The present invention relates to a photographic sheet material and method for its preparation. It has particular application to sheet material which is especially suitable for photographic printing, particularly by the diazo-type process, although it may be applied as well to other types of photographically sensitized material.

In the prior art there are, of course, many examples of coated sheet materials which are designed or intended for photographic work and which have surfaces which are well adapted for development of dye images and which lend themselves to erasure and modification of the photographic material. Sheets of cloth, textile, paper, film base, etc., for this purpose, particularly paper sheets, are ordinarily sized and/or coated with suitable pigment materials of various types. These pigments are bound to the base sheet by an appropriate resinous binder. A wide variety of precoating materials including pigments alone, binders alone, and combinations, have been used for photographic purposes and, more specifically, for diazo-type coatings of sheet materials. These coating materials generally contribute to surface smoothness and they tend to improve the dye density, especially when images are developed from dye formers such as diazonium compounds.

Pigments commonly used in diazo-type precoatings include silicas, starches, aluminas, alumino-silicates, and synthetic polymeric materials. Binders commonly employed include such materials as sodium caseinate, gelatin, water-soluble cellulose resins, paper sizing glues, and the like. Synthetic aqueous polyvinyl dispersions such as polyvinylacetate, polystyrene and various acrylate and methacrylates may be used. These materials, when water soluble, are preferably applied for precoating purposes in the form of water emulsions. The emulsions are, of course, desirable for compatibility with the photosensitive materials to be applied later. The precoating is applied to the suitable base which may be paper, cloth or even film base. Ordinarily paper is preferred for diazo-type reproduction sheets and the following discussion relates mainly to its use. This precoating is applied to the base sheet prior to application of the sensitizing solution. The paper can be coated either by the diazo type manufacturer or, if desired, by the mill which fabricates the paper or cloth base.

In formulating the diazo-type precoat composition and applying it to the base, certain difficulties are commonly encountered; whereas the pigment component of the precoat is advantageous to intensify the dye, as the latter is developed. Frequently, the pigment materials most often used are too easily removed unless substantial quantities of binder are used. They are particularly subject to being rubbed off or to cracking or to "crocking" on handling the sheet material. If too much binder is employed in an effort to more securely fasten the pigment to the base sheet, this tends to submerge the pigment, keep it somewhat out of contact with the image-forming dye materials, and thus tends to reduce the dye density which the pigment is intended to improve.

In other words, a pigment-binder ratio which gives an optimum dye density, when subsequently sensitized and printed or developed, may exhibit too great a tendency to rubbing off of the pigment or to "crocking." If the proportion of binder is increased sufficiently to offset this tendency, then the dye density may be reduced to an objectionable degree.

Precasting materials which use a high binder concentration, or which consist of only a binder as is often the case, may also cause operating difficulties when processing photographic materials. In particular, when putting diazo-type sheets through the developing and printing machines, binder materials such as polyvinylacetate emulsions which are often used as precoat, or part of the precoat, tend to become tacky during processing of the print. In such cases, the sheets tend to stick or adhere to machine parts in the developing section of the equipment, causing difficulty in mechanical handling of the sheets and causing damage to the photographic surface.

It is an object of the present invention to avoid the disadvantages mentioned above by improving both the composition of the precoat and the method of applying it. According to the present invention, it has been discovered that the disadvantages of precoats, as suggested above, can be greatly reduced or eliminated by incorporating in the precoat composition some emulsified hydrophobic normally solid material of waxy consistency in appropriate quantities. Such quantities are usually relatively small, e.g., of the order of 2 to 20% of the solids in the precoating composition.

For example, hydrocarbon waxes, rosins, rosin-wax mixtures and hydrocarbon polymeric materials such as polyethylene, polypropylene and the like may be employed. Mixtures of any two or more of these also may be used. Paraffin waxes, combinations of rosin and paraffin wax, and polyethylene are particularly preferred. These emulsions may also be used as components of the diazo-type sensitizing solution if desired. However, their effectiveness is better when they are used in the precoat layer. When properly used, these hydrophobic emulsions of waxy material reduce the precoat pigment rub-off or "crocking" substantially. They also reduce the tackiness of the film-forming materials which are used as binders or as precoats. They reduce the tendency for the resinous binder to take up the dye and reduce dye density. At the same time, they do not interfere with the dyes or their development.

The invention will be more fully understood by reference to the following specific examples.

**Example 1**

A paper base sheet material was coated uniformly with a precoating material consisting of the following:

- 6 parts by weight of silica
- 10 parts by weight of polyvinylacetate emulsion
- 4 parts by weight of paraffin wax emulsion
- 100 parts by weight of water

This precoated paper was dried and sensitized with the following composition:

- 2 parts by weight of 4-dimethylaminobenzenediazonium chloride
- 5 parts by weight of zinc chloride
- 3 parts by weight of sodium 6-7-dihydroxyanaphthalene-2-sulfonate
- 5 parts by weight of citric acid
- 4 parts by weight of thiourea
- 5 parts by weight of ethylene glycol
- 100 parts by weight of water

After application of the sensitizing coating, the paper was dried and exposed to light under a translucent original. Development was obtained by exposure to aqueous ammonia vapor. Ordinarily paper-base line print of high dye density resulted which resisted pigment rub-off much better than a similar print made from the same precoating materials less the paraffin wax emulsion. An instrument known as a "Crockmeter," designed by the Lowell Textile
Institute, Lowell, Massachusetts, was employed to compare the pigment rub-off. It was also used in the experiments below.

**Example II**

A paper base material was uniformly coated with the following precoating material:

- 6 parts by weight of silica
- 10 parts by weight of polyvinylacetate emulsion
- 4 parts by weight of polyethylene emulsion
- 100 parts by weight of water

This precoated paper was dried and sensitized with the following composition:

- 2 parts by weight of 4-dimethylaminobenzenediazonium chlorozincate
- 5 parts by weight of zinc chloride
- 3 parts by weight of sodium 6-7-dihydroxynaphthalene-2-sulfonate
- 5 parts by weight of citric acid
- 4 parts by weight of thiourea
- 5 parts by weight of ethylene glycol
- 100 parts by weight of water

The sensitized paper was dried and exposed to light under a translucent original as in the case of Example I. Development was obtained by exposing the sheet to aqueous ammonia vapors. A bright, blue-line print of high density resulted, as in Example I, which also resisted pigment rub-off much better than a similar print made from the same precoating, leaving out the polyethylene emulsion.

**Example III**

Paper base material was uniformly coated with the following precoated material:

- 6 parts by weight of silica
- 10 parts by weight of polyvinylacetate emulsion
- 4 parts by weight of paraffin wax-resin emulsion
- 100 parts by weight of water

This precoated paper was dried and sensitized with the following composition:

- 2 parts by weight of 4-dimethylaminobenzenediazonium chlorozincate
- 5 parts by weight of zinc chloride
- 3 parts by weight of sodium 6-7-dihydroxynaphthalene-2-sulfonate
- 5 parts by weight of citric acid
- 4 parts by weight of thiourea
- 5 parts by weight of ethylene glycol
- 100 parts by weight of water

The sensitized paper was dried and exposed to light under a translucent original. Development was carried out by exposure to aqueous ammonia vapors as in the preceding examples. A bright, high density blue-line print resulted which resisted pigment rub-off much better than a similar print made using the same precoating materials but omitting the paraffin wax-resin emulsion component. The dye density was not at all impaired. As in the preceding cases comparative tests of rub-off were checked with the "Crockmeter."

**Example IV**

A paper base sheet was uniformly coated with a composition as follows:

- 50 parts by weight of polyvinylacetate emulsion
- 4 parts by weight of paraffin wax emulsion
- 50 parts by weight of water

This precoated paper was dried and sensitized with the following composition:

- 2 parts by weight of 4-dimethylaminobenzenediazonium chlorozincate
- 5 parts by weight of zinc chloride

**Example V**

Paper base material was coated uniformly with a precoating material of the following composition:

- 12 parts by weight of modified corn starch
- 2 parts by weight of talc
- 4 parts by weight of sodium caseinate
- 4 parts by weight of paraflax wax emulsion
- 100 parts by weight of water

The precoated paper was dried and sensitized with the following:

- 2 parts by weight of 4-(N-benzyl-N-ethylaminobenzene-diazonium chlorostannate)
- 0.5 part by weight of citric acid
- 0.5 part by weight of aluminum sulfate
- 2.0 parts by weight of 1,3,6-naphthalenetrisulfonic acid
- 100 parts by weight of water

The sensitized paper was dried and exposed to light under a translucent original. The photograph thus obtained was developed by passing the exposed sheet through the following alkaline solution:

- 50 parts by weight of borax
- 20 parts by weight of sodium carbonate
- 10 parts by weight of thiourea
- 8 parts by weight of chlorogluconol
- 6 parts by weight of resorcinol
- 2 parts by weight of sodium salt of isopropynaphthalene-sulfonic acid
- 1000 parts by weight of water

In this case, a bright, high density black line resulted which resisted pigment rub-off very satisfactorily, in fact, much better than a similar print made from the same sheet with the same precoating but omitting the paraffin wax emulsion. As in previous examples, the pigment rub-off was compared in the Lowell Textile Institute "Crockmeter." Brightness of color was fully equivalent. Difficulties often arise in the smoothness with which diazotype paper traverses the exposure section of a white print machine. In addition, curl is often encountered in processing diazotype materials. A further aspect of my invention is to eliminate these two objections by placing a backwash of the wax emulsion in an amount of 2 to 20% by weight of the wax in the emulsion. Similarly, curl will be eliminated by precoating and sensitizing both surfaces of the paper while utilizing the compositions of any of the examples.

It will be apparent that the pigment which is employed is of the nature of a white opaquifying pigment such as is typified by silica, alumina and the like.

While the examples mention only a few diazonium compounds and coupling components, it is to be pointed out that any of the usual diazonium compounds or couplers employed in this art may be used. In this connection reference is made, for example, to the components referred to in U.S. Patent 2,501,874, diazos derived from
N,N-diethyl-p-phenylenediamine; N-ethyl-p-phenylenediamine; N-phenyl-p-phenylenediamine; N,N'-diethyl-2-ethoxy-p-phenylenediamine; N-ethyl-2-methyl-p-phenylenediamine; N,N-hexyl-2-hydroxyethyl-p-phenylenediamine; N-β-hydroxyethyl-N-methyl-p-phenylenediamine; 4-N-morpholino-p-phenylenediamine; 4-N-morpholino-2,5-dibutoxy-p-phenylenediamine; 4-N-morpholino-2,5-diethoxy-p-phenylenediamine.

According to customary procedures, these diazos are used in the form of their salts stabilized with zinc chloride, tin chloride, cadmium chloride and the like.

Examples of couplers, other than those mentioned in the examples, are 2,5-xylene; 2,3-dihydroxy naphthalene; resorcinol, octyl-resorcinol; p-methyl-N-phenyl pyrazolone; the amide of a-resorcylic acid; 2-hydroxynaphthalene-3,6-disulfonic acid; H-acid; acetyl acetonilide; 2,3-dihydroxynaphthalene-6-sulfonic acid; a-resorcylic acid and the like.

It will be obvious that various combinations of the hydrophobic material may be used with various pigments and it is intended by the claims which follow to cover the modifications which would suggest themselves to those skilled in the art, as far as the prior art permits.

What is claimed is:

1. A non-tacky photographic sheet comprising a base support sheet, carrying in that order a precoat which includes a white opacifying pigment, a resinos binder, and from 2 to 20% based on the total weight of solids in the precoating composition of an emulsified hydrophobic solid material of waxy consistency selected from the group consisting of paraffin wax, rosin, the mixture of rosin and paraffin wax, water-insoluble polyethylene and water-insoluble polypropylene, said precoat carrying a photo-sensitive diazo type layer.

2. An article as defined in claim 1 wherein both surfaces of the base sheet are carrying said precoat, one of said precoat carrying a photosensitive layer containing a diazonium compound and a coupling component.

3. A sheet according to claim 1 wherein the emulsified hydrophobic material is a paraffin wax emulsion.

4. A sheet according to claim 1 wherein the emulsified hydrophobic material is an emulsified water-insoluble polyethylene.

5. A sheet according to claim 1 wherein the emulsified hydrophobic material is a rosin emulsion.

6. A sheet according to claim 1 wherein the emulsified hydrophobic material is the mixture of a paraffin wax and rosin.

7. A sheet according to claim 1 wherein the base is paper.

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