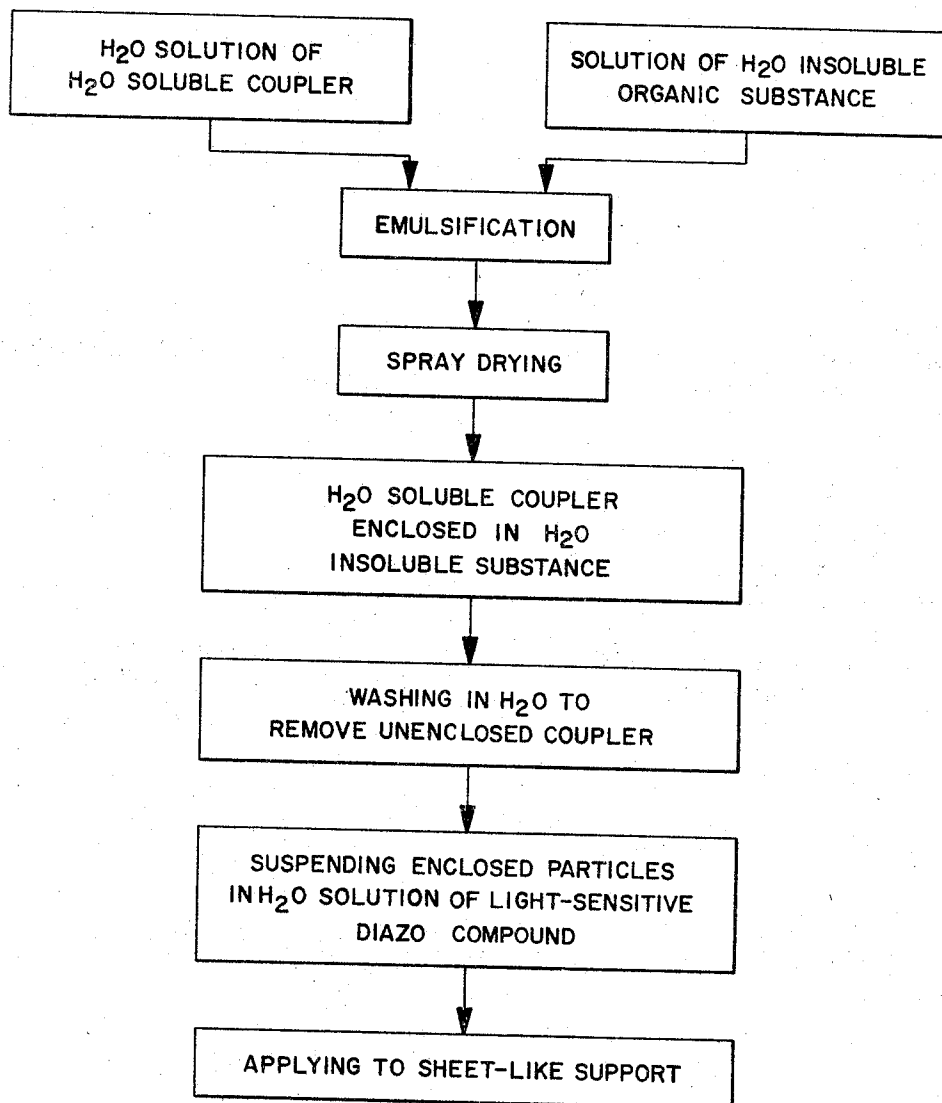


May 30, 1967

J. MUNDER ET AL
METHOD FOR PREPARING HEAT-DEVELOPABLE TWO-COMPONENT
DIAZOTYPE REPRODUCTION SHEET
Filed Dec. 20, 1963

3,322,556



INVENTORS
JOHANNES MUNDER
HELLMUT ZIEGLER

BY

Peter J. Millig

ATTORNEY

1

3,322,556

METHOD FOR PREPARING HEAT-DEVELOPABLE TWO-COMPONENT DIAZOTYPE REPRODUCTION SHEET

Johannes Munder, Wiesbaden-Biebrich, and Hellmut Ziegler, Wiesbaden-Schierstein, Germany, assignors, by mesne assignments, to Keuffel & Esser Company, Hoboken, N.J.

Filed Dec. 20, 1963, Ser. No. 332,288

Claims priority, application Germany, Dec. 22, 1962, K 48,553

4 Claims. (Cl. 117-34)

The present invention relates to diazotype reproduction materials and refers more particularly to heat-developable two-component diazotype reproduction materials and to processes for preparing said materials.

In the diazotype process, two methods of development are used: the dry process and the semi-wet process. In the dry process, the reproduction materials contain both diazo compound and coupler, and development of the exposed material is effected by means of gaseous ammonia. In the semi-wet process, the reproduction materials contain only diazo compound and development is effected by applying a solution of coupler to form an azo dye-stuff in the unexposed parts of coating.

The development step in both processes has disadvantages such as the noxious ammonia odors in the dry process and the need for a coupler bath in the semi-wet process. These disadvantages apply to apparatus requirements also. Therefore, attempts have been made to obtain a more simple development process by means such as steam.

The coupling of a diazo compound with a coupler containing hydroxy group takes place most readily in an alkaline to neutral pH region. Most experiments in this area have been directed towards the displacement of the pH value from the acid into the alkaline region with the help of certain additives. This can be done by the removal of a volatile acid or the production of alkaline substances from non-alkaline substances. Copies obtained in this way are inferior to the ammonia prints with respect to contrast and keeping qualities.

Further, the coupler and the diazo compound have been used in layers separated from each other by a fusible third layer to prevent premature coupling. Such a diazotype material is costly because three layers are applied to the supporting material; the middle one being free of pores and thus requiring careful attention.

One object of the present invention is to provide a method for the preparation of a two-component diazotype reproduction material developable, without the use of gaseous ammonia or a developer bath, by heat.

Another object is to provide a method for the preparation of a heat-developable two-component diazotype reproduction material which has good contrast, good keeping qualities, and ease of manufacture.

Other objects will become apparent from the specification, drawing, and claims.

Briefly, the present invention relates to a method for the preparation of a heat-developable diazotype reproduction material having on a sheet-like support a light-sensitive coating comprising a diazo compound and a coupler. The coupler consists of an alkali metal salt, alkaline earth metal salt, ammonium salt or amine salt of a phenolic or enolic hydroxy compound in the form of small particles enveloped in a water-insoluble substance melting at 50 to 200° C.

In the method according to the present invention, the water-soluble coupler is dissolved in water and then the solution is finely dispersed in a solution of water-insoluble

2

wax or resin to produce a water-in-oil emulsion. Alternatively, the aqueous solution may be formed by dissolving in water the base-less coupler and the equivalent quantity of the corresponding inorganic or organic base.

Emulsification can be effected by means of a high speed mixer (Ultra-Turrax-Mixer), or vibration mixer (Vibro-Mixer). Then the water in-oil-emulsion is spray-dried. In the resulting fine powder, the water-insoluble organic substance encloses the azo coupling component in a protective film, and when necessary, the fine powder may be washed with a solvent in which the protective film is not soluble, to remove any unenclosed azo coupling component adhering to the particles. Water or dilute acid can be used. When an emulsion of a sufficiently fine division and a suitable atomizing spray nozzle are used, a powder having a particle size of about 25 microns is obtained directly. If, however, fractionation should be necessary to obtain the desired powder of a particle size of not more than 30 microns, screening or wind shifting is done.

The coupling component in the form of tiny particles enveloped in the wax or resin is preferably used in a maximum grain size of 30 microns. If coarser particles are used it becomes difficult to obtain evenly coated diazotype material in accordance with the invention.

As the coupler or coupling component is inorganic due to its phenolate or enolate form, the necessary conditions for the coupling reaction to take place are already present. It does not occur, however, until the water-insoluble skin which envelops each individual particles of the coupler is melted by the action of heat.

For the skin enveloping the coupler component, any water-insoluble organic substance is suitable provided it has a narrow melting range within the region of 50 to 200° C., is colorless or only weakly colored, is fluid in its molten state, is sufficiently rigid at room temperature to afford continuing isolation, and does not react with the diazo compound used. Substances fulfilling these conditions include natural resins such as colophony, rosin resins and shellac; conversion products of natural resins, such as hydrogenated resins, calcium and zinc resinates, resin esters and synthetic resins modified with natural resins; maleic resins; oil-free alkyd resins; light colored phenol resins of the novolac type; alkyl phenol resins and terpene phenol resins; coumarone resins; vinyl polymers such as polyvinyl acetals, polyvinyl acetates, polyvinyl chloride, polyvinylidene chloride, polyvinyl ether polyacrylic acid ester, polystyrene and interpolymers of the vinyl compounds with one another and with other polymerizable compounds; polymers of aliphatic, unsaturated, hydrocarbons; ketone resins; chlorodiphenyl resins; epoxy resins and silicone resins.

Among substances having melting ranges in the lower portion of the temperature range given above, those with a narrow melting range, e.g. of not more than 10° C., are preferred.

As coupling component, any alkali metal, alkaline earth metal, ammonium or amine salt of a phenolic or enolic hydroxy compound that can couple with a diazo compound to form a dyestuff under the influence of heat can be used. The following can be used: 2,3-dihydroxynaphthalene; acetoacetic acid anilide; 2,3-dihydroxynaphthalene-6-sulfonic acid; 2-naphthol-3-carboxylic acid; 2-naphthol-3-carboxylic acid methyl ester; 2,4-dihydroxybenzamide; 1-methyl-3-hydroxy-benzene-4 glutaric acid; phenol - 3 - urea; 2,4,2',4' - tetrahydroxy - diphenyl; 2-naphthol-3,6-disulfonic acid sodium salt; and 1-phenyl-3-methyl-pyrazolone-(5).

Suitable diazo compounds have adequate stability in

3

the temperature range used for the heat development and couple in the presence of heat to form a dyestuff. Examples of such diazo compounds are: 2,5-diethoxy-4-benzoylamino-benzene diazonium chloride; 4-phenylaminobenzene diazonium hydrogen sulfate; 4-diazo-2,5-dimethoxy-4'-methyl diphenyl sulfide (HCl-salt); 4-morpholino benzene diazonium fluoborate; 4-morpholino-2,5-diethoxy benzene diazonium chloride; 4-morpholino-2,5-dimethoxy-benzene diazonium chloride; 4-dimethyl-amino-benzenediazonium chloride; 4 - (4' - ethoxyphenyl) 2,5-diethoxy-benzene diazonium chloride; 4-ethyl-benzyl-amino-benzene diazonium chloride; 2-ethoxy-4-diethyl-amino benzene diazonium chloride; and 4-benzylamino-2,5-diethoxybenzene diazonium chloride.

In addition to the diazo compound and the coupler, additives usually included in diazotype materials may also be present. Common additives are tartaric acid, citric acid, zinc chloride and thiourea. It is advantageous to include a wetting agent such as saponine to aid dispersion of coupler particles in an aqueous solution of the diazo compound. It is also advantageous for a binder such as carboxymethyl cellulose, solution starch, casein, gelatine or synthetic resin dispersions to be used to ensure firm adhesion of the particles to the supporting material. Base papers commonly used in diazo printing can be used as sheet-like supports, and transparent foils of cellulose hydrate, cellulose esters, polyamides polyester, polycarbonates, polyvinyl compounds and the like are suitable. The preference, however, is for paper and similar cellulose products.

To prepare a copy, the reproduction material of the present invention is exposed under a master to actinic radiation to decompose diazo compound in the exposed areas. It is then brought into contact with a hot body such as a hot roller or plate to melt the protective film and thus permit coupling to occur. A copy can also be produced by the contact process if a master with an image on one side only is placed between an infrared source and the reproduction material in such a way that the image side of the master and the non-sensitized side of the light-sensitive reproduction material are in contact. Under the influence of the infrared rays, the image parts of the master generate more heat than the image-free parts. With a suitable dosage of radiation, this heat is sufficient to melt the water-insoluble skin enveloping the coupler particles in the parts adjacent to the image parts, and thus permits the coupling to occur in the image areas. The images are fixed by exposure to light, the unused diazo compound left in the image-free parts being thereby decomposed.

A third method whereby copies can be produced is the reflex process. The reproduction material is placed between the infrared source and the master in such a way that the image side of the master and the non-sensitized side of the light-sensitive material are in contact. The master may in this case have images on both sides. The infrared rays are converted to heat in the image parts to form a heat image. The heat image melts the protective film on the coupler particles and permits coupling to occur. In this case too, the unused diazo compound in the image-free parts is decomposed by subsequent exposure to light.

Reproduction coatings in accordance with the present invention have the advantage that they are simple to produce. They can be developed by a mere heating process, i.e., without any adjuvant such as alkali or steam, give prints with very good contrast and have good keeping qualities.

Example

50 grams of the sodium salt of 2-naphthol-3,6-disulfonic acid were dissolved in 175 grams of water and the solution emulsified by means of a high speed mixer (Ultra-Turrax-Mixer) in a solution of 200 grams of a maleinate resin having a melting range between 69 and 77° C., such as "Hobimal" P 59, in 1800 grams of trichloro-

4

ethylene. The emulsion was sprayed by an air stream at about 30 atmospheres at the rate of 12 ml./min. into a conic vessel heated to 90 to 95° C. so that the main part of the water and all of the trichloroethylene was evaporated and removed by the air. The resin enclosed the particles of the moist sodium salt as a protective film. Any unenclosed coupling substance which adhered to the particles was removed by several washings with water. The resultant particles had an average particle size of 20 microns, and were used directly after drying at 40° C.

The following mixture was applied to a paper support:

20 grams of the coupling powder enclosed by the resin
2 grams of 4-dimethylamino-benzene diazonium chloride (zinc chloride salt)
1 gram of citric acid
8 grams of thiourea
0.2 gram of saponine
2.5 grams of casein
67 grams of water.

The above mentioned resin sold under the trade name "Hobimal" P 59 is a polyester resin prepared by condensing maleic acid, rosin, and a polyhydric alcohol.

The support coated with the suspension was dried in an air stream at 30 to 40° C.

After exposure to a UV arc lamp behind a master the material was developed by means of heated rolls and plates having a temperature of 110 to 120° C. by contacting the material with the latter for a short period of time. A blue violet copy corresponding to the master was obtained.

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

What is claimed is:

1. A method for the preparation of a heat-developable two-component diazotype reproduction material comprising the steps of: emulsifying an aqueous solution of a coupler in a solution of water-insoluble organic substance melting between 50 and 200° C., said coupler being a salt of a base of the group consisting of alkali metals, alkaline earth metals, ammonia and amines, and an acid organic hydroxy compound of the group consisting of phenols and enols; spray-drying the emulsion at a temperature below the boiling point of water to form fine moist particles of coupler enclosed in said substance, said particles of enclosed coupler having a maximum particle size of 30 microns; washing said particles with water to remove unenclosed coupler from the surface of said particles; suspending said particles in an aqueous solution of light-sensitive diazo compound capable of coupling with said said coupler under the influence of heat; coating a sheet-like support uniformly with the suspension; and drying the coated support at 30 to 40° C. to produce a heat-developable two-component diazotype reproduction material.

2. A method in accordance with claim 1 in which said coupler is selected from the group consisting of alkali metal, alkaline earth metal, ammonium and amine salts of: 2,3-dihydroxy naphthalene; acetoacetic acid anilide; 2,3-dihydroxynaphthalene-6-sulfonic acid; 2-naphthol-3-carboxylic acid; 2-naphthol-3-carboxylic acid methyl ester; 2,4-dihydroxy benzamide; 1-methyl-3-hydroxy-benzene-4-glutaric acid; phenol - 3 - urea; 2,4,2',4'-tetrahydroxy diphenyl; 2-naphthol-3,6-disulfonic acid; an 1-phenyl-3-methyl-pyrazolone-(5).

3. A method in accordance with claim 1 in which said diazo compound is a member selected from the group consisting of: 2,5-diethoxy-4-benzoylamino-benzene diazonium chloride; 4-phenylaminobenzene diazonium hydrogen sulfate; 4-diazo-2,5-dimethoxy-4'-methyl diphenyl sulfide (HCl-salt); 4-morpholino-benzene diazonium

5

fluoborate; 4-morpholino-2,5-diethoxybenzene diazonium chloride; 4-morpholino-2,5-dimethoxy benzene diazonium chloride; 4-dimethylamino benzene diazonium chloride; 4-(4'-ethoxy-phenyl) - 2,5 - diethoxy-benzene diazonium chloride; 4-ethylbenzylamino-benzene diazonium chloride; 2-ethoxy-4-diethylaminobenzene diazonium chloride; and 4-benzyl-amino-2,5-diethoxybenzene diazonium chloride.

4. A method in accordance with claim 1 in which said coupler is the sodium salt of 2-naphthol-3,6-disulfonic acid, said substance is a maleinate resin melting between 60 and 77° C., and said diazo compound is 4-dimethyl-amino benzene diazonium chloride (zinc chloride salt).

5

10

6

References Cited

UNITED STATES PATENTS

2,680,062	6/1954	Sus	117—36.8
2,939,009	5/1960	Tien	117—36.1
3,016,308	1/1962	Macaulay	117—36.1
3,202,510	8/1965	Hollmann	117—34

OTHER REFERENCES

10 Kosar: "Photo. Sci. & Eng.," volume 5, No. 4, July-August 1961, pages 239-243.

MURRAY KATZ, *Primary Examiner.*