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PHOTOLITHOGRAPHIC PRINTING PLATES AND PROCESS FOR PRODUCING SAME

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ABSTRACT OF THE DISCLOSURE

In a process for producing a lithographic printing plate comprising exposing an imaging medium comprising a developer layer containing a developing agent capable of oxidation in the presence of a hydrophilic organic colloid to form an image receptive to greasy printing ink, and over the developer layer a hydrophilic organic colloid photosensitive emulsion capable of reacting with the developer to produce a visible metal image, and the emulsion containing a hardener, in which the colloid has a hardness equivalent to that of a gelatin layer containing from about 2 grams to about 15 grams of dry formaldehyde per gram of gelatin, which exposed imaging medium is contacted with an activator solution for the developer to produce a lithographic plate, the improvement comprising reducing the water absorption characteristics of printing plate by contacting the imaging medium with an antiswelling agent which is preferably a solution of an alkali metal halide, sulfate or nitrate.

This invention relates to photographic reproduction processes. More precisely, the invention disclosed herein relates to processes involving photolithographic printing plates and especially to methods for improving photolithographic printing plates which comprise silver halide photographic emulsions.

Photolithographic printing plates are well known to the art. For example, photolithographic plates useful in the practice of the present invention and manners of producing same are disclosed in more detail in U.S. Patent 3,146,104 which is incorporated herein by reference. The essential elements of photolithographic printing plates are a suitable substrate and generally a plurality of layers, at least one of which comprises a radiation sensitive, e.g., light sensitive, system which in most cases comprises a silver halide and an organic binder material, generally gelatin. Usually one of the additional layers of said plates comprises a developing agent and more often than not, the developing agent is disposed in a layer adjacent the radiation sensitive layer. The uppermost layer of said plates comprises gelatin which is generally prehardened to a particular degree.

Essentially, the production of photolithographic plates involves the exposure of said plates to a pattern of activating radiation modified by an image pattern and development thereof. In the development process, the character of the organic binder material of the uppermost layer undergoes changes. For example, the binder in the developed portions is rendered oleophilic, e.g., ink receptive, whereas the binder in the non-developed portion maintains its oleophobic, e.g., water receptive character. Thereafter, ink is applied to the plate and adheres preferentially to the oleophilic portions thereof. Accordingly, a plurality of copies can be printed from the plates in accordance with known techniques.

An outstanding problem in the production of suitable photolithographic printing plates involves a phenomenon known to the art as "blinding." Essentially, the problem of "blinding" is caused by the absence of adequate or definitive differentiation between the ink receptive and water

receptive portions of the developed photolithographic plate. Accordingly, "blinding" indicates that the ink receptivity of the oleophilic portion of the developed lithographic plate is adversely impaired and poor quality reproductions are obtained therefrom. Oftentimes "blinding" can occur immediately after the printing step is begun. For example, in some instances, as many as 50 or more copies must be printed before the photolithographic plate develops sufficient ink receptivity to produce quality copies. However, "blinding" can also manifest itself during the printing run, for example, after about 100 or more copies are produced. Presently, the only way to adequately correct the problem of "blinding" is to produce another photolithographic plate. Accordingly, such a problem is time consuming and uneconomical and any process whereby "blinding" can be eliminated or effectively minimized would be indeed a notable contribution to the art.

A principal object of the present invention is to provide improved photolithographic plates.

Another object of the present invention is to provide an improved process for producing photolithographic plates.

Still another object of the present invention is to provide a process for improving the ink receptivity of photolithographic plates.

Still another object of the present invention is to provide a process for correcting the problem of "blinding" which may arise at any time during the production of copies from photolithographic plates.

Another more specific object of the present invention is to provide an improved acid stop bath for processing photolithographic plates.

Still other objects and advantages of the present invention will in part be obvious to those skilled in the art or will in part appear hereinafter.

Broadly, the above objects and advantages are realized in accordance with the practice of the present invention by adjusting the water absorption characteristics of the binder in that layer of the photolithographic plate which is ultimately rendered oleophilic and oleophobic. According to a hypothesis which I have postulated—but to which I do not intend to be bound—the water absorption characteristics of the binder employed in said layers is an important factor in maintaining differentiations between the oleophilic and the oleophobic portions of the layer. In turn, in maintaining such differentiations, the overall ink receptivity of the photolithographic plate is advantageously improved. This hypothesis is consistent with my observation that "blinding" can be virtually eliminated in photolithographic plates by reducing the water absorption characteristics of the gelatin layer comprising the oleophilic and oleophobic portions.

In accordance with one embodiment of my invention, improved photolithographic plates are produced by employing as the binder in the uppermost layer of said plates, gelatins which inherently have low water absorption characteristics. Many manners of producing gelatins having low moisture absorption characteristics are known to the art. For example, on pages 69 and 70 of "The Theory of the Photographic Process" by Mees, Revised Edition, published by the MacMillan Company in 1954, two such methods are disclosed. In accordance with one of the methods disclosed therein, gelatins of reduced water absorption characteristics can be produced by lowering the pH of the sol from which the gelatin is produced before drying same. In the practice of the present invention gelatins of suitable reduced water absorption characteristics are produced by adjusting the pH of the sol to less than about 5.

In accordance with another method disclosed therein, gelatins of reduced water absorption characteristics suit-

able in the practice of the present invention can be produced by increasing the concentrations of the original sol to amounts above about 10 percent.

However, in accordance with the most preferred embodiment of my invention, I prefer to reduce the water absorption characteristics of the gelatin layers by applying solutions comprising specific materials to photolithographic plates during the development processing thereof.

In accordance with one aspect of this embodiment of my invention, photolithographic plates of improved initial ink receptivity can be produced. Plates produced in accordance with this aspect can be used to produce printed copies with a high degree of assurance that the phenomenon of "blinding" will not be encountered therewith. Another aspect of this embodiment of my invention involves the application of the solutions to photolithographic plates which have been processed according to development techniques presently known to the art and which manifest "blinding" during the copy printing step. In accordance with this aspect, said "blinding" can be eliminated without the need of producing a new photolithographic plate.

The specific materials which I have found to be useful in the preferred embodiment of the present invention are known broadly as anti-swelling agents for the binder materials employed in photolithographic plates. Such anti-swelling agents for gelatin are disclosed in pages 64 and 65 of "The Theory of the Photographic Process" by Mees, Revised Edition, published by the MacMillan Company. However, in the practice of the present invention, the organic and inorganic salts of the alkali metals are definitely preferred. Accordingly, especially preferred anti-swelling agents are the sulfates, tartrates, citrates, acetates, halides, nitrates and the like of the alkali metals and especially the above mentioned salts of sodium and potassium. In the practice of my invention, aqueous solutions of the above mentioned salts are preferably employed but partially aqueous solutions can be used if desired. The concentration of said salts in the solutions can vary depending primarily on the solubility of the particular salt employed but normally solutions of less than about 20 percent by weight of the salts are suitable.

The benefits which flow from the practice of the present invention are realized by applying the aforesaid solutions to the lithographic plates preferably after the development of the image pattern therein. An especially suitable and preferred method of applying said solutions involves employing same in combination with acids as "stop baths" since such "stop baths" are normally employed in the processing of photolithographic plates. In accordance with this method, the developed plate is contacted with a solution comprising an alkali metal salt and an amount of acid sufficient to reduce the pH of the solution to preferably less than about 2.0. I prefer to use the acids such as citric, glycolic and phosphoric acid or others with similar dissociation constant. Normally, the plate is immersed in the "'stop bath" for about 20 seconds but somewhat longer times can be employed.

It is also to be understood that the alkali metal salts need not be added directly to such "stop baths." For example, the developed lithographic plate can be contacted with solutions of said salts either before, but preferably after, the plate is immersed in said "stop baths."

Also, the solutions of the alkali metal salts can be applied to the developed lithographic plate while the plate is employed to produce printed copies. For example, dilute solutions of said salts can be employed as fountain solutions during the copy printing step.

I especially prefer to contact the photolithographic plates with my solutions prior to the use of said plates to reproduce copies therefrom. For example, plates processed in accordance with this technique do not manifest "blinding" during the copy printing step. Moreover, plates processed in this fashion immediately manifest a high degree of ink receptivity. Accordingly, the initial copies reproduced therefrom are of high quality and need not be discarded as is oftentimes the situation presently in the art. However, it is to be understood that my solutions can also be advantageously employed to correct any "blinding" which occurs during the printing step with plates processed in accordance with development techniques presently known to the art. For example, I have found that such plates need not be discarded since the "blinding" can be eliminated by contacting said plates with the solutions of the present invention.

My invention and manners of practicing same as well as the advantages to be derived therefrom will be better understood by reference to the following examples which illustrate details of my invention. It is to be understood that the following examples are illustrative in nature and in no way are they to be construed so as to limit my invention beyond those limitations expressly set forth in the present specification or in the claims which appear hereinafter.

In the following examples, the photolithographic plate material involved is similar to that described in FIGURE 2 of U.S. Patent 3,146,104. Said patent describes photolithographic plates which are representative of the type used in the practice of the present invention. The plate material employed essentially comprises a support and a plurality of layers thereon. The layer adjacent the support comprises gelatin and a polyhydroxybenzene silver halide developing agent which, upon reaction with silver halide, can produce an oxidation product which renders the binder, e.g., gelatin oleophilic. Over said developer containing layer is an unfogged gelatino-silver halide emulsion layer while over said emulsion layer is a fogged gelatino-silver halide emulsion layer uniformly hardened with a hardener.

EXAMPLE 1

A lithographic plate material, as described above, was exposed to a line positive, processed for about 20 seconds in a 4 percent aqueous sodium carbonate monohydrate solution and treated for about one minute in an aqueous stop bath of the following formulation:

	Percent by weight
Phosphoric acid (85%)	1.5
Potassium sulfate	5.0

The plate was squeegeed to remove excess liquid and run on a lithographic press.

Lithographic plates processed in the stop bath solution of the above formulation have not manifested "blinding" even though such plates have been used to print 500 copies or more. Moreover, said copies, even those produced initially, were of high quality.

Substantially, the same results are obtained when sodium sulfate, sodium chloride, potassium bromide or like salts heretofore mentioned in the same or lesser concentrations are substituted for the potassium sulfate shown above.

EXAMPLE 2

Substantially the same procedure as in Example 1 was followed but a stop bath of the following formulation was substituted for the stop bath of Example 1:

	Percent by weight
Phosphoric acid	13
Benzyl alcohol	14
Triethylene glycol	73

Stop baths conforming to the formulation above are described in detail in U.S. Patent 3,146,105.

After about 100 copies were printed, "blinding" occurred and the run was terminated. However, instead of producing a new photolithographic plate, the plate of the example was immersed in an aqueous solution of sodium sulfate. The solution comprised about 10 percent by weight sodium sulfate. The plate was then run on a lithographic press and high quality copies produced therefrom.

EXAMPLE 3

A lithographic plate material was exposed to an image pattern and developed in accordance with the procedure of Example 1. After development, a portion of the plate was immersed in the "stop bath" of Example 2 whereas another portion thereof was immersed in an aqueous "stop bath" of the following formulation:

	Percent by weight
Sodium chloride	5
Phosphoric acid (85%)	1.5

The plate was then run on a lithographic printing press. After one printing, the copy produced from the portion of the plate immersed in the "stop bath" of the above described formulation was of high quality indicating an improved ink receptivity of the portion of the plate processed in accordance with the practice of my invention. In contrast thereto, the copy produced from the portion of the plate immersed in the "stop bath" of Example 1 did not manifest such quality until after about 50 prints were produced.

This example illustrates the efficacy of the solutions of the present invention in not only eliminating "blinding" but also in improving the overall initial ink receptivity of lithographic plates. Accordingly, plates processed in accordance with the practice of the present invention can produce high quality print copies immediately, whereas presently in the art, the initially printed copies must oftentimes be discarded because of their inferior quality.

Another surprising advantage in the use of photolithographic plates processed in accordance with the practice of my invention resides in the fact that the copies reproduced therefrom more accurately reflect the quantity as well as the tonal quality of the original data or information comprising the exposure pattern. For example, oftentimes original data in the form of fine lines or light lines cannot be reproduced in copies produced from plates processed in accordance with known techniques. This is true even though the fine lines or light lines can be seen in the developed photolithographic plate. Apparently, such developed areas do not manifest sufficient ink receptivity to permit same to be copied. However, in accordance with the practice of my invention, such areas do develop sufficient ink receptivity and fine line or light line data is accurately reproduced in the copies. Also the tonal quality or contrast of the original data is more accurately reproduced in copies printed from photolithographic plates produced in accordance with my invention.

Many modifications of the incidental features offered in the above examples for the purpose of illustrating my invention may be introduced thereto without departing from the spirit and scope of the invention defined in the appended claims.

Having described my invention together with manners of practicing same as well as preferred embodiments thereof, what I declare as new and desire to secure by U.S. Letters Patent is as follows:

1. In the process of producing a lithographic printing plate from an imaging medium comprising a developer layer containing a developing agent capable of oxidation in the presence of a hydrophilic organic colloid to form an image receptive to greasy printing ink, and over the developer layer a hydrophilic organic colloid photosensitive emulsion capable of reacting with the developer to produce a visible metal image, and the emulsion containing a hardener, in which the colloid has a hardness equivalent to that of a gelatin layer containing from about 2 grams to about 15 grams of dry formaldehyde per gram of dry gelatin, which imaging medium is exposed and contacted with an activator solution for the developer to produce an element useful as a lithographic plate by reasons of differences in ink receptivity between the exposed and non-exposed areas of the medium, the improvement comprising reducing the water absorption characteristics of the printing plate by contacting the imaging medium with an antiswelling agent.

2. A process as in claim **1** wherein the hydrophilic colloid photosensitive emulsion comprises a gelatin-silver halide emulsion.

3. A process as in claim **2** wherein the antiswelling agent is an alkali metal halide, sulfate or nitrate, and wherein the antiswelling agent is applied to the imaging medium as a solution after exposure of the imaging medium.

4. In the process of producing a silver image in an exposed imaging medium comprising in order, a first layer comprising a silver halide developing agent capable of oxidation in the presence of a hydrophilic organic colloid to form an image receptive to greasy printing inks, a second layer comprising an exposed hydrophilic organic colloid silver halide emulsion and a third layer comprising a fogged hydrophilic organic colloid silver halide emulsion containing a hardener, in which the colloid has a hardness equivalent to that of a gelatin layer containing from about 2 grams to about 15 grams of formaldehyde per pound of gelatin, which imaging medium is contacted with an activator solution for the silver halide developing agent thereby producing an element useful as a lithographic plate, the improvement comprising contacting the plate with a solution comprising contacting an antiswelling agent for the hydrophilic organic colloid.

5. The process of claim **4** wherein said solution comprises a salt chosen from the group consisting of the halides, sulfates and nitrates of an alkali metal.

6. The process of claim **4** wherein said solution comprises sodium sulfate.

7. The process of claim **4** wherein said solution comprises sodium chloride.

8. The process of claim **4** wherein said solution comprises potassium sulfate.

9. The process of claim **4** wherein said solution comprises potassium chloride.

10. The process of claim **4** wherein said solution comprises an acid.

11. The process of claim **4** wherein said plate is contacted with said solution after ink has been added to said plate.

12. A photographic stop bath for use in processing photolitographic printing plates which comprises a solution comprising phosphoric acid and a salt chosen from the group consisting of the halides, sulfates and nitrates of an alkali metal.

13. The stop bath of claim **12** wherein said salt is sodium chloride.

14. The stop bath of claim **12** wherein said salt is sodium sulfate.

15. The stop bath of claim **12** wherein said salt is potassium chloride.

16. The stop bath of claim **12** wherein said salt is potassium sulfate.

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