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PAPER, PARTICULARLY PRINTING PAPER, AND METHOD OF MAKING SAME

Filed March 29, 1957

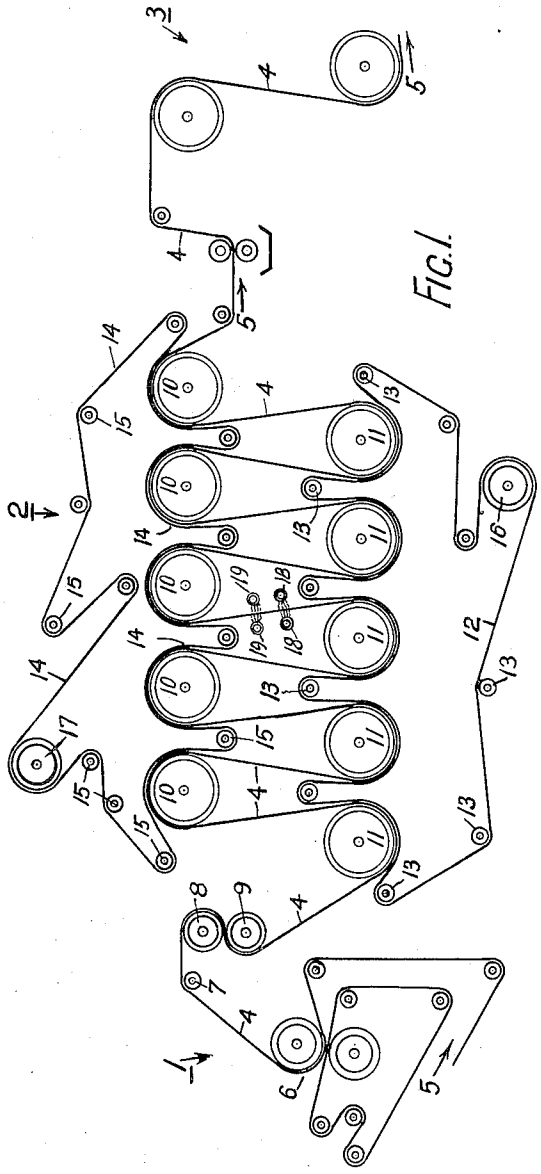


FIG. 1.

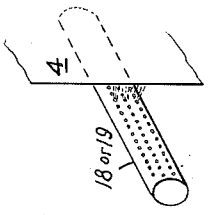


FIG. 4.

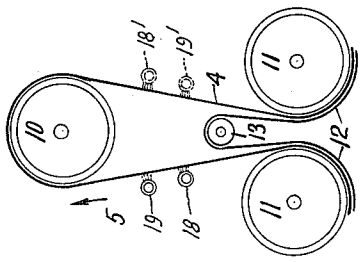


FIG. 3.

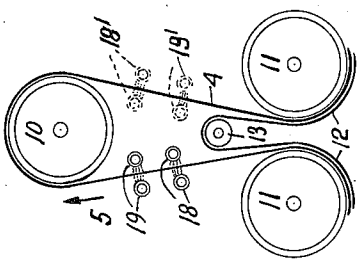


FIG. 2.

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PAPER, PARTICULARLY PRINTING PAPER, AND METHOD OF MAKING SAME

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16 Claims. (Cl. 162—163)

This invention has reference to the manufacture of paper. It has for its main object to provide a new kind of paper which is particularly suitable for use as printing paper especially newsprint or book print, although it is also applicable with advantage to other types of paper, for instance packing paper, wrapping paper and paper for other purposes.

Basically, paper according to the invention is produced in the same manner as known types of paper from wood pulp stock prepared in any conventional manner chemically, semi-chemically or mechanically, in paper machines of the Fourdrinier type, of the cylinder type or of any other type. Accordingly, the appearance of the improved paper which varies according to the different types of raw materials and/or methods employed in its manufacture, is substantially the same as that of the corresponding types of normal paper and, when intended for use as printing paper, care is taken for the pores to remain open which means to say that the paper "breathes," a characteristic of the greatest importance particularly when the paper is intended for use in high-speed printing.

Another object of the invention is to provide a new and improved type of printing paper which when compared with paper of substantially the same composition and make, is less oil and water absorbent.

A still further object of the invention is to provide a new and improved type of printing paper of a reduced ratio of oil and water absorption, which does not allow any substantial flow or spread of printing ink to occur across the paper.

A still further object of the invention is to provide a paper which, due to its reduced absorption of oil and water, can be made thinner than normal paper intended for the same purpose, without showing any trace or substantial trace of print on its reverse side and which, at the same time, is lighter and cheaper to produce than such normal paper.

According to the invention, porous paper, especially printing paper made of cellulose pulp, has applied to its surface a water-insoluble metallic salt embedded and substantially evenly distributed within a thin continuous layer consisting of the reaction product of at least one resinogenous agent with the cellulose and other substances contained in the paper and capable of reacting with said resinogenous agent, said layer being applied to the paper surface in such a manner that it firmly adheres thereto without filling or clogging the pores of the paper. The water-insoluble salt contained in the layer so applied, which forms the predominant part thereof, reduces the absorption by the paper of water and oil and permanently increases the affinity of the paper to printing ink.

The term "resinogenous agent" used in this specification comprehends all agents capable of forming with cellulose, lignin and with certain other substances contained in wood pulp, a compound which is, or resembles, a synthetic resin, said agents being mainly formaldehyde, urea, phenol and furfural.

The application of the metallic salt and resinogenous agent or agents to the paper is effected in the form of a mist, i.e, in micro-colloidal dispersion by means of steam during a phase in the manufacture of the paper in which

the latter contains between 20 to 60% by weight of water and is held at a temperature between about 80 to 100° C.

The paper produced according to the invention, besides being oil and water resistant, shows high affinity to printing ink, especially to ink made of carbon black and mineral oil. Due to the reduced oil absorption a smaller amount of ink is required for printing, resulting in a considerable saving of printing ink. On account of the affinity of the ink to the layer, the print applied to paper made according to the invention adheres better to the paper and dries more rapidly, particularly if the consistency or viscosity of the printing ink is adjusted to suit the speed of the printing press.

Due to the reduced lateral spread of the ink the print on paper made according to the invention is sharper and generally of better appearance than print on normal paper of the same composition and made by the same paper-making process, the outlines of the print being more clearly defined and neater, and "smutching" of printed lines being substantially eliminated. As paper made according to the invention may be lighter and cheaper than normal paper, considerable saving in transport cost, particularly of newsprint, can be achieved and the drying time for the ink is shortened, thereby rendering the production of both the paper and of the print more economical, in addition to the improvement in quality of the print referred to above.

Like normal paper, that produced according to the invention is capable of being re-used after disintegration, in the usual manner.

In order to more particularly describe the invention reference is made to the accompanying drawing which diagrammatically illustrates one phase in the manufacture of paper in a Fourdrinier machine, and to the examples hereafter described. In said drawing:

FIG. 1 is an elevational view showing only the parts relevant to the invention of a paper machine of the Fourdrinier type, and incorporating means for carrying the invention into effect,

FIGS. 2 and 3 are views showing on a larger scale some variants in the arrangement of the means required for carrying out the invention; and

FIG. 4 is a perspective view depicting a fragment of one form of a spray tube for use according to the invention and its relationship to a paper web.

FIG. 1 of the drawing shows a portion 2 of the drying section of the machine arranged between the paper pressing section 1 and a further drying section 3 thereof. The continuous paper sheet or web 4 produced in the machine, the direction of progress of which is indicated by a sequence of arrows 5, leaves the last press 6 of the pressing section 1 over a guiding roller 7 and a smoothing press which comprises rollers 8 and 9. In the smoothing press the paper web which comes from the web-forming portion of the machine (not shown) via the pressing section 1, still contains about 65 to 70% by weight of water, but has in this phase sufficient solidity to be self-supporting.

The first drying section 2 comprises a number of spaced, steam-heated drier rollers 10 and 11 arranged at two levels in such a manner that the web passes the rollers in a winding path and thus overlies the drier rollers 10, 11 at the two levels, in alternation. A felt band or blanket 12 guided by a series of driving and supporting rollers 13 in appropriate arrangement guides the web 4 and keeps it in engagement with the temporarily lower surfaces of the drier rollers 11 at the lower level. Similarly, a felt band or blanket 14 guided by a series of driving and supporting rollers 15 in appropriate arrangement guides the web 4 and keeps it in engagement with the temporarily upper surfaces of the drier rollers 10 at the upper level. By the time the web 4 leaves the portion 2 of

the drying section, its water content is reduced to between about 10 to 20% by weight. A drier roller **16** is also provided in the path of the felt band **12** and, similarly, a drier roller **17** in the path of the band **14**, the rollers **16**, **17** serving for drying the felt band portions which have absorbed water in the section **2** before they re-engage the web **4** at the station where it enters the section **2**.

According to the invention sets of tubes **18** and **19** are provided in the portion **2** of the drying section **2** between the two sets of drier rollers adjacent the web **4**, the tubes **18** and **19** being arranged in close vicinity to the web, extending transversely to the direction of travel of the web, and being each provided with a series of spray apertures such as shown in FIG. 4, or with nozzles, directed towards the web surface. The tubes **18** are connected to a supply of a first treating solution for the paper, the nature of which is described hereafter and which for brevity is termed "solution A." This solution is forced through the tubes **18** and aprayed by steam under pressure over the surface of the web **4**. The tubes **19** on the other hand are connected to a supply of another solution, termed "solution B," which is capable of chemically reacting with solution A as described hereafter, solution B being also blown upon the web surface by steam under pressure. In each case the steam pressure is of the order of 20 to 70 lbs. per sq. inch. At the station or stations impinged upon by the two solutions the web still contains between about 60% and about 20% of water, and the ambient temperature within the drying section **2** is between about 80 to 100° C.

As can be seen from FIG. 1, and more clearly from FIG. 2, in one specific arrangement the tubes **18** for supplying solution A are arranged at either side of the path of the web **4** between two drier rollers **11** and **10**, and the tubes **19** for supplying solution B in close relationship to the tubes **18**, likewise at either side of the path of the web but nearer to the drier roller **10**. Thus the two solutions impinge upon both sides of the web, solution B being applied to the web immediately after the application thereto of solution A so that reaction of the two solutions, which results in the formation of a film or layer on the web, is effected practically instantaneously.

FIG. 2 also shows in dotted lines a second set of tubes **18'** and **19'**, respectively, arranged at either side of the web after the latter has passed the drier roller **10** on its way to the next drier roller **11'**, the tubes **19'** being nearer to the latter than the tubes **18'**. Such additional sets may be required if the web passes the section at a comparatively high speed, or if it is desired to obtain a thicker film or layer on the paper web, and it will be understood that still further sets of pipes for spraying solution A and solution B upon the web surface under steam pressure may be provided in the drying section **2**, if this should be required.

FIG. 3 shows a modified arrangement of the spray tubes **18**, **19** and **18'**, **19'** respectively, suitable for use where only one side of the paper web **4** requires the application to its surface of a film or layer for the purposes of this invention.

In each arrangement the spray apertures are of very small diameter, or the nozzles designed as atomizers, in order to ensure a very fine distribution of the solutions in the form of a mist, i.e. in micro-colloidal dispersion, and thus the greatest possible uniformity in the distribution of the solutions over the web surface during the application under steam pressure.

Solution A referred to above is an aqueous solution of a higher fatty acid soap constituted by an alkali metal and/or ammonium salt of a long-chain saturated or unsaturated carboxylic acid. The latter may be a synthetic fatty acid or a mixture of synthetic fatty acids having chain lengths of at least **11** obtained by oxidation of natural or synthetic hydrocarbons or by hydrogenation of carbon monoxide. Preferably however, the carboxylic acid is a natural carboxylic acid having a chainlength of from 12 to 20 carbon atoms, suitable natural fatty acids being, for instance oleic acid, lauric acid, myristic acid, palmitic acid and stearic acid. Suitable alkali salts of these fatty acids are, for instance, sodium oleate, potassium stearate and ammonium stearate, either alone or in mixture, but similar alkali salts of these and other fatty acids in watery solution are also usable in the process.

These alkali salts are dissolved in hot or boiling water before being used in the process according to the invention, or if so desired, the aqueous solution of an alkali salt of a fatty acid may be prepared shortly before use by saponification in heat of one of the aforementioned fatty acids with equimolecular or an excess quantity of an alkali hydrocarbon such as ammonium hydroxide or potassium hydroxide or of an alkali carbonate, such as sodium carbonate. Saponification may also be effected by, or in the presence of, a suitable organic amine such as triethanolamine.

Solution B, to which reference is made above, is a solution in hot water of an inorganic or organic salt or salts of a metal having a valency of at least two.

In order to fix the metallic soap produced in fine distribution on the paper surface by the reaction of the salts contained in solution B with the acid or acids contained in solution A, it is embedded within a thin continuous layer produced, according to the invention, of at least one resinogenous agent with the cellulose, lignin and certain other substances contained in the paper. This layer is applied to the paper surface together with the constituents of the soap by spraying the paper surface with that resinogenous agent which, as pointed out previously, may consist of any one of the group consisting of formaldehyde, urea, phenol and furfural. All these substances are soluble in water and can therefore be applied to the paper surface in aqueous solution together with either solution A or solution B or both.

Formaldehyde, urea and furfural may be applied to the web, optionally, either together with solution A or with solution B or with both said solutions. As phenol is acidic, it can only be applied together with solution B.

The following are examples of solutions A and B such as used in accordance with the present invention.

Example 1

Solution A: 30 gms. of stearic acid, 5 gms. potassium hydroxide, 10 gms. of hexamethylene-tetramine are added to and dissolved in 5 liters of water by heating.

Solution B contains 20 gms. of aluminium sulfate and 11 cc. of a 40% solution of formaldehyde to 5 liters of water.

Example 2

Solution A: 30 gms. oleic acid, 10 gms. sodium carbonate, 10 gms. ammonium hydroxide and 5.5 cc. of a 40% solution of formaldehyde are added to and dissolved in 5 liters of water.

Solution B contains 10 gms. of aluminium potassium sulfate and 5.5 cc. of a 40% solution of formaldehyde to 5 liters of water.

Example 3

Solution A: 22 gms. naphthenic acid, 49 gms. ammonium hydroxide and 11 gms. of urea, with or without an addition of 10 gms. of hexamethylene-tetramine are added to and dissolved in 5 liters of water by heating.

Solution B contains 10 gms. of freshly prepared aluminium acetate to 5 liters of water.

Example 4

Solution A: 27 gms. linoleic acid, 10 gms. ammonium carbonate, 10 gms. hexamethylene-tetramine and 3 cc. of a 40% solution of formaldehyde are added to and dissolved in 5 liters of water by heating.

Solution B contains 10 gms. ferrous sulfate and 3.3 gms. of para-formaldehyde in 5 liters of water.

Example 5

Solution A: 29 gms. stearic acid, 10 gms. triethanolamine, 20 gms. ammonium hydroxide, 10 gms. hexamethylene-tetramine are added to and dissolved in 5 liters of water by heating.

Solution B contains 5 gms. of aluminium sulfate, 5 gms. of aluminium acetate and 11 gms. of phenol to 5 liters of water.

Example 6

Solution A: 30 gms. stearic acid, 20 gms. hexamethylene-tetramine, 10 gms. ammonium hydroxide and 11 gms. of furfural are added to and dissolved in 5 liters of water by heating.

Solution B contains 10 gms. aluminium sulfate and 5.5 cc. of a 40% solution of formaldehyde in 5 liters of water.

Example 7

Solution A: 22 gms. stearic acid, 11 gms. potassium carbonate and 5.5 gms. urea are added to and dissolved in 5 liters of water by heating.

Solution B contains 11 gms. of zinc sulfate and 5 gms. of urea to 5 liters of water.

Example 8

Solution A: 27 gms. stearic acid, 11 gms. potassium carbonate, 11 cc. of a 40% solution of formaldehyde are added to and dissolved in 5 liters of water by heating.

Solution B contains 5.5 gms. of manganese sulfate and 5.5 gms. of furfural in 5 liters of water.

The proportions of active substances in water described in the foregoing examples were found to be of advantage for a speed of paper progress through a papermaking machine of the type described, of between 10 to 15 ft./sec., and for a water content of the paper at the station of application, between 30 and 20% by weight. For higher paper speeds it is possible to arrange two series of spray tubes 18, 19 and 18', 19', in succession, as described for instance with reference to FIGS. 2 and 3, or to arrange even more sets of spray tubes in succession. Alternatively, it is possible to use for higher paper speeds, higher concentrations of active substances in water.

For paper speeds of the order of 30 to 35 ft./sec., for instance, the concentrations of the active substances may be doubled or even trebled. This means to say that for solution A the concentration of alkali metal and/or ammonium salt of a long-chain saturated or unsaturated carboxylic acid may vary between about 20 to 100 gms. to each 5 liters of water, while in solution B the concentration of an inorganic or organic salt or salts of a metal having a valency of at least 2 may vary between about 10 gms. and 35 gms. to each 5 liters of water.

Similarly, the concentration of the resinogenous substance or substances in either solution or in both solutions, as the case may be, may vary between about 5 gms. and 20 gms. to each 10 liters of water used in solution A and solution B conjointly.

I desire it to be understood that I do not wish protection by Letters Patent to be limited to the aforedescribed details, as these are capable of further modification within the scope of the appended claims.

If, for instance, it is desired to obtain or increase the water and grease resistance of the paper produced according to the invention, a protective colloid or colloids may be incorporated in the layer by adding same to the treating solution or solutions. Suitable colloids are gluten and alginic acid.

On the other hand it should be noted that while for carrying out the method according to the invention any water-soluble salt of a metal having a valency of at least two and capable of forming with the long-chain carboxylic acid of an alkali salt a substantially water-insoluble salt, can be used in theory, many such salts will

be excluded in practice, for instance for reasons of economy or because of the toxicity of such salts.

The treatment of paper according to any one of the aforedescribed examples leaves the weight of the paper practically unchanged, the increase of weight being of the order of about 0.01 to 0.1%.

What I claim is:

1. In a method of making paper from paper pulp containing at least cellulose, lignin and water as constituent materials in a continuous process which includes the steps of forming a paper web and drying said web on a paper machine, the steps which comprise applying to the freshly-formed paper web a first aqueous solution comprising a long-chain carboxylic acid alkali salt, and a second aqueous solution comprising a water-soluble salt of a metal having a valency of at least two and capable of forming with the long-chain carboxylic acid of said alkali salt a substantially water-insoluble salt, and a water-soluble resinogenous agent reactive at elevated temperature with the cellulose and lignin to form a resinous layer on the web surface, said second solution being applied to said web after said first solution is applied thereto while said web continues to move through said machine and said solutions being applied to the paper surface under steam pressure in micro-colloidal dispersion during a phase in the drying step on the paper machine in which the paper web contains from 60 to 20% by weight of water and is at a temperature between about 80 to 100° C.

2. A method as defined in claim 1, wherein said solutions of said alkali salt and said water-soluble metal salt are applied to the surface of the paper web in close succession to secure the immediate formation on the web of a water-insoluble salt of a long-chain caboxylic acid.

3. A method as defined in claim 2, wherein said long-chain carboxylic acid is a natural carboxylic acid having a chain-length of from 12 to 20 carbon atoms, and said salt is a member of the group consisting of sodium, potassium and ammonium salts.

4. A method as defined in claim 2, wherein the long-chain carboxylic acid of said salt is a synthetic fatty acid having a chain-length of at least 11 carbon atoms.

5. A method of making paper from paper pulp containing at least cellulose, lignin and water as constituent materials in a continuous process which includes the steps of forming a paper web and drying said web, the steps which comprise applying to the freshly-formed paper web a first solution comprising a long-chain carboxylic acid alkali salt, and a second solution comprising a water-soluble salt of a metal having a valency of at least two and capable of forming with the long-chain carboxylic acid of said alkali salt a substantially water-insoluble salt, and a water-soluble resinogenous agent consisting of at least one member of the group consisting of formaldehyde, urea, phenol and furfural, said second solution being applied to said web after said first solution is applied thereto while said web continues to move through said machine and said solutions being applied to the web surface under steam pressure in microcolloidal dispersion during a phase in the drying step in which the paper web contains from 60 to 20% by weight of water and is at a temperature between about 80 to 100° C., said agent being contained in at least one of said solutions.

6. The method defined in claim 5, wherein said long-chain carboxylic acid is a natural carboxylic acid having a chain-length of from 12 to 20 carbon atoms and said salt is a member of the group consisting of sodium, potassium and ammonium salts, said solutions of the water-soluble alkali salt and the water-soluble salt of a metal having a valency of at least two being applied to the surface of the paper web in close succession of time each in the form of a mist.

7. The method as claimed in claim 6, wherein said water-soluble alkali salt, said water-soluble salt of a metal having a valency of at least two and said water-soluble resinogenous agent are applied to the web surface in the

form of two solutions in hot water made to impinge upon the web in close time succession, said first solution containing for each 5 liters of water between 5 and 100 gms. of a long-chain carboxylic acid of from 12 to 20 carbon atoms and a quantity of alkali sufficient to at least neutralize the acid whereas said second solution contains for each 5 liters of water between 5 and 50 gms. of a water-soluble salt of a metal having a valency of at least two, and the concentration of the said resinogenous agent is between 5 gms. and 20 gms. to each 10 liters of water used in the first solution and in the second solution conjointly.

8. The method as claimed in claim 7, wherein said first solution contains to 5 liters of water about 30 gms. of stearic acid, about 5 gms. potassium hydroxide and about 10 gms. of hexamethylene-tetramine, and wherein said second solution contains to 5 liters of water about 20 gms. of aluminium sulfate and about 11 cc. of a 40% solution of formaldehyde.

9. The method as claimed in claim 7, wherein said first solution contains for each 5 liters of water about 30 gms. oleic acid, about 10 gms. sodium carbonate, about 10 gms. ammonium hydroxide and about 5.5 cc. of a 40% solution of formaldehyde, and wherein said second solution contains for each 5 liters of water about 10 gms. of aluminium potassium sulfate and about 5.5 cc. of a 40% solution of formaldehyde.

10. The method as claimed in claim 7, wherein said first solution contains for each 5 liters of water about 22 gms. naphthenic acid, about 49 gms. ammonium hydroxide and about 11 gms. of urea, and wherein said second solution contains to 5 liters of water about 10 gms. of freshly prepared aluminium acetate.

11. The method as claimed in claim 7, wherein said first solution contains for each 5 liters of water about 27 gms. linoleic acid, about 10 gms. ammonium carbonate, about 10 gms. hexamethylene-tetramine and about 3 cc. of a 40% solution of formaldehyde, and wherein said second solution contains for each 5 liters of water about 10 gms. ferrous sulfate and about 3.3 gms. of paraformaldehyde.

12. The method as claimed in claim 7, wherein said first solution contains for each 5 liters of water about 29 gms. stearic acid, about 10 gms. triethanolamine, about 20 gms. ammonium hydroxide and about 10 gms. hexamethylene-tetramine, and wherein said second solution contains for each 5 liters of water about 5 gms. of aluminium sulfate, about 5 gms. of aluminium acetate and about 11 gms. of phenol.

13. The method as claimed in claim 7, wherein said first solution contains for each 5 liters of water about 30 gms. stearic acid, about 20 gms. hexamethylene-tetramine, about 10 gms. ammonium hydroxide and about 11 gms. of furfural, and wherein said second solution contains for each 5 liters of water about 10 gms. aluminium sulfate and about 5.5 cc. of a 40% solution of formaldehyde.

14. The method as claimed in claim 7, wherein said first solution contains for each 5 liters of water about 22 gms. stearic acid, about 11 gms. potassium carbonate and about 5.5 gms. urea, and wherein said second solution contains to 5 liters of water about 11 gms. of zinc sulfate and about 5 gms. of urea.

15. The method as claimed in claim 7, wherein said first solution contains for each 5 liters of water about 27 gms. stearic acid, about 11 gms. potassium carbonate and about 11 cc. of a 40% solution of formaldehyde, and wherein said second solution contains for each 5 liters of water about 5.5 gms. of manganese sulfate and about 5.5 gms. of furfural.

16. A paper formed from paper pulp containing at least cellulose, lignin and water as constituent materials by the steps which comprise forming a paper web, partially drying said web on a paper machine to a water content of 20 to 60% and a temperature of 80 to 100° C., applying to said web at said temperature and with said water content a first aqueous solution comprising a long-chain carboxylic acid alkali salt, and a second aqueous solution comprising a water-soluble salt of a metal having a valency of at least two and capable of forming with the long-chain carboxylic acid of said alkali salt a substantially water-insoluble salt, and a water-soluble resinogenous agent reactive at elevated temperature with the cellulose and lignin to form a resinous layer on the web surface, said second solution being applied to said web after said first solution is applied thereto and said solutions being applied to the paper surface while said web continues to move through said machine under steam pressure in micro-colloidal dispersion, and completing the drying of said web.

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