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2,999,016

DRAWING MATERIAL

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This invention relates to drawing and highly accurate reproduction processes such as used by draftsmen and for the production of templates suitable for factory operations and the production of precise maps and the like.

Patent 2,718,476 to Eichorn describes dimensionally stable materials for these purposes which are based on woven glass cloth material impregnated with a polyester resin. It has now been found that it is possible to obtain the same degree of dimensional stability without the need for using glass cloth by using a base material which is a transparent or translucent film of polyester material. These films may range in thickness from .001" to .010", but are usually .003" to .007" thick. This material has additional advantages because it is more transparent than the glass cloth material, it is free from fibers giving it a smoother drawing surface and eliminating the fiber pattern from the background on reproductions made through the material. It is more flexible and therefore can be handled more freely. It has better initial tear strength and its cost is lower.

One of the most important uses for the new material is in the production of templates, particularly for aircraft construction. This is done by making full scale drawings on the new material for the templates or patterns and then reproducing them on the actual construction materials such as aluminum, magnesium, etc. The usual drawing materials such as tracing paper and tracing cloth do not have sufficient dimensional stability for this purpose because they are hygroscopic and expand or contract with changes of atmospheric moisture as well as with temperature changes thus making it impossible to hold the minute tolerances and exact dimensions necessary for precision machining.

Prior to the development of the glass cloth material mentioned above, countless hours were expended in scribing production drawings on metal templates such as sheet aluminum. Many attempts were made to draw on some more stable material or to directly attach a less stable sheet of paper or the like to the metal template. Thus drawings have been made on metal foil, or paper drawings made to scale have been attached to metal or other backing by use of various plastic or adhesive compositions. Numerous attempts have also been made to transfer such drawings to templates by means of photosensitive material, but because of the opaque nature of the backing material, these processes have generally relied on a reflex photographic process. The transparent nature of the present material offers a wide variety of reproduction processes for transferring the image drawn on the stable polyester film to the metal template.

In its simplest form, the polyester film is provided with a pencil and ink receptive surface suitable for drawings made in the usual manner as on tracing paper and tracing cloth. These drawings can be readily reproduced on to metal templates or any other base where a high degree of dimensional stability is essential. In another form, the polyester foil is provided with a scribing layer which is opaque to actinic light. When using this material, the original drawing is made by scribing techniques which are preferred in many cases where the highest accuracy is desired. The invention also contemplates photo-sensitive coatings applied over the pencil and ink receptive surfaces or over the scribing surface. These materials make it

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possible to produce duplicate masters from an original drawing or to make a reproduction from an ordinary drawing on to the scribing material. The reproduced outline may then be followed by the scribing technique to form a master which acts as a photographic negative to form further reproductions. The invention also contemplates the use of metallic scribing layers which may be applied to the surface of the foil by evaporation in high vacuum or by deposition from chemical solutions instead of the organic scribing layers. When the metallic scribing layers are used, it is also possible to apply a photosensitive resist over the metallic layer and after developing the resist image, the unprotected metal may be etched away by means of a suitable chemical solution to form an image which is readily photographically reproduced.

These photosensitive resists may also be applied over opaque organic layers which may be etched away by an organic solvent. For example, M. Hepher and E. E. Leoning (Kodak Ltd., Harrow, England), published a method for dissolving away an organic layer through a photo mechanical resist using polyethylene glycol to prevent undercutting.

Besides the use in template work as described above, the new materials and processes of the present invention will find considerable use in mapping work. The scribing materials in particular will find considerable use in this field. A high degree of precision is essential in this work because color separation plates are very often made. Those portions of a complete compilation map which are to be reproduced in any one color are scribed on one sheet of the dimensionally stable material. Each scribed sheet then becomes a negative from which the corresponding color plate is made for printing the map. Obviously, the different color plates must all register when the finished maps are produced so a high degree of dimensional stability is essential in the scribing material. The material provided with a metallic scribing layer and a photo-mechanical resist layer thereover is particularly suitable in this work since the photo-mechanical resist can be used to print lettering and symbols which can then be produced in negative form by etching away the metallic coating.

The polyester film used in the present invention is formed from a dibasic acid and a glycol. In particular, the polyester resin formed from terephthalic acid and ethylene glycol forms a film of excellent dimensional stability, particularly when the molecules are properly orientated. This film is marketed by the E. I. du Pont de Nemours Co. under the name of "Mylar." The linear polymers formed by the reaction of the terephthalic acid and ethylene glycol are oriented along the fiber axis in the production of the film in order to obtain the desired characteristics. This type of film will be referred to hereinafter as a film of oriented polyester resins formed principally from terephthalic acid and ethylene glycol. This polyester film has good light transmission, flexibility and dimensional stability. Both surfaces may be smooth or one or the other surface may be provided with a dull or matte finish formed in the polyester film itself. The matte surface may provide slightly better adhesion for some of the coatings which are used although it is not essential for adhesion of these coatings. It has been found that coatings including a substantial proportion of an alkyd resin have good adhesion to the polyester film. However, the alkyd resin may be modified by the addition of other resins including nitro-cellulose, urea formaldehyde and melamine formaldehyde resins. As examples of alkyd resins which may be used in these coatings, the "Rezyl" resins of the American Cyanamide Co. particularly numbers 387-5, 330-5, 435-1 and the "Glyptal" resins particularly No. 2522 of the General Electric Co. may be used. These are basically glycerol phthalate which is oil modified for example with castor oil or soya

oil. Rezyl resin 387-5 is described in the National Paint, Varnish and Lacquer Association, supplement 2 to circular 738, dated September 1952 at page 61a and according to the above publication the solids content of Rezyl 387-5 is 41% phthalic anhydride, 33% soy bean oil, and the resin has an acid number maximum of 12.

In order to make these coatings receptive to pencil and ink lines, considerable pigment is incorporated. Particularly, siliceous pigment materials may be used including pure silica and silicates such as diatomaceous talc. However, the pigment should be transparent in order to transmit light for photographic purposes and for this reason, pure silica is usually preferred as the pigment.

Some typical examples of suitable coatings for pencil and ink acceptance are given below:

Example I

10 lbs of pigment (SiO_2)
5 lbs. of alkyd resin solids
5 lbs. of nitrocellulose solids
1 oz. of cobalt naphthenate containing 6% cobalt (dryer)
40 lbs. of solvents

The solvents may be selected from suitable esters, ketones and the like, such as ethyl acetate, butyl acetate, and methyl ethyl ketone.

The proportion of solids to solvents may be varied depending upon the manner of application of the coating. The above formula is intended for meniscus coating, but the coating may also be applied by spraying, etc.

Example II

2.4 lbs. of silica pigment
1.8 lbs. of alkyd resin solids
4 lb. of melamine formaldehyde resin (Melmac, American Cyanamid Co.)

Photosensitive coatings may be applied over these pencil and ink coatings. For example, gelatin-silver halide emulsions for contact, reflex or projection printing can be used. In addition, wash off emulsions sensitized with bi-chromates of other hardening agents which may also contain silver halide as a pigment can also be used. Diazotype coatings particularly of the type which form a sepia image opaque to actinic light may be applied and also ferri-photosensitive coatings such as blueprint and particularly brownprint which contains a soluble silver salt in addition to the light sensitive ferric salt making the image opaque to actinic light and suitable for further reproduction. The materials provided with these photosensitive coatings can be used for making prints of a full scale drawing. Changes, additions and corrections can then be made on these prints with pencil or ink and the revised drawing used for the reproduction of templates, maps, etc. These photosensitive materials are also useful for making duplicate originals when no changes are necessary.

The following is an example of a diazotype coating which can be applied over the pencil and ink receptive coating.

Example III

50 grams diazo diethyl aniline
60 grams citric acid
20 grams boric acid
25 grams resorcinol
20 grams thiourea
10 grams zinc chloride
150 cc. polyvinyl acetate (10% solution in alcohol)
50 grams silica pigment
50 grams ethyl cellulose
125 cc. water
Ethyl alcohol to make 4000 cc.

It is also possible to apply a diazo type photosensitive coating on the polyester foil which has not been provided with a pencil surface. For example, this may be

done by applying a thin coat of alkyd resin followed by a thin coat of an emulsion of vinyl acetate and Ethocel containing a small amount of pigment and then applying two coats of the diazotype formulae of Example III.

A brownprint composition containing the usual light sensitive ferric salt, silver nitrate and keeping salts in a gelatin carrier may be applied on the pencil and ink receptive coating.

The scribe coatings which may be applied to the polyester film generally also require an alkyd or polyester resin in substantial proportion. The coating is loaded with pigments and/or dyes to give it the required degree of visual or actinic opacity as required. The addition of nitrocellulose can be incorporated provided the other ingredients are properly balanced and this may be desirable in order to give the coatings sufficient hardness. The usual opaque pigments such as titanium dioxide are suitable particularly for light colors. A high proportion of pigment improves the cutting properties of the scribe coating because its presence decreases the cohesion of the resin which makes up the rest of the coating. Even when the coating includes sufficient pigment to make it opaque for reproduction purposes a dye may also be incorporated to give the material a more pleasing color.

In cases where it is necessary to do tracing through the scribe material, the pigment may be omitted entirely to give maximum visible light transmission and an actinic light absorbing dye may be incorporated to make the coating opaque for reproduction purposes.

The following examples illustrate the scribe coatings. These coatings may be applied directly on the polyester foil.

Example IV

35 White opaque scribe coating:

2 lbs. of alkyd resin
9 lbs. of titanium dioxide
¼ oz. cobalt naphthenate drier
9 lbs. solvent (xylol, toluol and/or ethyl acetate)

If a colored opaque scribe coating is desired, colored pigments such as chrome yellow, molybdate orange and carbon black may be added or suitable colored dyes may be added.

A transparent coating would be obtained by leaving out all of the pigments and using only a dye opaque to actinic light. However, in this case the cutting properties would not be as good but could be improved by additives without sacrificing much transparency.

Other resins may be added to these coatings. For example, urea and melamine formaldehyde may be added up to about 10% of the resin content. Nitro cellulose may be added up to 75% of the resin content if suitable plasticizers are also added.

Photosensitive coatings may be applied over these scribe coatings. These are useful so that an image can be reproduced on top of the scribing coating and all or part of it cut into the scribing layer with a suitable tool. The following are examples of diazotype and blueprint photosensitive coatings which may be applied over the scribe coatings.

Example V

Diazotype coating:

65 50 grams diazo compound of diethyl aniline
50 grams citric acid
25 grams boric acid
50 grams 2,3-dihydroxy naphthalene
2½ grams resorcinol
70 80 grams Ethocel (an ethyl cellulose supplied by the Hercules Powder Co.)
50 cc. water bring up to 4000 cc. with alcohol

This coating can be applied directly on the scribe coatings.

Example VI

Blueprint coating:

- 50 cc. resin emulsion such as polystyrene, polyvinyl acetate and urea formaldehyde
- 24 cc. hydroxy ethyl cellulose (Cellosize of Union Carbide Co.)
- .8 cc. glyoxal (30% solution)
- .9 of a gram citric acid
- 25 grams ferric sodium oxalate
- 2.6 grams potassium ferricyanide
- 115 grams water
- .2 of a gram wetting agent

As an alternative form of scribing layer or coating, metal films may be applied to the polyester foil. For example, metals may be readily evaporated on to this foil in high vacuum. Particularly, the softer metals such as copper, lead, zinc and tin are suitable for this purpose, also suitable alloys such as solder may be used. Metal coatings and similar coatings may also be applied to the polyester foil by deposition from aqueous chemical solutions. For example, silver and lead sulphide may be deposited in this manner.

Photosensitive layers may be applied over these metallic scribe coatings which may be of the general type already discussed for application to the scribe coatings having an organic resin base and these scribe coated materials will function in the manners already described. However, these metallic scribe coatings have an additional advantage in that a light sensitive colloid type of photosensitive coating may be applied over the metallic layer. After exposure to light and development, these coatings form a photomechanical resist image protecting parts of the metallic coating and exposing others. By using suitable chemical etching agents such as nitric acid and other acids and ferric chloride, it is possible to remove the exposed parts of the metallic coating. In this manner, additional information such as lettering, symbols and the like may be added to scribed drawings or maps.

The light hardenable colloid photosensitive layer may consist of a bichromated gelatin or glue, a gelatin or glue sensitized with a diazo or diazido compound (the diazido compounds disclosed in U.S. Patent No. 2,663,640 would be suitable for this purpose) or a resin sensitized with an unsaturated ketone which is light sensitive of the type disclosed in the Murray Patent No. 1,965,710 of July 10, 1934.

Having thus described the invention what is claimed is:

1. A dimensionally stable flexible sheet material for carrying a highly precise image which may be copied comprising a base film of oriented polyethylene terephthalate and an adherent over-coat of a film forming resinous material comprising a substantial proportion of an unsaturated fatty oil modified glycerol phthalate alkyd resin which is provided with a material opaque to actinic light whereby a dimensionally stable master can be obtained by treatment of the opaquing material to provide areas of different opacity for use in reproductions by actinic light processes in which the actinic light is affected by the difference in opacity resulting from the treatment thereof in different areas.

2. The invention according to claim 1 in which an abrasive material is incorporated in the alkyd resin to provide a pencil take and ink receptive surface for the opaquing material in pencil or in ink.

3. The invention according to claim 1 in which a siliceous abrasive material is incorporated in the alkyd resin to provide a pencil take and ink receptive surface.

4. The invention according to claim 1 in which the opaque material is incorporated in the alkyd resin.

5. The invention according to claim 4 in which the opaque material is a dye.

6. The invention according to claim 4 in which the

opaquing material is fine granular material and provides excellent scribing characteristics to the alkyd resin.

7. The invention according to claim 4 in which the opaquing material is titanium dioxide in sufficient proportions to assure effective scribing removal of the alkyd resin overcoat.

8. The invention according to claim 1 in which the opaquing material is a photosensitive substance selected from the group consisting of silver halides, bichromates, diazo compounds and ferric salts.

9. The invention according to claim 1 in which a light sensitive diazo compound of the type which will react with an azo dye coupling component in alkaline medium to form an azo dye applied with an organic film forming carrier is the opaquing material.

10. The invention according to claim 1 in which a photosensitive coating is provided on the surface of the alkyd resin including a light sensitive diazo compound of the type which will react with an azo dye coupling component in alkaline medium to form an azo dye applied with an organic film forming carrier including a vinyl resin, said alkyd resin and said photosensitive coating being removable with a scribing tool.

11. The invention according to claim 1 in which an adherent photosensitive coating is applied on the surface of said alkyd resin including a light sensitive diazo compound of the type which will react with an azo dye coupling component in alkaline medium to form an azo dye applied with an organic film forming carrier including ethyl cellulose, said alkyd resin and said photosensitive coating being removable with a scribing tool.

12. The invention according to claim 1 in which the opaquing material includes an adherent photosensitive coating on the surface of the alkyd resin including a light sensitive blueprint composition applied with an aqueous dispersion of resin particles.

13. The invention according to claim 1 in which the opaquing material includes an adherent photosensitive coat on the surface of said alkyd resin including a light sensitive blueprint composition applied with an aqueous dispersion of resin particles, said resin particles including ethyl cellulose.

14. The invention according to claim 1 in which an adherent photosensitive coating is applied on the surface of the alkyd resin including a light hardenable colloid composition including a bichromate.

15. The invention according to claim 1 in which opaquing material is included in the alkyd resin and the alkyd resin is provided with abrasive particles providing a pencil take and ink receptive surface and a photographic over-coat is provided on the surface of the alkyd resin whereby photographic reproduction, drawing and scribing can be performed to provide the desired master for reproduction.

16. The invention according to claim 1 in which the oriented polyethylene terephthalate film is transparent.

17. The invention according to claim 2 in which the oriented polyethylene terephthalate film is transparent.

18. The invention according to claim 3 in which the oriented polyethylene terephthalate film is transparent.

19. The invention according to claim 4 in which the oriented polyethylene terephthalate film is transparent.

20. The invention according to claim 5 in which the oriented polyethylene terephthalate film is transparent.

21. The invention according to claim 6 in which the oriented polyethylene terephthalate film is transparent.

22. The invention according to claim 7 in which the oriented polyethylene terephthalate film is transparent.

23. The invention according to claim 8 in which the oriented polyethylene terephthalate film is transparent.

24. The invention according to claim 9 in which the oriented polyethylene terephthalate film is transparent.

25. The invention according to claim 10 in which the oriented polyethylene terephthalate film is transparent.

26. The invention according to claim 11 in which the

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oriented polyethylene terephthalate film is transparent.

27. The invention according to claim 12 in which the oriented polyethylene terephthalate film is transparent.

28. The invention according to claim 13 in which the oriented polyethylene terephthalate film is transparent.

29. The invention according to claim 14 in which the oriented polyethylene terephthalate film is transparent.

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