Jan. 31, 1961 F. E. KENDALL 2,969,731

STENCIL MANUFACTURE

Filed May 24, 1954

Fig. 1

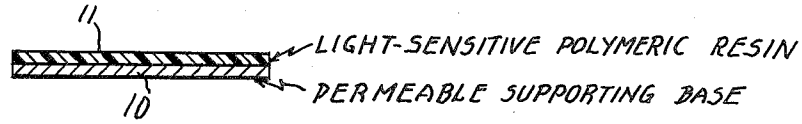


Fig. 2

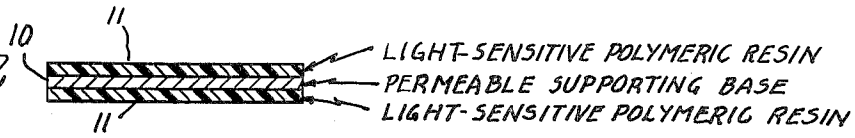


Fig. 3

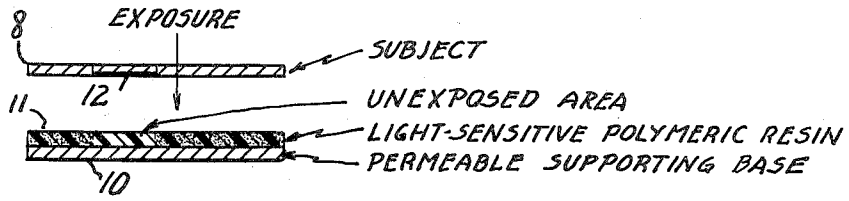


Fig. 4

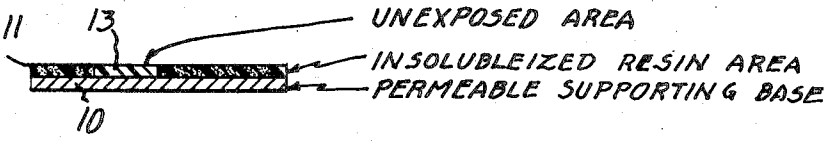


Fig. 5

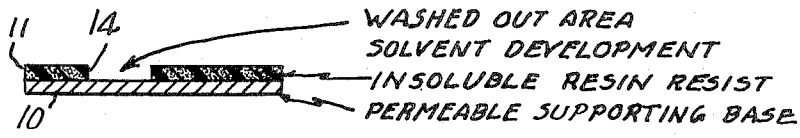


Fig. 7

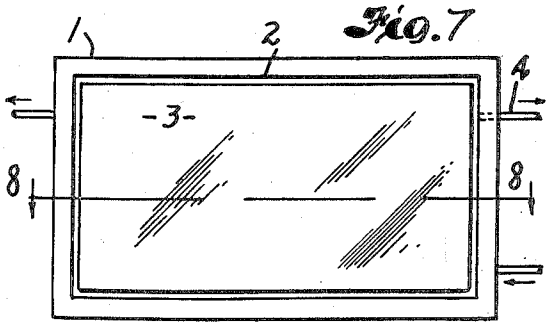


Fig. 8

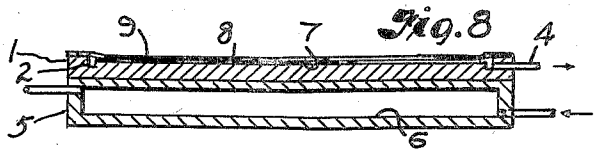
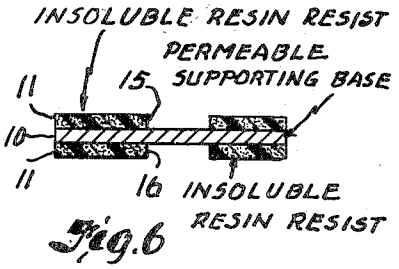


Fig. 6



INVENTOR.
FRED E. KENDALL
By Oberlin & Limbach
ATTORNEYS

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STENCIL MANUFACTURE

Fred E. Kendall, 30550 Landerwood Drive, Chagrin Falls, Ohio

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3 Claims. (Cl. 101—128.3)

This invention relates as indicated to a novel stencil and method of preparing the same, and more particularly to a method of producing an improved duplicating stencil resist having a much longer life than any heretofore produced.

For many years duplicating paper or the like has been cut, die-impressed and embossed in the preparation of stencils for use on mimeograph and other types of duplicating machines. More recently, an electrolytic method of marking metals through a die-impressed pressure sensitive resist or engraved plastic resist has been widely accepted by the metal marking industry and is now preferred in contrast to the older methods utilizing steel die stamps, acid and ink stamps, and pantograph or engraving tools. Such electrolytic method has utilized a die-impressed pressure-sensitive paper stencil which has been reinforced with various types of synthetic or natural resins and waxes adapted to be readily displaced by pressure rolling or by impact against electrotype or etched plates. After die-impressing, a liquid marking medium which may be either an ink or an electrolytic fluid, for example, is then applied to the stencil sheet and will pass through the porous fibrous layer where thus exposed and mark an underlying work surface accordingly. There are many modifications of this general marking method, practically all of which are susceptible of improvement in accordance with my present invention.

Stencils of the type above discussed are very convenient of use and give satisfactory results when first employed. They are, however, not very long-lived and the results obtained from any one stencil tend to become less and less satisfactory until the stencil must eventually be discarded. Many interested in the stencil problem have attempted to solve it through the technique of applying water soluble colloids containing photosensitive compounds to a supported porous member. After the coating has dried, a photonegative or a photopositive transparency is placed in contact with the coating, and by exposure to a proper light source, some curing of the light exposed coating may be caused to take place. The unexposed area may then be washed out with water and the exposed area treated in a hardening solution.

While the technique last described above has certain obvious virtues, it has also involved certain features which are unfortunate for my purpose. Colloidal proteins which have been light-sensitized with bichromates produce fairly well-defined copy but since they are hydrophilic they never become truly water impermeable but will imbibe water (including electrolytes) and thus serve as electrical conductors. This obviously renders them unsuitable for electrolytic stencil work.

It is accordingly a principal object of my invention to provide a novel stencil which may be produced by employment of an appropriate photographic negative or positive or other mask and which will have sharp definition and an extremely long life.

Another object is to provide a method of manufacturing such stencil which will be relatively simple and expeditious and will not require a high degree of skill on the part of the craftsman.

Still another object is to provide a stencil of the type indicated comprising a layer of pervious material and a layer of impervious material wherein such layer of impervious material is relatively thick, wear-resistant, and impervious to liquids employed therewith, including electrolytes.

Other objects of the invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, said invention then comprises the features hereinafter fully described and particularly pointed out in the claims, the following description and the annexed drawing setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principle of the invention may be employed.

In said annexed drawing:

Fig. 1 diagrammatically illustrates the layer of permeable supporting base material coated with a layer of a light sensitive polymeric resin;

Fig. 2 diagrammatically illustrates such permeable material coated on both sides with layers of such resin;

Fig. 3 shows the manner in which such material may be exposed to light passing through an appropriate negative to produce exposed and unexposed areas;

Figs. 4 and 5 illustrate the production of the finished stencil through solvent development;

Fig. 6 corresponds to Fig. 5 but with both sides of the permeable supporting base coated with the resin;

Fig. 7 is a top plan view of a special vacuum printing frame which I prefer to employ in the production of my new stencil; and

Fig. 8 is a longitudinal section taken on the line 8—8 on Fig. 7.

In accordance with my invention, I employ an impervious film or layer of a synthetic resin on a sheet of pervious material such as yoshino long fiber paper, such resin or lacquer being photosensitive and rendered insoluble due to photo-chemical action upon exposure to light.

More particularly, I prefer to employ photo-sensitive or photo-reactive resins which are soluble in organic solvents such as the polymeric cinnamic esters which have been photosensitized as taught in Minsk et al. Patent 2,610,120, for example. A preferred material comprises a cinnamic acid ester of polyvinyl alcohol as a combined carrier and light sensitive material, and as a sensitizer for the composition a nitro aryl compound having a nucleus containing from 6 to 10 carbon atoms, from 1 to 3 nitro groups being attached to such nucleus, the mono-nitro compounds being free of amino, hydroxyl, and formyl groups in a position ortho to the nitro group, such nitro aryl compounds being free of an amino and a hydroxyl group in positions ortho to each other, and free of carboxyl and sulpho groups. Reference may be had to said Minsk el al. patent for further details regarding the preparation of such photosensitive coating material and also to Minsk et al. Patents 2,670,285, 2,670,286, and 2,670,287.

Instead of applying an extremely thin film of the resin to an impervious supporting surface as taught by Minsk et al., I apply a relatively thick film of the resin to a permeable medium which may be of no greater thickness than such film itself. This photosensitive resin or lacquer may be applied to one or both sides of such pervious material in any convenient manner. It readily lends itself to application by weir coating or by roll coating on automatic equipment. Indeed, it may be applied simply by immersing the supporting medium (such as yoshino paper) therein and wiping off the surplus through fixed

wiping bars. Conventional spraying techniques familiar in the paint industry may be employed, but this will ordinarily require that the pervious supporting medium be supported in an appropriate frame.

In order to produce my new stencil having a relatively thick resin coating or coatings without danger of poor development, undercutting, and poor definition, I utilize the novel vacuum printing frame shown in Figs. 7 and 8 of the drawing. Such frame comprises a flat metal plate 1 (preferably aluminum) having a narrow groove 2 milled therein parallel to the outer edge of the plate and defining the printing area. Such groove may be about a quarter of an inch deep and a quarter of an inch wide and may be spaced about one inch in from the outer edge of the plate. The printing area 3 of the plate defined by such groove will desirably be milled about 1/16 inch lower than the outer rim of the plate in order to assist in ensuring that air is uniformly removed in the manner explained below. A tube 4 communicates with groove 2 and leads to any convenient source of vacuum (not shown). Plate 1 is mounted on a hollow metal base 5 having an inner chamber 6 through which cooling water is adapted to be circulated. Printing area 3 may be painted black or it may be covered with a black piece of non-reflective paper or the like.

The photosensitive coated material 7 is placed upon such printing area 3 of plate 1 and the photonegative or photopositive transparency 8 is superimposed thereon. It is, of course, very important that the reproducing copy be in intimate contact with such coated photo-resist material, and I accordingly place a clear piece of flexible plastic sheet material 9 over the above assembly and extending laterally beyond groove 2. This flexible transparent plastic sheet may, for example, be of cellulose acetate, cellulose nitrate, cellulose propionate, cellulose butyrate, polyvinyl acetate, vinylidine chloride, melamine formaldehyde, methyl methacrylate, polyamides (nylon), and other well-known polymers and co-polymers. Such plastic sheet may be clamped to the outer border of plate 1 but, if thin and flexible enough, it may be retained in place and provided with an adequate seal simply through the action of the vacuum now produced in groove 2. Such vacuum, of course, draws down the plastic sheet firmly upon the superimposed photonegative and photosensitive coated material to press the same firmly and snugly together. After an exposure which may ordinarily be from about 2 to about 10 minutes depending on the light source, the thickness of the photosensitive coating, and the copy being reproduced, the vacuum may be relieved and the exposed photosensitive coated material removed. A considerable quantity of heat is normally produced and absorbed during this process and cooling water will accordingly be circulated through chamber 6.

As shown in Fig. 1 of the drawing, the photosensitive coated material may comprise a permeable supporting base 10 of sheet material such as yoshino long fiber paper coated on one side with the preferred light sensitive polymeric resin 11, or as shown in Fig. 2 such permeable sheet material may be coated on both sides with the resin film or layer 11. When the coated material of Fig. 1 is exposed to light passing through negative 8 having a light impermeable area 12, the coating 11 will include exposed and unexposed areas corresponding to the light transmitting and light impermeable areas of the negative. Thus, as shown in Figs. 4 and 5, the unexposed region 13 remains soluble and may be washed out by appropriate solvent development as shown in Fig. 5 to expose the underlying permeable material 10 in a sharply defined area 14 forming the stencil design. Similarly, as shown in Fig. 6, when both sides of the thin permeable layer 10 have been coated with the resin, the stencil design will be formed by solvent development of the unexposed regions 15 and 16 on directly opposite sides of permeable sheet 10. When both sides of sheet 10 are thus coated with the resin resist layers, it is especially important that sheet 10 be thin and of good light transmitting quality so that the resin on the underside of the sheet will be exposed sufficiently to render the same insoluble. The resin on the underside of the sheet will, moreover, in such cases likewise preferably be in the form of a relatively thin film.

I have been successful in applying the resin to a permeable sheet in the form of a film as thin as such sheet itself and up to a thickness of 0.01 inch. Ordinarily, the resin film should have a thickness of from about .0015 to .008 inch, and preferably from about .002 to .005 inch. The permeable supporting sheet will preferably be from ½ mil to 1 mil in thickness for the production of fine line stencils and from 1 to 3 mils in thickness for production of broad line stencils.

While Minsk et al. Patent 2,610,120 recommends a variety of solvents such as aromatic alcohols, ethers, ether alcohols, furfural, benzaldehyde, morpholine and acetophenone, for example, and either immersion of the coated plates therein or treatment by a technique resembling that followed in vapor degreasing, I employ resin coatings which may be of considerably greater thickness than those contemplated by Minsk et al., and accordingly I prefer to employ a hot developer at a temperature of from about 50° to 95° C. when employing a developer such as dichlor-ethylene and trichlor-ethylene. It is also desirable to maintain some slight motion of the stencil while immersed in the hot developer, or to circulate the latter, since otherwise incomplete washing out of the unexposed areas may be experienced.

I have found, however, that a different type of developer is more suitable for my purpose and may be employed without heating. Examples of such developers are cellulose acetate solvents such as ethylene glycol mono-methyl ether acetate, ethylene glycol monoethyl ether acetate, and ethylene glycol mono-butyl ether acetates.

A wide variety of pervious supporting media may be employed in the manufacture of my new stencil, the life required and the type of copy to be reproduced largely dictating the selection of the particular medium to be employed. As above indicated, yoshino long fiber pervious paper may be utilized and, if desired, such paper may be wet strengthened in the manner described in my co-pending application Serial No. 293,418, filed June 13, 1952, now abandoned. The hot developing technique referred to above, however, tends to wash out the wet strengthening material, and it will accordingly usually be preferred to wet strength the exposed stencil portion by application of dilute organic soluble resin solutions after such development has taken place. The exposed fibers may be considerably strengthened in this manner without blocking of the interstices therebetween. While certain stencils prepared in accordance with my aforesaid application Serial No. 293,418 are currently producing an average of about 3,000 to 4,000 marks each before they require to be discarded, with the same size copy and exactly the same assembly I have been able to obtain 25,000 marks with my new stencil in accordance with the present invention. By employing somewhat more expensive pervious supporting media, it is possible to obtain an even larger number of marks.

Excellent stencils have been produced using silk screen as the supporting medium, the life of the stencil being limited only to the wearability of the resin film resist. Another preferred supporting medium is a very fine woven fabric of Fiberglas. Nylon, rayon, orlon, Dacron, linen, cotton, wool and metal cloth may all be employed. They should, of course, be selected to provide the proper uniform distribution of voids or interstices for passage of the marking material therethrough.

Inasmuch as I prefer to employ a resin resist film of substantially greater thickness than that contemplated by Minsk et al. in the production of their lithographic plates, I have encountered a certain amount of difficulty

due to undesirable hardness or brittleness of such film. I have accordingly added plasticizers to the resin in amount up to 20% by weight of the total weight of the solids present in the solution of the photosensitive resin or lacquer without any apparent deleterious effect upon the photosensitivity of the latter. Inasmuch as such lacquer is very expensive, the addition of the plasticizer not only renders the same more suitable for my purpose, but also serves considerably to reduce the cost thereof. Phthalates as a class and more particularly dimethyl phthalate, dibutyl phthalate, diamyl phthalate, dimethoxyethyl phthalate, and dibutoxyethyl phthalate have proven satisfactory. Organic phosphates as a class and more particularly tricresyl phosphate and triphenyl phosphate have likewise proven satisfactory. Orthonitrobiphenyl may also be used. In general, plasticizers for such resins are familiar to those skilled in the art and any suitable plasticizer may be employed.

It was expected that a considerable portion of the added plasticizer might be washed out of the resin film when the latter is subjected to the action of the developer. While some such effect has been apparent, the resin resist layer of the finished stencil has been sufficiently strong and flexible without local weak spots or unrelated voids.

I prefer, however, to incorporate the plasticizer in the developer (either the hot or cold type referred to above) as this method is very convenient and inexpensive and has been found to be unexpectedly effective. Nor does it interfere with the action of the developer.

It is often desired to incorporate some color into the finished product, and I have found that certain dies which are soluble in the organic solvents used with either the resin or the developer may be incorporated in sufficient amount to impart quite dense color with no deleterious effect on the finished product. Malachite green, nigrosine black, wool fast blue, plasto blue, spirit blue, and other dyes have been mixed into the photosensitive lacquer to impart the desired color to the film. While a certain proportion of the dye may wash out during the developing operation, sufficient remains to achieve my purpose. The dyes may in fact be dissolved in the developer which will thereupon impart color to the retained plastic film during the developing operation.

My new method of producing stencils is suitable for use with any copy which lends itself to photographing and from which a photonegative or photopositive transparency may be prepared. Where the number of copies desired is sufficient to justify, entire pages of print, for example, may be reproduced in this manner and copies run off on a mimeograph machine. Halftones may be reproduced with excellent detail and stencils produced in accordance with my invention may readily be applied to the silk screen process. My new stencils are especially useful for employment with electrolytes for electrolytic etching and marking, particularly of metals. They have proved extremely wear-resistant, are not hydrophilic, and produce very sharp and definite outlines.

Reference may also be had to Allen Patent 2,566,302 which discloses copolymers suitable for employment in accordance with my invention. Styrene and 1-cinnamyl styrene are copolymerized to form a resin which I place upon my permeable supporting sheet. After exposure to light, the resist may be developed with a suitable solvent such as chlorobenzene, xylene, or decahydronaphthalene.

In general, I prefer to employ light sensitive polymeric cinnamic acid esters such as cinnamic acid esters of polyvinyl alcohol and cellulose, with their light sensitivity enhanced or fortified by inclusion of nitro compounds, anthrone compounds, quinone compounds, diaminodiphenyl carbinol, diaminodiphenyl methane, and diaminodiphenyl ketone compounds as taught in the previously mentioned Minsk et al. patents. These sensitized resins are light sensitive in the ultra-violet range. G. A. Schröter (Kunststoffe, 41, 291–4 (1951)) also describes a photosensitive resin which I may employ. Rubber hydrohalides and nitrocellulose are sensitized with isocyclic and heterocyclic compounds containing at least three ring systems, including compounds containing the ring systems of anthracine, acridine, and phenozine.

Reference is hereby made to a continuation-in-part application of the foregoing subject matter, entitled "Stencil Means and Manufacture Thereof," and assigned Serial No. 507,696.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims or the equivalent of such be employed.

I therefore particularly point out and distinctly claim as my invention:

1. The method of producing a wear-resistant stencil which comprises uniformly coating a thin flexible sheet of permeable material with a film of a cinnamic acid ester resin sensitized to the action of light, superimposing an article having opaque and transparent areas, exposing such coated sheet to the action of light transmitted through such article to render the exposed portions insoluble in developer, washing such exposed film in solvent developer effective to dissolve out the unexposed portions and disclose the underlying permeable sheet to produce the stencil design, such developer containing a plasticizing agent for such cinnamic acid ester resin adapted to be absorbed thereby during such washing operation to render such resin coating flexible and non-brittle.

2. The method of claim 1 wherein such sensitized cinnamic acid ester resin is sensitized by a nitro aryl compound having a nucleus having from 6 to 10 carbon atoms, from 1 to 3 nitro groups being attached to such nucleus, the mono-nitro compounds being free of amino, hydroxyl and formyl groups in a position ortho to the nitro group, such nitro aryl compounds being free of an amino and a hydroxyl group in positions ortho to each other, and free of carboxyl and sulpho groups.

3. The method of producing a wear-resistant stencil which comprises uniformly coating a thin flexible sheet of permeable material with a film of a cinnamic acid ester resin sensitized to the action of light, superimposing an article having opaque and transparent areas, exposing such coated sheet to the action of light transmitted through such article to render the exposed portions insoluble in developer, washing such exposed film in solvent developer selected from the class consisting of ethylene glycol mono-methyl ether acetate, ethylene glycol monoethyl ether acetate, and ethylene glycol mono-butyl ether acetates, to dissolve out the unexposed portions and to disclose the underlying permeable sheet to produce the stencil design, such developer including therein a plasticizing agent for such film effective to render the latter non-brittle.

References Cited in the file of this patent

UNITED STATES PATENTS

1,354,478	Gestetner	Oct. 5, 1920
1,675,561	Keel	July 3, 1928
2,064,764	Playford et al.	Dec. 15, 1936
2,131,225	Kirch et al.	Sept. 27, 1938
2,182,325	Tucker	Dec. 5, 1939
2,184,288	Danglemajer	Dec. 26, 1939
2,318,959	Muskat et al.	May 11, 1943
2,405,508	Lindsay	Aug. 6, 1946
2,500,877	Sharples	Mar. 14, 1950
2,610,120	Minsk et al.	Sept. 9, 1952
2,637,255	Pleydell et al.	May 5, 1953
2,670,285	Minsk et al.	Feb. 23, 1954
2,670,286	Minsk et al.	Feb. 23, 1954
2,670,287	Minsk et al.	Feb. 23, 1954
2,685,510	Yackel	Aug. 3, 1954
2,732,301	Robertson et al.	Jan. 24, 1956

FOREIGN PATENTS

633,293	Great Britain	Dec. 12, 1949