## United States Patent Office.

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## PROCESS OF SENSITIZING PAPER.

SPECIFICATION forming part of Letters Patent No. 637,637, dated November 21, 1899.

Application filed July 22, 1899. Serial No. 724,792. (No specimens.)

To all whom it may concern:

Be it known that I, JOHANNES MEYER, a citizen of the United States, residing in the city of New York, in the borough of Brooklyn 5 and State of New York, have invented certain new and useful Improvements in Processes of Sensitizing Paper and other Surfaces, of which

the following is a specification.

This process is based upon the discovery of to the valuable properties of the silver phosphates when combined with organic acids, such as acetic, tartaric, citric, and succinic acids. The silver phosphates have so far not been employed for photographic or other pur-15 poses and the only mention of any application made of them is to be found in Hardwich's Manual of Photographic Chemistry. He writes: "Other insoluble salts, such as the phosphate and citrate, render the paper 20 more sensitive than when it has been treated with a soluble salt of silver only." The great value of the silver phosphates consists in their property of forming emulsions with suitable organic acids, which behave in all respects 25 like the well-known emulsions of the silver haloid salts with albumen, gelatin, or collodion. I have discovered that the silver phosphates, aside from being soluble in ammonia, phosphoric acid, and nitric acid so-30 lutions, as was well known, form solutions with a number of organic acids—as, for instance, acetic, tartaric, citric, and succinic acid; but under certain conditions silver phosphates will form, in conjunction with an or-35 ganic acid, a true emulsion. I have studied the behavior of silver phosphate toward tartaric acid in this direction most carefully, and as the tartaric acid-silver-phosphate emulsion—is chiefly employed I will now proceed 40 to give directions how to prepare and how to use it.

To an aqueous solution of one dram of silver nitrate a well-diluted solution of sodium phosphate is added. The resulting silver 45 phosphate is well washed by decantation and brought to the volume of one fluid ounce. To this silver phosphate held in suspension we add five drams of tartaric acid dissolved in five drams of water, at the same time im-50 parting to the containing vessel a quick rotary motion. In this way is obtained a white jelly-

like mass of a volume of two ounces containing a quantity of silver phosphate equivalent to the dram of nitrate we started from. It is essential that all the chemicals, including the 55 water, be chemically pure. To render this emulsion more fluid, it is either slightly heated or agitated with a glass rod or by shaking the bottle. In this state it is used for coating the paper or other surfaces on which it is desired 60

to print. The proportions given above are the best for practical use. The preparation of the emulsion is, however, easier for one not experienced in this special line of work, by mix- 65 ing a fluid ounce of silver phosphate with a smaller quantity of tartaric acid-for instance, two drams of acid in two drams of water—when the emulsion will set more readily. When the emulsion is left in its 70 jelly-like state, crystallization will set in after some time, while a portion of the silver is retained in the solution. Citric acid seems to have the greatest affinity for silver phosphate. Twelve drams of citric acid mixed with the 75 fluid ounce of silver phosphate, before referred to, will produce a clear transparent solution which has remarkable sensitiveness and qualities. The emulsion or solution of silver phosphate in organic acid thus obtained 80 is then applied in any suitable manner to the surface to be sensitized. It may be applied by means of a soft flat camel's-hair brush to paper, after which it is permitted to dry. When this sensitized photographic paper is 85 exposed under a negative to direct or shaded sunlight, a positive picture of great accuracy and agreeable tone is obtained. When the paper is first coated with albumen or gelatin or any similar substance, a photographic 90 print can be produced in less time than by the silver haloids heretofore employed, and not only sunlight, but also artificial, especially electric, light can be used for producing a direct print. The photographic print thus 95 obtained can be toned by any of the wellknown toning solutions, and finally fixed by means of sodium hyposulfite. The print is then washed until no trace of the hyposulfite is left in the same. In place of paper any 100 other material—such as wood, celluloid, lithographic stone, silk, cotton, or other textile

fabric and other material—can be coated with the composition and pictures of great delicacy and beauty, not inferior to prints on

paper, be produced thereon.

The advantages of my improved process of sensitizing paper and other surfaces are that silver phosphates can be employed without the aid of a viscous substance, like albumen or gelatin, that the silver-phosphate emulsion 10 or solution can be spread over almost any surface like a paint or dye, and that only a very weak solution of sodium hyposulfite and a short immersion of the prints are required to remove the unchanged silver and render

15 the prints permanent. When the prints are left in the fixing-bath for a longer time than a minute, the sulfuration of the prints will commence, which is induced by the organic acid, and which will be 20 completed to blackness of the picture in a few minutes more. Though sulfur-toning is believed to have many objectionable features. the prints made by the process described do not suffer in appearance if the sulfuration is 25 not too long continued. The use of albumen will prevent the prints which have been toned by sulfur from becoming yellow and faded by atmospheric oxidation. These results were obtained by a number of tests continued 30 through a considerable period of time. The dominant color of the prints made by the silver-phosphate emulsion or solution is a brown or auburn shade, which darkens considerably with the drying of the prints. Toning may 35 therefore be dispensed with in many applications in the arts. When the prints are made on textile fabrics, they are generally brown in

tone; but this can be changed in the case of cotton to black by passing a hot flat-iron over 40 the same, while prints on silk will not undergo this change. Though the predominating color of the silver-phosphate prints is brown, many of them show various other tones, and it must be assumed that certain

45 negatives act as media for the transferring of color qualities and influence the production of the tone to a certain degree under conditions not yet known. When a silver-bromid emulsion is added to a silver-phosphate

50 emulsion, the sensitiveness of the emulsion is so increased that even the light of a common petroleum-lamp is sufficient to produce a direct print. The sensitiveness of the emul-

sion is also increased by the addition of a small quantity of citric acid. The solution of sil- 55 ver phosphate in citric acid when applied to a plain piece of paper and exposed under the negative to direct sunlight produces a print of a very agreeable bluish tone, which will compare favorably with other prints in accu- 60 racy, in the high lights, and in the depth of the shadows.

Paper coated with albumen and sensitized with a silver-phosphate emulsion or solution has great durability and will not deteriorate 65 under climatic influences. It can be used therefore at any time for printing without im-

pairing the quality of the print.

By my improved silver-phosphate emulsion or solution positive pictures can be made with 70 but little trouble and in a very short time. The print is removed from the printing-frame directly to the fixing-bath, to which sodium bicarbonate is added when the original color of the print is to be preserved. The print 75 remains in the fixing-bath for a short time and is then freed from any adhering traces of sodium hyposulfite by washing it in hot or cold water for about five minutes.

I do not claim in this application the com- 80 position for sensitizing paper and other surfaces, as a separate application has been filed for the same on September 5, 1899, Serial No.

729,522.

Having thus described my invention, I 85 claim as new and desire to secure by Letters Patent—

1. The process herein described of sensitizing paper and other surfaces, which consists in preparing a compound of silver phosphate 90 and an organic acid, and then applying said compound to the surface to be sensitized, substantially as set forth.

2. The process herein described of sensitizing paper and other surfaces, which consists 95 in preparing an emulsion of silver phosphate and tartaric acid and then applying this emulsion to the surface to be printed, substantially as set forth.

In testimony that I claim the foregoing as 100 my invention I have signed my name in presence of two subscribing witnesses.

JOHANNES MEYER.

Witnesses:

PAUL GOEPEL, M. H. WURTZEL.