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UNITED STATES PATENT OFFICE.

RUDOLF LANGHANS, OF BERLIN, GERMANY.

PROCESS OF METALLIZING WITH PRECIOUS METALS.

SPECIFICATION forming part of Letters Patent No. 666,321, dated January 22, 1901.

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To all whom it may concern:

Be it known that I, RUDOLF LANGHANS, a subject of the Emperor of Austria-Hungary, residing at No. 6 An-der-Stadtbahn, Berlin, Prussia, German Empire, have invented a new and useful Improved Process of Metallizing with Precious Metals; and I do hereby declare that the following is a full, clear, and exact description of the invention, which will enable others skilled in the art to which it appertains to make and use the same.

The present invention relates to the metallizing of objects with precious metals; and it provides for an improved process by the aid of which objects of any kind, shape, and substance (both inorganic and organic) can be metallized, both entirely and partly, with precious metals in a by far more advantageous and simpler manner than heretofore. Especially, my present invention is adapted for metallizing with platinum and other metals of the platinum group, with mixtures or alloys of such metals, with gold, and with mixtures or alloys of gold with one or more of the metals of the platinum group.

The base of my present invention is the use of certain organic compounds of precious metals—that is to say, those compounds which sulfur derivatives of the aliphatic series form with precious metals and with halogen (chlorin, bromin, and iodine) compounds of precious metals, such as compounds of the sulfur derivatives of the alcohol radicals, (mercaptans, sulfids, alkyl disulfids, and so-called “sulfin compounds,”) of the sulfur derivatives of the aldehydes, (thioaldehydes, mercaptals,) and of the sulfur derivatives of the ketones (thioketones, mercaptols) with halogen (chlorin, bromin, and iodine) compounds of precious metals, or with free or pure precious metals, as also hydroxids, nitrites, and nitrates of such of said compounds as are formed with the free or pure precious metals. (For composition, preparation, &c., see, for instance, *Beilstein, Handbuch der Organischen Chemie*, first tome, third edition, pages 347 to 369.) Up to the present invention the said metalliferous aliphatic sulfur derivatives have not found any use in the arts, but were of a mere scientific interest only. Now I have discovered that they possess properties which make them very well adapt-

ed for the purpose in view. They melt at a comparatively low temperature, and in the molten state they form an oily fluid which, being mobile, allows to be very regularly and uniformly distributed over surfaces of the finest configuration. A slight raising of the temperature of the fluid suffices to cause its reduction to metal, and as this reduction takes place slowly and progressively the metal is separated out in the state of a homogeneous and dense deposit, showing a brilliant mirror-like surface. The metallic deposit is well coherent in itself and adherent to the foundation, so that it does not allow to be removed by rubbing, but can be burnished. Moreover, it is perfectly stable, whereby is meant that it does not transform into the state of black or sponge as, for instance, do the metallic deposits produced by means of ethyl platinum chlorid, hydrogen platinum cyanid, and the like. Besides, the deposit can easily be welded by means of a Bunsen flame fed with gas under pressure. On the other hand, the gaseous products of decomposition containing chlorin and sulfur do not in the least attack the substance to be metallized. For metallizing with gold a temperature of 50° to 150° centigrade will suffice, whereas with metals of the platinum group a temperature of 150° to 350° centigrade is required.

By virtue of the above properties of the compounds specified I am enabled to metallize even objects made out of a combustible material—such, for instance, as paper, fabrics, and other fibrous structures—without damaging such foundation; but I am also enabled to burn away a combustible foundation, so that the pure metal is left behind as a true imitation of the combustible foundation. For instance, I am enabled by my present invention to transform the well-known fibrous foundation for manufacturing incandescent mantles into a mantle composed of gold or of one or more metals of the platinum group or of any alloy of gold and such metals—a problem not hitherto resolved; but I may as well coat a refractory surface—for instance, one of glass, porcelain, and the like—with a brilliant mirror of gold, platinum, iridium, and the like.

From what is said it results that my present invention essentially consists in wetting

the object to be metallized with a solution of one or more of the said metalliferous aliphatic sulfur derivatives prepared with a volatile or volatilizable solvent, allowing the solvent to volatilize, wetting anew with the fluid, if required, heating up to the melting-point of the compound or mixture of compounds used, and finally raising the temperature above the decomposition-point of said compound or mixture of compounds.

If the object to be metallized is made out of a combustible material—as, for instance, paper, wood, fibers, and the like—and it is not desired to destroy such foundation, the temperature is raised only so much as required to cause decomposition of the metallizing compound used, whereas when the shaped combustible foundation is intended to merely serve as a model, form, or “mold,” so to speak, such a degree of heat is applied as will cause the fabric or other combustible material or structure used as the foundation to burn away.

I wish it to be understood that the terms “metallizing” and “wetting” as used in the present specification and the annexed claims are intended to comprise the former, coating with metal, impregnating with metal, and transforming into metal, and the latter coating, painting, impregnating, or in any other wise providing the object or foundation with the solution of the metallizing compound or compounds.

Of the metallizing compounds cited I at present prefer as the most advantageous ones those of the radicals of the fatty alcohols, especially their sulfids, (so-called “sulfin salts,”) and in all cases where a combustible foundation is not to be destroyed. I prefer to use the ethyl sulfid platinum chlorid and protochlorid, whereas when the foundation is to be burned away I prefer the nitrates obtained from the said halogen compounds by means of argentic nitrate.

As solvents may be used volatile liquid hydrocarbons, alcohol, chloroform, and the like. I, however, prefer to employ bromoform, as this solvent allows highly-concentrated solutions to be prepared.

In order that my invention may be fully understood, I proceed to describe some examples of how to reduce it to practice.

First. Productions of mirrors, specula, and reflectors.—A refractory back—for instance, a concave parabolically-shaped back out of porcelain—is carefully freed from any adhering impurities, coated, as by painting with a pencil, with a bromoformic solution of ethyl sulfid platinum chlorid and the bromoform allowed to volatilize, when the coated back is first gently heated up to the melting-point of the coating and then the temperature raised above the decomposition-point of the coating.

When the decomposition is complete, the back shows to be covered with a very uniform and brilliant coherent layer of platinum. The platinum mirror thus obtained may finally be

burned in by raising the temperature up to a red heat.

Second. Production of metallized folia, for instance, for use in galvanic gas-batteries.—Sheets of paper, asbestos, or slate are wetted with a bromoformic solution of ethyl sulfid platinum chlorid and the bromoform allowed to volatilize, when heat is applied first gently up to the melting-point of the chlorid and finally to its decomposition-point. In case of sheets of paper or cardboard being used as the foundation, if such foundation is intended to be left unaltered, so as to produce, for instance, paper sheets impregnated with platinum, the final heat has to be such as will not cause the paper to be carbonized—that is to say, the final heat applied should not be higher than 300° centigrade.

Third. Production of blanks for rapid telegraphy.—The signs to be transmitted are written upon a non-conductive sheet—for instance, a sheet of paper or cardboard using the solution of the metallizing compound as the ink and a pen made out of platinum or iridium as the writing instrument—the signs are allowed to perfectly dry, and then the sheet is passed through a pair of cylinders heated up to the decomposition-point of the metallizing compound—for instance, ethyl sulfid platinum chlorid. On leaving the cylinders the sheet shows to be provided with metallic signs, which extend through the paper from one side to the other.

Fourth. Transformation of fibrous structures into pure metallic ones.—A combustible structure—for instance, the fabric used for manufacturing incandescent mantles—is impregnated with a bromoformic solution of nitrated ethyl sulfid platinum, (obtained by mixing a solution of ethyl sulfid platinum protochlorid with argentic nitrate and filtering,) the impregnated fabric is placed on the mold and allowed to dry, and when perfectly dry it is burned as in manufacturing incandescent mantles, whereby the structure is caused to shrink more or less, according as the solution employed is more or less concentrated and the fabric more or less dense. The platinum mantle thus obtained should finally be exposed to welding heat applied by means of a Bunsen flame fed with gas under pressure. The welded structure allows to be pressed or chased, hammered, and burnished.

Fifth. Production of small metal tubes for manufacturing filaments for electric incandescent lamps.—A well-polished artificial thread—for instance, a thread produced from a cellulose solution—is passed through a bromoformic solution of nitrated ethyl sulfid platinum, dried and gently heated so as to well distribute the coating compound, when it is coated with the earthy oxids, previously reduced to a very fine powder, and finally heated above the decomposition-point of the metallizing compound to such a temperature as will destroy the cellulose thread or foundation.

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Obviously my invention may also be used to replace the well-known preparations of precious metal with balsam of sulfur.

What I claim as my invention is—

5 1. The process of metallizing with precious metals which consists in wetting a foundation with a solution of a compound or compounds of precious metals with aliphatic sulfur derivatives prepared with a volatile solvent,
10 drying, heating first up to the melting-point of the metallizing compounds, and then raising the heat above the decomposition-point of said compounds, substantially as and for the purpose specified.

15 2. The process of metallizing with precious metals which consists in wetting a foundation with a bromoformic solution of a compound or compounds of precious metals with aliphatic sulfur derivatives, drying, heating first
20 up to the melting-point of the said metallizing compound or compounds, and then raising the temperature above the decomposition-point of the said compound or compounds, substantially as and for the purpose specified.

25 3. The process of metallizing with precious metals which consists in wetting a foundation with a solution of precious metals compounded with sulfids of aliphatic alcohol radicals, drying, and heating, substantially as described.
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4. The process of metallizing with precious metals which consists in wetting a combustible foundation with a solution of precious metals compounded with sulfids of aliphatic
35 alcohol radicals, drying and heating, substantially as described.

5. The process of metallizing with precious metals which consists in wetting a porous combustible foundation with a solution of precious metals compounded with sulfids of aliphatic alcohol radicals, drying and heating, substantially as and for the purpose described. 40

6. The process of metallizing with precious metals which consists in wetting a porous combustible foundation with a solution of nitrated compounds of precious metals with sulfids of aliphatic alcohol radicals, drying, and heating so as to burn away the foundation, substantially as and for the purpose specified. 45 50

7. The process of metallizing with precious metals which consists in impregnating a fabric with a bromoformic solution of nitrated compounds of precious metals with ethyl sulfid, drying and heating, so as to burn away
55 the fiber, substantially as and for the purpose specified.

8. The process of metallizing with precious metals which consists in impregnating a fabric with a bromoformic solution of nitrated compounds of precious metals with ethyl sulfid, drying, heating so as to burn away the fiber, and welding the metallic structure obtained, substantially as and for the purpose specified. 60 65

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

RUDOLF LANGHANS.

Witnesses:

WOLDEMAR HAUPT,
HENRY HASPER.