H. W. F. LORENZ.

SENSITIVE SAFETY PRINT.

APPLICATION FILED APR. 16, 1909.

969,549. **Patented Sept. 6, 1910.**

Fig. 1.

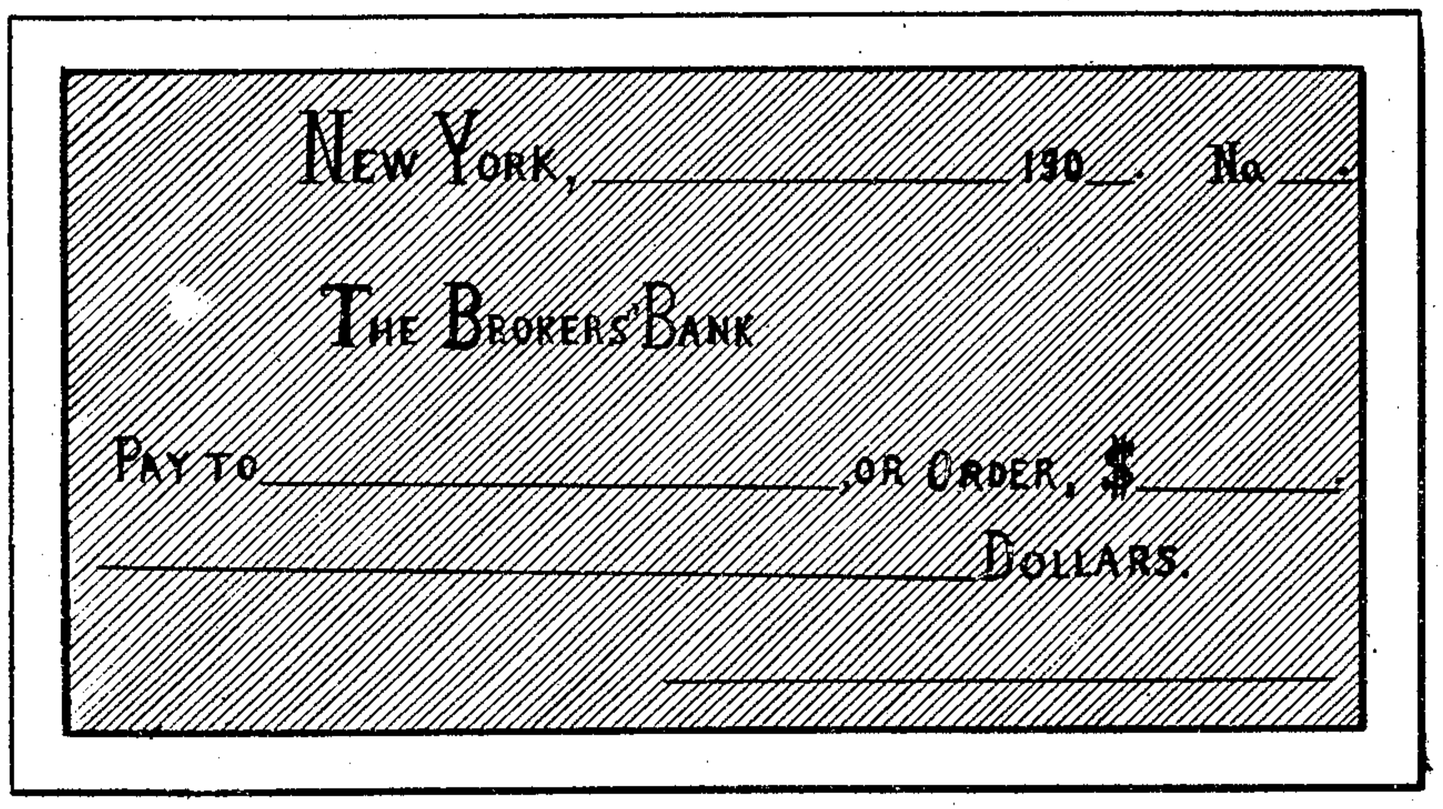
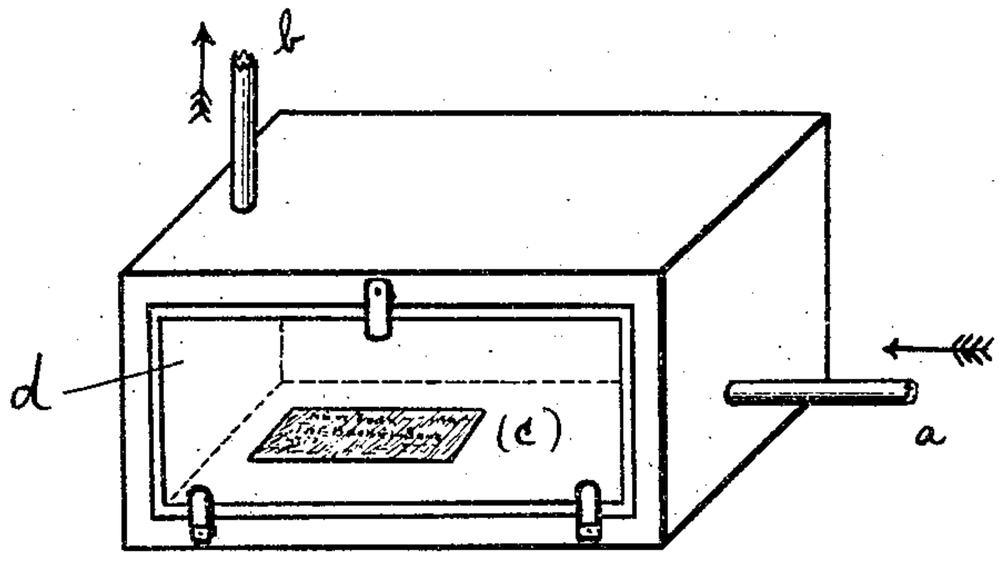


Fig. 2.



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UNITED STATES PATENT OFFICE.

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SENSITIVE SAFETY-PRINT.

969,549. Specification of Letters Patent. Patented Sept. 6, 1910.

Application filed April 16, 1909. Serial No. 490,386.

To all whom it may concern:

Be it known that I, HENRY W. F. LORENZ, a citizen of the United States, and a resident of the city of Jersey City, in the county of Hudson and State of New Jersey, have invented a new and Improved Sensitive Safety-Print, of which the following is a clear, full, and exact description.

This invention relates to the manufacture of sensitive safety prints such as are intended to be used for checks, letters of credit, bank notes, postage, revenue and trade stamps, bonds, stock certificates, and the like security papers.

Reference is to be had to the accompanying drawings which form part of this specification.

Figure 1 represents a check which is formed according to my invention. Fig. 2 represents a suitable form of a closed receptacle in which the check is treated according to my process.

Sensitive prints on paper have in the past been made by dissolving a water-soluble coloring matter in a vehicle consisting of glycerin, gum arabic and water and printing therewith. The great objection to such prints is that they can be easily washed off with water, are readily soiled by moist hands, etc. The great desideratum has been and is to have a print that is sensitive chemically, but insoluble in water. One method of obtaining such a print is to make a print as above-stated, drying and passing it through, or immersing it in, a proper fixing solution, (*i. e.* for brilliant green a solution of tannic acid), washing and drying. This process is very disadvantageous. Very few coloring matters can be passably fixed in this manner, and even these few are very liable to discolor the unprinted paper; the whites are not clear. The latter defect can be somewhat removed in some cases by passing the fixed print a short time through a very weak bleaching solution, and again washing. Even this is unsatisfactory.

The object of my invention is a sensitive safety print insoluble in water, obtained without passing the print through, or immersing it in, a fixing bath, washing bath, etc. I use no baths. By my process I am enabled to use, also, a very large number of coloring matters. The unprinted part of the paper remains white, and is not clouded or discolored by the running of the color.

My prints can be immersed in water, or washed with water, without "bleeding" of the color.

It is obvious that in carrying out my process of making sensitive safety prints on paper for the hereinbefore mentioned purpose it must be modified (1) to suit the chemical nature of the coloring matter, and (2) the method of printing, whether the latter is surface printing or printing from intaglio,—steel, etc., engravings. In all cases I start with a soluble, chemically sensitive, coloring matter which in the finished print has been converted into a water-insoluble coloring matter (usually but not necessarily, a socalled "lake color"). "The term 'lake color' is used to distinguish pigments made from dyestuffs and coloring matters, by precipitating the coloring matter as an insoluble compound, which is thus used for pigmental purposes, to distinguish them from natural pigments, such as ocher, umber, etc., and from chemical colors manufactured by direct combination, or decomposition of distinct salts, *e. g.*, such colors as lead chromates, Chinese blue, etc." "The lakes formed from basic colors are combinations of the color and some acid or semi-acid body. Just as the acid colors behave as if they were the acid of a simple salt, so the basic colors act as if they were the bases of the salts formed by their union with the acids." Some colors, for instance, some acid colors, are in the free state insoluble but their sodium (or ammonium) salts are soluble (*e. g.* Congo red, alkali blue). In such cases I may start with the soluble sodium salt, and, by means of a stronger acid body, liberate the insoluble acid color. By a "chemically sensitive" coloring matter, or dyestuff, I have in view particularly such as are sensitive to the chemicals that can be used advantageously in removing writing inks,—acids, alkalies, bleaching agents. Colors not possessing special sensitiveness (*e. g.* alizarin, etc.) are excluded from my process.

The precipitants I prefer to use are, for basic colors, tannic acid, although I do not confine myself to this one substance; for acid or slightly acid colors I employ basic bodies, inorganic or organic, preferring ordinarily the usual metallic compounds employed in lake making, *e. g.* barium chlorid or acetate, lead and aluminium compounds,

etc. For some, at least, of the direct dyeing cotton colors I can get along without a precipitant (cotton red 4 B, etc.).

In preparing an ink for printing I employ ordinarily, as chief ingredients, the soluble coloring matter and its corresponding precipitant and prefer to have present, as a third ingredient, what I call a volatile "deterrent." This can be a volatile acid, like acetic acid, or a volatile base like ammonia, or anilin, depending upon the chemical nature of the coloring matter and lake. The object of the "deterrent" is to deter, or prevent, the precipitation of the insoluble lake or coloring matter, (thus insuring a more complete and permanent fixing on the paper) until the ink has been transferred upon the paper in printing. Or the deterrent may be simply a volatile dissolving medium for the lake. There should also preferably be present a proper diluting medium (and, in the case of a printing ink for engraved plates, an ink base like blanc fixe, *e. g.* precipitated barium sulfate, sublimed lead, etc.) to give the ink proper working qualities. When the precipitant, or volatile deterrent, is of a liquid nature (*e. g.* lactic acid or anilin can in some cases be such), it can itself serve also as a diluent, in which case a special diluent is not necessarily required.

As a final step in my process of making a sensitive print on paper, the print must be exposed to steam vapor. With some colors it is possible to fairly fix the color by heating the print to a temperature sufficiently high (say 115° C.) for driving off the volatile part of the vehicle, but many colors discolor at the required heat.

A sample check made according to my invention is illustrated in Fig. 1. The fine lines (shading) represent a sensitive print (tint), whereas the letters and figures represent a sensitive intaglio print.

In Fig. 2, which shows a simple form of closed receptacle, or steaming box, steam enters at (*a*) and passes out at (*b*). (*d*) represents a removable glass door through which is seen the check (*c*) being subjected to steam vapor.

A few examples will illustrate different modifications of my process.

By soluble varnish I mean a composition approximately consisting of—

Gum arabic	30 parts.
Glycerin	50 "
Water	20 "

Inks for Surface Printing.

Brilliant green, $C_{23}H_{24}N_2Cl_2$:

Color	3
Soluble varnish	25
Water	8
Glycerin	8
Acetic acid, 50%	.5

Heat on water or steam bath, let cool and add:

Tannic acid	6
Water	6
Acetic acid	1 (50%).

Print, and expose print to steam vapor. It is preferable to carry out this steaming process in an inclosed vessel under a steam pressure of ½–2 atmospheres.

Methyl violet, B. B. extra (Badische):

Color	3
Soluble varnish	6
Tannic acid	6
Acetic acid	2 (50%).

(Acetic acid can be omitted.)

Mix thoroughly, and print. Expose print to steam vapor.

Reactions: Solutions of free alkali (sodium hydrate) give a red-brown discoloration of print. Oxalic acid: bluer. Muriatic acid: bleaches. Ammonia: violet-soluble. Solution of bleaching powder and solution of oxalic acid applied alternatively: bleach.

Victoria blue, B. (Badische), $C_{33}H_{32}N_3Cl$: Use same as last color. Expose to steam vapor.

Reactions: Sodium hydrate solution: red-brown. Muriatic acid: gray. Bromin: bleached. Bleaching powder solution and oxalic acid solution applied alternatingly: slowly bleached.

Fuchsin, $C_{19}H_{26}N_3ClO_4$:

Color	4
Soluble varnish	5
Tannic acid	6
Water	3
Acetic acid	2 (50%).

Print and expose to steam vapor.

Reactions: Solutions of sodium hydrate: yellow-brown. Oxalic acid: blue. Muriatic acid: yellow, bleaches. Bromin, dilute: bluer. Bleaching powder and oxalic acid used alternately: slowly bleaches.

Light green S. L. (Badische): Use same as last color. Expose to steam vapor.

Reactions: Solutions of sodium hydrate: red-brown. Muriatic acid: dark gray-brown. Bromin: bluish-gray. Bleaching powder and oxalic acid: slowly bleached.

Paper yellow 3 G. X. (Badische):

Color	2
Sol. varnish	4
Water	1
Glycerin	1
Barium acetate (or barium chlorid)	2

Prints yellowish-red. With barium chlorid, prints light yellowish-brown. Steamed=original color in both cases. Print and expose to steam vapor.

Reactions: Solutions of sodium hydrate: red, dark, soluble. Oxalic acid: grayish. Muriatic acid: blue-black. Bromin: grayish. Bleaching powder and oxalic acid used alternately: bleaches slowly.

Cotton red 4 B., $C_{34}H_{26}N_6O_6S_2Na_2$:

Color	1
Sol. varnish	7

Print and expose to steam vapor.

Reactions: Solutions of sodium hydrate: yellowish. Oxalic acid: blue-gray. Muriatic acid: blue. Bromin: bleached. Bleaching powder and oxalic acid used alternately: bleached.

Print and expose to steam vapor.

Congo red, $C_{32}H_{22}N_6O_6S_2Na_2$:

Color	1
Ammonia water, .90 sp. gr	1
Add soluble varnish	2

Print and expose to steam vapor. If the steam vapor contains acetic acid vapors, (a volatile fixing agent) the free color is precipitated (blue). Otherwise the print is red (fixed by steam).

Reactions of red print: Solutions of oxalic or muriatic acid: blue. Acetic acid; blue, with violet shade. Sodium hydrate: red-brown, soluble. Ammonia: red, soluble. Bromin: gray, slowly bleached.

Inks for Steel Plate Printing Primarily, but can also be Used for Surface Printing.

Iodeosin B, $C_{20}H_8O_5I_4$:

Color	4
Lactic acid	12
Sublimed lead	12
Blanc fixe	15

Print and steam.

Color of print: Re

Reactions: Solutions of sodium hydrate, or ammonia: blue red, soluble. Muriatic acid: yellow-red. Oxalic acid: yellow-red.

Cotton red 4 B., $C_{34}H_{26}N_6S_2Na_2$:

Color	20
Lactic acid	10
Glycerin	5

Color: Brown.

Print and steam.

Reactions: Solutions of oxalic and muriatic acids: blue. Ammonia: red-brown, light. Bromin: bleached. Alkali: red.

Rosolic acid, $C_{19}H_{14}O_3$:

Color	1
Lactic acid	6
Blanc fixe	2
Sublimed lead	2

Print and steam.

Color: Yellow red.

Reactions: Solutions of alkalies: blue-red, soluble. Oxalic and muriatic acids: yellow, soluble. Bromin: brown. Bleaching powder and oxalic acid: slowly bleached.

Carminic acid, $C_{22}H_{24}O_{12}$ (Merck):

Color	1
Lactic acid	6
Aluminium hydrate	2
Sublimed lead	3

Color: Dry heat changes to a purple-gray.

Reactions: Solutions of oxalic acid: yellow-red. Sodium hydrate: purple, soluble. Bromin: bleached, etc.

Victoria blue B. (Badische) $C_{33}H_{32}N_3Cl$:

Color	.5
Casein	2.
Tannic acid	1.
Acetic acid	.2
Lactic acid, add sufficient to make ink of proper working consistency.	

Reactions: Solutions of sodium hydrate: red-brown, soluble. Ammonia: blackish. Muriatic acid: light green. Hypochlorite and oxalic acid: gray, slowly bleaching.

Brilliant green:

Color	2
Anilin	1
Tannic acid	5
Acetic acid	1

Print and steam.

Reactions: Solutions of ammonia: green, soluble. Sodium hydrate: gray. Muriatic acid: brown. Bleaching powder, and oxalic acid: slowly bleached.

It is evident that in the above mentioned examples of printing inks there can be a considerable variation in the proportions of the various ingredients. The quantity of diluting medium should be enough to give the ink proper working qualities.

Any number of printings can be made on the same paper in different colors and the whole fixed simultaneously by steam vapor.

Where I speak of a soluble varnish above I do not necessarily confine myself to the mixture of gum arabic, glycerin and water. I can also use, for instance, a mixture of starch, glycerin and water, or similarly working pastes or varnishes.

I claim:

1. A sensitive safety print on paper, consisting of a paper substance printed with an ink composed, primarily, of a chemically sensitive, soluble substance, which is capable of forming a lake insoluble in water, dissolved in a vehicle containing a precipitant, gum, diluent and a volatile reagent which will prevent the precipitation of said insoluble lake, said print being rendered water-insoluble by exposure to steam vapor.

2. A sensitive safety print on paper, for

checks, letters of credit, bank notes, postage stamps, revenue and trade stamps, bonds, stock certificates, railroad tickets, and all manner of security papers, consisting of a paper substance overprinted with an ink composed, primarily, of a chemically sensitive, soluble substance, which is capable of forming a lake insoluble in water, dissolved in a vehicle containing a precipitant, diluent and a reagent which will prevent the precipitation of said insoluble lake, said overprint being rendered water-insoluble by exposure to steam vapor.

3. A sensitive safety print on paper, for checks, letters of credit, bank notes, postage, revenue and trade stamps, bonds, stock certificates, railroad tickets, and all manner of security papers, consisting of a paper substance printed with an ink composed, primarily, of a chemically sensitive, soluble substance which can be converted into a water-insoluble body, dissolved in a vehicle consisting of a precipitant and a diluent, said print being rendered water-insoluble by exposure to steam vapor.

4. A sensitive security print on paper, consisting of a paper substance printed with an ink composed, primarily, of a chemically sensitive, soluble substance, which is capable of being converted into a water-insoluble body, dissolving it in a vehicle consisting of a precipitant and a volatile oil-like diluent, with or without an inert base to give proper working qualities, printing therewith and exposing the print to steam vapor.

5. A sensitive safety print on paper, comprising a paper substance printed with an ink consisting of a soluble, chemically sensitive dyestuff capable of being converted into a water-insoluble body, dissolved in a volatile, oil-like diluent, with addition of a precipitant for said dyestuff, said print being rendered water-insoluble by exposure to a sufficiently high temperature for driving off the volatile part of the vehicle.

6. A sensitive safety print on paper for checks, letters of credit, bank notes, postage, revenue and trade stamps, bonds, stock certificates, railroad tickets, and all manner of security papers, consisting of a paper substance printed with an ink composed, primarily, of a chemically sensitive, soluble substance which is capable of being converted into a water-insoluble body, dissolved in a liquid diluting medium, with or without other ingredients for securing proper printing and fixing qualities, said print being rendered water-insoluble by exposure to steam vapor.

7. A sensitive safety print on paper, consisting of a paper substance printed with an ink consisting of a chemically sensitive coloring matter, capable of being converted into a water-insoluble body, mixed with a vehicle consisting of a precipitant and volatile oil-like diluent, with or without other ingredients for securing proper printing qualities, said print being rendered water-insoluble by exposure to steam vapor.

8. A sensitive safety print on paper for checks, letters of credit, bank notes, postage, revenue and trade stamps, bonds, stock certificates, railroad tickets, and all manner of security papers, consisting of a paper substance printed with a sensitive ink, said ink, when transferred on the paper substance, being, primarily, water-soluble but rendered, secondarily, water-insoluble by exposure to steam vapor.

9. A sensitive security paper, consisting of a paper substance printed with a sensitive ink, said ink, when transferred on the paper substance, being, primarily, water soluble, but rendered, secondarily, water-insoluble by exposure of the print to a sufficiently high temperature.

10. A sensitive safety print on paper, consisting of a paper substance overprinted with a sensitive ink, said ink being, primarily, water-soluble but rendered, secondarily, water-insoluble by exposure to steam vapor.

11. A sensitive safety print on paper, comprising a paper substance printed with a water-soluble, chemically sensitive, ink, rendered water-insoluble by steam vapor.

12. A sensitive safety print on paper, consisting of a paper substance overprinted consecutively with differently colored inks, said inks, when thus transferred on the paper substance being, collectively, water-soluble but rendered simultaneously water-insoluble by exposure of the print to steam vapor.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

HENRY W. F. LORENZ.

Witnesses:
ELIZA INNES,
MARIE LORENZ.