

[54] **LONG-WEARING SILVER-HALIDE  
GELATIN OFFSET PRINTING PLATE**

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[56] **References Cited**

**UNITED STATES PATENTS**

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[57]

**ABSTRACT**

A long-wearing silver-halide gelatin offset printing plate having a photosensitive emulsion layer of about 3 mils on a metal base, preferably aluminum, which is subjected to long development, after light exposure, with a tanning developer and which is thereafter baked for from 520 to 30 seconds at a temperature of from 275° C to 375° C to thereby achieve a hardened film of uniform thickness. The thickness of the hardened, baked film at the point of first wear on the printing plate varies from about 3 to 7 microns. In comparison with the number of good quality prints obtainable from heretofore known plates, e.g., 500 to 1,000 prints, the present plate gives from 20,000 to 500,000 good quality prints.

**7 Claims, No Drawings**

## LONG-WEARING SILVER-HALIDE GELATIN OFFSET PRINTING PLATE

This invention relates to a long-wearing, silver-halide gelatin offset printing plate which increases the number of good quality prints obtainable from the usual 500 to 1,000 to 20,000 to 500,000 as a result of the adjustment of four variables which are, in the order of importance:

- a. development time;
- b. degree of tanning and hardening by baking after development;
- c. thickness of the applied emulsion coating; and,
- d. thickness at the point of first wear.

Offset printing plates are conventionally made by uniformly coating silver-halide gelatin emulsions on dimensionally stable metal sheets, exposing to light and treating with tanning developer to tan the gelatin in proportion to the light intensity and time of exposure are well known and widely used for offset printing. The image in the tanned areas takes up the printing ink less readily than the image in the non-tanned areas so that the plate provides the tone and details of a negative transparency without the use of a screen, as used in photomechanical half-tone, to print a positive impression in continuous tone upon practically any type or grade of paper.

In the present invention, washing following tanning development removes the non-exposed portions of the gelatin and, thereby, uncovers portions of the oleophobic metal substrate. The preferred metal base used in the present invention is aluminum which is anodized to provide an intact hydrated alumina surface film (hydrophilic or oleophobic) which serves as a subbing layer for the uniformly coated emulsion. The uniformly applied emulsion coating at about 2.5 to 4.0 mils in (c), above, provides a printing film, after baking in step (b), which will have a thickness of from 3 to 7 microns. It is essential to assure the minimum thickness of 3 microns by adjusting the gelatin solids content in the water-containing emulsion.

In accordance with the invention, the development conditions differ from those used in conventional tanning development of silver-halide plates in that the time of development is lengthened to at least 10 seconds and up to 5 minutes or more, whereby the quinones in the tanning developer effect a high degree of insolubilization of the gelatin in the emulsion at the light-exposed portions, this insolubilization in the liquid development stage being continued during the baking process after the plate has been removed from the developer bath, washed and dried.

The baking conditions of from 520 to 30 seconds at 275° C to 375° C convert the developed film into a stable, long-wearing printing plate bearing hydrophilic and hydrophobic portions which produce high quality printing and clean margins and which are especially useful for making printing plates exposed by low intensity, short duration light source, such as a cathode ray tube.

A third critical factor is the thickness of the uniformly applied emulsion coating which results at the exposed portions in a printing film exhibiting a thickness of from 3 to 7 microns at the point of first wear.

Heretofore, there have been attempts to improve collotype copper printing plates based upon alum hardened gelatin sensitized by alkali dichromate, developed under water and brushed to remove the softened portions, as shown in MacBride, U.S. Pat. No. 2,226,314. MacBride's improved plates have a life of about 1,000 prints (see page 1, column 2, line 35), and the printing improvement is achieved by immersing the completely dried plate in a hygroscopic fluid that does not attack the gelatin and does not cause the plate to become tacky, and which permits the plate to take ink readily. MacBride's concept is to prepare a more durable plate which produces better printing quality (page 3, column 1, lines 1-7) by liquid treatment.

In contrast, the present invention produces a long-wearing plate having a surprising degree of durability by the combined expedients of fundamentally altering the development time, a separate baking operation, and controlling the applied thickness so that the thickness of the processed film at the point of first wear will be from 3 to 7 microns.

The following illustrates a method of preparing the long-wearing plate of the invention.

### A. GELATIN SILVER EMULSION

A mixed silver bromide-iodide grain (4 percent to 4.5 percent of halide being iodide), precipitated in a slight excess of bromide ion, is preferred. The grains are highly crystalline and are generally hexagonal in horizontal projection. The grains which appear to be triangular are actually hexagonal with three very short sides. The grains may be variable in size and range from 0.5 to 5 microns in width with the average size being in the range to 3 to 5 microns (i.e., average or typical particle).

A good photographic gelatin, such as calfskin gelatin, is used in the ratio of 1 part of gelatin to 2 parts of silver-halide. At the point of coating the emulsion, the solids content should be 15 percent to 20 percent, by weight (gelatin and silver-halide), and should be essentially free of harmful electrolyte; although, some situations may require retention of electrolyte or even additional electrolyte.

### B. THE ALUMINUM SUBSTRATE

A 6-mil thick grained aluminum sheet is preferred, but a sheet of any desired thickness may be used if it has the requisite structural strength.

The emulsion is coated onto the grained surface which provides an anti-halation background and improved adhesion.

The aluminum of the sheet should have an intact hydrated alumina film between it and the photographic emulsion since where the alumina film is broken free, silver is deposited without any photographic processing. Free electrolyte assists electrolytic reduction of silver-halide grains at the exposed substrate aluminum.

The surface to be coated with photographic emulsion must be free of organic contaminant. Therefore, the substrate should be lightly rubbed in a warm detergent solution, well rinsed with tap water, and finally, with distilled or deionized water. As soon as the substrate is dry, it should be coated with the photographic emulsion.

### C. COATING

Coating should be by any method allowing the application of a uniform smooth coating. The substrate thickness variation should be of the order of the photographic coating thickness. Since this cannot be closely controlled in an economical fashion, an accurate, precise spraying method is preferred. Any of the commercial methods which are described in the ASTM D 823-53 Standards for use in producing films of uniform thickness of paint, varnish, or lacquer may be used, e.g., dip coating, spray coating, and blade or knife coating.

Conditions of coating vary, depending upon coating speed, equipment, etc. However, since photographic emulsions of the solids level herein indicated melt in the range of 35° C to 40° C, the temperature at the spray head should be slightly higher while the plate being coated should be slightly cooler to allow conformation of the coating to the terrain variations in the substrate.

Before use, the water content of the coating must be reduced. Generally, standing in a cool, dark room at 25 percent relative humidity and 22° C for periods of at least 30 minutes has proved to be adequate. Conditioning for several days is not harmful, but neither is it advantageous. In the case of special requirements, such as the need for improved resolution in ultimate image or shortened processing time, desiccant liquids or air can be used. In any case, one should not melt the photographic emulsion.

### D. EXPOSURE

Bearing in mind that the exposure will vary with the performance desired and the emulsion used (for example, image resolution is better with brief exposure), exposures for the long plate wear of this invention should be in the range of 100

to 300 ft. candles in intensity, from 2 to 20 seconds, as obtained for example, on a contact printer at 0 rheostat setting and using four 60 watt bulbs, with 10 seconds being preferred.

### E. DEVELOPMENT

A variety of developing agents are useful, but they must have the ability to tan gelatin. Therefore, the developer should be based upon catechol (pyrocatechol), pyrogallol, hydroquinone, or mixtures, or derivatives of catechol or hydroquinone.

The preferred developer consists of:	
Metol	0.089 grams
Sodium sulfite	0.333 grams
Pyrogallol	0.111 grams
Potassium carbonate	1.389 grams
Water	100 mls.

The developer solution should be fresh and not depleted by exposure to air, and should comprise 100 mls. of the above developer solution to 30 sq. in. of exposed plate. The developer may be used again and again if it is protected from air and is replenished.

Preferably, as for example with the preferred developer solution, development time should be for 1 minute at 22° C. The time may be shortened to as little as several seconds by increasing the temperature. Development may be shorter or longer, but there appears to be little need, if any, in going beyond 5 minutes of development. If the time is shorter than 1 minute, the plate life will normally be shorter.

Following development, the plate is dipped into 40 percent ammonium thiocyanate solution for about ½ second and is rinsed under flowing lukewarm water (about 50° C) for about 20 to 30 seconds (gentle massage may be used) to remove non-image emulsion. The image is cleaned by rinsing in cold tap water and finally in distilled water. The image is then suspended at 25 percent relative humidity to drip dry for ½ hour, but desiccant solutions or dry, warm gas may be used to hasten drying. The image is then dried on a warm surface (75° C to 100° C) briefly and baked. It is to be noted that the water content of the image must be reduced before baking, and a number of methods are available, some of which are quicker than others.

A fine grained emulsion requires a more severe bake than does the preferred emulsion herein. The preferred baking step is carried out for 30 seconds in a 360° C oven, but it is recognized that other methods may be used involving shorter processing periods. The plate is removed from the oven and allowed to cool to room temperature, and it is then baked again with the other side of the plate to the rear of the oven. In this manner, the entire plate is subjected to uniform and controlled heat. Of course, two-step baking can be avoided by use of a well-balanced oven or by the use of mechanical devices to assure uniform baking.

As soon as it can be handled conveniently, the plate is placed on an offset press, etched with fountain solution and run. Ink is accepted immediately and more than 100,000 copies of good quality are printed.

### F. COATING METHOD USED

The coating methods used are adequately described in ASTM D 823-53 (reapproved 1965). In the motor driven blade film applicator, a Gardner Coater was used, available from Gardner Laboratory, Inc. of Bethesda, Md.

For most coatings, as shown in ASTM D 823-53, Method D, a motor driven laboratory coating rod (R.D.S. Laboratory Coating Rod, available from R.D. Specialties, Webster, N.Y.) was used. Long-wear, durable plates were made using bar No. 20 (about 0.60 mil, 20 percent solids). Comparable coatings with No. 8 and No. 3 bars did not provide long-wearing durable printing plates. Coatings were made using No. 12 and No. 16 bars, but processing conditions leading to durability were not used.

Some coatings were made using a Baker Film applicator (available from Gardner Laboratory, Inc., above) with the applicator set at 0 mil for C<sub>0</sub> and at 3 mils for C<sub>3</sub>. These coatings represent a minimum of 3 microns to a maximum of 7 microns after baking.

The plate thickness was determined by measuring under a light-section microscope using the non-destructive test described in literature available from Carl Zeiss, the manufacturer, and also described in the article by W. Illig. The measuring of anodized layers on aluminum was obtained, for example, by the method described in *Z. Metalloberfläche*, Vol. 13 (1959), Issue 2, pp. 33-35.

Table I, below, illustrates five plates which were made in development times of 3 and 5 minutes, while Table II shows the effect of developing times between 10 and 60 seconds and baking times between 30 and 300 seconds.

TABLE I

Number of Copies Printed to First Sign of Wear  
(10 Second Exposure Time for All Plates)

Plate	Development Time (Mins.)	Baking Program	No. of Copies Printed
A	5	4-50 sec. at 365°C with position alternated	203,000
B	5	2-30 sec. at 360°C alternate bakes	87,000
C	5	4-60 sec. at 365°C alternate bakes	134,000
D	5	4-130 sec. at 360°C alternate bakes	163,000
E	3	2-30 sec. at 360°C alternate bakes	343,000

TABLE II

Effect of Baking and Development  
Time on Plate Durability

Plate	Development time (sec.)	Baking Conditions temperature (°C)	time (sec.)	Number of copies printed before 1st wear
F	10		300	36,500
G	10		30	20,000
H	60	360	30 & 30	206,000

### EXAMPLE I

Aluminum having a grained surface was coated using an eccentric bar set at 3 mils thickness with a silver halide-gelatin emulsion (10.75g silver halide, mainly AgBr with 4.5 percent AgI, 5 gms gelatin, 15 percent solids) and allowed to dry under ambient conditions (about 20° C to 25° C) for 3 hours.

Using a contact printer and a Buckbee-Mears USAF 1951 Resolving Power Test Target as mask, a latent image was formed by exposure for 8 seconds at 60-foot candles intensity. This image was developed in 200 mls of tanning developer at ambient conditions for each plate, described in Tables I and II, the tanning developer having the following composition:

Ingredient	Amount
Metol	0.178 g
Pyrogallol	0.222 g
Sodium Sulfite	0.666 g
Potassium Carbonate	2.778 g
Water	200 ml

After development is completed, removal of the non-imaged gelatin-silver halide coating is best achieved by brief immersion (for 30 seconds) in 40 percent aqueous ammonium thiocyanate, followed by lukewarm tapwater flowing over the plate. Gentle rubbing with the fingertips or with a soft sponge hastens removal and does not damage the image film when done with care.

Lesser concentrations of ammonium thiocyanate can be used, for example, 20 percent aqueous solution, and shorter immersion times can be used, for example, as short as 1 to 2 seconds.

Following tanning development and removal of the non-imaged gelatin-silver halide coating, the resulting plate consisted of an image film which was oleophilic (ink-accepting) and background alumina which was hydrophilic (fountain solution-accepting). Thus, the ink was confined to the image areas, and the printed copy was sharp and clean.

After storage under ambient conditions for 40 hours, the plate was conditioned in a desiccator containing a 20 percent relative humidity for 24 hours. It should be understood that storage and conditioning can be for shorter periods of time, or entirely deleted.

The plates A to H were then baked as set forth in Tables I and II, and as described below.

The following detailed examples set out the baking preparation of Plates A to E, inclusive, in Table I, and illustrates the conditions of tanning development and baking which lead to enhanced plate durability, as summarized in Table II.

Plate A was baked four times for 50 seconds each time in a small muffle furnace at a temperature of 365° C for a total of 200 seconds. The plate was arranged so that neither the image nor the substrate directly under the image touched a hot surface, thus, avoiding image damage. After each of the first three bakings, the position of the plate in the furnace was alternated back to front to compensate for any temperature variations which might exist at the back and front of the furnace.

Heat was applied to the image by convection and through conduction from the ends of the substrate. Substrate heat advanced slowly because the image was generally at least 3 to 4 inches from the plate end contacting the hot furnace surface and the cross-section of the substrate was small, e.g. a 6-mil sheet. The furnace used was manufactured by Jelrus Technical Products Corporation of New Hyde Park, N.Y., and was type TF-2 with the temperature accurately controlled with a thermocouple and controller.

The application of heat was gradual, and loss of moisture was gradual and slow during the baking cycles. This is necessary because where moisture loss is too rapid, image damage occurs, as in the case of heating by direct contact of the substrate in the image area with a hot surface. It is recognized, of course, that under these baking conditions the temperature of the gelatin image and the temperature of the oven never reached equilibrium, and the temperature of the gelatin is therefore unknown.

Plate B was baked twice for 30 seconds each time with one alteration of position, or for a total of 60 seconds, and the same procedure was followed as for Plate A.

Plate C was baked four times for 60 seconds each time, or for a total of 240 seconds, at a temperature of 365° C with the alternate positioning and procedure described above for Plate A, and Plate D was baked four times for 130 seconds each time, or for a total of 520 seconds, at 360° C in the same manner.

Plate E was baked twice for 30 seconds each time, or for a total of 60 seconds, at 360° C and as described for Plate B, above.

Plates B and E, both baked for 2 cycles at 30 seconds at or near 360° C, both provided excellent, long-wearing plates.

In the above examples, a baking cycle involves placing a plate into the muffle furnace for the requisite time, removing it and allowing it to cool to room temperature. Longer wearing plates were also made at 275° C. However, 2, 28-hour heating

cycles were required, and such is not practicable in a commercial printing plate.

Continuous baking cycles longer than 30 seconds at these high temperatures produced some gelatin deterioration. However, where the particle size of the silver halide in the gelatin emulsion was smaller, the images were more thermally resistant.

The durability of Plates A to E is summarized in Table I, above. The number of copies printed from each plate before the first signs of wear appear are set forth in the last column of the Table.

A more detailed discussion of the factors of long development, high temperature baking cycles, and critical thickness values is presented after Example II hereinbelow. However, it is noted that the reduction in thickness from the coating stage during which the uniformly thick 3-mil silver halide-gelatin film is applied to the baking stage at temperatures of 365° C (plus or minus 5° C) is from about 300 microns to about 10 microns. A typical measurement using a bar coating at a level of 15.31 percent coating solids provides coating thicknesses in the range of 0.000,276 to 0.000,484 inches. After baking, the thickness varies in a range of from about 3 to 10 microns, and best results as to the durability are achieved between 3 and 7 microns.

#### EXAMPLE II

This example illustrates the effect of baking and development time on plate durability, as summarized in Table II above.

Plates F, G, and H in this example are made by the same method as set out for the plates of Example I, e.g., the bar coating, contact printing, tanning development, and washing to expose metal oleophobic portions, followed by the baking cycles, but with specific variations as shown in Table II, e.g.:

a. The development time for Plate F is 10 seconds, the development time for Plate G is 10 seconds, and the development time for Plate H is 60 seconds;

b. the baking temperature/time cycle for Plate F is 275° C for 300 seconds, for Plate G 375° C for 30 seconds, and for Plate H two cycles are carried out, each for 30 seconds and each at a temperature of 360° C.

As shown in Table II, the improvement of Plate F, which is made by a long bake at the lower part of the baking range, 275° C, is to improve the service life of the plate over the McBride-type plate, which has a life of 1,000 printing impressions to a high level of over 36,000 printing impressions, e.g. a 36-fold improvement.

By shortening the time of the baking cycle while raising the temperature to compensate for shortened time, the Plate G, made in accordance with the invention, exhibits a service life of 20,000 printing impressions, e.g. a 20-fold improvement.

Surprisingly, by shortening the baking cycles to 30 seconds and by using at least 2 baking cycles as shown for Plate H, the service life is greatly improved by more than 200-fold, e.g. to a value of 206,000 printing impressions before first wear, and this follows because of longer development time which assures tanning insolubilization.

The tanning insolubilization illustrated in the above-preferred examples may be effected, as is well known in the art, with any one of the phenolic developing agents commonly used, e.g. with either pyrogallol, pyrocatechin, or hydroquinone, in the presence of alkali metal or ammonium sulfite and alkali, e.g. alkali metal carbonate or alkali metal hydroxide. Conventional tanning developers require minimum quantities of sulfite, up to 2 grams per liter and with alkali metal carbonate up to 16 grams per liter, depending upon the phenolic developing agent used. With pyrocatechin in alkali metal carbonate, metol is commonly added. Generally, pyrogallol with added metol is also preferred. Typical formulas are well known and are shown, for example, at pages 664-666 of "Photographic Chemistry," Vol. 2, by Pierre Glafkides. These typical developers may contain preservative, such as ascorbic

acid, and contrast enhancing agents, such as organic sulfides or thiourea.

It is realized that in the practice of this invention alternative methods of heating can be chosen which are equivalent to the method used herein. For example, the plate could be moved in controlled fashion under heating elements set at increasing temperatures.

The term "oleophobic metal" as used herein is not limited to aluminum, but is art known to include materials, such as iron, zinc, and others.

While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. A long-wearing oleophobic metal base oleophilic silver-halide gelatin offset image printing plate comprising a photosensitive silver-halide emulsion layer deposited in a uniform layer from aqueous gelatin medium in a thickness of at least about 2.5 mils up to about 4 mils on an oleophobic metal base which after exposure is developed for 10 seconds to about 300 seconds with a tanning developer and thereafter has removed therefrom the non-exposed portions of the silver-halide gelatin emulsion layer to uncover the portions of the oleophobic metal substrate therebeneath, and which is dried to remove water and thereafter baked in one or more cycles for a period of time varying between 10 and 520 seconds at a temperature of from 275° C up to about 375° C, the temperature and period of time being such that the bake-hardened film is shrunk to a uniform thickness of from about 3 to 10 microns.

2. A long-wearing oleophobic metal base oleophilic silver-halide gelatin offset image printing plate as claimed in claim 1 wherein said metal base is aluminum.

3. A method of making a long-wearing oleophobic metal base oleophilic silver-halide gelatin offset image printing plate

comprising:

providing a photosensitive silver-halide emulsion layer deposited uniformly from aqueous gelatin medium in a thickness of at least about 2.5 mils up to about 4 mils on an oleophobic metal base;

exposing the plate to actinic image information;

after exposure developing the plate for at least 10 seconds up to about 300 seconds with a tanning developer;

removing the non-exposed portion of the silver-halide gelatin emulsion layer to uncover the portions of the oleophobic metal substrate therebeneath;

drying to remove water from said layer and base; and

thereafter baking the plate in one or more cycles for a period of time varying between 10 seconds and 520 seconds at a temperature of from 275° C up to 375° C to provide exposed, developed and bake-hardened oleophilic silver-halide gelatin film offset image portions shrunk to a substantially uniform thickness of from about 3 microns to about 10 microns upon said oleophobic metal base.

4. A method as claimed in claim 3, wherein the silver-halide emulsion layer is provided to a thickness of at least about 3 mils and the exposed, developed, and bake-hardened oleophilic silver-halide gelatin film offset portions are shrunk to a thickness of from about 3 microns to about 7 microns.

5. A method as claimed in claim 3, wherein the development is for a period of from between about 10 seconds and about 60 seconds.

6. A method as claimed in claim 3, wherein baking is carried out in at least 2 cycles of about 30 seconds each.

7. A method as claimed in claim 4, wherein the development is for a period of from between about 60 seconds and 300 seconds and the baking takes place at a temperature of from 275° C and 375° C in at least 2 cycles of about 30 seconds each.

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