

UNITED STATES PATENT OFFICE.

WILHELM TRIEPEL, OF BERLIN, GERMANY.

PROCESS OF PRODUCING PICTURES AND PHOTOGRAPHIC-PRINTING PLATES.

No. 901,218.

Specification of Letters Patent.

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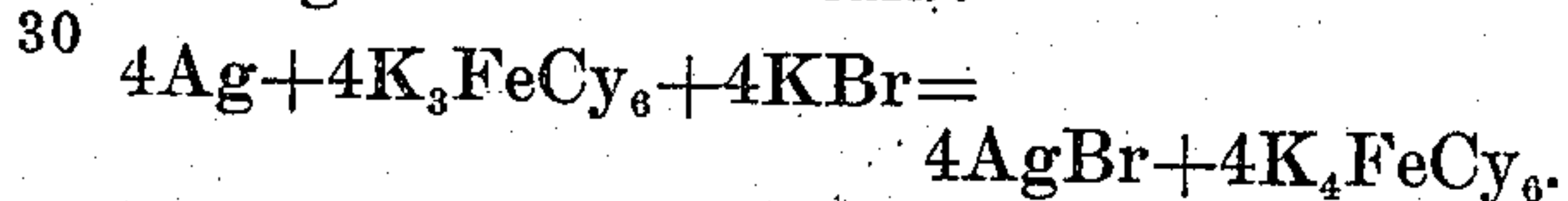
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To all whom it may concern:

Be it known that I, WILHELM TRIEPEL, doctor of philosophy, a subject of the German Emperor, and residing at 59 Fasanenstrasse, in the city of Berlin, Germany, have invented certain new and useful Improvements in Processes of Producing Pictures and Photographic-Printing Plates, of which the following is a specification.

The present invention relates to the known process of obtaining pictures and printing plates from colloidal films with the aid of bichromate, these films being brought into contact with pictures which consist of metals and which have been formed by direct exposure or development.

For executing the process, use is preferably made of the known reaction which provides the metals, for example, the metallic silver of a photographic copy, in a solution; the latter substantially consists of alkali salts of such acids the silver salts of which are insoluble in acids (haloid salts or sulfocyanids) and ferricyanids, and, moreover, also contains bichromates for "tanning" the colloidal film. Such solutions or mixtures react, as is known, with the metals which are on the pictures, approximately according to the following chemical formula:



The potassium ferrocyanid (K_4FeCy_6) which is formed is reconverted again by the bichromate which is present into potassium ferricyanid, whereby products of reduction of chromic acid (chromate of chromic oxid) are formed which on their part have the capability of "tanning" colloidal substances.

Now in spite of the conversion of the silver into bromid of silver taking place almost instantaneously in the above mentioned reaction, I have nevertheless been able to establish the fact that it is not possible to obtain pigment copies which are free from objection according to this known process, because the second stage of the re-action, that is to say, the reduction of the bichromate by the potassium ferrocyanid, requires a longer period of time, during which the potassium ferrocyanid diffuses into the film and therefore fails to reduce the bichromate at the spots or places where it has formed. On the other hand I have found that when copies are thus obtained, the details of the original pictures do not remain when the pictures are de-

veloped, but that the pigmented gelatin floats away. If it is attempted, however, to remove this defect in known manner by an addition of alum and citric acid, flat pictures without sufficient depth are as a rule obtained, because when a small proportion of the bichromate is reduced by the potassium ferrocyanid, the gelatin which has been previously tanned by the alum, receives another tanning to such a degree that its diffusing action is practically destroyed and the remaining potassium ferrocyanid cannot diffuse to greater depths and thus be permitted to re-act in the denser portions of the silver copy. My attempts to remove these above mentioned defects have led to the result that this is quite possible when I work as follows: Namely, I add to the known baths, the composition of which has been described above, substances which influence catalytically the oxidation of the potassium ferrocyanid by bichromate, and hence the re-action of the latter, that is the tanning of the gelatin, to effect oxidation of the potassium ferrocyanid in the places where it has formed. Thus a picturesque tanning is effected, whereupon the defects mentioned disappear at once.

As substances which have a catalytic action, I have found suitable the compounds of cerium, as well as the rare metals of the earth, iron, uranium, cobalt, nickel, vanadium, titanium, thorium, manganese, mercury, copper, etc. as well as mixtures of the mentioned compounds.

In order that the process may be clearly understood, I give the following example of one way of executing the same: If, in the first place, it is a question of pictures, in the case of which gelatin carries the picture, so-called developing copies, I prefer firstly to tan these preliminarily in known manner, before I employ them for the present pigment process, and I treat them first in a bath which contains alum, formaldehyde and similar substances which have a tanning action, wash them well and dry them. I then soak the tanned or untanned pictures well in water again, and press them on a pigmented paper which is impregnated with a solution or mixture. I compose these solutions or mixtures about in proportions for which the following example may be given, it being pointed out that the relative quantities of the individual chemicals may be varied within wide limits according to the effect which is to be obtained in each case. 2.0 grms.

potassium ferricyanid, 1.5 grms. potassium bichromate, 2.0 grms. potassium bromid, 0.4 grms. sulfate of the dioxid of cerium, 0.2 grms. nitrate of the sesquioxid of cerium, 100 c. cms. water.

In making a solution like the above, it is preferable to dissolve the salt of cerium by itself in some cold water, and to add this solution to the other chemicals. The quantity of the salts of the sesquioxid of cerium as well as the salts of the dioxid of cerium may also be increased if necessary. For the employment of different catalysators beside one another, it is preferable in many cases to use a bath of less concentration, for which the additional following example may be given: 1.5 grms. potassium ferricyanid, 1.0 grms. potassium bichromate, 1.0 grms. potassium bromid, 0.2 grms. iron-alum, 0.06 grms. citric acid, 0.2 grms. nitrate of sesquioxid of cerium.

The results can be modulated in the most varied manner by corresponding variation of the baths.

I have found it favorable to add frequently small quantities of such substances to these sensitizing solutions which, as alum, tungstate of sodium and the like, have a tanning action on gelatin, and to modulate their tanning action by adding inorganic or organic acids, acid salts or alkaline compounds of organic acids, which do not exercise a reducing action on the chromic acid, and which are suited to convert the metals which have a tanning action into a complex compound. Likewise, suitable quantities of readily volatile substances, as alcohol, acetone and the like, or also glycerin and the like, may be added to the sensitizing baths. The addition of these volatile substances increases the moisture absorbing properties of the surface.

For daylight copies, for example, those on celloidin paper, I have found suitable, among others, a solution which is composed approximately as follows: 2.0 grms. potassium ferricyanid, 2.0 grms. potassium bromid, 1.5 grms. potassium bichromate, 0.2 grms. sulfate of dioxid of cerium, 0.2 grms. nitrate of sesquioxid of cerium, 100 c. cms. water.

Instead of the potassium salts employed in the foregoing examples, the corresponding sodium and ammonium compounds can, of course, also be employed. Further, the different components of the impregnating solutions may be allowed to act not only in their entirety, but also separated and in optional composition, partly on the silver print and partly on the pigment paper.

The pigmented paper, as long as it is pressed on to the silver copy, can be developed in hot water, or also the pigmented paper can be separated from the copy after sufficient contact under cold water, then transferred in the usual manner on to paper, glass,

metal, etc., and lastly developed. In order to obtain a pigment copy from a silver print in one of the two ways, a time of contact of from 3 to 5 minutes suffices generally speaking.

The faded copy which remains behind can be obtained again in the original strength by means of one of the usual developers and be used again in the same manner after it has been well washed.

If the development of the pigment print is proceeded with while the pigmented paper is in contact with the copy, it is preferable to liberate the finished picture in known manner from the compounds of silver which have formed, as well as from silver which has possibly remained unchanged, as, say, by thiosulfate, possibly with an addition of ferricyanids, for the purpose of avoiding darkening.

I have also found that when employing celloidin pictures, even when these are on fairly old paper, it is preferable in individual cases to soften these celloidin pictures previously in a solution of alcohol and glycerin, to which, if the copies still contain silver, haloid metals or other salts, for example, ammonium chlorid, which precipitate silver, are added. The addition of these substances is for the purpose of modifying the excess of soluble silver salts so that it no longer acts upon the sensitized solution, fixing being thereby rendered unnecessary. When strong solutions have been employed for impregnating the pigmented paper, it is preferable to remove the excess of the solutions by weak pressure.

The pictures and printing plates which are produced according to the above process with the help of the baths containing catalytic substances are specially remarkable for their more brilliant depths and more picturesque modulation, as compared with known pigment pictures obtained hitherto in a similar manner. Also the reproduction of even the finest details succeeds excellently. The production of pigment pictures, particularly from daylight copies, is particularly successful, although the quantities of silver which are contained in the film of the picture are only exceedingly small.

The individual chemicals which are employed for making the baths do not require to act in their entirety on the colloidal film, but can act, in optional composition, partly on the silver print and partly on the film. The process can be employed in all the methods of the art of reproduction which are based on tanning colloidal films by reproduction-products of chromates.

What I claim as my invention and desire to secure by Letters Patent is:—

1. A process of producing pictures, photographic printing plates and the like from colloidal films, consisting in impregnating

a colloidal pigmented film with a solution containing haloid salts, ferricyanids, bichromates and in addition substances which act catalytically, in pressing a metallic picture 5 formed by direct exposure which is to be pigmented on to the impregnated colloidal film, in separating the picture and the film and in washing them.

2. A process of producing pictures, photographic printing plates and the like from 10 colloidal films, consisting in impregnating a colloidal pigmented film with a solution containing alkali salts of such acids the silver salts of which are insoluble in acids, ferricyanids, bichromates and in addition sub- 15 stances which act catalytically, in pressing a metallic picture formed by development which is to be pigmented on to the impregnated colloidal film, in separating the picture 20 and the film and in washing them.

3. A process of producing pictures, photographic printing plates and the like from colloidal films, consisting in impregnating a colloidal pigmented film with a solution con- 25 taining haloid salts, ferricyanids, bichromates and in addition substances which act catalytically, in softening in a liquid which contains glycerin a metallic picture which is to be pigmented, in pressing the softened 30 picture on to the impregnated colloidal film, in separating the picture and the film and in washing them.

4. A process of producing pictures, photographic printing plates and the like from 35 colloidal films in the case of unfixed silver copies still containing soluble silver salts, consisting in impregnating a colloidal pigmented film with a solution containing haloid salts, ferricyanids, bichromates and in addi- 40 tion substances which act catalytically, in softening in a liquid which contains a salt which precipitates silver a metallic picture which is to be pigmented, in pressing the softened picture on to the impregnated col- 45 loidal film, in separating the picture and the film and in washing them.

5. A process of producing pictures, photographic printing plates and the like from 50 colloidal films, consisting in impregnating a colloidal pigmented film with a solution containing haloid salts, ferricyanids, bichro-

mates and in addition substances which act catalytically, in soaking in a liquid which contains glycerin and alcohol a metallic picture which is to be pigmented, in pressing 55 the soaked picture on to the impregnated colloidal film, in separating the picture and the film and in washing them.

6. A process of producing pictures, photographic printing plates and the like from 60 colloidal films, consisting in impregnating a colloidal pigmented film with a solution containing haloid salts, ferricyanids, bichromates and in addition substances which act catalytically, in soaking in a liquid which 65 contains glycerin and alcohol a celloidin picture on rather old paper which is to be pigmented, in pressing the soaked picture on to the impregnated colloidal film, in separating the picture and the film and in washing them. 70

7. A process of producing pictures, photographic printing plates and the like from colloidal films, consisting in impregnating a colloidal pigmented film with a solution containing haloid salts, ferricyanids, bichro- 75 mates and in addition substances which act catalytically, in pressing a metallic picture formed by direct exposure which is to be pigmented on to the impregnated colloidal film, in separating the picture and the film, in 80 washing the colloidal film, in transferring the latter to a suitable material and in developing the film.

8. A process of producing pictures, photographic printing plates and the like from 85 colloidal films, consisting in impregnating a colloidal pigmented film with a solution containing haloid salts, ferricyanids, bichromates and in addition substances which act catalytically, in pressing a metallic picture 90 formed by direct exposure which is to be pigmented on to the impregnated colloidal film, and in developing the film on the metallic print.

In testimony whereof I have hereunto set 95 my hand in presence of two subscribing witnesses.

WILHELM TRIEPEL.

Witnesses:

HENRY HASPER,
ARTHUR SCHROEDER.