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LIQUID PRINTING INK CONTAINING A LIGNIN COMPOUND

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1

This invention relates to printing inks.

The printing of magazines, newspapers, containers, fabrics and similar sheet material with known printing inks presents important practical problems in respect to the manner and speed of drying the printed ink films and the quality of the resulting prints.

The principal object of this invention is to provide new and improved printing inks which obviate important limitations or shortcomings of known printing inks. More particularly, this invention is to provide printing inks which are useful for high speed printing of good quality at much less expense than the known inks used for such work. Another object is to improve high speed printing operations by the provision of printing inks which give the effect of quick drying and form prints of high quality without requiring the forced volatilization of a solvent, or the oxidation or polymerization of a drying oil varnish, or the use of a metallic drier, or the application of a precipitating medium, or the use of heating or other complex or expensive equipment with the printing press.

Another object of my invention is to provide improved printing inks which will produce printed matter of high quality at either high or low printing speeds, and by which prints may be formed having distinct printed characters of desired color or gloss and free not only from smudging and offsetting but also from the formation of craters or ridges as often encountered in the use of known inks for high speed printing.

A further object of my invention is to provide valuable fast drying inks which contain water as a large part of their composition.

Still another object is to provide such water-containing inks which are waterproof when printed.

Other objects, features and advantages of this invention will appear from the following illustrative description of its principles and of preferred embodiments thereof, while the improvements and combinations claimed as my invention will be set forth particularly in the appended claims.

My invention involves a recognition and utilization of the principle that if printing inks are made with a liquid carrier and a resinous binder for coloring matter in such relation to each other

2

and to the sheet material to be printed that the binder ordinarily will be held dispersed in the carrier, and that the binder has a strong affinity for said material and is not "skin-forming" in nature but freely releases the liquefying component of the carrier to said material upon contact therewith, and that the liquid thus released is readily absorbed or spread out and disseminated by said material, the inks so obtained will form prints of good quality by setting immediately to a smudge- and rub-resistant state equivalent to dryness, without requiring any further operation.

The inks so made in effect "break" upon contact with the sheet material, such that the binder and the pigment adhere to the material, without bleeding, as rub-resistant films in the forms of the printing elements from which they were impressed, while the liquefying component is released and quickly disseminated or absorbed away to a harmless state beneath or around these films. The bulk of the liquid thus disseminated from the printed ink bears such a minute relation to the bulk of the sheet material printed that it does not materially affect the quality of the printed matter, and since the printed films immediately attain the quality of dryness the printed matter can be immediately backed up, folded, stacked, bound or otherwise handled without damage. If it is desired in any particular case, of course, the disseminated liquid or moisture can be largely removed after the printing by allowing it to become volatilized or dissipated by natural processes, or by artificial heating or other treatment.

According to this invention, therefore, printing inks are provided which set quickly by contact with the paper or other fabric being printed. Their liquefying component is released to the paper or fabric, which absorbs or disseminates it from the printed films so as to leave imprints of coloring matter bound to the surface of the paper by a suitably hard, adherent resinous substance. Since this drying action is not dependent upon other treatment, the printing and immediate handling of the printed matter can be carried out with facility at high printing press speeds. The inks embodying my invention set more rapidly even than conventional newspaper inks, but, in contrast to the poor quality of prints made from

the latter, they form rub-resistant films when printed which have their pigment held firmly to the paper in resinous matter as prints of high quality.

I have discovered that printing inks embodying these principles and advantages can be obtained by employing lignin or a derivative or equivalent of lignin having its characteristic molecular structure as an essential resinous substance of the binder for the coloring matter, and dispersing the binder and the coloring matter in a liquid carrier having a solvating or solubilizing action upon lignin so as to form an ink of the desired body and printing quality.

I have also found that the liquid carrier to be employed can be composed advantageously of a thin liquid or diluent, such as water, which has a distinct affinity for cellulosic material or the like and which alone will not dissolve or disperse enough of the resinous binder to make a printing ink, together with an organic substance, a solubilizer for lignin, which is soluble in or miscible with the diluent and which renders the whole carrier capable of taking up and dispersing the binder.

Lignin is a resinous substance existing abundantly in the plant world. Large amounts of it produced in wood pulping or paper making are discarded as a waste material. Lignin serves in nature as a binder or lining for the woody cells or fibers of plants, constituting about one-fourth of the weight of wood. Thus it has a natural affinity for cellulose, and this same affinity is exhibited, if to a lesser degree, between lignin from fiber liberation on the one hand and the paper and other sheet materials ordinarily used for printing, on the other. Paper, paperboard and cotton textiles are all cellulosic materials, and so are regenerated cellulose, cellulose acetate, cellulose nitrate and various other substances used for making sheet materials or fabrics. Printing inks employing a lignin from fiber liberation as a binder according to my invention exhibit the properties required to print well on these materials and also on sheet materials coated with substances which are cellulosic in character or with substances which have a pronounced affinity for paper or like cellulosic material, such as coatings containing clay or other fillers in starch or other base material that adheres to paper.

In addition to its distinct affinity for or adhesiveness to such sheet materials, a lignin from fiber liberation as used in inks according to my invention exhibits the further desired properties of permitting free release or migration of liquefying components across the boundaries of the printed ink films to the paper or other sheet material when the ink is printed, of being sufficiently open or non-sealing in nature to permit this dissemination of liquid and avoid skin formation that would entrap the liquid, and yet when printed of forming films which are dense, hard and strong enough for high quality printing. Further, the lignin from fiber liberation permits the body or printing consistency of the ink and the gloss or color of the print to be controlled as desired by methods of formulation such as disclosed hereinafter, or by others known to the printing ink art.

The usefulness of lignin for the present purpose is attributable to its characteristic molecular structure, namely, it is an organic polymer containing a multiplicity of hydroxy and methoxy radicals in the macromolecule. Other resinous substances of the same nature, i. e. natural or synthetic organic polymers possessing the characteristic molecular structure or nucleus of lignin, may be used for the same purpose. The term "a lignin from fiber liberation" is used herein to mean lignin or any of these equivalent substances. The printing and drying qualities of inks using a lignin from fiber liberation according to my invention are believed to result basically from electrostatic relationships between the lignin from fiber liberation and components of the liquid carrier, on the one hand, and between them and the sheet material upon which the inks are printed, on the other.

Among the known lignins from fiber liberation which have been found satisfactory are lignin in its various forms, such as soda, sulphate or other lignins derived from hardwood, softwood, straw, corncobs or the like and precipitated lignin from waste sulphite liquor such as lignosulfonates. Others which may be used include lignin complexes, such as methanol lignin, butanol lignin, ethanol lignin, phenol lignin, glycol lignin, acid lignin, reduced lignin, extracted lignin and soda or sulphate lignin products; products derived from wood which consist principally of pyro-lignin or its derivatives; and resinous materials containing lignin, such as certain precipitated wood extracts, enriched wood pulps and other like substances containing lignin structures either naturally or as an addition to other matter. Soda and sulphate lignins are each obtainable in two forms, of which one is a precipitated or water-insoluble lignin and the other is a water-soluble lignin.

To obtain the basic characteristics of the new inks and yet modify their minor qualities to advantage for certain printing uses, a lignin from fiber liberation may be blended or reacted with other compatible organic plastics or resins, either natural or synthetic. The binder of the ink in such embodiments is a composite resinous substance containing a lignin from fiber liberation. For example, I have found composite substances useful which are made by cooking or fusing a lignin from fiber limitation with a thermoplastic resin such as gum, wood rosin, ester gum, Batu gum, damar gum, alkyd-type resins modified by chemical combination with natural resin acids, or the like. In this way the qualities of the films produced by printing the inks may be regulated as to gloss, adhesion to coated papers, water resistance or the like, or blending may be utilized to regulate the consistency of the ink for different methods of printing or different printing press speeds.

The liquid carrier of the new inks may be composed of substances selected from a wide variety, although the range of selection for particular formulations may vary with the particular lignin from fiber liberation employed or with particular qualities that may be desired to be emphasized especially in certain inks. In general, the substances useful as solubilizers for dispersing lignins from fiber liberation are organic compounds which exert solvating action upon macromolecular structures such as lignin, breaking them up or dispersing them to a state of solvation by the action of polar groups in molecules of relatively small size as compared with the lignin macromolecules. Of this nature are compounds among the following: amino compounds, including cyclic and alkyl-hydroxy amino compounds and their esters; keto compounds including amides, lactones, ketones, lactams and aldehydes, including hydroxy and methoxy aldehydes; and hydroxy compounds including alkyl nitro-hydroxy com-

pounds and poly-hydroxy compounds and their ethers and esters.

The diluent used in the carrier should be a thin liquid having polar characteristics, a low molecular weight and a strong affinity for the sheet material to be printed, which liquid in the presence of the solubilizer will carry enough dispersed resinous binder and coloring matter to give a body or consistency suitable for printing and to produce printed films satisfactorily binding the pigment or other coloring matter to the paper. I have found that water peculiarly meets the requirements. It not only possesses the requisite thinness or fluidity and affinity for paper or the like but also has the important advantages of extreme cheapness, non-inflammability and relative stability against chemical action or evaporation on the printing press.

In embodiments using water as the diluent, the solubilizer employed may be a water-miscible organic substance which in water acts as a solvating agent for lignin. In general its structure contains or has the basic character of a substance containing one or more polar groups corresponding to some polar groups contained in lignin. Thus it may be a keto compound, a polyhydroxy compound or a cyclic or alkyl amino compound of the nature stated.

I have further discovered that particularly desirable inks containing a lignin from fiber liberation as a binder or bodying substance and water as a carrier component can be produced by the use of alkyl aminohydroxy compounds and esters thereof as solubilizers, such as 2-amino-2-methyl-1, 3-propanediol, 2-amino-2-ethyl-1, 3-propanediol, 2-amino-2-methyl - 1 - propanol, 2-amino-2, 4-pentanediol, tris (hydroxymethyl) amino methane, and the like. The first and last mentioned of these are normally solids, while the others normally are liquids.

These particular solubilizers facilitate the production of smooth, clear dispersions of enough lignin from fiber liberation in water to secure inks having almost any desired printing qualities when colors have been incorporated. They are so effective that the desired content of resinous binder can be dispersed in water, to obtain a dispersion of thin body, by using between about 5 and 20% of the solubilizer. This avoids having the quality of the ink restricted too much by the necessity of using a large proportion of solubilizer, which would enhance costs and in some cases entail a sacrifice of non-inflammability, gloss, or printing quality. The body or printing consistency of inks using these solubilizers generally can be adjusted to suit the requirements of any particular printing press or type of printing work by regulating the ratio of the solubilizer content to the content of lignin from fiber liberation in the ink. To increase the solubilizer content gives a thinner body with the same content of lignin from fiber liberation.

The following further exemplify solubilizers which are useful pursuant hereto in various formulations of inks containing a lignin from fiber liberation: Lactones, such as 4-hydroxy pentanoic acid lactone; aliphatic ketones, such as acetone and methylethyl ketone; aliphatic alcohols, such as ethyl alcohol and higher aliphatic alcohols; 1,3-ketols or beta-hydroxy ketones, such as 4 - hydroxy-4-methyl pentanone; nitro-aliphatic alcohols, such as 2-nitro - 2 - methyl-1-propanol, 2-nitro-1-butanol, 1-nitro-2-butanol, 2-nitro-1-pentanol, 3-nitro-3-methyl-2-pentanol, 2-nitro-3-hexanol, 3-nitro-4-heptanol and 5-nitro-4-octanol; aliphatic hydroxy and amino aldehydes containing 6 or less carbon atoms; aldehyde- and amino-alcohols; amino-glycols; hexamethylenetetramine; amino-ketones, such as 4-amino-4-methyl pentanone; glycols and polyglycols, such as ethylene glycol, dipropylene glycol, etc., ethers thereof such as the mono ethyl, mono methyl and mono butyl ethers of diethylene glycol (carbitols) and the corresponding ethers of ethylene glycol (cellosolves), and esters thereof, such as their acetates, propionates, etc.; and alkyl aromatic dicarboxylic acid esters, such as dimethyl phthalate.

A preferred procedure for making the new inks is to mix or dissolve the solubilizer in the diluent to obtain a carrier or solvating liquid, then add the resinous binder and disperse it thoroughly, with the aid of agitation or heat or of both if desired, and thereafter mill in or otherwise incorporate the coloring matter.

When a strong solubilizer is employed in the new inks it tends to render the printed ink films insufficiently water resistant for many uses. The lignin from fiber limitation may be washed off the paper with water, even though not soluble in water. I have discovered, however, that water resistance can be imparted to the inks when desired by the addition of a waterproofing agent. I have found further that organic compounds may be used as waterproofing agents which fall into several classes, including: First, those having little or no solvating power for lignin which are insoluble in water and yet stay dispersed in an aqueous dispersion of lignin with the aid of a third substance, such as the solubilizer used to effect dispersion of the lignin; second, those which are soluble in water and have little or no solvating power for lignin; and third, those which normally are liquid and have sufficient solvating power for lignin to serve as a dispersing liquid or solubilizer in the carrier of the ink. The useful waterproofing agents are all organic compounds possessing such affinity for the macromolecules of lignin that they adhere to them as part of the printed ink films and render those films water resistant. They would precipitate lignin from an aqueous dispersion thereof if added to such dispersion in unlimited amount.

In the use of such non-solvating compounds as components of water-containing lignin inks, a limited amount of the water proofing agent between 1 and 20% of the weight of the ink generally is employed. This preferably is added after the lignin from fiber liberation has been dispersed in the aqueous liquid carrier, or during its dispersion, so as to be incorporated with the aid of the solubilizer present.

Where water-containing inks are made to contain waterproofing compounds of the second and third types above-mentioned, the remarkable situation may obtain of having all liquid ingredients of the ink water-like or water soluble to some degree, and yet of achieving water resistance or water-proofness in the printed ink films as their liquefying component or carrier is disseminated away by the sheet material printed.

Waterproofing compounds of the third type may constitute substantially the entire liquid carrier of an ink in cases where water is not used; but lignin-containing inks of this type are less useful than the others because they are more expensive and they exhibit slow drying qualities.

Among the organic compounds which I have

found useful as waterproofing agents are hydroxy aromatic, hydroxy fatty acid, keto and oxime compounds that lack solvent power for lignin.

The compounds useful as waterproofers include, more particularly, beta-hydroxy aldehydes or aldols, glycerol aldehydes, dihydroxy aldehydes, dihydroxy ketones, amino-keto compounds, methoxy-keto compounds, hydroxy dialdehydes, dihydroxy aldehyde ketones, hydroxy diketones, dialdehyde ketones and aldehyde diketones; for example, beta-hydroxy ethanal, beta-hydroxy propionaldehyde, aldol, glycol acetol, hydroxy lactones, urea, paraformaldehyde, gammavalerolactone, glyoxal, and methylene disalicylic acid. Such compounds may be mono- or poly-hydroxylated, and they may be aliphatic or aromatic, depending upon the particular composition desired. Useful aromatic hydroxy compounds are the benzene diols, such as 1,3-benzenediol (resorcinol) and 1,4-benzenediol (hydroquinol); also the benzenetriols, such as 1,2,4-benzene triol, pyrogallol and phloroglucinol; also higher homologous benzene derivatives of corresponding structure, such as 1,5-dihydroxynaphthalene, alizarin, anthragallol, rufigallol, vanillin (4-hydroxy-3-methoxy benzaldehyde) and para-hydroxyacetophenone; and also methoxy phenols, such as hydroquinone monomethyl ether.

According to some embodiments hereof, fast drying inks which form waterproof prints are made by first dispersing water-insoluble lignin in a carrier composed of water and a solubilizer as above mentioned, e. g. an amino-hydroxy compound or a polyhydroxy compound such as ethylene glycol. Then a waterproofer having little or no solvating power for lignin, for example, paraformaldehyde, hydroquinone monomethyl ether, 1,5-dihydroxynaphthalene, p-hydroxyacetophenone, resorcinol, pyrogallol, rufigallol, anthragallol, methylene disalicylic acid, or another such waterproofer as above mentioned, is incorporated in the dispersion to obtain a vehicle into which the desired pigments are milled or ground.

According to other embodiments, fast drying inks are made with a dispersion of water-soluble lignin in an amino ketone, such as formamide, or a like compound which both disperses the lignin and renders the printed ink waterproof. Water is added to this dispersion to produce a homogenous vehicle for the ink pigments which has the consistency and the fast drying quality desired in the finished inks.

According to still other embodiments of my invention, an amino ketone such as formamide, to serve in a dual capacity as liquid carrier and waterproofer, is used to make a dispersion of water-insoluble lignin, and water which otherwise would precipitate this lignin is added in conjunction with an organic solubilizer or "coupling" agent. The latter preferably is an amine such as the cyclohexylamines, alkylaminoethanols (ethyl diethanolamine, etc.) and the like. Then the pigment and any other desired coloring matter is milled or ground in to finish the ink.

I have found, further, that the new inks may be given increased stability against setting or hardening on a printing press by incorporating therein a water-retaining carbohydrate, such as starch or glucose, or a carbohydrate derivative effective as a humectant, such as 1,2,3,4,5,6-hexanehexol.

I have also found that wetting agents may be incorporated in the new inks to advantage in some cases, to reduce the surface tension of the carrier and cause its liquefying component to penetrate or disseminate faster in the paper or other sheet material when released from the binder as the ink is printed. Higher molecular polar-nonpolar compounds, such as sulfonated fatty alcohols, long-chain amines, hydrogenated fatty acids or chlorinated alcohols may be used for this purpose; for example, polyoxyalkylene hexanepentol laurate.

The new inks may contain various other components or substituents, as may be desired, such as aqueous substances or oils, organic solvents or diluents and various types of coloring matter. According to some embodiments water soluble lignin is used to take advantage of its limited solubility in water. In other embodiments water insoluble lignin, such as precipitated lignin obtained from hardwood soda black liquor or hardwood sulphate liquor, is employed with a larger proportion of organic solubilizer, to take advantage of its particular qualities.

The following examples illustrate formulations of inks embodying my invention. Precipitated soda lignin and precipitated sulphate lignin can be used interchangeably with little or no change of these formulations.

Example I

	Parts by weight
Water	47
2-amino-2-methyl-1,3-propanediol	16
Precipitated soda lignin	23
Diethylene glycol monobutyl ether	2
Carbon black	12
	100

This makes an ink of medium body which is noninflammable and does not bleed in oil or paraffin. It is not waterproof. The 2-amino-2-methyl-1,3-propanediol is dissolved in the water to produce a carrier or composite liquid used for dispersing the lignin to produce a varnish. Then the diethylene glycol monobutyl ether is added and the pigment is incorporated by grinding.

Example II

	Parts by weight
2-amino-2-methyl-1,3-propanediol	10.00
Water	51.00
Paraformaldehyde	4.50
Precipitated soda lignin	20.00
Diethylene glycol monobutyl ether	1.80
Hansa yellow	12.70
	100.00

This is a fast drying yellow ink. It has greater water resistance than Example I.

Example III

	Parts by weight
Water soluble soda lignin	25
Formamide	36
Water	18
Urea	5
Waxy starch—"Amioca"	2
Carbon black	14
	100

Here the ink has a binder of water soluble lignin, and yet it forms water-repellant prints. This composition is good for printing on coated or magazine paper stock.

Example IV

	Parts by weight
Water soluble soda lignin	25
Formamide	27
Water	27
Urea	5
Waxy starch	2
Carbon black	14
	100

This is similar to Example III.

Example V

	Parts by weight
Precipitated soda lignin	17.3
2-amino-2-methyl-1,3-propanediol	12
Water	35.2
Diethylene glycol monobutyl ether	1.5
Gamma-valerolactone	25
Carbon black	9
	100

This example contains pigment and a binder of precipitated lignin dispersed in a carrier containing water, an amino-hydroxy compound solubilizing the lignin in the water, and a lactone as a waterproofing agent.

The four examples next following (VI to IX) respectively illustrate the employment of an aliphatic polyaldehyde, an aromatic polyhydroxy compound, an aromatic aldehyde, and a hydroxyketone as waterproofing agents.

Example VI

	Parts by weight
2-amino-2-methyl-1,3-propanediol	10.00
Water	51.00
Paraformaldehyde	4.50
Precipitated soda lignin	20.00
Diethylene glycol monobutyl ether	1.80
Peacock blue	12.70
	100.00

This is a blue ink formulated for high speed newspaper printing. It is fast drying and has fair water resistance. A similar ink of red color is obtained by substituting para red for the peacock blue.

Example VII

	Parts by weight
Precipitated soda lignin	22.75
Diethylene glycol monoethyl ether	34.50
Water	25.00
Dihydroxynaphthalene-1,5	7.25
Carbon black	10.50
	100.00

This makes a good printing ink of heavy body useful for printing on coarse absorbent materials such as cotton textiles.

Example VIII

	Parts by weight
Precipitated soda lignin	21
Diethylene glycol monoethyl ether	32.2
Water	30
4-hydroxy-3-methoxy-benzaldehyde	7
Carbon black	9.8
	100

Example IX

	Parts by weight
Precipitated soda lignin	22.75
Diethylene glycol monoethyl ether	34.5
Water	25.00
p-Hydroxyacetophenone	7.25
Carbon black	10.5
	100

Example X

	Parts by weight
Precipitated soda lignin	15.00
2-amino-2-methyl-1,3-propanediol	11
Water	54
Hydroquinone monomethyl ether	5
Carbon black	14
Toner	1
	100

This makes an ink of thin body adapted for rotogravure printing.

Example XI

	Parts by weight
Precipitated soda lignin	15
2-amino-2-methyl-1,3-propanediol	10
Water	35
Ethylene glycol	19
Paraformaldehyde	5
Carbon black	14
Toner	1
Tetradecylamine	1
	100

This composition is adapted for printing on newsprint or similar absorbent material. When the lignin content is increased to 23% and the water content is reduced to 27% a heavier bodied ink is obtained which is suitable for printing on ordinary calendered paper (uncoated).

Example XII

	Parts by weight
Blended lignin-resin (precipitated soda lignin, 34%; W. W. gum rosin, 66%)	20
2-amino-2-methyl-1,3-propanediol	12
Water	54
Carbon black	14
	98

This composition makes a very fast drying ink of good gloss and medium body, not waterproof.

Example XIII

	Parts by weight
Blended lignin-resin (precipitated soda lignin, 30%; Batu gum (natural resin), 70%	20
2-amino-2-methyl-1,3-propanediol	12
Water	54
Carbon black	14
	100

This composition makes a very fast drying ink of thin body which forms water-resistant prints.

Example XIV

	Parts by weight
Precipitated soda lignin	26
Formamide	34
Water	16
2-methyl-2,4-pentanediol	4
Hexamethylene tetramine	5
Carbon black	14
Triethanolamine	1
	100

This ink has excellent water resistance.

Example XV

	Parts by weight
Precipitated soda lignin	24
Formamide	33
Water	15
2-methyl-2,4-pentanediol	4
Triethanolamine	1
Cornstarch	4
Carbon black	14
Hexamethylene	5
	100

This ink has good water resistance and is especially formulated for low shrinkage on hard papers.

Example XVI

	Parts by weight
2-amino-2-methyl-1,3-propanediol	10
Water	37
1,2,3,4,5,6-hexanehexol	10
Paraformaldehyde	5
Precipitated soda lignin	23
Carbon black	14
Toner	1
	100

The amount of lignin from fiber liberation utilized in the inks of the present invention is ordinarily between 12 and 30% of the total ink composition. The water content of the inks generally is in the range of 20 to 55% of the total ink composition.

It will be understood that the foregoing details and examples are presented to illustrate the invention and are not to be regarded as restrictive except as may be required by a fair construction of the appended claims. A wide variety of compositions or formulations may be prepared by those skilled in the art to embody features and principles disclosed above and claimed hereinafter as my invention.

I claim:

1. A liquid printing ink consisting essentially of coloring matter and a binder dispersed in a hydrophilic liquid carrier containing water, the predominant constituent of said binder being a lignin from fiber liberation.

2. A liquid printing ink consisting essentially of coloring matter and a binder dispersed in a hydrophilic liquid carrier containing water, the predominant constituent of said binder being a soda lignin.

3. A liquid printing ink consisting essentially of coloring matter and a binder dispersed in a hydrophilic liquid carrier containing water, the predominant constituent of said binder being a sulfate lignin.

4. A liquid printing ink consisting essentially of coloring matter and a binder dispersed in a hydrophilic liquid carrier containing water, the predominant constituent of said binder being a lignosulfonate precipitate from waste sulfite liquor.

5. A liquid printing ink consisting essentially of coloring matter and a binder dispersed in a composite liquid carrier containing water and a lower hydroxyalkane containing a —NH_2 group dispersing said binder in said carrier, the predominant constituent of said binder being a lignin from fiber liberation.

6. A liquid printing ink consisting essentially of coloring matter and a binder dispersed in a composite liquid carrier containing water and 2-amino-2-methyl-1,3-propanediol dispersing said binder in said carrier, the predominant constituent of said binder being a lignin from fiber liberation.

7. A liquid printing ink consisting essentially of coloring matter and a binder dispersed in a composite liquid carrier containing water, and 2-amino-2-methyl-1-propanol dispersing said binder in said carrier, the predominant constituent of said binder being a lignin from fiber liberation.

8. A liquid printing ink consisting essentially of coloring matter and a binder dispersed in a composite liquid carrier containing water, and tris (hydroxymethyl) aminomethane dispersing said binder in said carrier, the predominant constituent of said binder being a lignin from fiber liberation.

9. A liquid printing ink consisting essentially of coloring matter, a binder and a hydrophilic liquid carrier containing water, a lower hydroxyalkane containing a —NH_2 group dispersing said binder in said carrier, and a lower aliphatic aldehyde that enhances the water resistance of the printed ink, the predominant constituent of said binder being a lignin from fiber liberation.

10. A liquid printing ink consisting essentially of coloring matter, a binder and a hydrophilic liquid carrier containing water, a lower hydroxyalkane containing a —NH_2 group dispersing said binder in said carrier, and paraformaldehyde that enhances the water resistance of the printed ink, the predominant constituent of said binder being a lignin from fiber liberation.

11. A liquid printing ink consisting essentially of coloring matter, a binder and a hydrophilic liquid carrier containing water, a lower hydroxyalkane containing a —NH_2 group dispersing said binder in said carrier, and glyoxal that enhances the water resistance of the printed ink, the predominant constituent of said binder being a lignin from fiber liberation.

12. A printing ink comprising coloring matter, approximately 12–30 percent of a lignin from fiber liberation, water, and approximately 5–20% of a lower hydroxyalkane containing a —NH_2 group, all percentages by weight of the ink.

13. A printing ink comprising coloring matter, a binder, the predominant constituent of said binder being a lignin from fiber liberation, approximately 20–55 percent of water, approximately 5–20 percent of a lower hydroxyalkane containing a —NH_2 group, and approximately 1–20 percent of a lower aliphatic aldehyde, all percentages by weight of the ink.

14. A liquid printing ink consisting essentially of coloring matter and a binder dispersed in a composite liquid carrier containing water and a lower hydroxyalkane containing a —NH_2 group dispersing said binder in said carrier, the predominant constituent of said binder being precipitated soda lignin.

15. A liquid printing ink consisting essentially of coloring matter and a binder dispersed in a composite liquid carrier containing water and a lower hydroxyalkane containing a —NH_2 group dispersing said binder in said carrier, the predominant constituent of said binder being sulfate lignin.

16. A liquid printing ink consisting essentially of coloring matter and a binder dispersed in a composite liquid carrier containing water and a lower hydroxyalkane containing a —NH_2 group dispersing said binder in said carrier, the predominant constituent of said binder being a lignosulfonate precipitate from waste sulfite liquor.

17. A printing ink consisting essentially of coloring matter and a binder dispersed in an aqueous liquid carrier containing formamide, the predominant constituent of said binder being a lignin from fiber liberation.

18. A printing ink consisting essentially of coloring matter and a binder dispersed in an aqueous liquid carrier containing formamide as its predominant constituent, the predominant constituent of said binder being a lignin from fiber liberation.

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