfactory. After the cement is applied, an emulsion transfer paper consisting essentially of a paper base with a photo-sensitive emulsion, is applied at once to the cement—the emulsion side being in contact with the cement. The laminated panel is then allowed to cure in a well ventilated dark room at about 70° F. to 80° F. for ten to fifteen days, after which the paper backing may be stripped from the panel. The panel is then ready for exposure and development in the usual way.

It will be apparent from the above description of the invention that a basic material is incorporated either in the primer coat, which contains a drying or semi-drying oil, or in the white matte transfer lacquer, or in a special sealer coat between the two. It is also within the scope of this invention to introduce the basic material into one or all of these coats. Any basic material which does not fog a photographic emulsion and has a buffer or alkaline reaction suffi-

cient to impart a pH of 7 to 12 to the coats to which it is added, is satisfactory in carrying out the invention. The following basic materials were found effective when incorporated in the primer: sesqui calcium silicate and dicalcium silicate, prepared in accordance with U. S. Patent 2,263,606, Portland cement, aluminous sement, barium carbonate and alkaline earth metal aluminates which have been dehydrated just below their sintering point, and which contain up to about .8% free metal oxide. These materials may also be used in the sealer coat or in the matte transfer lacquer. In addition, barium hydroxide, calcium hydroxide, sodium silicate, sodium caseinate, monoethanolamine, diethanolamine, triethanolamine, trimethylbenzyl ammonium hydroxide, similar amines, carbonates and hydroxides may be used in the sealer or lacquer coats, provided they do not fog the photo-sensitive emulsion and produce a pH between 9 and 12. It has been found that zinc oxide is ineffective in any of the coats, because its pH is below 7. On the other hand, the alkali metal hydroxides and carbonates are unsatisfactory because they saponify the film-forming oils, thereby causing peeling and blistering when the films are exposed to moisture. These materials have a pH greater than 12.

The film-forming materials of the sealer coat may be proteins like zein and casein, or resinous as polymeric methacrylate esters or cellulose derivatives, such as nitrocellulose, ethyl cellulose, ethyl acetate, and mixed ethers.

No sealer is necessary if the basic material is incorporated either in the primer or in the transfer lacquer. It is permissible, and is within the scope of this invention, to use a basic material in both the primer and the lacquer and, in addition, to introduce a sealer containing a basic material. The basic material used in such a case may be the same material in all the coats, or, if desired, a different material in each coat. If the basic materials are added to the primer, they should be selected from the least water soluble types, i. e., calcium silicates, etc. The more water soluble types may be used in the sealer coat or in the top coat.

It is also within the scope of this invention to utilize in these coating compositions any binder, vehicle, plasticizer, solvent or other ingredient which either does not cause fogging of the photo-sensitive emulsion or the fogging normally caused by them can be prevented through the use of basic materials.

Our invention is useful in all such processes which involve the application of a photo-sensitive film over a paint containing incompletely oxidized drying or semi-drying oils. The best example of such a use is the photo-template reproduction of industrial patterns used extensively by the aircraft industry.

Primers prepared in accordance with our invention may be recoated with standard transfer lacquer within six hours after application. Analogous primers containing no basic materials, or only rather inactive bases, like zinc oxide, have to be dried for over ninety-six hours before the standard transfer lacquer is applied, in order to assure that the emulsion applied subsequently will not fog during storage.

Sealer coats and transfer lacquers containing basic materials may be applied over standard primer within sixteen to eighteen hours after application. The use of our invention obviates the necessity of a baking operation for the primer

and at the same time reduces substantially the time necessary for the preparation of systems that do not fog the photo-sensitive emulsion on storage. This is very much desired, particularly by aircraft companies, as a means of speeding up production.

It is apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, and therefore, it is not intended to be limited except as indicated in the appended claims.

We claim:

1. A photo-template comprising a rigid base having an oil primer in contact therewith, superimposed upon the primer a transfer lacquer, a photo-sensitive emulsion cemented thereto, and a mild alkaline material incorporated in one of the coats between the metal and the photo-sensitive emulsion said alkaline material being innocuous to the said emulsion.

2. The product of claim 1 in which the alkaline material has a pH between 7 and 12.

3. The product of claim 1 in which the primer contains a vegetable oil having drying properties.

4. The product of claim 1 in which a sealer coat containing the alkaline agent is applied between the transfer lacquer and the primer.

5. In the process of preparing photo-templates in which a rigid base is primed with an oil primer and subsequently a photo-sensitive emulsion is attached thereto by cementing a transfer paper to the primed base and thereafter stripping the paper from the base, the improvement which comprises incorporating in a coating composition applied to the base before the transfer paper is cemented thereto an alkaline agent having a

pH between 7 and 12 which is innocuous to the said emulsion.

6. The process of preparing non-fogging photo-templates which comprises applying a composition having approximately the following formula:

Parts by weight	
Soya bean oil modified alkyd resin-----	14.90
Solvent -----	34.80
Portland cement-----	8.90
Extenders -----	26.95
Pigment -----	13.70
Drier -----	.95
	100.00

allowing the same to dry for about six hours; applying a sealer coat thereto containing 8 parts of zein and .65 part of an ethanolamine dispersed in about 91.35 parts of a mixture of alcohol and water, allowing the same to dry; and thereafter applying a transfer lacquer containing nitrocellulose as the film-forming agent, a plasticizer, basic calcium silicate and an extender; allowing the composition to dry; and thereafter cementing thereto a photo-sensitive transfer paper; stripping the paper from the laminated material; and thereafter exposing and developing the photo-sensitive emulsion.

7. The product of claim 1 in which the alkaline material is in the said oil primer.

8. The composition of claim 1 in which the alkaline material is inorganic.

9. The composition of claim 1 in which the alkaline material is an amine.

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