UNITED STATES PATENT OFFICE.

WILHELM OSTWALD, OF LEIPSIC, GERMANY.

PROCESS FOR REPRODUCING DESIGNS, PICTURES, LETTER-PRESS, AND THE LIKE.

No. 798,528. Specification of Letters Patent. Patented Aug. 29, 1905.

Application filed November 16, 1903. Serial No. 181,403.

To all whom it may concern:

Be it known that I, WILHELM OSTWALD, doctor of philosophy and professor, a subject of the King of Saxony, residing at Linnéstrasse 2/3, Leipsic, Saxony, German Empire, have invented new and useful Improvements in Processes for Reproducing Designs, Pictures, Letter-Press, and the Like, of which the following is a specification.

The problem in all reproducing processes consists in applying color to predetermined parts of the receiving-surface while leaving other places free. According as this process is to consist of an alternation between a uniform application of color and a ground remaining unaltered or of a constant gradation of the color from a greatest strength to a zero value in the unaltered ground, line and half-tone processes may be distinguished. In order to form a reproduction, the spacial differences corresponding to the picture must be made to appear upon the receiving-surface. The most simple method of effecting this is by mechanical means—as, for example, in ordinary letter-press printing, where the ink is mechanically applied by means of an even roller upon the projecting faces of the characters from which the reproduction is made. In lithography the different behavior of the fatty design and of the wet ground with respect to fatty ink (which only remains adhering to the fatty design when rolled) serves for producing this spacial arrangement of the ink. Generally speaking, therefore, any means which influences the spacial arrangement of the substance necessary for the impression is also applicable for producing reproductions. Such a means, which has not hitherto been employed for the technical purpose of reproduction, is the influencing of diffusion by the spacial arrangement of such factors as exert an influence on the starting or the speed of the diffusion. By diffusion is to be understood, generally speaking, the spontaneous progression or alternation of a substance in the form of a fluid or gas from conditions of higher concentration to those of less concentration. Of particular importance for the present purpose are such diffusion processes as take place in porous or fibrous structures—such as paper, fabrics, felt, and the like—when one side of them is brought into contact with the substance capable of diffusion. The progress thereof takes place both by the intermediary of any vaporized particles and by means of capillarity, somewhat in the manner of the spreading of a blot of ink in blotting-paper. If, for example, a predetermined substance is permitted to diffuse from a plane surface in which it is uniformly distributed in a receiving-surface—for instance, a sheet of paper—a uniform layer of the substance will proceed into the paper. If this substance produces coloring itself, or if by means of a reaction of any kind—such, for example, as a chemical reaction—it may be converted into a coloring product a uniformly-colored surface is obtained. This is no longer the case, however, when anything is interposed which prevents the progress of the diffusion. If, for instance, a pattern or stencil of any other substance is interposed, a reproduction of the same will be produced, as the coloring will be produced only at those places at which the diffusion is not prevented by the substance of the pattern or the like, all other parts remaining uncolored. These patterns may be produced, for example, by forming upon paper, which of itself permits of diffusion, designs by means of an ink which wholly or partially prevents diffusion. If this restraining means is applied in varying strengths, half-tone pictures may be obtained. If, however, it is desired to reproduce line originals, a single strength or property of the restraining means will be sufficient. Such a means for restraining diffusion in paper may consist of size, gum, or bronze color, resin, paraffin, collodion, or, generally speaking, of a substance in which the diffusing substance is insoluble or but slightly soluble. The procedure may also be reversed—that is to say, diffusion may be facilitated in certain places. This may be effected by reducing the thickness of the pattern by mechanical means or by forming designs by means of substances which facilitate diffusion. One takes, for instance, a sheet of celluloid and writes on it with a solution of sulfid of sodium, ferrous chlorid, or another reductive substance, whereby the impervious celluloid is transformed at the desired places into cellulose, which allows the diffusion.

The diffusion medium may be constituted by a liquid or dissolved substance or by a gas or vapor. While liquid diffusion may advantageously be employed for forming patterns on fabrics, gas or vapor diffusion is preferable in the case of reproductions upon paper. If the coloring-matter itself is employed as the diffusion agent, the phenomenon occurs that the coloring-matter entering the receiving-surface spreads through it also by diffu-

sion. Its contours will therefore become hazy in time. This may be desirable for many purposes, but conditions may exist in which it is required to obviate this. In such cases a substance may be provided in the receiving-surface which, together with the diffusion substance, produces such a coloring-matter or coloring-matter former as will undergo no further diffusion. For example, ammonia-gas may be employed as diffusion substance, and in the receiving-surface it may meet with a mercurous salt provided therein, forming therewith the known black amid compounds.

In order to give an illustration of the multiplicity of manners in which the process indicated above on general lines may be carried into practice, the following examples may be described, although these of course only indicate the possibilities of the process without by any means exhausting the same.

A. Ammonia may be employed as diffusion substance. This substance presents extremely great mobility, and consequently very rapid diffusion. The receiving-surface may in the first place be prepared with such coloring-matters as litmus, curcuma, Congo red, or the like in an acidulated condition, these substances assuming another color owing to the basic properties of the ammonia. Further, the receiving-surface may be prepared with such salts as give with ammonia a precipitate which is either colored itself or is converted into a colored compound by further treatment. Thus from paper which has been prepared with a manganese salt manganese hydroxid is precipitated by ammonia and in contact with the atmosphere is changed into a brown higher oxygenated oxid. The unchanged manganese salt may be permitted to remain therein or it may be removed by washing with water. A manganese picture produced in this manner may by further treating it with a mixture of a slowly-oxidizing substance and a substance giving a colored oxidation product—for instance, a mixture of hydrochlorid of anilin and chlorate of sodium—owing to its catalytic action, form other coloring-matters upon itself, and thereby be decolored and strengthened.

If the paper is prepared with a mercurous salt, ammonia produces a brown-black amid compound. If the ammonia is permitted to act upon a fabric which contains a soluble aluminate, a ferric, chromic salt, or a chromate, the corresponding hydroxid is deposited in the fibers and may serve as a mordant for fixing any desired mordanting coloring-matters, such as alizarin. If in the receiving stratum an acid solution of the said salts is present mixed with glue, this is rendered insoluble by the separating out of the hydroxids after the reaction of the ammonia. This phenomenon may likewise be employed partly for fixing such dissolved coloring-matter as is retained faster by the glue than by fabric—for instance, non-substantive coal-tar dyestuffs, as malachite-green anilin violet, and partly for retaining by the coagulation of the glue any mechanically-combined coloring-substance present, such as lampblack, indigo, ocher.

B. *The employment as diffusion medium of acetic acid.*—In this case also such coloring-matters may be employed as present in the acid condition colors other than in the basic condition. Paper colored violet-red with an alkaline solution of phenol-phthalein is decolored, curcuma-paper rendered brown through alkali becomes pale yellow, &c. Further, the receiving-surface may be prepared with a mixture of iodid of potassium and iodate of potassium. By the action of the acetic acid iodin is liberated therefrom, and by reaction upon starch present in the paper, by its oxidizing action or by another suitable coloring reaction, gives a picture of the desired properties. Salts of weak acids may also be present in the receiving-surface and there may be liberated by the acetic acid, then developing their especial reaction. For example, the receiving-surface may contain nitrite of sodium and a substance, such as phenol, which is not changed by this salt, but by free nitrous acid. On the other hand, an insoluble carbonate or oxid or hydroxid—for instance, of lead—present in the receiving-surface may be converted by acetic acid into a soluble salt, which is removed by washing, whereupon the residue may be converted by a chemical reaction—for instance, by sulfid of sodium—into a colored compound, if necessary. If for any of these purposes acetic acid should be too weak an acid, it may be replaced by formic acid, hydrochloric acid, or the like.

C. *Chlorin, bromin, or iodin as diffusion medium.*—In this case the receiving-surface may be prepared with such colors as are bleached by halogens, or it may contain such substances as give coloring-matters by the oxidizing action of halogens, such as the leuco compounds of the dyestuffs—for instance, rosanilin, phenylated rosanilin, and such like.

D. *Nitrous acid or higher oxids of nitrogen as diffusion substance.*—In this instance all the numerous coloring reactions of organic substances which nitrous acid effects—for instance, on phenols aromatic amids may be utilized.

E. *Sulfurous acid or sulfur dioxid as diffusion substance.*—This may be employed either for bleaching colors present in the receiving-surface or their reducing properties on substances present in the receiving-surface utilized.

F. *Alcohol as diffusion substance.*—The receiving-surface is lightly dusted with the powder of a coloring-matter readily soluble in alcohol, such as an anilin dyestuff, especially a phenylated rosanilin. The diffusing alcohol then condenses on the powder, dis-

solves it, and produces a correspondingly-strong coloring, or the receiving-surface is provided with a coating of resin-powder. This is softened by the alcohol-vapor and becomes viscous. It then combines with the support and is able to retain coloring-matters when mixed with it.

G. *Formaldehyde as diffusion substance.*—The receiving-surface may either contain a substance, such as gold-chlorid which is reduced by the formaldehyde, or the formaldehyde acts upon a surface containing glue, renders this insoluble, and thereby renders possible all reproduction processes which depend upon the utilization of the difference between soluble and insoluble size.

In the production of patterns or stencils the first consideration is whether the reaction employed acts positively or negatively. The former is the case when a colored ground is decolored, the latter when upon a clear ground a dark color is produced. A pattern which is formed by impermeable lines or contours upon a permeable support reproduces these contours in dark coloring with a positive reaction, while with a negative reaction it is light upon a dark ground. Such a pattern would therefore be called "positive." If, on the other hand, the ground of the pattern is impermeable, it will give with a positive reaction light lines or contours upon a dark ground and the reverse with a negative reaction. This is a negative pattern. A positive pattern is formed by drawing or writing upon a permeable support with a substance rendering it impermeable. For example, inscriptions may be made with Japan black, a varnish containing asphalt on paper, thereby producing lines which are far less permeable to the best diffusion substances than the paper. If the diffusion medium is an acid, the inscription may be made with a solution of fatty or resin soap, from which an impermeablizing substance is separated by the acid. It is also permissible to add to the ink with which the lines are produced a substance which chemically neutralizes the diffusion substance—for example, magnesia for acetic acid. For producing a negative pattern the procedure may be such that inscriptions are formed upon an impermeable support with an ink which produces permeability. Thus paper may be coated with gum-sandarac upon which inscriptions are made with soda-lye especially previously colored. Upon washing with water the coating disappears on the inscriptions and the lines become permeable. Another process consists in forming the inscriptions with a colored solution of dextrine, the surface being uniformly rolled after drying with Japan black. If after drying the sheet is placed in water, the dextrine is dissolved, taking with it the Japan black which is on it. This may be facilitated by rubbing with a soft brush. Upon the same principle numerous pairs of different substances may be combined when a solution is available for one which does not dissolve the other. It is also frequently important that the picture obtained shall present the same conditions as to left and right hand—that is to say, that it shall not be reversed, for example, when a copy of writing is to be produced. In order to attain this end, it is only necessary to so form the pattern that the side upon which the inscription is formed is toward the diffusion-cushion and the rear side toward the receiving-surface. A pattern formed with Japan black upon thin paper permits of producing prints of quite satisfactory sharpness. The procedure may be the same with positive and negative patterns.

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

The process for reproducing designs, pictures, inscriptions and the like, consisting in conducting a substance by a spontaneous diffusion through a permeable pattern or stencil to a receiving-surface containing a substance capable of reaction with said conducted substance by spontaneous diffusion to form colored products.

In witness whereof I have hereunto signed my name, this 3d day of November, 1903, in the presence of two subscribing witnesses.

WILHELM OSTWALD.

Witnesses:
RUDOLPH FRICKE,
LEON ZEITLIN.