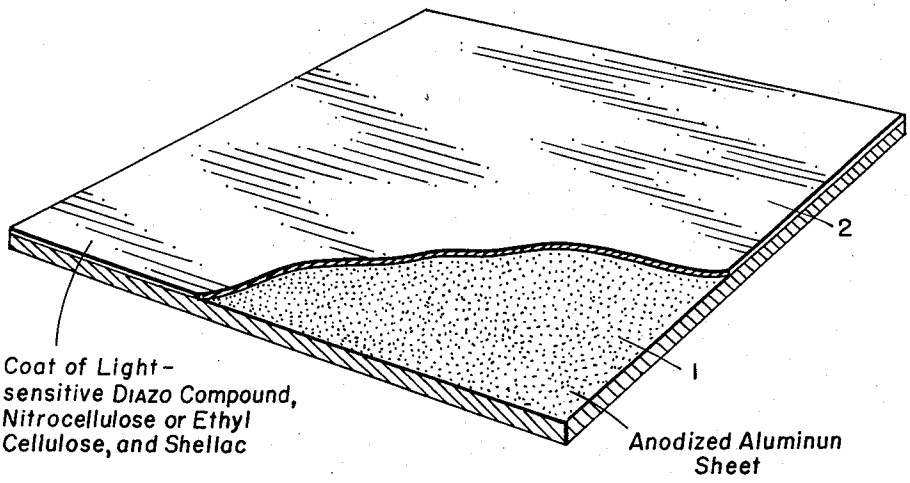
Jan. 27, 1959 R. P. WEEGAR ET AL 2,871,119

DIAZOTYPE REPRODUCTION MATERIAL AND METHOD

Filed Feb. 21, 1955



INVENTORS:
RALPH P. WEEGAR
HENRY C. UNKAUF
BY
Marzall, Johnston, Cook & Root
ATT'YS

United States Patent Office 2,871,119 Patented Jan. 27, 1959

2,871,119

DIAZOTYPE REPRODUCTION MATERIAL AND METHOD

Ralph P. Weegar, Villa Park, and Henry C. Unkauf, Chicago, Ill., assignors to Eugene Dietzgen Co., Chicago, Ill., a corporation of Delaware

Application February 21, 1955, Serial No. 489,440

8 Claims. (Cl. 96—49)

This invention relates to a diazotype reproduction material and method of manufacture. More particularly, it relates to the provision of a light-sensitive diazotype layer on a metal surface.

Water and organic solvent-impervious metal surfaces pose difficult problems in the application and fixation thereon of materials which provide photographic light-sensitive layers. In the provision of photographic light-sensitive layers on other base materials, an absorbent surface is commonly treated with a solution of light-sensitive components which serve to reproduce a desired image. Thus, for example, diazotype reproduction media are produced by treating an absorbent surface with a solution containing azo dye components in an uncombined form. The most commonly used base material is paper, and the components are usually in aqueous solution. Sufficient penetration is obtained to insure bonding of the paper and the sensitizing composition, and the ultimate dye image. Cellulose esters and ethers are also in common use as base materials, and they are impregnated with a sensitizing solution by the addition of penetrating or swelling agents which have a solvent action on the base material, to insure the necessary bonding.

The prior methods are, however, unsuitable for coating liquid-impervious metal surfaces, there being insufficient bonding with the base material to provide a uniform layer of the sensitizing components which is permanently bonded and is resistant to wear and abrasion. Furthermore, the dye images reproduced on the surface by exposure and development have little permanency, and in order to prevent easy removal of the images, it is necessary to overcoat them with a transparent coating. Even such a coating on a metal is easily scratched, chipped and otherwise damaged in ordinary handling, shipping, and storage.

There are a number of advantages in the use of dimensionally stable aluminum base materials, especially in the production of aluminum templates or the like, and it is highly desirable to provide an aluminum base coated with a light-sensitive layer.

It is therefore an object of the invention to provide a new and improved diazotype reproduction material and method of manufacture, particularly a dimensionally stable photographic reproduction material.

A particular object is to provide a reproduction material which includes an aluminum base and a light-sensitive diazotype layer thereon.

A further object is to provide a diazotype reproduction element which furnishes excellent uniform permanent reproduction and which is resistant to the various conditions encountered.

An additional object is to supply a reliable and effective method for providing a light-sensitive diazotype layer on an impervious aluminum surface, which surface absorbs substantially no water or organic solvent, so that it is unreceptive to aqueous and organic solvent solutions, for all practical purposes, and there will be no or only insubstantial adherence or binding of the solutions and their ingredients to the surface.

Another object is to coat an aluminum base or support employing a principally non-aqueous organic solvent solution of a light-sensitive diazo compound.

Still another object is to provide a base of aluminum sheet material and the like, and a strongly adherent diazotype layer thereon, which may be exposed to light under a drawing or pattern to mark the base rapidly and accurately for cutting or shaping into a template, pattern, structural part and the like.

An additional object is to provide a method of preparing an aluminum body having a design on its surface.

Yet another object is to provide a diazotype coat on an aluminum base material having the desired properties of transparency or translucency, little color, storage stability and resistance to chemical and physical attack under the conditions normally encountered.

Other objects include the manufacture and application of new and improved coating compositions, and coats and coated base materials, and the provision of new and useful methods. These and other objects and advantages of the invention will appear on consideration of the specification taken in conjunction with the attached drawing, in which the single figure is a broken perspective view of a sheet of anodized aluminum provided with a diazotype layer or coat, according to a preferred embodiment of the invention.

The invention provides a photographic reproduction material which includes an aluminum base material, and a coat of a light-sensitive diazo compound and a cellulose ester or ether, particularly, nitrocellulose or ethyl cellulose.

A method for providing a diazotype layer on an aluminum surface is provided in the invention, which method includes coating the aluminum surface with an organic solvent solution of a diazo compound and the cellulose derivative. The wet coat is dried to provide a light-sensitive surface on the body, the light-sensitive surface is exposed to light of varying intensity, and the resulting print is developed to produce an aluminum body having a design on its surface.

The aluminum surface is rendered receptive to the sensitizing composition by pitting or roughening, so that the surface is covered with a multitude of closely spaced fine pits, cavities or indentations. The surface is pitted by anodizing, alodyning, Diversey etching, or sand blasting, for example.

The aluminum surface thus rendered receptive to the sensitizing composition is provided with an outer layer or coating of a light-sensitive diazo compound and ethyl cellulose or nitrocellulose, by applying the components in an organic solvent solution. Adherence to the surface is improved when the solution, and thus the resulting coat, additionally contains a resinous material of the shellac type. Development of the subsequent print is also benefitted thereby.

An important phenomenon cooperating in the invention is that although the films of the cellulose derivatives are not alone pervious to ammonia and water vapor, and to the developing solutions, so that a diazo layer cannot be overcoated satisfactorily with them, the thin films are sufficiently pervious when mixed with the diazo components to exhibit good developing properties. On the other hand, the films or coats may be regarded as water resistant and have excellent stability to heat, ammonia, water and water vapor, not swelling, loosening or dissolving, and they are very rugged and durable.

Diazo compounds which are organic solvent soluble and suitable for the sensitizing compositions of the invention include, for example, those which are derived from aromatic p-diamines of the benzene series, particularly

those which are N-mono or di-substituted on the undiazotized amino groups, with or without aliphatic substitution on the benzene ring. Also included are resinous condensation products of aldehydes, such as formaldehyde, with these light-sensitive diazo compounds, and the p-amino phenyl sulfones of the diazo compounds. The boron trifluoride, the stannous chloride, the cadmium chloride, and the zinc chloride double salts of the aforementioned light sensitive organic solvent soluble diazo compounds are included. Specific examples of such compounds which are used in the production of diazotype images of high contrast are the diazo derivatives of p-amino-N-methyl aniline, p-amino-N-di-methyl aniline, p-amino - N - ethyl aniline, p-amino-N-di-ethyl aniline, p-amino - N - methyl-N-ethyl aniline, p-amino-N-ethoxy aniline, p-amino-N-methyl-N-ethoxy aniline, p-amino-N-ethyl-N-ethoxy aniline, p-amino-N-diethyl - m - toluidine, and 1-amino-3-methyl-4-ethylamino benzene, all in the form of their diazo double salts with zinc chloride, cadmium chloride, stannous chloride, or boron trifluoride, or their diazo p-amino-phenyl sulfones, or their diazo-formaldehyde resinous condensation products.

As coupling components, any compound which will function as a coupling component may be employed either in the coating composition together with the diazo compound in order to produce a two-component system, or in the developing solution as a color forming developer. In either case, the coupling component selected will be one which will produce the desired color or a combination of coupling components which will produce a multi-color effect. Examples of preferred coupling components are: 2,3-dihydroxy naphthalene and its 6-sulfonic acid derivative, phloroglucinol, methyl phloroglucinol, resorcinol, resorcinol-mono-methyl ether, di-chloro resorcinol, m-hydroxy phenyl urea, acetoacetanilide, acetoacetylcyclohexyl amide, 7-hydroxy naphthalene-1-biguanide, 7-hydroxy-1,2-naphthimidazole, 2-amino-8-naphthol-3,6-disulfonic acid, 2-, 7-dihydroxy naphthalene, 1-naphthol-4-sulfonic acid, and 1-amino-8-naphthol-3,6-disulfonic acid.

The sensitizing compositions may contain the usual adjuncts such as metal salts, to intensify the dyestuff image, i. e., aluminum sulfate, titanium ammonium fluoride, nickel sulfate and the like, and acids designed to retard precoupling such as citric acid, maleic acid, tartaric acid, boric acid and the like.

The diazo composition can also advantageously include a filler such as colloidal silica, hydrated silica, diatomaceous earth, bentonite, mica and the like. The filler acts to raise the softening point of the coating, promote development of a print by inducing porosity, and provide a mat surface.

The sensitizing composition is a principally non-aqueous organic solvent solution of the diazo ingredients and the cellulose ester or ether, and preferably, a shellac type resinous material. The ingredients are balanced for mutual compatibility and the properties desired. The solvent and film-forming ingredients are selected for solubility and are adjusted to a viscosity suitable for application and which will properly suspend the filler, and to provide a continuous abrasion-resistant film. The solvents are preferably selected from the group of lower aliphatic alcohols, lower aliphatic ketones, lower aliphatic glycol esters and lower aliphatic glycol ethers, and they are specially selected to furnish a controlled rate of drying on application to the base material. Thus, the solvents are balanced to result in a drying rate which is slow enough to avoid condensation or pick-up of water and to avoid premature drying in the rollers or other equipment, yet rapid enough to dry rapidly and completely in a satisfactory manner after application, furnishing a thin uniform strongly adhering and non-tacky surface coat. For example, a drying rate of 5–10 minutes at 150–175° F. in commercial coating equipment is provided.

The primary solvent for the mixture is methanol or ethanol, or acetone or methyl ethyl ketone may be substituted in whole or in part. The primary solvent is present in a major proportion by weight of the total of the organic solvents, preferably in a proportion of 60–90% of the solvents. The primary solvent is blended with a minor proportion, preferably 10–40%, of a higher boiling alcohol or the equivalent, which serves to prevent overly rapid drying with consequent "blushing." The medium boiling lower aliphatic alcohols having 4 carbon atoms or more and which are liquid at room temperature, such as butyl alcohol and amyl alcohol, are desirably employed, and they may be substituted in whole or in part by lower aliphatic glycol esters or ethers, such as the esters or ethers of ethylene glycol, propylene glycol and glycerine. In a controlled low humidity, normal or isopropanol may be used alone.

A preferred combination of solvents is a mixture of 90–85% of methanol and 10–15% of butanol, or an equivalent mixture.

In the compositions which are ammonia developed after printing, a small amount of a lower aliphatic glycol, such as ethylene glycol, propylene glycol and glycerine, may be included to assist in picking up water vapor in developing. The proportion of glycol is preferably about ¼ to 1 part by weight to 1 part of the cellulose derivative. This function together with that of the secondary or higher boiling solvent is also provided by Cellosolve esters, such as the lower aliphatic Cellosolve esters, preferably β-alkoxy ethyl acetate.

In the sensitizing composition, the cellulose ether or ester binder is preferably employed in a proportion of about ¼ to 5 parts by weight to 1 part of diazo compound. The reference to diazo compound does not include the coupling components and the adjuncts. Preferably, a shellac type resinous substance is included in a proportion of about ¼ to 1 part by weight to 1 part of cellulose ether or ester.

About 30 to 60 parts by weight of solvent per part of the cellulose binder are employed, equivalent to a proportion of binder of about 3.3% to 1.6% based on the solvents. About 20 to 200 parts by weight of solvent are employed per part of diazo compound, so that the diazo compound is present in a proportion of about 5 to 0.5% of the solvents. It is ordinarily preferred to incorporate about 0.5 to 5 parts of filler per part of diazo compound.

The composition includes merely sufficient water to dissolve those components of the diazo system which are insoluble or difficultly soluble in organic solvents, but not enough to preicpitate the cellulose ester or ether, or the shellac, and the proportion of water thus amounts to a maximum of about 3% by weight of the complete sensitizing composition.

The sensitizing composition prepared in the above manner is applied to the receptive aluminum surface by brushing, spraying, bead-coating, roller coating, silk screening, or the like, to provide a thin coat on the surface. The material is dried in the dark, at a temperature of from about room temperature to about 250° F., the upper temperature being limited by the stability of the diazo components. An adherent sensitized layer is thus firmly bonded to the aluminum surface. The reproduction material so produced can be exposed to light of varying intensity in accordance with a design to be reproduced thereon, e. g., under a pattern to be reproduced, and the images developed by exposure to ammonia vapors in the case of the two-component or dry-developing process, or by spraying, dipping, swabbing or sponging with a developing solution in the case of the one-component or moist-developing process.

When the original pattern or drawing is produced on a dimensionally stable medium, such as photo-template glass cloth, the final diazotype reproduction on the aluminum surface will be an exact true-to-scale duplicate copy of the original. The resulting copy is unaffected by atmospheric moisture and requires no over-spraying or

lacquering, as there is no rubbing or peeling off of the surface, and the image is well protected. The sensitized aluminum materials and the resulting prints may be transported and employed in various localities; for example, they have found widespread application in the manufacture of metal templates in the aircraft industry.

The following example is furnished to assist in providing a complete understanding of the invention, but it is to be understood that the invention is not limited thereto nor to the specific compositions, proportions and conditions set forth therein, which are given only for purposes of illustration.

Example

The example illustrates production of a direct (positive image) dimensionally stable blue line print, ammonia developed, on an aluminum metal sheet.

The solution is prepared, having the following compositions:

Methanol	cc.	3,000
n-Butanol	cc.	250
Water	cc.	235
Citric acid	gms.	55
Zinc chloride	gms.	47
Thiourea	gms.	55
2,3-di-hydroxynaphthalene-6-sulfonic acid	gms.	25
p - Diazo - N - diethyl - m - toluidine, zinc chloride double salt	gms.	55

These ingredients, thoroughly mixed and filtered, are added to the following mixture:

Methanol	cc.	3,500
n-Butanol	cc.	500
Shellac (bleached, dewaxed)	gms.	100
Nitrocotton (RS 5–6 sec.)	gms.	200
Diatomaceous earth (Johns-Manville "Celite")	gms.	75

The final mix is stored in a covered crock until ready for use.

An aluminum metal sheet, deep-etched (anodized), 12′ long, 4′ wide, and 0.125″ thick, represented by the numeral **1** in the drawing, is uniformly spray coated in a layer about 0.0001–0.0002″ thick with the above-described sensitizing solution, and dried in the dark, so that a coat or film **2** is provided on a surface of the sheet and strongly adheres thereto. A print is made on the sensitized metal sheet, using as the original pattern, a 12′ x 4′ sepia intermediate print on plastic-impregnated glass cloth. The metal plate is contact printed by means of an arc light, and is developed by placing it in a wooden box, 14′ long, 5′ high, and 1′ wide, filled with ammonia and water vapors.

The resulting blue-line positive copy is an exact, true-to-scale, positive reproduction of the sepia intermediate print, having a very small distortion.

The above mix may also include 100 cc. of ethylene glycol or propylene glycol, to assist in developing. In place of the nitrocotton, 200 gms. of ethyl cellulose (Hercules N–50) can be employed.

Other two-component diazo systems can be substituted such as p-diazo-N-methyl-N-hydroxy-ethyl aniline, zinc chloride double salt, and resorcinol, which produces a direct sepia print; and p-diazo-N-ethyl-N-ethoxy aniline, stannous chloride double salt, and 2,3-di-hydroxy-naphthalene, which produces a direct blue line print. A one-component diazo system can also be employed, such as p-diazo-N-ethyl-N-benzyl aniline, cadmium chloride double salt, and naphthalene-1,3,6-tri-sulfonic acid, sodium salt, developed with phloroglucinol and resorcinol solution, which produces a direct sepia line print; and 4-diazo-N-benzoyl-2,5-dibutoxy aniline, zinc chloride double salt, developed with phloroglucinol solution, which produces a direct black line print. Other combinations of light-sensitive diazo compounds, or light-sensitive diazo compounds and azo coupling components, soluble in the types of organic solvents described, and suitable for the preparation of photographic light-sensitive layers, i. e., which will provide a photographic reproduction, visually reproducing a drawing on exposure to light and developing by undergoing a substantial color change, can be substituted for the compounds employed.

In this manner, a new and improved photographic reproduction material constituting a sensitized aluminum base is provided. This material is especially useful for rapidly and accurately reproducing a drawing or pattern on the surface of the aluminum, for producing templates, structural members and the like. Aluminum sheets may be coated simply and rapidly at any location, transported as desired and exposed under a drawing suited for the intended purpose. The method and material find especially advantageous use in quantity production.

What is claimed is:

1. An aluminum base and an adherent coat of a light-sensitive diazo compound, a member selected from the class consisting of ethyl cellulose and nitrocellulose, and shellac.

2. A pitted aluminum sheet and an adherent coat of a light-sensitive diazo compound, a member selected from the class consisting of ethyl cellulose and nitrocellulose, and shellac.

3. An aluminum base and an adherent coat of a light-sensitive diazo compound, ethyl cellulose, and shellac.

4. An aluminum base and an adherent coat of a light-sensitive diazo compound, nitrocellulose, and shellac.

5. The method for providing a light-sensitive diazo-type layer on an aluminum surface which comprises coating said surface with an organic solvent solution of a light-sensitive diazo compound, a member selected from the class consisting of ethyl cellulose and nitrocellulose, and shellac.

6. The method for providing a light-sensitive diazo-type layer on an aluminum surface which comprises coating said surface with an organic solvent solution of a light-sensitive diazo compound, a member selected from the class consisting of ethyl cellulose and nitrocellulose, and shellac, said solvent being selected from the class consisting of lower aliphatic alcohols, lower aliphatic ketones, lower aliphatic glycol esters, and lower aliphatic glycol ethers.

7. The method for providing a light-sensitive diazotype layer on an aluminum surface which comprises coating said surface with an organic solvent solution of a light-sensitive diazo compound, a member selected from the class consisting of ethyl cellulose and nitrocellulose, and shellac, said solvent being a mixture of methanol and butanol.

8. The method of preparing an aluminum body having a design on a surface thereof which comprises coating a pitted surface of an aluminum body with an organic solvent solution of a light-sensitive diazo compound, a member selected from the class consisting of ethyl cellulose and nitrocellulose, and shellac, drying the thus coated body, exposing the resulting light-sensitive surface of said body to light of varying intensity in accordance with a design to be reproduced, and developing the resulting print.

References Cited in the file of this patent

UNITED STATES PATENTS

2,409,564	Heinecke et al.	Oct. 15, 1946
2,593,928	Slifkin	Apr. 22, 1952
2,714,066	Jewett et al.	July 26, 1955

FOREIGN PATENTS

539,314	Great Britain	Sept. 4, 1941
563,804	Great Britain	Aug. 30, 1944
711,626	Great Britain	July 7, 1954