

UNITED STATES PATENT OFFICE.

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HELIOCAUSTIC ART COMPANY, OF SAME PLACE.

PROCESS OF PRODUCING PHOTOGRAPHS ON HARD SURFACES.

SPECIFICATION forming part of Letters Patent No. 474,850, dated May 17, 1892.

Application filed August 23, 1890. Renewed September 12, 1891. Serial No. 405,566. (No specimens.)

To all whom it may concern:

Be it known that I, ARMAND MÜLLER-JACOBS, a citizen of the Republic of Switzerland, and a resident of New York, in the
5 county of New York and State of New York, have invented certain new and useful Improvements in the Process of Producing Photographs, &c., on Hard Surfaces, of which the following is a specification.

10 My invention has reference to a new process of producing photographs, images, and pictures on hard surfaces, as glass, metal, porcelain, &c.; and the invention consists in
15 applying to such a surface a coating of a solution of guaiaretic acid or of the guaiaretate of a metal or organic base and submitting the so-coated surface under a photographic negative or a transparent positive of
20 the image to the action of the light, whereby the parts of the coating exposed to the light through the unaffected parts of the negative or transparent positive become hard and insoluble, then developing the coated surface,
25 and finally applying to the film a suitable acid, whereby the picture is etched into the surface. The hard portions of the film which are not affected by the acid are then removed.

I have found that the guaiaretic acid ($C_{20}H_{26}O_4$) or its metallic salts, or those made
30 of guaiaretic acid with organic bases, by exposure to light change their properties as to solubility and as to resistance to oxidizing agents. The guaiaretic acid, as well known, is, freshly prepared, soluble in alcohol, ether,
35 bisulphide of carbon, chloroform, acetic acid, benzole, and other substances; but by exposure to light it becomes less or entirely insoluble in these substances, like asphaltum or resins—that is to say, the salts of abietic
40 acid, ($C_{44}H_{64}O_5$.) As far as my researches go guaiacetic acid ($C_{19}H_{22}O_6$) is formed by this action, which latter is still more oxidized by certain likewise-acting substances. A similar
45 effect takes place by exposing the salts of guaiaretic acid with metals or organic bases, also the chlorine, bromine, and iodine substitution products or the corresponding salts to the action of light. Certain colors—for instance, anilin-violet, magenta-red, safranine—
50 when combined in minute quantities with guaiaretic acid or its salts accelerate the ac-

tion of the light—i. e., they act as sensitizers. I furthermore found that a thin coating of this acid or its salts laid upon a hard surface and exposed to the light for a certain time
55 becomes impermeable by dilute universal or organic acids. These properties of guaiaretic acid or its salts, as aforesaid, render them useful for the production or reproduction of pictures, photographs, ornaments, &c., by means
60 of the actinic rays.

In carrying out my invention to produce a photograph, picture, image, or ornaments on a hard surface, as metal, porcelain, glass, lithographic stone, &c., I first dissolve one
65 hundred parts of crystallized guaiaretic acid, or, to obtain a more sensitive film, one hundred and twenty parts of dry amorphous guaiaretate of silver or of a corresponding quantity of the zinc, lead, or magnesium salt
70 (which latter are less sensitive than the silver salt) in five hundred parts of pure benzole. I may use the salts colored with three to four per cent. of aniline-violet or another
75 aniline color or colors. I then prepare a rubber solution by dissolving seven and one-half parts of dry caoutchouc in five hundred parts of benzole. I may also use a collodion solution instead of rubber, the collodion solution
80 containing one to two per cent. of nitro-cellulose; but I prefer the above-described composition of rubber. Both solutions are then thoroughly mixed together and the well-cleaned surface on which the picture is to be produced is carefully coated with the mixture
85 thus obtained in the dark. Then the so-coated surface is exposed under a negative or transparent positive to the action of light, a ten to twelve minute's exposure to direct sunlight being sufficient to harden the exposed parts
90 and to render them insoluble in the developing-bath, and the best I found to be composed of a mixture of one part of benzole and five parts of spirits of turpentine. Of course
95 other developers can be used. The parts of the film which are not affected by the action of the light are thereby removed and the picture appears on the surface. The plate is then dried and etched by appropriate acids, according to the nature of the surface to
100 which the sensitive film is applied; or it may be printed from directly with lithographic ink.

Another method of applying the light sensitive properties of the guaiaretic acid or of the guaiaretates to the art of production of pictures, images, or ornaments is the following: I mix a neutral aqueous solution of ten parts of pure guaiaretic acid in any alkali with one hundred parts of a dilute solution of gelatine. Then I coat the well-cleaned surface with this solution and dry it in the dark in a horizontal position by a heat not exceeding 120° Fahrenheit. The object is then put into a tray containing a weak solution of sulphuric, hydrochloric, or any other suitable acid to precipitate the guaiaretic acid in the gelatine film, or in a weak solution of a salt of a metal—for instance, of nitrate of silver, sulphate of magnesium, &c.—to form a guaiaretate. The film can be more sensitized if it is brought after thoroughly washing in a very dilute bath of an aniline color, as above mentioned. After a second drying the film is exposed and the negative or transparent positive and developed by means of the benzole developer. The gelatine film is then, after drying, hardened by chromic or common alum, tannic acid, or any other suitable substance. The surface having the thus-prepared picture can afterward be etched with the appropriate acid.

30 The guaiaretic acid which I use is prepared in the following way: Two parts of guaiacum are dissolved in ten parts of alcohol, filtered, and concentrated to a thin sirupy solution, Then it is mixed with a warm concentrated

solution of one part of potassium hydrate. After twenty-four hours standing it forms a mass of the consistency of pulp and is pressed through a filtering-cloth. The remainder is thoroughly washed first with alcohol and then with water and crystallized by means of dilute alcohol.

Having thus described my invention, I claim as new and desire to secure by Letters Patent—

1. The process of producing photographs, images, and pictures on hard surfaces, which consists in coating the surfaces with a solution of guaiaretic acid or of the guaiaretate of a metal or organic base, subjecting the so-coated surface under a negative or transparent positive to the action of the light, and after developing the same subjecting the surface to a suitable acid, by which the photograph or image is etched into the surface, substantially as set forth.

2. In the art of photography, the process which consists in coating a surface with a guaiaretic acid or its metal or organic salts as the essential sensitizing medium, substantially as set forth.

Signed at New York, in the county of New York and State of New York, this 5th day of August, A. D. 1890.

ARMAND MÜLLER-JACOBS.

Witnesses:

CHARLES KARP,
JOHN J. POWERS.