

1

2

3,418,469

## DIAZO REPRODUCTION

Robert M. Gold, Brooklyn, N.Y., assignor to Keuffel & Esser Company, Hoboken, N.J., a corporation of New Jersey

No Drawing. Filed Apr. 5, 1965, Ser. No. 445,704

10 Claims. (Cl. 250—65)

### ABSTRACT OF THE DISCLOSURE

A method is provided for image formation on diazo-type material and includes the use of developable diazo-type composition having an outer coating of a layer of discrete solid particles of a thermoplastic polymeric material which is ordinarily permeable to diazotype developing fluids, but when heated will form a coalesced impermeable film. Imagewise heating such material to form a film pattern of coalesced fluid impermeable polymer and application of a developer fluid, such as ammonia vapors or an alkaline solution of azo dye coupler, results in selective development of azo dye images in accordance with the film pattern.

The present invention relates to diazo reproduction and refers more particularly to materials and methods for making diazo reproductions.

At the present time, diazo materials are exposed to actinic radiation through a transparent or translucent original, thereby destroying the light-sensitive diazo compound in the exposed areas. The undecomposed diazo compound is then combined with a coupling component in the presence of an alkali to form a dye. It is not presently possible to copy two-sided printed materials or graphic information on opaque bases by this procedure, nor is it possible to make a reversal copy by this procedure.

Therefore one object of the present invention is to provide materials and methods for making diazo reproductions, which overcome the disadvantages of the prior art.

Another object is to provide materials and methods for copying opaque and two-sided originals.

Another object is to provide materials and methods for making direct and reversal copies.

Another object is to provide methods for making diazo reproductions by the reflex technique.

Another object is to provide methods for making diazo transparencies without ultraviolet radiation.

Another object is to provide methods for making diazo intermediates from originals having printed matter on both sides.

Other objects will become apparent in the course of the following specification.

The objects of the present invention may be realized by impressing an image on a diazo material overcoated with a layer of discrete coalesceable thermoplastic particles, by means of infrared radiation or ultraviolet radiation, and developing the image by means of ammonia vapors or a liquid developer. The diazo material may be of the dry-developing variety or the semi-moist variety. In the dry-developing type, the diazo compound and the coupler are on the same support. In the semi-moist type, only the diazo compound is on the support; the coupler is in the aqueous developer. The discrete coalesceable thermoplastic particles may also be coated together with the diazo compound. The diazo material preferably comprises a diazo layer on a support which is substantially vapor and liquid-impervious. Paper may be used but plastic films are better.

In one example of the present invention, a conventional dry-developing diazo material was overcoated with

a discontinuous layer of discrete coalesceable thermoplastic latex particles which coalesce above a given temperature. The uniform, discontinuous layer was substantially transparent except for a slight haze which was barely visible. The discontinuous layer was permeable to vapors and liquids. The resulting sheet was used in a normal manner by contact exposure to ultraviolet radiation which decomposed the diazo compound in the light-struck areas and by development in ammonia vapors to produce a positive reproduction of good quality.

The novel uses of such a material involve thermographic methods coupled with retention of the original conventional methods. Thermal imaging may take place in a thermographic copying machine using an original with infrared-absorbing graphics. The thermal exposure coalesces the latex particles in the image areas so that the particles adhere to each other and to the support in these areas. The coalesced particles thus form a vapor barrier or mask that prevents development in heated areas while the uncoalesced particles permit coupling in the unheated areas. Development with ammonia produces a reversal copy of the original. Subsequent uniform exposure to ultraviolet radiation stabilizes the image.

Exposure in the thermoprinting machine may be either by front-printing or back-printing. The former permits copying two-sided or opaque originals.

Thermographic and photographic exposure techniques may be combined in any sequence to obtain composite copies of two or more originals. The film substrate prevents ammonia permeation through the support to the underlying diazo layer, but paper and cloth substrates were still suitable for producing excellent reproductions. To prevent possible loss of image contrast due to ammonia development through the back of the porous paper or cloth support, a barrier coating of ammonia-impermeable polymer may be used.

A semi-moist diazo material was also used. The sensitized layer was overcoated with the latex and used for photographic or thermographic copying to give positives, negatives, or combinations of both. Development in the semi-moist developer proceeds normally for the ultraviolet-exposed copy, since the uncoalesced particles permit penetration of the developer into the sensitized layer.

Development of the thermally exposed material proceeds only in the unheated areas. In the heated areas, the coalesced particles were water-repellent and impervious to the developer solution.

Another example of this invention employs a developing sheet which releases alkali vapors upon heating. Preferably, the alkali-releasing temperature is below the particle-coalescing temperature to prevent serious image degradation. In this case, after thermal (or ultraviolet or both) exposure, the diazo material was placed in intimate contact with the alkali-releasing sheet with the particle layer in contact with the alkali-releasing sheet. The composite was then passed through a heating machine which heats the paper to the alkali-releasing temperature. Alternatively, an infrared-absorbing layer on the alkali sheet permits development by infrared radiation in a thermographic machine.

It was found in the present invention that some conventional diazo materials having a precoat layer of discrete, thermoplastic particles could be employed in this novel process to yield images of fair quality, but optimum results were obtained by laying down the discontinuous layer as an overcoat to obtain a maximum masking effect. This gave more complete barrier protection for the developing step.

Suitable supports for the diazo layer were paper, film, cloth and similar bases. Where the support is transparent, the reproduction may be used as a transparency for

projection purposes or as an intermediate for further reproduction.

Some suitable photosensitive diazo compounds were 4-diethyl-amino-benzene diazonium borofluoride; 2,5-dimethoxy-4-morpholino-benzene diazonium borofluoride; 2,5-diethoxy-4-morpholino-benzene-diazonium borofluoride; 4-ethylbenzylamino-benzene diazonium chloride; and mixtures thereof. Other photosensitive diazonium compounds may be used.

Some suitable couplers were 2,4-dihydroxy-benzamide; 1-methyl-3-hydroxy-4-acetyl-amido-benzene; 3-hydroxy-2-naphthoic acid ethanolamide hydrochloride; diresorcinol sulfide; 4-bromo-3,5-dihydroxy-benzoic acid amide; resorcinol; (2-hydroxy-4-methyl)-beta-phenyl-glutaric acid; 3-hydroxy-2-naphthoic acid ethylene-diamine amide hydrochloride; and mixtures thereof. Other couplers may also be used.

Some suitable latexes were Rhoplex B-85 acrylic resin latex, Vinac WR-20 polyvinyl acetate emulsion, poly-EM non-ionic polyethylene emulsion, emulsion M polystyrene emulsion, Poly-EM-11 anionic polyethylene emulsion. The latexes were diluted to 1 to 10 percent by volume for coating purposes. The particles were discrete when coated but were coalesced by the application of heat. The layer of discrete particles is permeable to ammonia and to aqueous developer, but the coalesced particles are impervious to ammonia and to aqueous developer. By proper selection of the latex, drying at moderate temperatures was permissible without causing coalescence.

Commercially available diazo material may be used as the starting material. It is coated with the layer of discrete coalesceable thermoplastic particles in a thin and transparent layer. In fact, the layer is barely discernible except as a slight haze on transparent supports.

It is apparent that the described examples are capable of many variations and modifications. All such variations and modifications are to be included within the scope of the present invention.

What is claimed is:

1. A diazo reproduction material consisting essentially of:

a substantially fluid-impermeable support; a layer of light-sensitive diazotype composition coated on said support, said composition comprising a light-sensitive diazonium compound capable of forming a dye with azo coupler compound; and

a fluid permeable layer of solid discrete heat-coalesceable thermoplastic polymer particles uniformly coated over said light-sensitive composition layer, said polymer being, when in the form of a film, substantially fluid impermeable.

2. A diazo reproduction material consisting essentially of:

a substantially fluid-impermeable support; a layer of light-sensitive diazotype composition coated on said support, said composition comprising a light-sensitive diazonium compound and an azo coupler compound capable of forming a dye with said diazonium compound; and

a fluid permeable layer of discrete coalesceable thermoplastic polymer particles uniformly coated on said layer of diazotype composition.

3. A diazo reproduction material according to claim 1 wherein said permeable layer consists essentially of discrete, coalesceable, thermoplastic particles of acrylic resin.

4. A diazo reproduction material according to claim 1 wherein said permeable layer consists essentially of discrete, coalesceable, thermoplastic particles of polyethylene.

5. A diazo reproduction material according to claim 1 wherein said permeable layer consists essentially of discrete, coalesceable, thermoplastic particles of polystyrene.

6. A diazo reproduction material according to claim 1 wherein said permeable layer consists essentially of discrete, coalesceable, thermoplastic particles of polyvinyl acetate.

7. A method of image reproduction comprising: heating imagewise the material defined in claim 1, thereby coalescing areas of said layer of polymer particles corresponding to said heated image and forming a fluid impermeable image pattern in said layer; and

applying to said imaged material a developer fluid capable of promoting the formation of an azo dye in said diazotype composition, whereby said developer fluid penetrates the permeable areas of said polymer particle layer and effects dye formation in those portions of said diazotype composition immediately underlying said permeable areas.

8. A method of image reproduction according to claim 7 wherein said developer fluid comprises an alkaline solution of an azo coupler compound.

9. A method of image reproduction according to claim 7 wherein said developer fluid is an alkaline vapor.

10. A method of image reproduction according to claim 7 including a further fixing step, after the application of developer, comprising exposing said material to ultraviolet radiation.

#### References Cited

##### UNITED STATES PATENTS

|           |         |                        |          |
|-----------|---------|------------------------|----------|
| 2,597,306 | 5/1952  | Eaton et al. ....      | 96—49 XR |
| 2,691,587 | 10/1954 | Greig .....            | 96—49    |
| 2,732,299 | 1/1956  | Morrison .....         | 96—49    |
| 3,027,256 | 3/1962  | Klimkowski et al. .... | 96—49    |
| 3,046,128 | 7/1962  | Klimkowski et al. ...  | 96—75 XR |
| 3,272,629 | 9/1966  | Hills .....            | 96—75    |
| 3,284,201 | 11/1966 | Meijs et al. ....      | 96—49 XR |

##### FOREIGN PATENTS

|           |        |         |
|-----------|--------|---------|
| 1,336,307 | 7/1963 | France. |
| 1,377,477 | 9/1964 | France. |

NORMAN G. TORCHIN, *Primary Examiner.*

C. L. BOWERS, JR., *Assistant Examiner.*

U.S. Cl. X.R.

96—49, 75; 117—36.8