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PLANOGRAPHIC PLATE AND METHOD OF MAKING THE SAME

Douglas A. Newman, Sea Cliff, and Allan T. Schlotzhauer, Locust Valley, N. Y., assignors to Columbia Ribbon & Carbon Manufacturing Company, Inc., Glen Cove, N. Y., a corporation of New York

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This invention relates to planographic printing plates and to the methods of making the same.

Relatively inexpensive planographic plates for use in instances where the number of copies desired is not too great have had increasingly favorable reception for the reason that better copies can be provided than is possible with alternate reproduction systems, for example, hectographic. The full acceptance of plates of this character, however, has been hampered by the fact that a plate which gives copies of the highest quality is somewhat too costly for most users, while a plate within an acceptable cost range has not been found which will give sufficiently good results to warrant the change-over in the user's equipment.

An object of the invention, therefore, is the production of a planographic plate capable of producing a reasonable number of copies of the foremost quality, and which can be made at a cost sufficiently low to be attractive to users of duplicating equipment, and particularly those whose requirements as concerns numbers of copies are moderate.

Planographic plates of the type with which the invention is concerned normally have a base of a cellulosic material such as paper treated to give it high wet-strength and low wet-extensibility so as to withstand the moistening treatment and stresses undergone in the printing operation. Furthermore, the surface must have the appropriate hydrophilic-oleophilic balance to operate as a planographic plate.

Various treatments and coating compositions have been suggested in the past in an effort to provide a paper base plate which meets the above need, but none have been entirely successful for the reason that to produce plates capable of rendering acceptable copies, the numerous treatments to which they must be subjected bring the cost of the plate to a level where it cannot be used economically as a substitute for other duplication methods.

We have discovered, however, a coating solution which satisfies the exacting requirements for a planographic printing surface and which at the same time has additional properties which materially reduce the effort and expense required in the treatment of paper plates therewith, in addition to effecting other savings. The essential ingredient is a dibasic acid styrene copolymer, normally in the form of an ammonium or other alkali salt, and is marketed under the trade name "Amberlite W–1," which expression is used hereinafter to designate compounds of this character. This material itself is inexpensive when compared with most materials which are in any way suitable for such coatings. Furthermore, when the same is incorporated in a coating solution insolubilized and dried, a tough, stable, rubber-like film is formed, whereby plates coated therewith may be stored without deterioration. This coating is also found to have the proper balance between its hydrophilic and oleophilic properties, especially for plates which are to be used in work where long operating life is not the primary consideration.

Unlike most materials capable of providing films which lay the surface fibers of the paper and have suitable planographic properties, "Amberlite W–1" is suitable as a wet-strength sizing material for paper, and, in addition, has

the property of being rendered insoluble by the action of heat at comparatively low temperatures.

The nature of the solution formed when "Amberlite W–1" is used as the film-forming constituent likewise has a marked effect upon the cost of production in that more continuous films are obtainable with fewer treatments than when previously known planographic surfacing materials are used.

Other features and advantages will hereinafter appear.

A planographic plate or sheet of the character with which the invention is concerned normally consists of a base web of paper formed by the consolidation of suitable fibers using paper-making equipment of a known type. During the process of manufacture, the fiber is mixed in the beaters with a sizing material, or the web when formed is impregnated with such sizing material, selected to impart wet-strength to the web and decrease the water penetration thereof. This is necessary in order that the finished plate, which is used by continuously wetting the same, will have sufficient strength to withstand the stresses imposed thereon by a printing press in operation with minimum damage or deterioration, and further, so that changes in size and shape of the sheet which would distort an image imprinted thereon to an unacceptable degree are avoided. A sized sheet of this character is then provided with one or more coatings of a material which will lay any surface fibers and provide a surface having the appropriate hydrophilic-oleophilic balance. It has become customary to use a plurality of superposed coatings for the purpose since it is known that imperfections such as fiber ends and pinholes, which seriously affect the quality of work of which the sheet is capable by introducing objectionable background "tone," are much more effectively covered when several light coatings are used in place of a single heavy one. The sheet must be subjected to a drying treatment after each sizing or coating and, depending upon the quality and properties desired, may be calendered one or more times.

The improved surface coating which includes "Amberlite W–1" as the essential constituent thereof is found to have important advantages over the other coatings now known to be usable for this purpose. While the planographic properties of this material are the equivalent of those of materials formerly in use, we have found that it also possesses remarkable covering properties, so that flaws in the nature of fiber ends and pinholes are eliminated to an acceptable degree with fewer coats and a consequent saving in production costs.

Not only is an "Amberlite W–1" film having a thickness equal to that of a film formed of previously used materials, the full equivalent thereof with regard to covering properties, but an additional feature of this material makes it economically possible to apply heavier and denser coatings in a single operation. The most practical and expeditious impregnation or coating of paper webs is conducted using apparatus in the nature of a vat through which the web may be passed, for example, the size tub normally used in connection with paper making machinery. Such an arrangement, however, is usable with coating baths of low viscosity only. Since the continuity of the resulting film depends upon the concentration of the solution, and since solutions of higher concentration have increased viscosity, the application of planographic surfaces to a paper web using materials previously known has required either that several low viscosity applications be made in the size tub, or the more complicated equipment be used to handle the higher viscosity solutions. "Amberlite W–1," however, has the advantage of being readily dispersible in water to form solutions of a comparatively high concentration at a relatively low viscosity. For example, solutions having a concentration substantially in excess of five per cent have a viscosity such that they can be readily handled in the size tub while concentrations of this order using other known planographic coating ingredients would be so viscous as to preclude effective application using this apparatus.

The wet-strength sizing treatment to which paper to be used as a planographic plate is subjected, normally employs a material such as melamine having desirable moisture-resistance. Such materials previously used for this

purpose, however, have not had suitable fiber laying and planographic properties, so that the treatment of the web after sizing has been necessarily such as to provide a completely superimposed planographic surface coating thereon.

One important feature of the invention resides in the discovery that "Amberlite W–1," in addition to being capable of forming the planographic surface of a paper plate, is also suitable for use as the essential constituent of the sizing bath, since it has the property of reducing the water absorption of the paper fiber and thus increasing the wet-strength of the paper and reducing its wet-extensibility to a point where it can withstand the stresses imposed during its use in a printing machine under moistened conditions.

When a paper plate is constructed using "Amberlite W–1" as the main ingredient of the wet-strength size, as least two other important and unexpected savings are realized. In the first place, with other sizing materials, for example melamine, while the treated paper has suitable wet-strength properties, it is not economical to recover the fiber which finds its way into the broke, i. e. the improperly deposited pulp mixture or damaged paper, since the reacted size is not readily separated therefrom to permit its reclamation. When "Amberlite W–1" is used, however, alkali solutions readily separate the size from the fiber so that the latter may be reclaimed for further use. In the second place the characteristics of "Amberlite W–1" are such that the impregnation of a web, or coating thereon may be rendered insoluble in a number of ways, some of which accord so well with normal paper making procedures that the cost for such treatment is materially reduced as compared with treatments necessary when using other materials. The "Amberlite W–1" size, in its water-soluble alkali salt form, is capable of being reacted with solutions containing heavy metal salts to form a material having the nature of a water insoluble salt. Furthermore the "Amberlite W–1" size, when the major portion thereof is in the form of an ammonium salt, as is normally the case, may be subjected to heat and thus converted into a material having the nature of an insoluble acidic form of the dibasic acid styrene copolymer. In addition, the degree of completion of the latter reaction, while a function of both time and temperature, is found to reach acceptable percentages with remarkably low temperatures applied for reasonably short periods of time. This property is an important feature of the invention for the reason that the temperatures normally employed in paper-making machinery are not particularly high, and the discovery of "Amberlite W–1" as a size and coating for planographic plates permits their production without resorting to additional handling and processing steps as is normally the case with materials heretofore known. For example, it has been found that a web treated with "Amberlite W–1" may have the sizing thereon thoroughly insolubilized by subjection to a temperature of 100° C. for only five minutes. In fact the treatment at 100° C. for as little as two minutes has been found to give acceptable results in many cases. Such a low temperature insolubilizing treatment conducted directly on the conventional paper-making equipment thus renders the usual additional steps such as insolubilizing washes, or passes through special high temperature or long exposure equipment unnecessary.

With reference to the materials used in and products of the foregoing reactions, terminology is herein adopted and consistently used hereinafter, such that the water soluble alkali salts, as well as the form of heavy metal salts, or insoluble acidic forms, are all comprehended in the general expression "dibasic acid styrene copolymer."

The most complete advantage is taken of the invention when solutions containing "Amberlite W–1" are used both as the wet-strength size and as the planographic surface coating for the paper. When the sizing treatment is finished it will be found that the surface fibers of the paper are partially laid and that the sheet already has planographic properties to a substantial degree. Under these circumstances, it is usually necessary to apply a single finishing coat only, which assures proper coverage of possible flaws and which may receive any treatment directed toward determining the exact planographic properties required under the circumstances.

The following examples illustrate the materials and steps which may be used in carrying out the invention. The particular ingredients and steps hereinafter described, while representing the forms of the invention at present

preferred, and listed in the order of preference, are of course only a few of many possible variations, depending upon the circumstances and requirements of the particular case:

FORMULA #1

Ingredients:	Parts by weight
"Amberlite W–1"	25
Clay	18
"Aerosol O. T."	10
Sodium pyrophosphate	0.3
Water	75

FORMULA #2

Ingredients:	Parts by weight
Copper sulphate	3
Aluminum sulphate	1
Ferric chloride	0.5
Chromic trioxide	0.5
Water	95

Formula #1 represents a preferred form of the improved surface coating solution for providing a paper sheet with suitable planographic properties. It will be noted that a proportion of clay filler has been added to give the coating a desirable "tooth" which assists in retention of the image-forming material. The ingredient designated as "Aerosol" is essentially dioctyl sodium sulfosuccinate and an inert diluent serving as a wetting agent to enhance the surface covering properties the solution, and the sodium pyrophosphate acts as a buffer for maintaining the solution at a suitable pH value.

Formula #2 represents a preferred insolubilizing solution suitable for treatment of a planographic coating of the type consisting essentially of "Amberlite W–1."

Example I

The preferred process includes the steps of sizing the base stock with any suitable solution of "Amberlite W–1," either in the beaters or by subsequent impregnation of the web, insolubilizing the same by subjection to a temperature of 100° C. for two minutes, applying a single coating to the planographic surface of the web using Formula #1 and insolubilizing the same by treatment with a metallic salt wash consisting of Formula #2. An alternative to the use of Formula #2 as an insolubilizing agent would consist in repeating the heat treatment described above after the surface coating has been applied. This would provide a surface whose planographic properties are suitable under certain circumstances, although the use of Formula #2 or its equivalent is normally preferable for reacting the surface coating where copies of the best quality are required.

Example II

An alternate process includes the steps of sizing the base stock with any suitable previously-known solution for imparting wet-strength to the paper, insolubilizing the same by the appropriate treatment, and thereafter coating the planographic surface of the web one or more times with Formula #1 and proceeding as described in Example I.

Examples III and IV

Paper sized in accordance with Examples I and II respectively may then be treated by coating the same with any suitable coating material to provide a water-repellent barrier. Thereafter a coating consisting of Formula I is superimposed on the barrier and the procedure continued as in Example I.

Example V

A base sheet having a printing image of oleous ink-receptive material formed thereon is treated by coating the same with Formula I. Since this is an aqueous solution it is repelled by the image and coats only the background area of the web surrounding the image. The coating is then insolubilized either by heating or by the use of Formula II as described for Example I. The background is thus coated with material which is hydrophilic, and when wet becomes oleophobic permitting the sheet to be used as a planographic plate.

It will be understood, of course, that the quality of the image and the number of copies obtainable may be

varied by adjusting certain factors in the plate construction such as the amount of filler and its particle size, the degree and number of calendering or pressing treatments used, and the extent of insolubilization treatment to which the coatings are subjected.

Thus, it will be seen that we have provided a planographic plate having a surface coating such that the same is suitable for making a moderate number of copies of exceptionally good quality and which can be produced at a cost which is less than any substantially equivalent plate heretofore known. Furthermore, the coating material used readily lends itself to the usual treatments for modifying its properties in any desired manner, and is also capable of being applied to a base sheet after the image has been formed thereon to impart thereto the properties necessary for its use as a planographic plate. In addition, the invention is seen to include the process of forming a planographic plate wherein the material used to impregnate and coat the base so affects the process steps required that a planographic plate which is the equivalent of those previously used can be produced in a more expeditious and less complicated manner.

Variations and modifications may be made within the scope of this invention and portions of the improvements may be used without others.

We claim:

1. A planographic plate comprising a base having a coating essentially of a dibasic acid styrene copolymer; and an ink receptive, water repellent image formed on said coating.

2. A planographic plate comprising a cellulosic base having a coating essentially of a water-insoluble dibasic acid styrene copolymer; and an ink-receptive, water-repellent image formed on said coating.

3. A planographic plate comprising a cellulosic base impregnated with a wet-strength sizing and having a surface coating, said sizing and coating each being essentially of a dibasic acid styrene copolymer; and an ink-receptive, water-repellent image formed on said surface coating.

4. A planographic plate comprising a base having a coating essentially of a dibasic acid styrene copolymer in the form of a salt; and an ink-receptive, water-repellent image formed on said coating.

5. A planographic plate as defined in claim 4 in which said salt is in the form of an ammonium salt.

6. A planographic plate comprising a cellulosic base impregnated with a wet-strength sizing and having a surface coating, said sizing and coating each being essentially of a dibasic acid styrene copolymer in the form of a salt; and an ink-receptive, water-repellent image formed on said surface coating.

7. A planographic plate comprising a cellulosic base impregnated with a wet-strength sizing and a surface coating, the latter being essentially of a dibasic acid styrene copolymer; and an ink-receptive, water-repellent image formed on said surface coating.

8. A planographic plate comprising a cellulosic base impregnated with a wet-strength sizing and a surface coating, the latter being essentially of a dibasic acid styrene copolymer in the form of a salt; and an ink-receptive, water-repellent image formed on said surface coating.

9. The process of making a planographic plate comprising the steps of coating a surface of a cellulosic base with a solution which is essentially an aqueous dispersion of an alkali salt of a dibasic acid styrene copolymer; insolubilizing the same; and forming an ink-receptive, water-repellent image on said coating.

10. The process of making a planographic plate comprising the steps of coating a surface of a cellulosic base with a solution which is essentially an aqueous dispersion of a dibasic acid styrene copolymer in the form of an ammonium salt; insolubilizing the same by subjecting the coating to a temperature of not over 100° C. for not over two minutes; and forming an ink-receptive, water-repellent image on said coating.

11. The process of making a planographic plate comprising the steps of impregnating the material of a cellulosic base with a wet-strength solution; thereafter coating a surface of said base with a planographic surface forming solution, each of said solutions being essentially an aqueous dispersion of a dibasic acid styrene copolymer in the form of an alkali salt; and forming an ink-receptive, water-repellent image on said planographic coated surface.

12. The process of making a planographic plate comprising the steps of impregnating the material of a cellulosic base with a wet-strength solution; thereafter applying a single coating only to a surface of said base using a planographic surface forming solution, each of said solutions being essentially an aqueous dispersion of a dibasic acid styrene copolymer in the form of an alkali salt; and forming an ink-receptive, water-repellent image on said planographic coated surface.

13. The process of making a planographic plate comprising the steps of impregnating the material of a cellulosic base with a solution which is essentially an aqueous dispersion of a dibasic acid styrene copolymer in the form of an ammonium salt; consolidating said material into a web, insolubilizing the impregnant by subjecting the web to heat; applying a single coating only to a surface of said web using a solution which is essentially an aqueous dispersion of a dibasic acid styrene copolymer in the form of an alkali salt, and insolubilizing said coating; and forming an ink-repective, water-repellent image on said single coating.

14. The process of making a planographic plate comprising the steps of impregnating the material of a cellulosic base with a solution which is essentially an aqueous dispersion of a dibasic acid styrene copolymer in the form of an ammonium salt; consolidating said material into a web, insolubilizing the impregnant by subjecting the web to heat; applying a single coating only to a surface of said web using a solution which is essentially an aqueous dispersion of a dibasic acid styrene copolymer in the form of an ammonium salt, and insolubilizing said coating by subjecting said coating to heat; and forming an ink-receptive, water-repellent image on said single coating.

15. The process of making a planographic plate comprising the steps of impregnating the material of a cellulosic base with a solution which is essentially an aqueous dispersion of a dibasic acid styrene copolymer in the form of an ammonium salt; consolidating said material into a web, insolubilizing the impregnant by subjecting the web to heat; applying a single coating only to a surface of said web using a solution which is essentially an aqueous dispersion of a dibasic acid styrene copolymer in the form of an alkali salt, and insolubilizing said coating by reacting the same with a metallic salt solution; and forming an ink-receptive, water-repellent image on said single coating.

16. The process of making a planographic plate which includes the steps of impregnating a cellulosic base material with a wet-strength sizing; thereafter passing the same through a vat coating process wherein the vat contains a solution which is essentially an aqueous dispersion of a dibasic acid styrene copolymer in the form of an alkali salt; and forming an ink-receptive, water-repellent image on said vat coating.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,293,293	Allison	Feb. 4, 1919
1,759,956	Reed	May 27, 1930
2,072,487	Snyder	Mar. 2, 1937
2,078,535	Hagedorn et al.	Apr. 27, 1937
2,154,219	Shepherd	Apr. 11, 1939
2,186,946	Wood	Jan. 16, 1940
2,230,981	Toland et al.	Feb. 4, 1941
2,298,943	Howard	Oct. 13, 1942
2,311,889	Toland	Feb. 23, 1943
2,319,033	Bernstein et al.	May 11, 1943
2,356,879	Pense et al.	Aug. 29, 1944
2,373,287	Bassist	Apr. 10, 1945
2,391,620	Quarles	Dec. 25, 1945
2,402,469	Toland et al.	June 18, 1946
2,428,716	McGill	Oct. 7, 1947
2,486,804	Seymour	Nov. 1, 1949
2,542,784	Van Dusen	Feb. 20, 1951

(Other references on following page)

OTHER REFERENCES

Ser. No. 397,138, Fikentscher et al. (A. P. C.), published May 11, 1943.

Collins et al.—Wet Strength Paper. Boyce Publishing Co., N. Y. Copy available in Scientific Library. Only pages 34, 47 and 76 cited.

Information Bulletin 372—Annotated Comprehensive List of Trade Names of Synthetics. Research Assn. of British Rubber Mfrs. Copy available in Division 50. Only page 14 cited.

Paper Trade Journal, April 3, 1947, pages 49–56. (Copy in Scientific Library.)