

UNITED STATES PATENT OFFICE

2,230,981

PRINTING PLATE

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No Drawing. Application July 23, 1940,
Serial No. 347,044

26 Claims. (Cl. 41—41.5)

This invention relates to planographic printing plates and is a continuation in part of earlier applications, Ser. No. 311,294, filed December 28, 1939 and Ser. No. 170,762, filed October 25, 1937.

5 In the preparation of planographic printing plate surfaces, it is now customary, in most cases, to employ metal plates. The surfaces of these plates are required to be roughened by a graining operation which renders the surfaces capable
10 of retaining films of water and becoming thereby grease-repellent. The graining operation increases to an objectionable extent the cost of preparation of plates by both the time and labor required and the equipment employed. In addition
15 to its cost, the graining operation is objectionable due to the fact that plates prepared by it must be subjected to etching or gumming operations both during the preparation and operation of the plate. Furthermore, satisfactory grained
20 metal lithographic surfaces can be prepared on only a few relatively expensive metals.

It is a chief object of the present invention to improve planographic printing plates and to devise novel water-receptive portions of a planographic plate surface which may take the place
25 of grained plate surfaces and eliminate some etching and gumming treatments now required to be carried out in connection with grained metal plates, and which may make possible the
30 use of various metals and other materials to comprise a base for a printing plate.

The invention also aims to present a combination of materials adapted to provide a coated body which gives printing effects equivalent to, or
35 better than, the effects obtained with lithographic stone printing.

It is a further object of the invention to provide a colloid plate of novel limited water-receptive character, and generally to make available a simple, cheap and efficient printing plate capable of
40 effecting improved printing quality.

The nature of the invention and its objects, will be more fully understood from the following description, and the novel features will be more
45 particularly pointed out in the accompanying claims.

In making planographic printing plates, as indicated above, it is customary to provide a metal support and to rely on grained metal surfaces
50 for retaining water and repelling greasy inks in the non-printing portions of the plate. The usual practice is to employ the metals aluminum and zinc to comprise the support and to grain one side of the metal so that it may retain water by
55 capillary attraction. This is expensive and slow,

and involves tying up of many thousands of metal plates which have to be stored and which require therefore a large amount of space. In addition, graining machinery is costly and represents a very considerable investment of money. It may
5 therefore be seen that it is highly desirable to avoid the grained plate construction in preparing a planographic printing surface.

In accordance with our invention, we employ a synthetic hydrophilic resin in a film state to take the place of the grained metal surfaces described. We apply a thin layer of a resin, as for example from a suspension of polyvinyl alcohol (3% solution) on a suitable support. This film
10 is allowed to set and is then moistened. Printing portions are thereafter prepared on a film, as for example by the albumin process.

This albumin process consists in applying on the moistened film a coating material which consists of albumin and a material sensitive to actinic light such as ammonium bichromate, or other chromic salt. The film of sensitized albumin is allowed to dry and is then exposed under a negative to actinic light, whereby the exposed
20 portions of the albumin become hardened and grease-receptive. The plate is then rolled up with a developing ink, held under running water and developed by lightly rubbing as with a plectet of cotton to remove the ink and albumin from the non-exposed areas. This effects printing
25 portions of albumin which are sensitized to grease and non-printing surfaces of hydrophilic material which retain water by absorption and are thereby desensitized to grease.

It is pointed out that by applying the coating, the entire step of graining with all of its attendant difficulties is avoided. In addition, due to the hydrophilic character of the film described, moisture is retained by absorption, and capillary effects such as are required in the development
35 of a hygroscopic surface on a grained metal plate, need not be resorted to. With the hydrophilic plate surface, certain etching and gumming operations required in connection with the use of grained metal plates may be eliminated or greatly
40 reduced. The hydrophilic film functions somewhat in accordance with the principle of a colloid printing plate by absorbing water in the manner described. The use of a hydrophilic film of synthetic material to comprise the non-printing portions of a printing plate may be resorted to in
45 preparing other printing plates than the albumin plate described, as for example plates whose printing portions consist of coating materials
55

other than albumin, as bichromated gum and the like.

Various materials may be utilized to comprise a suitable support, as for instance metals of many types, plastic compositions, paper and the like. It will be observed that this is a definite advantage since with a plate of grained surface only metal may be utilized and only a few metals such as zinc and aluminum are satisfactory.

Various other solution strengths of polyvinyl alcohol may be employed, as 5% and 10% solutions and others. In addition to the polyvinyl alcohol resin cited as a suitable coating material for effecting non-printing portions of a plate, certain other resins may be employed as vinyl resins, such as vinyl acetates, halides, esters, copolymers of esters, ethers, ketones, alcoholates, and the like. Also we may employ some synthetic resins of a normally hydrophilic character and particularly synthetic hydrophilic colloids which may be put into solution or suspension and thus may be readily coated on a support to comprise a film, which will absorb water in a suitable manner for forming the non-printing portions of a planographic printing plate. Such films may comprise certain synthesized materials obtained from hydrocarbons, phenols, aldehydes, ketones, amines, natural resin acids, polyhydric alcohols and polybasic acids, vinyl compounds, rubber, sulphur and fatty oils. Only those materials obtained from the above noted reactants which, without dissolving, are hydrophilic in a proper degree for meeting lithographic printing limitations, or which may be made so by treatment with reagents, are suitable for purpose of coating in accordance with this invention and are intended to be included.

A few such resins from which plates less desirable than vinyl plates may be made comprise

(a) a product obtained from heating to 100° C. 150 parts of diethylene glycol and 70 parts of boric acid together with 80 parts of borax with agitation (aqueous solution); (b) a product obtained from treating polyvinyl alcohol with an aldehyde and a substance capable of condensing with the aldehyde, as a phenol; (c) a product obtained by treating a vinyl ester-aldehyde with another aldehyde; (d) a product obtained by heating methylolurea with a compound containing at least two free hydroxyl groups (aqueous solution); (e) and a condensation product resulting from treating aryl sulphonamido carboxylic acid amide with formaldehyde (aqueous solutions).

A further aspect of our invention deals with a plate having modified hydrophilic non-printing portions comprising a hydrophilic material combined with a chromic salt such as ammonium bichromate, particular reference being had to polyvinyl alcohol and other vinyl compounds.

The non-printing portions of this modified plate material should not be confused with printing portions of plates obtained from hardening albumin or other coatings with ammonium bichromate where the ammonium bichromate has been employed as a sensitizing agent for exposure to actinic light to render the various colloids hard and grease-receptive.

According to our improved method of treating a hydrophilic coating with a chromic salt, we provide for directly mixing a solution of a salt, such as ammonium bichromate, with a solution of polyvinyl alcohol and allowing a film of the product to dry without necessarily employing any action of light or other agents whatever,

although the action of light or other agents in some instances may not be objectionable. Our method is based upon the discovery that the use of a chromic salt, and in particular ammonium bichromate, with a vinyl compound such as polyvinyl alcohol in substantially any proportion, while toughening a film of the vinyl compound, fails to result in the development of a product which is completely water-repellent and hence adapted to receiving grease. This is the opposite case of that which results from combining bichromate with most colloids such as albumin, glue, and the like. These colloids are quickly hardened by bichromate to an extremely water-resistant mass which is easily rendered grease-receptive.

It will be seen that by utilizing the ammonium bichromate with a solution of polyvinyl alcohol, the porosity or water-absorptive character of a film of polyvinyl alcohol may be limited or reduced in a highly desirable manner. This limitation of water-receptivity is effected without the danger usually encountered of hardening the alcohol to a point where it becomes grease-receptive so that it would cause objectionable smurring in a plate. Heretofore, it has been considered impossible to allow ammonium bichromate to remain in a hydrophilic colloid film if water receptivity was desired, for the reason that when combined with colloid materials, the bichromate would continue to harden at a slow rate until sooner or later grease-receptive surfaces were formed. This aspect of our invention is based essentially on the discovery that the bichromate can be used to limit water-receptivity of a hydrophilic colloid without its necessarily developing grease-receptivity, especially when the treated colloid is moistened before possible contact with greasy or grease-forming materials.

The desirable hardening effect noted may result from the reaction which takes place upon the mere admixture of the bichromate and the colloid. It may be expedited, however, by subjecting the mixture to light, heat, and/or pressure. Although light is effective as an agent for expediting the reaction, we prefer not to use it in reacting the chromic salt with a vinyl compound such as the alcohol, for the reason that it renders the film dark yellow in color. Maintenance of the translucent character of the film, in a plate or in the print on a plate, is advisable, as it facilitates correction of errors, as well as preparation and handling of the plate.

A desirable treatment of a hydrophilic synthetic material to decrease water-receptivity may also be effected with a copper salt such as cupric chloride. We may desire to use certain other reagents to accentuate the action of the salt used, as for example ferric chloride or ferric sulphate mixed with a bichromate solution. It may further be desired to employ these and other agents, as heat and pressure and others, for treating other hydrophilic materials of the class referred to above. In employing the polyvinyl alcohol and the ammonium bichromate, various proportions may be employed of which one specific example consists in the following amounts:

	Oz.
5% polyvinyl alcohol suspension-----	7 70
Ammonium bichromate-----	1

If desired, about .7 c. c. of ferric chloride solution, 42° Bé., may be added to this mixture for cooperating with the chromic salt in decreasing the water-receptivity of the non-printing por-

tions. Either with or without the ferric chloride, suitable water-receptive films may be quickly obtained from this mixture. Thicker and more slowly drying films may be formed from mixtures of larger proportions of the resin.

The grained metal surfaces of zinc and aluminum plates, for which the coatings of the invention are a substitute, were designed to take the place of lithographic stone. Certain other substitutes have also been attempted from time to time by combining clay, or other filler materials, with a binder such as a colloid, or a cementitious material, or other type of bonding agent. Such mixtures are intended to form a suspension which may be coated upon a suitable base. In a coated state, the clay particles are designed to form a stone-like body having a water absorptive character generally resembling that of lithographic stone. Attempts to coat such suspensions have been unsuccessful. One reason consists in the fact that the suspensions cannot be prepared of a uniform consistency suitable for forming smooth coatings. These mixtures tend to coagulate and form a lumpy mass which prevents uniform application. Also, the dried coatings do not retain water in a satisfactory manner after being subjected, for a short time, to use on a press, and to the action of grassy inks. This is particularly due to the bonding agents, heretofore employed, becoming sensitized to grease in the non-printing portions of a plate surface which causes smurring or other undesirable ink transfer.

Another feature of the invention consists in the use of a hydrophilic material, of which the polyvinyl alcohol is particularly exemplary, with clays or other fillers to provide a suspension having a consistency well adapted to being uniformly spread over a base, and to forming a satisfactory printing surface which gives printing quality resembling that obtained from printing with lithographic stone. The colloidal character of polyvinyl alcohol, in particular, enables this substance to become intimately incorporated with the tiny filler particles which provides a suspension of highly uniform consistency, well adapted to forming a smooth coating and to being spread out in a very thin state.

In a dried coating of a mixture as described, the hydrophilic material functions as a bonding agent interposed in and around the filler particles, and also continues to accept water in the usual manner. This effects a permanent water reservoir between the filler particles which is not affected by any exposure to grease and which makes possible long life operation of the plate. At the same time, the filler particles lend a certain amount of hardness to the hydrophilic materials, may be utilized to reduce and also to maintain substantially constant the amount of water retained in any given surface area, and may provide a mild grain in the surface greatly resembling the grain of lithographic stone.

By the addition of a filler, the hydrophilic materials may be rendered more adhesive and, in some instances, such suspensions will stick firmly to materials on which the hydrophilic material alone cannot be bonded. One example of such a substance is rubber. The hardening effect of a filler such as clay may in some cases eliminate the use of the various hardening agents already discussed, and is further useful in facilitating penetration and retention of materials making up the printing image portions of the plate, and in inking such portions. With some proportions of

filler and hydrophilic material, swelling in the non-printing portions of a plate prepared from the mixture is substantially reduced or eliminated.

Preferred filler materials which may be placed in suspension with hydrophilic materials are calcium carbonate, kaolin and china clay. Others may be desired to be employed, as for example feldspar, fluorspar, barium sulphate, calcium chloride, and the like. A preferred hydrophilic material is polyvinyl alcohol. Hydrophilic substances such as vinyl compounds and others above referred to may also be employed. Various proportions of the hydrophilic material and filler may be used. One example thereof consists in the following mixture:

5% polyvinyl alcohol-----	pt--	1
China clay-----	oz--	2

Other amounts in the same proportion may be resorted to. If desired, the various hardening agents recited above may be desired to be employed with the mixture in some cases. Also, various treatments may be given a coating formed from these mixtures. For instance, a coating may be subjected to etching treatments if desired, or it may be subjected to immersion in various preserving materials or other reagents.

It will be seen that the invention provides improved printing plates, greatly superior to plates having grained surfaces for retaining moisture by capillarity. The hydrophilic coating, either with or without fillers, can be more cheaply and quickly prepared, and may effect improved printing quality. Various materials may be used to support the coating, and limitation to use of zinc or aluminum is obviated. The hydrophilic character of the coating is limited by several means to a highly satisfactory point. If the coating without filler is employed on a grained surface, it should be noted that it conforms to such grain, thereby presenting a secondary grained surface of softened or modified character which in some instances may be employed to effect finer halftone quality of printing. This is particularly the case where a paper support is used which presents a very fine grain for the coating to conform to. Various other graining effects such as roughening to promote water-receptivity by capillarity, may be resorted to, with the coatings. The addition of fillers in the manner described further enhances the desirable water receptive character of the hydrophilic materials generally, and provides a type of printing which is an excellent substitute for lithographic stone printing.

The term "hydrophilic" as employed in the specification is intended to mean "water-absorptive" and not "water-soluble." Where the material referred to may occur in both water soluble and water-absorptive states, as for example polyvinyl alcohol, which is soluble in hot water but which in a film state may be rendered only water absorptive to cold water, it is intended that the term "hydrophilic" refer to the material in a water-absorptive state.

While we have disclosed preferred reagents, materials and procedures, it should be understood that various changes and modifications may be resorted to therein, in keeping with the spirit of the invention as defined by the appended claims.

Having described our invention, we claim:

1. As a new article of manufacture, a printing plate presenting water-receptive areas comprising a polyvinyl alcohol.

2. As a new article of manufacture, a colloidal printing plate having printing areas and non-printing areas occurring therein, said non-printing areas comprising polyvinyl alcohol in a water-receptive state.
3. As a new article of manufacture, a colloidal printing plate having printing areas and non-printing areas occurring thereon, said non-printing areas comprising that hydrophilic product obtained from hardening polyvinyl alcohol with ammonium bichromate in the presence of ferric chloride.
4. As a new article of manufacture, a colloidal printing body having printing areas and non-printing areas occurring therein, said non-printing areas comprising hydrophilic polyvinyl alcohol and the exposed surfaces of said areas being roughened to further promote water-receptivity by capillary action.
5. A colloidal printing plate comprising a base and a material coated over said base, said material presenting printing areas and non-printing areas and said non-printing areas comprising water-receptive polyvinyl alcohol.
6. A colloidal printing plate comprising a base and a coating of polyvinyl alcohol on said base, said polyvinyl alcohol coating presenting selective non-printing areas having a substantially fixed degree of water receptivity.
7. A colloidal printing plate comprising a base and a film of polyvinyl alcohol coated on said base, said polyvinyl alcohol coating presenting hydrophilic non-printing areas, the polyvinyl alcohol comprising the non-printing areas being in a state of polymerization of such degree as to provide a water receptivity substantially equivalent in uniformity and definiteness of moisture retention to the water receptivity of a grained metal lithographic printing plate.
8. As a new article of manufacture, a colloidal printing plate having printing areas and non-printing areas occurring thereon, said non-printing areas comprising a hydrophilic product resulting from hardening polyvinyl alcohol with ammonium bichromate in the presence of ferric sulphate.
9. As a new article of manufacture, a printing plate presenting water-receptive areas comprising a vinyl compound.
10. As a new article of manufacture, a printing plate presenting water-receptive areas comprising co-polymers of vinyl esters.
11. As a new article of manufacture, a printing plate presenting water-receptive areas comprising polyvinyl alcohol and ammonium bichromate.
12. As a new article of manufacture, a printing plate presenting water-receptive areas comprising polyvinyl alcohol, ammonium bichromate and ferric chloride.
13. As a new article of manufacture, a printing plate presenting water-receptive areas including a polymerized vinyl compound and a chromic salt.
14. As a new article of manufacture a printing plate presenting water-receptive areas comprising a vinyl compound, a chromic salt and a salt selected from the group consisting of ferric chloride, ferric sulphate and the like.
15. As a new article of manufacture, a printing plate presenting water-receptive areas comprising vinyl acetate.
16. As a new article of manufacture, a printing plate presenting water-receptive areas comprising a vinyl ester.
17. As a new article of manufacture, a printing plate presenting water-receptive areas comprising a vinyl ether.
18. As a new article of manufacture, a printing plate presenting water-receptive areas comprising a vinyl compound and cupric chloride.
19. As an article of manufacture, a printing plate presenting water-receptive areas which comprise a mixture of a vinyl compound and a finely divided clay-like material.
20. As an article of manufacture, a printing plate presenting water-receptive areas comprising a mixture of a hydrophilic vinyl compound and a filler.
21. As an article of manufacture, a printing plate presenting water-receptive areas comprising a mixture of polyvinyl alcohol and a filler.
22. As an article of manufacture, a printing plate presenting water-receptive areas comprising a mixture of a hydrophilic vinyl resin, a finely divided, clay-like filler, and a hardening agent.
23. As an article of manufacture, a printing plate presenting a surface coating consisting of a mixture of a hydrophilic vinyl resin and a filler, a grease-receptive printing image impregnated in the filler and resin mixture to form printing and non-printing portions of a planographic printing surface.
24. As an article of manufacture, a printing plate presenting water-receptive areas comprising a vinyl resin, an ingredient for hardening the vinyl compound and an ingredient for imparting porosity thereto.
25. As an article of manufacture, a printing plate comprising a base, a coating on said base consisting of a mixture of a water-receptive vinyl compound and an ingredient for reducing swelling of the vinyl compound, printing portions supported on the said coating and bonded to the said ingredient and vinyl compound.
26. As an article of manufacture a printing plate presenting water-receptive areas comprising a hydrophilic film of a vinyl compound and an ingredient for modifying the water-receptivity of the vinyl compound.

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