US 20100189969A1

(19) **United States**

(12) **Patent Application Publication**

Oksanen et al.

(10) **Pub. No.: US 2010/0189969 A1**

(43) **Pub. Date: Jul. 29, 2010**

(54) **NON-FLUTING PRINTING SUBSTRATE AND METHOD FOR PRODUCING THE SAME**

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(21) Appl. No.: **12/597,233**

(22) PCT Filed: **Apr. 25, 2008**

(86) PCT No.: **PCT/EP08/55111**

§ 371 (c)(1),
(2), (4) Date: **Mar. 18, 2010**

Related U.S. Application Data

(60) Provisional application No. 61/022,410, filed on Jan. 21, 2008.

(30) **Foreign Application Priority Data**

Apr. 25, 2007 (FI) 20075286

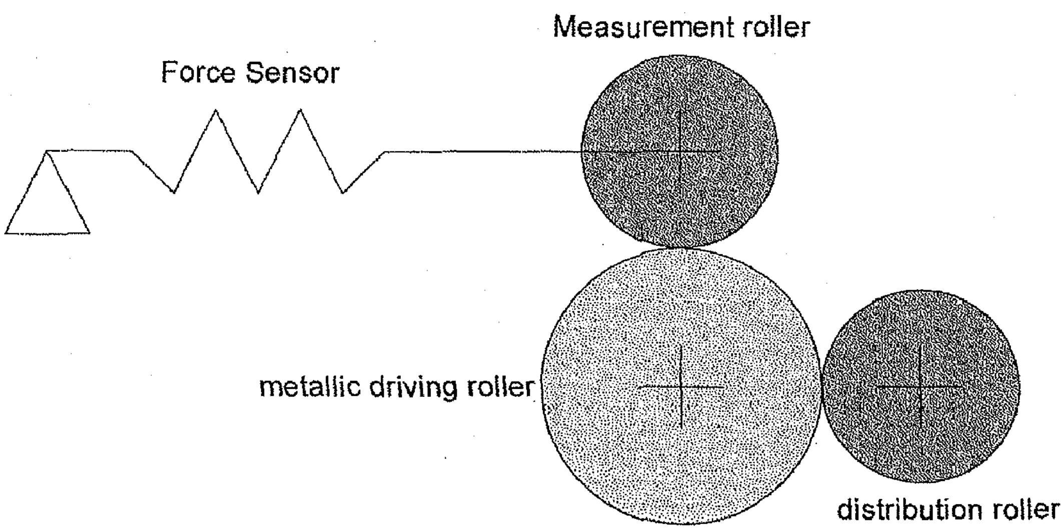
Publication Classification

(51) **Int. Cl.**
B41F 3/34 (2006.01)
B32B 3/10 (2006.01)

(52) **U.S. Cl.** **428/207**; 101/492; 428/195.1

(57) **ABSTRACT**

The present invention relates to a printed substrate comprising a substrate and a printing ink and is characterized in that at least one side of the substrate has a surface with such porosity that the Gurley-Hill air permeability value of the substrate is above 7000 s/100 ml, and it comprises an printing ink formulated as heat-set offset printing ink with reduced tack comprising at least one pigment and a mixture of at least two solvents boiling in the range of from 200° C. to 270° C.



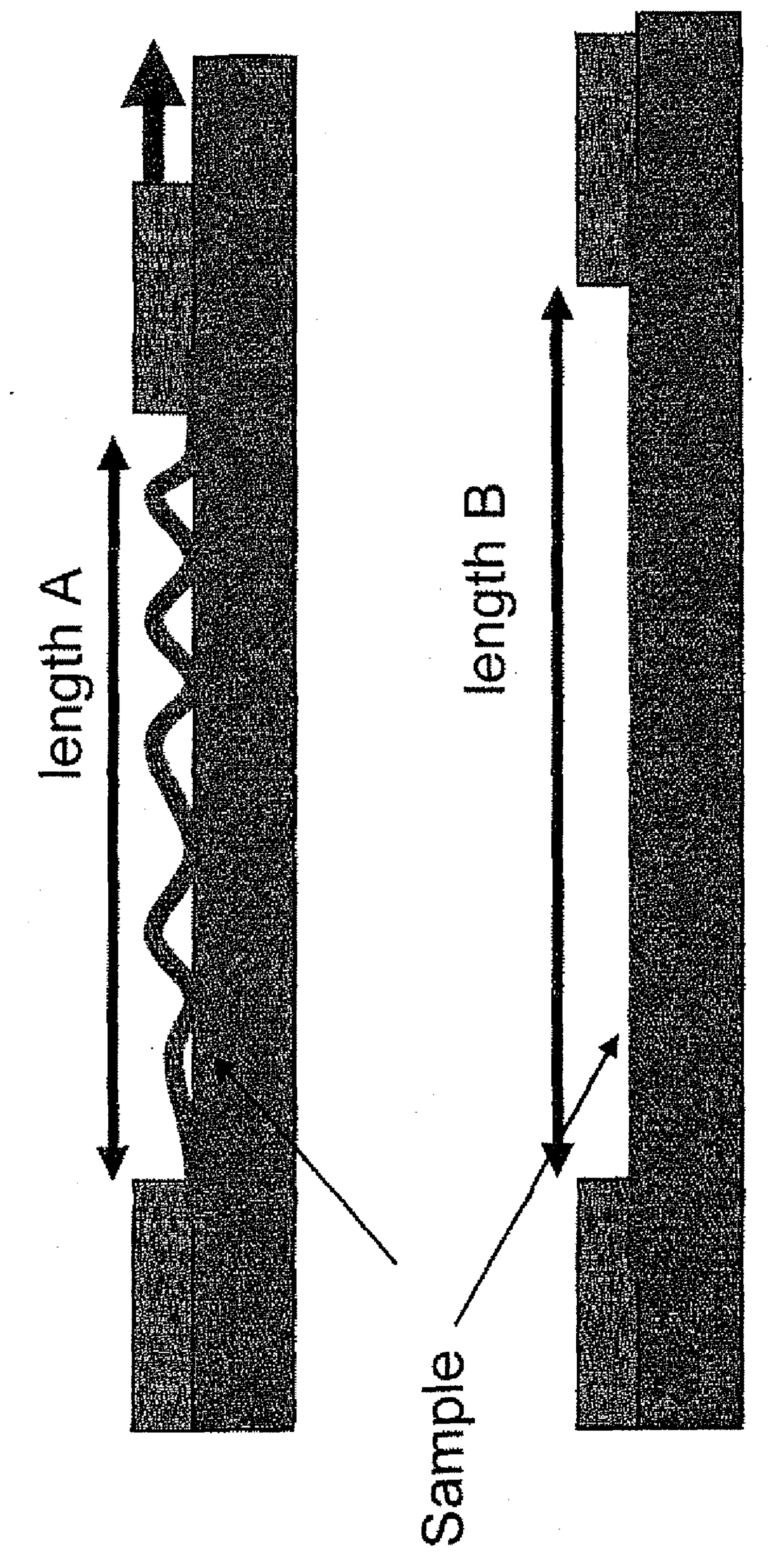


Fig. 1

The Idea of AFT Measurement

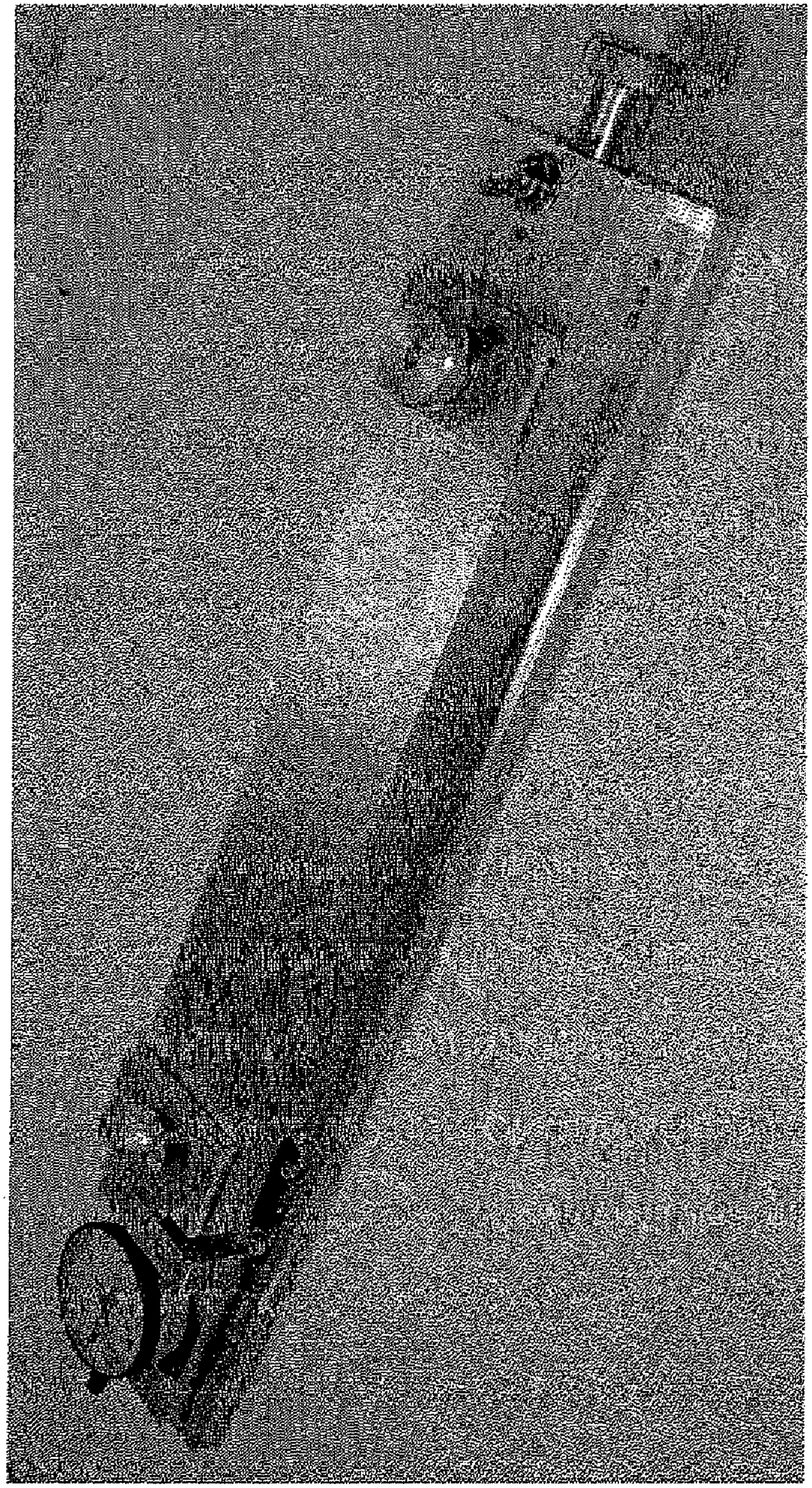


Fig. 2

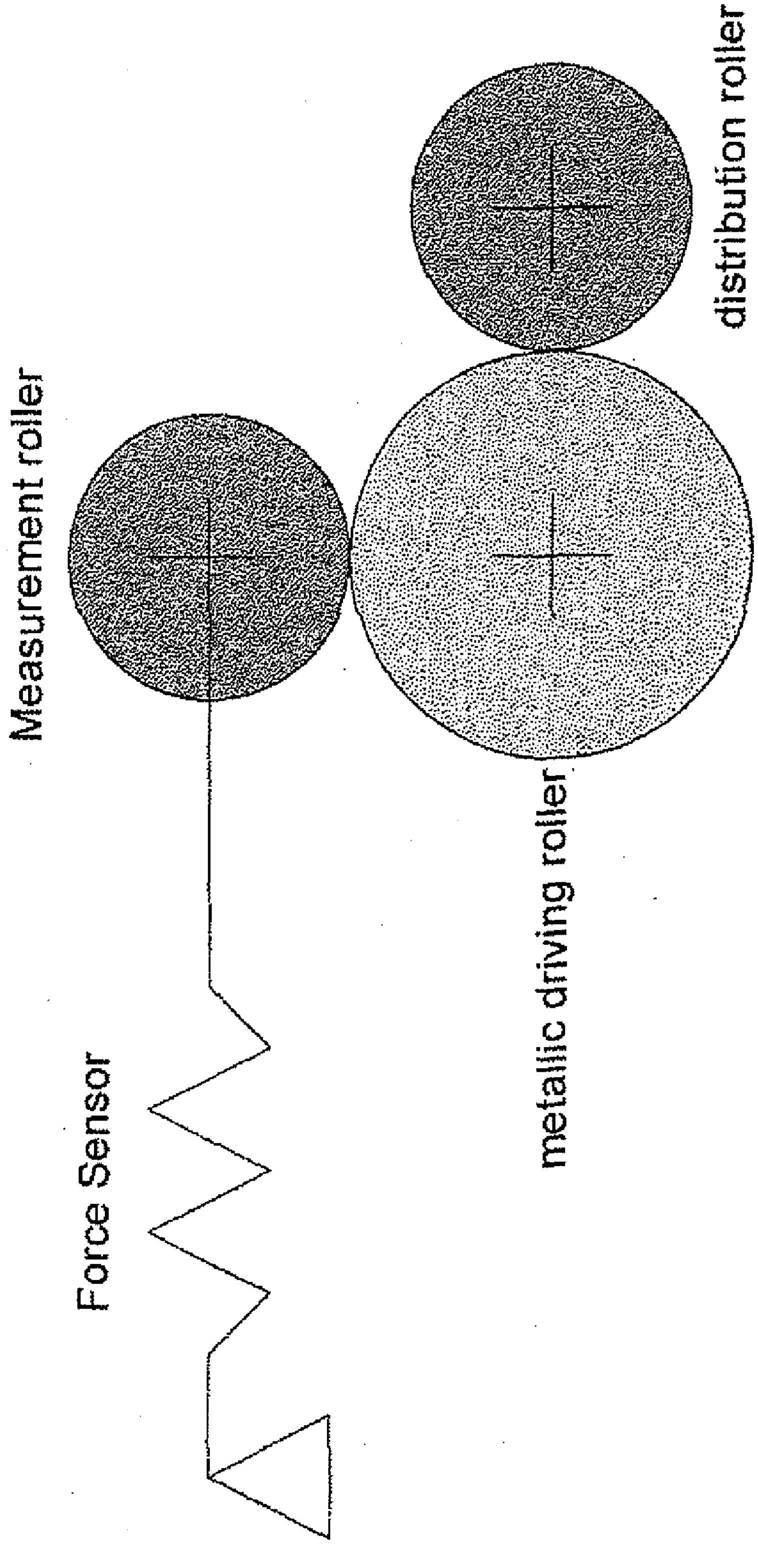

Measurement roller
distribution roller
metallic driving roller
Force Sensor

Fig. 3

NON-FLUTING PRINTING SUBSTRATE AND METHOD FOR PRODUCING THE SAME

[0001] The present invention relates to a printed substrate, and in particular to a printed paper. In terms of this invention substrate means to also include, but being not limited to, a paper. The printed substrate comprises at least one coating and a printing ink, formulated as heat-set printing ink. The printing ink has a reduced tack and comprises at least one pigment and a mixture of at least two solvents boiling in the range of from 200° C. to 270° C.

[0002] The term coating includes any surface treatment applied to at least one side of the substrate resulting in reduced porosity of the respective surface of the side of the substrate.

[0003] In terms of this invention, the expressions "heat-set offset printing inks, including heat-set web offset (HSWO) printing inks" are always to be understood such that the respective printing inks are formulated for heat-set offset printing, and hence do fulfil the properties being necessary as matter of principle for such printing inks.

[0004] In other words, the particular surface of the unprinted substrate can be achieved, for example but not limited to, by coating the substrate with a coating colour.

[0005] The porosity of the surface of the unprinted substrate is such that the Gurley-Hill air permeability value of the substrate is above 7000 s/100 ml, preferably above 10000 s/100 ml and most preferably above 12000 s/100 ml.

[0006] The printed substrate also comprises a non-fluting printing ink being formulated as heat-set printing ink. The printing ink has a reduced tack and comprises at least one pigment and a mixture of at least two solvents boiling in the range of from 200° C. to 270° C. and furthermore is designed to be printed onto the substrate during a heat-set offset printing process, in including, but not limited to, a heat-set web offset (HSWO) printing process. The printing process is for achieving inter alia the desired and advantageous effect of considerably less fluting in terms of AFT values being below 0.05%. According to preferred embodiments of the process described according to the present invention gloss and smoothness of the printed substrate are also improved.

[0007] The present invention also relates to a method of manufacturing the printed substrate by a heat-set offset, including a HSWO printing process. The term heat-set offset printing in the context of the present invention refers to heat-set offset printing making us of fount solutions that are water-based. In terms of this invention heat set offset printing means to include, however is not limited to, HSWO printing.

[0008] The present invention still further refers to the use of a substrate and a printing ink being formulated as heat-set offset printing ink. The printing ink has a reduced tack and comprises at least one pigment and a mixture of at least two solvents boiling in the range of from 200° C. to 270° C. It furthermore may comprise also a low boiling solvent. The printing ink is designed for producing a printed substrate showing considerably less fluting in terms of AFT values.

[0009] Not intending to be bound by this theory: during a heat-set printing process, the printing ink is usually dried in high-temperature ovens. In an early stage of the drying process of the printing process, moisture contained in the coated paper evaporates rapidly from non-imaged areas, resulting in considerable shrinkage in the cross direction of the coated paper within this non-imaged area. On the contrary, moisture of the coated paper located underneath an imaged area evaporates rather slowly, since the printing ink layer on the coated paper acts as a barrier to heat transfer and moisture evaporation, resulting in little shrinkage in the cross direction of the coated paper within this imaged area. As a result, the non-imaged area of the coated paper compresses the adjoining imaged area in the cross direction during the drying process, leading to buckling of the imaged area.

[0010] This phenomenon is known as "fluting" and it appears during heat-set printing, in particular during heat-set web offset printing, and causes customer complaints and various defects, such as for example waviness.

[0011] The problem is inter alia paper related and occurs due to the structure of the wood fibres forming the backbone of the paper web. Wood is an inhomogeneous compound of different fibres. These structures are stabilized by chemical bonds. Inside those fibres water molecules act as spacers, increasing fibre dimensions and affecting dimensions of the whole paper web. During the printing process, the fibres pick up more water and swell. In the hot air floatation dryer besides the printing ink, also the paper is dried. The water molecules between/inside the fibres evaporate, allowing the fibres to shrink and to come into close contact with each other. Thereby the paper web shrinks. New chemical bonds are formed between these fibres. Thus the dimensions of the paper are altered. Since after the printing process, there are areas of different water content in the paper web (i.e. water content in the imaged and non-imaged areas) this alteration of the dimensions of the web is more severe in some areas than in other adjacent areas. Due to the different swelling and shrinking extent of the fibres in these areas with different water content, waves form on the paper. The newly created chemical bonds are so strong that they will not be broken down completely after re-moistening.

[0012] In other words, within this description, the term "fluting" is defined as undulating creases, waves or bands that form in the printed paper after having passed a heat-set dryer. The corrugations appear in the direction of web travel and are, as mentioned before, more or less permanent, i.e. they do not relax until months after product delivery.

[0013] Many efforts have been made in order to overcome the problem of fluting during heat-set printing.

[0014] According to the prior art, new paper products are suggested, as for example described in Jon Tappi J., (2003) vol. 57, no. 1, January 2003, pp 92-97. There are papers described (launched by Oji Paper) which do not show fluting in web offset printing. It is stated that contractile forces, resulting from drying after web offset printing are minimized. However, the use of such paper causes higher costs and in some applications the publishers as well as the printer are limited in printing ink choice.

[0015] Also, coatings capable of avoiding fluting are suggested in the art. In Tappi J., (2000) vol. 83, no. 4, April 2000. It is described that the tendency to flute is to a great extent determined by the coating formulation, wherein less absorbent coatings are supposed to decrease fluting. No concise suggestions are made regarding particular coatings and printing inks being suited to be used thereon.

[0016] One should note that according to the prior art various concepts based on different theories have been suggested to avoid the fluting problem.

[0017] During the 2002 (69th) Pulp and paper research conference, Tokyo, Japan, 17-18 Jun. 2002 and in the respective report (P-06, pp 166-171 [Tokyo, Japan: Japan TAPPI, 2002, 186 pp]) it is described that drying temperatures in the range of 135° C. prevent fluting during offset printing processes. The drying conditions in an early stage of the printing process are described to be important in the prevention of fluting. The concept does not lead to reasonable results.

[0018] From the art the skilled person is confused about concepts that exist for solving the fluting problem, particularly occurring in heat-set printing processes.

[0019] There are remoisteners on the market for all alleviation of fluting, but they do not give reproducible results.

[0020] According to J. Pulp Pap. Sci., (September 1993) Vol. 19, no. 5, J214-219, the results of theoretical and experimental analyses are presented, directed to suggestions for the alleviation of fluting by changing in dryer design and operation.

[0021] U.S. Pat. No. 6,058,844 refers to a method of and an apparatus diminution of fluting or corrugation occurring in printed webs of light weight coated paper printed on both sides with thermosetting printing ink on HMO printing presses. The problem is solved by spreading the web in its width-wise direction as the printed web exits the printing ink drying and heat setting oven of the press and passes over the web cooling chill rolls. Thereby the printed web is held in a flat and smooth condition until it is cooled down and the printing ink takes permanent set. Spreading the web prior to and during cooling allows the printing inks to thermoset in a flat state, because the web is kept flat and free of flutes during thermosetting. The method and apparatus is described to facilitate operation of the press at higher speeds and with lighter grades of paper. However, experience with such devices does not show the indicated advantages.

[0022] Additionally, WO 2004/003293 describes a paper having some specific features, with an oleophilic surface of the coating being the most relevant of these features and the gist of that invention. In order to achieve a suitable surface characteristic, which is mentioned in this art, it is obligatory to use oleophilic substances on the surface of the paper to be printed, like SMA based additives (Raisaprint D100 or Raisaprint D200, see page 5 of WO 2004/003293). They are used to control surface chemistry and to achieve the oleophilic character of the surface. Coating paper with these substances is expensive and therefore not favorable.

[0023] U.S. Pat. No. 5,713,990 and U.S. Pat. No. 5,875,720 describe printing ink compositions comprising high boiling oils as solvents in the printing ink vehicles. Also, the bodied tung oil described as solvent in U.S. Pat. No. 6,206,960, which is present in the printing ink composition, decomposes only at temperatures greater than 350° C. The drying temperatures suggested during the printing process described in U.S. Pat. No. 6,206,960 are as high as 149° C. U.S. Pat. No. 6,709,503 discloses modified linseed oil as solvent in printing ink compositions, which solvent decomposes only at temperatures greater than 350° C. The drying temperatures during the printing process are described to be high. U.S. Pat. No. 5,427,615 introduces fatty acid ester solvents with high flash points, decomposing only at temperatures above 350° C.

[0024] U.S. Pat. No. 4,357,164 disclose a printing ink comprising low boiling solvents. However, U.S. Pat. No. 4,357,164 relates to a waterless lithographic printing process, which does not cornprise the use of a fount solution, i.e. does not give rise to the fluting problem at all.

[0025] It becomes apparent from the various different, still unsuccessful, approaches to reduction and prevention of fluting described in the art that there exists a strong need for better quality of printed substrate obtained by heat-set, including HSWO printing processes.

[0026] It is therefore an object of the present invention to provide printed substrate with superior properties in terms of considerably less fluting. Still further, the printed substrate preferably also shows superior gloss and superior smoothness.

[0027] Also, an improved heat-set offset printing process for obtaining a printed substrate with achieving less fluting is an object of this invention.

[0028] The objects of the invention are solved by the subject-matter described in the patent claims.

[0029] The invention relates to a printed substrate comprising a substrate and a printing ink-characterized in that at least one side of the substrate has a surface with such porosity that the Gurley-Hill air permeability value of the substrate is above 7000 s/100 ml, and it comprises an printing ink formulated as heat-set offset printing ink with reduced tack comprising at least one pigment and a mixture of at least two solvents boiling in the range of from 200° C. to 270° C.

[0030] According to an embodiment of the invention at least on solvent present in the ready-to-use printing ink boils in the range of from 210° C. to 230° C. At least one further solvent being present in the ready-to-use printing ink boils in the range of from 240° C. to 270° C. The mixture of at least two solvents being present in the ready-to-use printing ink comprise solvents that may have different aromatic contents.

[0031] Preferably, the pigment present in the ready-to-use printing ink is added in the form of a pigment paste.

[0032] According to an embodiment of the invention at least one solvent present in the ready-to-use printing ink has an aromatic content of 1% by weight, based on the solvent, and at least a second solvent being present in the ready-to-use printing ink has an aromatic content of 12% by weight, based on the solvent. Preferably at least one solvent being present in the ready-to-use printing ink is a mineral oil solvent.

[0033] According to most preferred embodiments of the invention the printed substrate comprises a solvent, which solvent was present in the ready-to-use printing ink in amounts of at least 1% by weight, based on the printing ink composition. All solvents present in the ready-to-use printing ink can be mineral oil solvents.

[0034] According to most preferred embodiments of the invention the ready-to-use printing ink comprises a varnish in an amount of from 15 to 30% by weight based on the ready-to-use printing ink. The varnish can comprise at least one self-structured resin. The varnish can be free of gelling agents. Preferably at least one varnish within the printing ink is free of gelling agents.

[0035] The porosity of the substrate surface of the printed substrate according to the invention can be achieved by coating. The coating can comprise a coating colour comprising at least one coating pigment and/or at least one bonding agent. The weight ratio of coating pigment to bonding agent can be in the range of from 1:100 to 100:1. According to preferred embodiments of the invention at least one coating pigment is selected from the group consisting of kaolins, talcs, gypsum and carbonates. The amount of the coating pigment can be in the range of from 70 to 90 percent by weight based on the coating colour. The coating pigment can be a plate shaped coating pigment.

[0036] According to preferred embodiments of the invention the particle size distribution of the coating pigment is such that at least 40% by weight of the coating pigment particles are smaller than 2 μm. The particle size distribution of the coating pigment can be such that at least 25% by weight of the coating pigment particles are smaller than 1 μm and also can be such that the particle size distribution of the coating pigment is such that at least 10% by weight of the coating pigment particles are smaller than 0.5 μm.

[0037] According to the invention the printed substrate has an AFT value of below 0.05%, preferably below 0.03%. The AFT value is measured on a piece of printed substrate in the dimensions of 27 cm×5 cm at standard conditions with an AFT-meter, as set out in more detail below.

[0038] The invention also refers to a heat-set offset printing process comprising

applying to a substrate with such porosity that the Gurley-Hill air permeability value of the substrate is above 7000 s/100 ml an printing ink formulated as heat-set offset printing ink with reduced tack comprising at least one pigment and a mixture of at least two solvents boiling in the range of from 200° C. to 270° C., and

achieving an AFT value of the printed substrate of below 0.05%.

[0039] Again, said AFT value is measured on a piece of printed substrate in the dimensions of 27 cm×5 cm at standard conditions with an AFT-meter.

[0040] The process according to the invention makes use of an printing ink as described herein, in particular the printing ink comprises as solvents a mixture of at least two solvents comprising solvents having different aromatic contents. As said before, at least one solvent being present in the ready-to-use printing ink has an aromatic content of 1% by weight, based on the solvent, and at least a second solvent being present in the ready-to-use printing ink has an aromatic content of 12% by weight, based on the solvent.

[0041] In the process according to the invention the porosity of the surface of the substrate used within the process can be achieved by coating. The coating can comprise a coating colour comprising a coating pigment and/or at least one bonding agent.

[0042] The invention also refers to a use of a substrate with such porosity that the Gurley-Hill air permeability value of the substrate is above 7000 s/100 ml, and a printing ink formulated as heat-set offset printing ink comprising at least one pigment and a mixture of at least two solvents boiling in the range of from 200 to 270° C. for producing a printed substrate.

[0043] The ready-to-use printing inks as used according to the invention may comprise a mixture of at least two solvents having different aromatic contents. At least one solvent present in the ready-to-use printing inks can have an aromatic content of 1% by weight, based on the solvent, and at least a second solvent present in the ready-to-use printing inks has an aromatic content of 12% by weight, based on the solvent.

[0044] It is surprising that the printed substrate according to the present invention shows considerably less fluting. The fluting is determined by way of AFT value determination as set out further down below in detail. The term "considerable less fluting" and the term "non-fluting" are herein used synonymously. The highly advantageous and desirable non-fluting characteristics of the printed substrate according to the invention are achieved by making use of a substrate, in particular a paper, having a surface as described herein. Still further the particular printing inks as described before are essential for providing the printed substrate according to the invention. Finally, of course the heat-set printing process in accordance with the invention makes it possible to obtain the printed substrate with the advantageous non-fluting properties.

[0045] According to the present invention a printed substrate is provided, which may include a paper made from a fiber-based raw material, wherein at least one side has a surface with such porosity that the Gurley-Hill air permeability value of the substrate is above 7000 s/100 ml, preferably above 10000 s/100 ml and most preferably above 12000 s/100 ml.

[0046] Gurley-Hill measurement is based on ISO 5636-5: 2003 standard. The air permeability through substrate is determined, while a higher value (in s/100 ml) corresponds to lower porosity of the sample. The skilled person is well aware of the process of Gurley-Hill measurement and the mentioned respective standard.

[0047] The printed substrate furthermore comprises a printing ink formulated as heat set printing ink comprising a mixture of at least two solvents, as described above. The fluting of the printed substrate is reduced, i.e. it shows low fluting (non-fluting) properties. Preferably the AFT value is reduced more than 40%, preferably more than 50%, compared to the respective AFT value for printed substrate comprising a standard paper and a standard printing ink. The terms "non-fluting" and low fluting preferably comply with the definition in terms of AFT-values being below 0.05% or even below 0.03%.

[0048] FIG. **1** illustrates principle of AFT measurement.

[0049] FIG. **2** shows an apparatus for AFT measurement.

[0050] The AFT device as shown in FIG. **2** is used by insertion of a sample of printed substrate of certain length and width into the clamps of the AFT device and the shadow pattern which is caused by fluting is observed visually in low angle light. The substrate, in particular the paper, is stretched until it becomes totally flat, i.e. until the shadow pattern caused by fluting has disappeared. The elongation of the strip by stretching is measured and is the length B minus length A. The AFT value is the elongation in mm divided by 250 mm (initial length of the sample between the clamps into stretching direction) expressed in percent. For this method the following further parameters were set:

[0051] Sample preparation for AFT measurement:

- **[0052]** Printed paper was obtained by HSWO printing.
- **[0053]** Fluting was measured on a green area printed on both sides.
- **[0054]** Yellow optical density was 1.2 and cyan optical density was 1.5 in the printed green area.
- **[0055]** Dimension of printed green area are 20 cm*20 cm (MD*CD)[1]. The printed area was surrounded by unprinted white paper.
- **[0056]** 27 cm*5 cm (CD*MD)[1] sample is cut over the printed green area.

[1]MD=machine direction, CD=cross machine direction.

[0057] Typical AFT values of commercial heat-set offset printed papers are 0.07-0.11% (see example below). A sample is considered non-fluting, if the AFT value is 0.05% or lower. Measurements are done at 23° C. and relative humidity of 50%.

[0058] Standard paper and standard printing ink in terms of this invention are, for example:

[0059] Paper: Commercially available double coated MWC paper. Grammage: 80 g/m^2. Gurley-Hill: 3320 s/100 ml. AFT value 0.085% by using standard printing ink and web exit temperature 130° C. Base paper of this commercial MWC paper is a wood containing base paper with a grammage of 45 g/m^2. The paper is precoated with calcium carbonate coating pigment, binder and additives. Top coating is based on clay and calcium carbonate coating pigment blend, binder and additives.

[0060] Ink: Commercially available heat-set offset printing ink. This printing ink is suited for printing on coated paper especially Light Weight Coated paper (LWC) and Super Calendared (SC) paper.

[0061] There are no hints in the prior art on how to provide printed substrate having such high quality in terms of non-fluting properties defined by AFT values after heat-set offset printing.

[0062] In particular, the idea that at least one side of the substrate has a surface with such porosity that the Gurley-Hill air permeability value of the substrate is above 7000 s/100 ml, preferably above 10000 s/100 ml and most preferably above 12000 s/100 ml, has never been disclosed. The same is true for a printed substrate having the superior properties not only in terms of non-fluting but also regarding improved gloss and smoothness. Still further, due to the low tack behaviour of the printing ink, the undesired consequences of picking and piling can be avoided.

[0063] The present invention provides superior printed substrate obtained by a heat-set printing process, in particular HSWO printing process. Using this technique, a very high printing quality with regard to accuracy of the image is achieved. Additionally, the printed substrate can be obtained at favorable costs. Any conventional heat-set offset printing machine can be used in order to prepare the printed substrate of the present invention.

[0064] For example, coating technologies can be used to obtain two, three, four, five or more surfaces. Such technologies comprise the use of a metering size press, a blade coater with jet applicator, a blade coater with roll applicator, a blade coater with SDTA (short dwell time applicator), a spray coater or curtain coater or the like or any combination of these.

[0065] The present invention provides superior printed substrate obtained by a heat-set offset printing process. Using this technique, a very high printing quality with regard to accuracy of the image is achieved. Additionally, the printed substrate can be obtained at favorable costs. Any conventional heat-set offset printing machine can be used in order to prepare the printed substrate of the present invention.

[0066] The invention is specifically based on paper allowing the porosity of the surfaces to be controlled. The paper surface is designed to be dense as defined herein in terms of porosity. Together with the printing inks described herein and their synergistic interaction with the substrate, the new and advantageous printed substrate showing the described and claimed superior properties is obtained.

[0067] According to the present invention, the fluting properties of the printed substrate in terms of AFT values are reduced, namely more than 40% reduction, more preferred more than 50% reduction is achieved when compared to the respective values for printed substrate comprising standard paper and standard printing ink, as described before.

[0068] Although the inventors do not wish to be bound to such theories, the non-fluting behaviour of the printed substrate can be achieved by the use of printing inks formulated as heat set offset printing inks comprising a mixture of at least two solvents boiling in the range of from 200° C. to 270° C. Preferably, at least one solvent which may be a mineral oil has an aromatic content of 1% by weight. Nevertheless, suited are also solvents with an aromatic content in the range of from of 0% by weight to 5% by weight, preferably in the range of from 0.5% by weight to 3% by weight.

[0069] According to the invention a second solvent, which again can be a mineral oil, has an aromatic content of 12% by weight. Nevertheless, suited are also solvents with an aromatic content in the range of from 10% by weight to 18% by weight, preferably 11% by weight to 15% by weight.

[0070] According to most preferred embodiments the mixture of at least two solvents present in the printing ink, which solvents may be mineral oils, has an aromatic content in the range of from 6% by weight to 10% by weight, 7% by weight to 9% by weight and most preferred an aromatic content of 8% by weight.

[0071] The presence of the low boiling solvent allows for drying temperatures during the heat-set printing process being sufficiently low to avoid fluting. Preferred web temperatures in the last zone of the heat-set dryer are between 85° C. and 120° C., more preferred between 90° C. and 110° C. and most preferred between 95° C. and 105° C. Suited drying temperatures are for example 120° C., 110° C., 100° C., 95° C., 90° C. or 85° C.

[0072] Preferred amounts of low boiling solvents usable within the compositions of the invention are greater than 1% by weight (based on ready to use printing ink compositions), more preferred greater than 5% by weight (based on ready to use printing ink compositions) and in particular of from 10 to 40% by weight (based on ready to use printing ink compositions).

[0073] The printing inks allow for a particular tack behaviour, which can be caused by the presence of respective varnishes. The varnishes have superior properties, because the above-defined aromatic contents allow for the presence of particular resins (so called self-structured resins) and hence can be designed such that also the tack of the final printing ink is reduced.

[0074] It has been found that the presence of the special varnish allowing for a particular tack as set out within this application in the printing ink compositions makes the same suitable for printing on the coated substrate described herein. Due to interaction of the substrate with the printing ink, the desired non-fluting behaviour of the printed substrate is achieved. Further, picking and piling can be reduced or even avoided.

[0075] As mentioned before, by use of the mixture of solvents, such as mineral oils, with different aromatic contents and preferred boiling ranges, the tack of the printing inks is reduced.

[0076] The low tack described herein means that at the tack is at least 10% lower than the tack of known non-fluting heat-set offset printing inks, preferably between 10% and 20% lower, more preferably between 12.5% and 17.5%, most preferably 15% lower.

[0077] According to ISO 12634:1996(E) tack is defined as: “Restoring force between two rotating rollers of a given width caused by the splitting of an printing ink or vehicle film on the roller surfaces.”

[0078] A definition mentioned in the ASTM standard for tack measurement: D 4361-97: “Tack—a function of the force required to split a thin fluid film of a printing ink or vehicle between two rapidly separating surfaces; it is a rheological parameter indicative of internal cohesion of the fluid.”

[0079] Tack of printing inks controls their high speed transfer properties. It may also be meaningful as to the ability to predict paper picking and wet trapping in multi colour printing. Conventional instruments determine the force exerted on a measuring roller that is positioned on the printing ink film of a driving roller.

[0080] FIG. **3** shows the construction of a traditional three-roller-tackmeter.

[0081] Different manufacturers of tackmeters have established their own arbitrary scales. In this invention a Tack-o-scope® (Testprint BV, Netherlands.) is used to measure tack.

[0082] Operation principle of tack measurement instruments is described below:

[0083] A defined weight of printing ink is placed on a three roller system. The roller system consists of a middle, metallic driving roller, an printing ink distribution roller and a measuring roller for tack determination. These two outer rollers are covered with an elastomer layer. After speed adjustment and temperature stabilization the axial force on the measurement roller is determined. This axial force is used as indication of tack. The higher the axial force, the higher the determined tack number.

[0084] The moisture gradient, i.e. the drying gradient, between the printed and unprinted surfaces is minimized, and fluting in heat-set printing, in particular in the heat-set web offset printing processes, is significantly reduced or even avoided with the substrate according to the invention. The obtained density makes it possible to minimize the moisture gradient for the substrate. Drying of the non-imaged areas relative to the imaged areas is delayed due to the dense substrate, thereby the moisture gradient is reduced, e.g. in the HSWO drying process. By reducing the moisture gradient, fluting is reduced.

[0085] In this context, substrate refers to any fiber-based paper, cardboard or fiber product, or the like. Paper can be made from chemical pulp, mechanical pulp, chemimechanical pulp, recycled fiber and the like as well as mixtures thereof. The paper can be in the form of a paper web, press-web, or sheets, or another form appropriate for its purpose. The paper can contain the proper filling and admixing materials.

[0086] In one embodiment of the invention, the surface of the base paper [stock] is provided with a coating colour comprising a coating pigment and/or bonding agent [adhesive]. Preferably, the weight ratio of coating pigment to bonding agent is in the range of from 1:100 to 100:1, more preferably 5:1 to 1:5. In one embodiment, the coating pigment is chosen from the group consisting of kaolins, talcs, calcium carbonates, gypsum, their mixtures and similar coating pigments. Preferred coating pigments are kaolins and talcs.

[0087] Typically there are 100 parts of coating pigment present in the coating formulation. The proportion of binder in the composition is typically from 10 to 15 parts, with parts meaning parts per weight.

[0088] According to a preferred embodiment, the coating colour comprises a plate-shaped coating pigment, wherein the amount of plate-shaped coating pigment is more than 70 parts, preferably more than 90 parts.

[0089] According to a further embodiment of the present invention, the coating colour comprises a spherical coating pigment.

[0090] The coating colour can comprise a bonding agent. According to a preferred aspect of the present invention, the bonding agent comprises a latex having a glass transition temperature in the range of from −30 to 35° C., more preferably in the range of from 0 to 25° C. The glass transition temperature can be determined by Differential Scanning Calorimetry (DSC), which is known for the person skilled in the art.

[0091] In a further embodiment, the bonding agent is chosen from the group consisting of starches, proteins, latexes, carboxy-methyl cellulose, polyvinyl alcohol, their mixtures, and the like. Preferred bonding agents are latexes.

[0092] In one advantageous embodiment, the porosity of the paper surface is controlled by a coating colour comprising a combination of binder and coating pigments. In one embodiment, the coating colour comprises 75 to 95 percent by weight of coating pigments. The coating pigment can be incorporated into a dispersion, and may appear as a composition, in which the coating pigments constitute 50 to 100 percent by weight of said composition. In one embodiment, the bonding agent constitutes 5 to 25 percent by weight of the total coating colour. The bonding agent can be added in form of a solution, and may appear as a composition, in which the bonding agent constitutes 10 to 100 percent by weight.

[0093] For surface treatment of the paper, any suitable bonding agent and coating pigment may be used. Moreover, for surface treatment, e.g. admixing materials that are suitable and known per se within the field may be added to the coating colour. The mixture may comprise 0 to 10 percent by weight of admixing materials.

[0094] In one embodiment of the invention, the paper is calendered, preferably after surface treatment.

[0095] In the paper production process according to the invention, suitable fiber-based base paper is used as so-called base paper [stock], printing paper according to the invention can be created, e.g., Light Weight Coated (LWC), Medium Weight Coated (MWC), Machine Finished Coated (MFC), Wood Free Coated (WFC) paper, or similar paper.

[0096] In one embodiment, filler materials, coating pigments, bonding agents and/or other chemicals are added to the fiber furnish in the paper production process. Any substances or chemicals known in the field may be used as filler materials, coating pigments, bonding agents and chemicals.

[0097] The coating colour comprised in the paper according to the present invention preferably comprises a coating pigment with such particle size distribution that at least 40% by weight of the coating pigment particles are smaller than 2 μm, at least 25% by weight of the coating pigment particles are smaller than 1 μm, and 10% by weight of the coating pigment particles are smaller than 0.5 μm. Particle size means to be the equivalent spherical diameter determined by a sedimentation technique (measured by using Sedigraph 5100).

[0098] According to one embodiment of the invention the substrate is surface treated with multi-layer treatment; the substrate can be double- or multi-coated. According to a preferred embodiment it is sufficient that only one of the two or more surface treatment layers have the desired low porosity.

[0099] According to one embodiment of the invention the substrate is surface treated by coating and/or surface sizing and the substrate is coated or surface sized with at least two layers one upon the other. According to a preferred embodiment of the invention the lowest layer adjacent to the substrate is coated.

[0100] According to one embodiment of the invention the substrate is surface treated by pre-coating the one or both surfaces of the substrate. According to one embodimeat the substrate is pre-coated with dense pre-coating. According to the preferred embodiment the substrate is further coated with at least one more coating layer, which may be dense or not.

[0101] The dense surface treatment layer can be any of the two or more surface treatment layers. According to one embodiment the dense layer is the uppermost surface treatment layer. According to another embodiment the dense layer is the intermediate surface treatment layer. According to another embodiment the uppermost surface treatment layer is not the dense layer, which enables a possibility to arrange, for example, better printability to the uppermost surface treatment layer.

[0102] According to one embodiment the thickness of the at least one dense surface treatment layer is 1 to 14 gsm (grams per square meter) per one side of the substrate, preferably between 7 to 14 gsm per one side. According to one embodiment the total coating thickness is 7 to 40 gsm per side.

[0103] The heat set offset printing process as described and claimed herein makes use of the printing inks and substrate as set out within this description. The process according to the present invention runs perfectly stable. The final product has a superior gloss and smoothness besides the desired AFT value.

[0104] The mineral oil solvents used in this invention are characterized by the boiling ranges, the aromatic contents and the aniline points. The boiling or distillation range [in ° C.] is determined by distillation according to DIN ISO 3405 or ASTM D 86. The initial and the final boiling points determine the boiling range. The aniline point [in ° C.] describes the solubility power of a solvent and is determined by DIN ISO 2977 or ASTM D 611. The aromatic content [in wt %] is determined by ASTM D 2140 or EC-A-A07 (UV). The Hydrocarbon type analysis is done by DIN 51378 and determines the content of aromatics (Car), naphthenics (Cn) and paraffinics (Cp) [in %].

Solvent Types Used in this Invention:

Component	distillation range (DIN ISO 3405, ASTM D 86)	Aniline point (DIN ISO 2977, ASTM D 611),	Carbon-type composition (DIN 51378, ASTM D 2140)		
			Car	Cn	Cp
Mineral oil A	280-310° C.	82	12	22	66
Mineral oil B	240-270° C.	84	<1	25	74
Mineral oil C	210-230° C.	84	<1	<1	99
Mineral oil D	240-270° C.	72	12	22	66

[0105] The cloudpoint temperature is a characteristic property, which is defined as the temperature at which a liquid (solution of a solid material and a solvent) begins to become cloudy. The solubility or compatibility of resins and varnishes is determined by cloud point measurements using a Chemotronic® device (Novomatics GmbH/Germany).

[0106] Furthermore, the present invention refers to the use of varnishes and printing inks as defined herein within a heat-set offset printing process.

[0107] The varnishes further comprise vegetable oil, preferably stand oil.

[0108] The varnishes preferably comprise a mixture of a main resin and a co-resin.

[0109] Preferably, the main resin is a self structured phenolic modified rosin resin with a viscosity of 30 Pas (35% in 6/9 AR blend*) and good compatibility (cloud point: 120° C. (in 6/9 AF new*). In addition self structured resins have non Newtonian flow behaviour. A skilled person can determine the structure of a resin by viscosity measurements on a rotational viscometer using p-Ostwald method. Standard Newtonian resins have a p-Ostwald factor of 0.9 to 1.0. Self structured resins have a p-Ostwald factor of 0.6 to 0.8. Examples for preferred self-structured phenolic modified rosin resins according to the present invention are e.g. Cray Valley Tergraf UZ87, Hexion Setaprint P7950, Arez PM1235.

[0110] Preferably, the co-resin is a hydrocarbon resin with a viscosity of 40 Pas (55% in 6/9*) and very good compatibility (Cloud point: 110° C. (in 6/9 AF*). Examples for preferred hydrocarbon resins according to the present invention are e.g. Neville Nevprint LG or Resinall R260.

[0111] The printing ink composition comprises a pigment paste in amounts of between 1% and 60% by weight, preferably between 25% and 50% by weight and most preferably between 30% and 45% by weight.

[0112] The varnishes are present within the non-fluting heat-set printing ink composition described herein in amounts of between 15% by weight and 50% by weight, preferably 15% by weight to 30% by weight, based on the printing ink composition.

EXAMPLE 1

Varnish "7131"

[0113] Resins used in offset technique are characterized by their solubility (Cloud point) and viscosity of the resin in a mineral oil distillate solution. These solutions can be prepared in Thermotronic® (Novomatics GmbH/Germany) varnish mixer. Depending on resin type, mixtures are made containing between 35% by weight and 55% by weight of hard resin and 45% by weight to 65% by weight mineral oil distillate with aromatic content adjusted to resin solubility (Testoils e.g.: DOW/Haltermann PKWF 6/9, 6/9AF, 6/9AFnew, 6/9AR, 6/9AR blend). Resin solution viscosities are determined by a rotational viscometer using a cone (25 mm diameter) and a plate at 23° C. The gap between cone and plate must be 0.05 mm. The viscosity is measured at a shear rate of 25 s^{-1}.

[0114] The varnish comprises a mineral oil with a low boiling range of from 240 to 270° C. (one part with an aromatic content of 15%, the other part with an aromatic content of 1%; the mixture is used to get a final aromatic content of 8%). It comprises vegetable stand oil. The main resin is a self structured phenolic modified rosin resin with a viscosity of 30 Pas (35% in 6/9 AR blend*)) and good compatibility (Cloud point: 120° C. (in 6/9 AF new*)). The co-resin is a hydrocarbon resin with a viscosity of 40 Pas (55% in 619*) and very good compatibility (Cloud point: 110° C. (in 6/9 AF*)). The resins are diluted in solvent and additives, heated to 180° C. and stirred for 30 min. After rheology and tack of the varnish was checked the varnish was cooled down to 130° C. and discharged.

[0115] The following table gives an overview over the ingredients of the varnish for illustration purposes:

Component	Varnish "7131"	wt. %
Mineral oil B	Boiling range 240-270° C., Aniline point 84° C., C_{ar} < 1%	25.0
Mineral oil D	Boiling range 240-270° C., Aniline point 72° C., C_{ar} 12%	20.5
Vegetable oil	Stand oil, viscosity: 50 poise	6.0
Self structured rosin resin	Viscosity: 30 Pas (35% in 6/9 AR blend), Cloud point: 120° C. (in 6/9 AF new)	43.5
Hydrocarbon resin	Viscosity: 40 Pas (55% in 6/9), Cloud point: 110° C. (in 6/9 AF)	5.0
Total [wt %]		100.0

[0116] The resins are diluted in solvents and additives, heated to 180° C. and stirred for 30 min. After rheology and tack of the varnish were checked the varnish was cooled down to 130° C. and discharged.

Varnish "1/3"

[0117] The following varnish is enclosed for illustration purposes and is not a new varnish.

[0118] The resins are diluted in solvent and additives, heated to 160° C. and stirred for 30 min. Then the gelling agent (diluted in solvent) was added and stirred for further 30 min. After rheology and tack of the varnish were checked the varnish was cooled down to 130° C. and discharged.

[0119] The following table gives an overview over the ingredients of the varnish:

Component	"1/3 varnish"	wt. %
Mineral oil C	Bp 210-240° C., Car < 1%, AP = 84° C.	33.8
Vegetable oil	Wood oil	5.0
Plasticizer	di-acid-di-ester	9.4
Phenolic modified rosin resin	Viscosity: 30 Pas (45% in 6/9AR blend*), Cloud point: 135° C. (10% in 6/9AF*)	32.4
Phenolic modified rosin resin	Viscosity: 35 Pas (40% in 6/9AR*), Cloud point: 115° C. (10% in 6/9*)	17.4
Gelling agent	aluminum chelate complex	0.9
Antioxidant	MTBHQ solution	1.5
Total		100

Varnish "4/7"

[0120] The following varnish is enclosed for illustration purposes and is not a new varnish.

[0121] This varnish comprises a mineral oil with a low boiling range of from 240 to 270° C. (aromatic content 15%), vegetable oil (wood oil) and a plasticizer (Di-Acid-diEster). The main resin in the varnish has low viscosity (30 Pas; 45% in 6/9AR blend*) and good compatibility (Cloud point: 135° C.; 10% in 6/9AF*). The co-resin has medium viscosity (35 Pas; 40% in 6/9AR*), medium compatibility (Cloud point: 115° C.; 10% in 619*) and gel reactivity. The varnish is gelled with an aluminium chelate complex.

[0122] The resins are diluted in solvent and additives, heated to 175° C. and stirred for 30 min. Then the varnish was cooled down to 160° C. and the gelling agent (diluted in solvent) was added and stirred for further 30 min. After rheology and tack of the varnish were checked the varnish was cooled down to 130° C. and discharged.

[0123] The following table gives an overview over the ingredients of the varnish:

Component	"4/7 varnish"	wt. %
Mineral oil D	Bp 240-270° C., C_{ar} = 12%, AP = 72° C.	34.1
Vegetable oil	Wood oil	5.0
Plasticizer	di-acid-di-ester	8.5
Phenolic modified rosin resin	Viscosity: 30 Pas (45% in 6/9AR blend*), Cloud point: 135° C. (10% in 6/9AF*)	32.0
Phenolic modified rosin resin	Viscosity: 35 Pas (40% in 6/9AR*), Cloud point: 115° C. (10% in 6/9*)	18.0
Gelling agent	aluminum chelate complex	0.9
Antioxidant	MTBHQ solution	1.5

[0124] The varnishes as described in Example 1 are suited to prepare non-fluting heat-set printing ink compositions, some of which compositions are described in the following Examples:

EXAMPLE 2

Non-Fluting Heat-Set Printing Ink Composition Series 140000

[0125] Series 14000D printing ink is based on varnish 7131. The printing ink composition was made of pigment paste (pigment level 30%). Mineral oil solvents with low boiling range (Boiling point (bp)=210-230° C., Aromatic content (Car)<1%, Aniline Point (AP)=84° C.) were chosen for improved drying. Mineral oil solvents with medium boiling range and better solubility (bp=240-270° C., Car=12%, AP=72° C.) were chosen for improved roller stability. A high pigment level allows thin printing ink films on printing press, which speeds up drying of the printing inks. For improved rub resistance and good coating colour of the paper sheets PE and PTFE wax pastes were added.

Composition of Printing Ink Series 140000:

[0126]

Component	Yellow	Magenta	Cyan	Black
Yellow pigment paste	33	—	—	—
Magenta pigment paste	—	40	—	—
Cyan pigment paste	—	—	34	—
Black pigment paste	—	—	—	41
Toner paste	0.5	—	—	—
Varnish 7131	49.5	40	49	44
PE wax paste	2	2	2	2
PTFE wax paste	1	1	1	1
Antioxidant solution	1	1	1	1
Mineral oil D	7	8	7	6
Mineral oil C	6	8	6	5
Total (wt. %)	100.0	100.0	100.0	100.0

[0127] The components of the printing ink were mixed in a dissolver at temperatures up to 60° C.

EXAMPLE 3

Non-Fluting Heat-Set Printing Ink Composition Series 14000T

[0128] Series 14000T printing ink is based on varnish 7131. The printing ink composition was made of pigment paste (pigment level 30%). Only mineral oil solvents with medium boiling range (bp=240-270° C.) were chosen for improved roller stability and lower tack. For better solubility mineral oil solvents with higher aromatic content were used in Cyan. A high pigment level allows thin printing ink films on the printing press, which speeds up drying. For improved rub resistance and good coating colour of the paper sheets PE and PTFE wax pastes were used.

Composition of Printing Ink Series 14000T:

[0129]

Component	Yellow	Magenta	Cyan	Black
Yellow pigment paste	33	—	—	—
Magenta pigment paste	—	40	—	—
Cyan pigment paste	—	—	34	—
Black pigment paste	—	—	—	41
Toner paste	0.5	—	—	—
Varnish 7131	49.5	40	50	44
PE wax paste	2	2	2	2
PTFE wax paste	1	1	1	1
Antioxidant solution	1	1	1	1
Mineral oil B	13	16	—	11
Mineral oil D	—	—	12	—
Total (wt %)	100.0	100.0	100.0	100.0

[0130] The components of the printing ink were mixed in a dissolver at temperatures up to 60° C.

EXAMPLE 4

Non-Fluting Heat-Set Printing Ink Composition Series 15000

[0131] Series 15000 is based on varnish 7131 and on the "4/7 varnish". The printing ink composition was made of pigment paste (pigment level 30%). Mineral oil solvents with low boiling range (bp=210-230° C.) were chosen for improved drying. Mineral oil solvents with high boiling range (bp=280-310° C., Car=12%, AP=82° C.) were chosen for improved roller stability. As yellow is printed last, a medium boiling range solvent can be used (bp=240-270° C.). A very high pigment level allows thin printing ink films on the printing press, which speeds up drying of the printing inks. For improved rub resistance and good coating colour of the paper sheets a higher amount of PTFE wax paste was used.

Composition of Printing Ink Series 15000:

[0132]

Component	Yellow	Magenta	Cyan	Black
Yellow pigment paste	39.2	—	—	—
Magenta pigment paste	—	46.5	—	—
Cyan pigment paste	—	—	39.8	—
Black pigment paste	—	—	—	48.3
Toner paste	0.6	—	—	—
4/7 Varnish	23.0	18.1	22.4	20.5
Varnish 7131	23.0	18.1	22.4	20.5
PTFE wax paste	2.1	2.1	2.1	2.1
Antioxidant solution	1.0	1.0	1.0	1.0
Mineral oil A	—	6.1	4.1	1.9

-continued

Component	Yellow	Magenta	Cyan	Black
Mineral oil B	4.1	—	—	—
Mineral oil C	7.2	8.2	8.2	5.6
Total (wt. %)	100.0	100.0	100.0	100.0

[0133] The components of the printing ink were mixed in a dissolver at temperatures up to 60° C.

EXAMPLE 5

Non-Fluting Heat-Set Printing Ink Composition Series 16000

[0134] Series 16000 is based on varnish 7131 and on "1/3 varnish". The printing ink composition was made of pigment paste (pigment level 30%). Mineral oil solvents with low boiling range (bp=210-230° C.) were chosen for improved drying. Additionally, mineral oil solvents with medium boiling range (bp=240-270° C.) were added for improved roller stability. Extender paste was used to increase solid content of the printing ink and to improve the solid lay of the printing ink on the paper. A very high pigment level allows for thin printing ink films on the printing press, which speeds up drying. For improved rub resistance and good coating colour of the paper sheets a little amount of PTFE wax paste was used.

Composition of Printing Ink Series 16000:

[0135]

Component	Yellow	Magenta	Cyan	Black
Yellow pigment paste	38	—	—	—
Magenta pigment paste	—	45	—	—
Cyan pigment paste	—	—	39	—
Black pigment paste	—	—	—	45
Toner paste	0.6	—	—	—
Extender paste	10	10	10	10
1/3 Varnish	18	14	19.5	17
Varnish 7131	20.5	14.5	18.5	17.5
PTFE wax paste	2	2	2	2
Antioxidant solution	1	1	1	1
Mineral oil B	3.4	7.5	7	6.5
Mineral oil C	6.5	6	3	1
Total (wt. %)	100.0	100.0	100.0	100.0

[0136] The components of the printing ink were mixed in a dissolver at temperatures up to 60° C.

COMPARATIVE EXAMPLE

[0137] AFT values for different known papers and printing inks printed thereon are shown. The printing ink used for all AFT measurements described in the table below is SunChemical "Challenge Intensive". The web exit for all measurements is 130° C.

Paper grade	Grammage, g/m^2	AFT value, %
LWC	51	0.104
LWC	57	0.109

-continued

Paper grade	Grammage, g/m^2	AFT value, %
LWC	65	0.094
WFC	70	0.088
MWC	80	0.085
WFC	80	0.084
MWC	90	0.086
WFC	90	0.075
WFC	100	0.076

[0138] Respective trials with printing inks as described herein printed on the paper according to this invention show the desired non-fluting behaviour of the resulting printed substrate/paper, i.e. AFT values are below 0.05%.

1. Printed substrate comprising a substrate and a printing ink characterized in that at least one side of the substrate has a surface with a porosity such that the Gurley-Hill air permeability value of the substrate is above 7000 s/100 ml, and

the printing ink is a heat-set offset printing ink with reduced tack comprising at least one pigment and a mixture of at least two solvents boiling in the range of from 200° C. to 270° C.

2. The printed substrate according to claim **1**, wherein the surface of the substrate is coated with at least two layers, at least one of which is said printing ink.

3. The printed substrate according to claim **1**, wherein at least one solvent present boils in the range of from 210° C. to 230° C.

4. The printed substrate according to claim **1**, wherein at least one solvent boils in the range of from 240° C. to 270° C.

5. The printed substrate according to claim **1**, wherein the mixture of at least two solvents comprise solvents having different aromatic content.

6. The printed substrate according to claim **1**, wherein the pigment is in the form of a pigment paste.

7. The printed substrate according to claim **1**, wherein at least one solvent present has an aromatic content of 1% by weight, based on the solvent, and at least a second solvent present has an aromatic content of 12% by weight, based on the solvent.

8. The printed substrate according to claim **1**, wherein at least one solvent present is a mineral oil solvent.

9. The printed substrate according to claim **1**, wherein the heat-set offset printing ink comprises at least one low boiling solvent in an amount of from 1 to 40% by weight, based on the printing ink composition.

10. The printed substrate according to claim **1**, wherein all solvents present are mineral oil solvents.

11. The printed substrate according to claim **1**, wherein the printing ink comprises a varnish in an amount of from 15 to 30% by weight based on the printing ink.

12. The printed substrate according to claim **11** wherein the varnish comprises at least one self-structured resin.

13. The printed substrate according to claim **1**, wherein the substrate surface having said porosity is a coated surface.

14. The substrate according to claim **13**, wherein the coating comprises a coating colour comprising at least one coating pigment, at least one bonding agent or both.

15. The printed substrate according to claim **14**, wherein both are present and the weight ratio of coating pigment to bonding agent is in the range of from 1:100 to 100:1.

16. The printed substrate according to claim **14**, wherein at least one coating pigment is selected from the group consisting of kaolins, talcs, gypsum and carbonates.

17. The printed substrate according to claim **14**, wherein the amount of the coating pigment is in the range of from 70 to 90 percent by weight based on the coating colour.

18. The printed substrate according to claim **14**, wherein the coating pigment is a plate shaped coating pigment.

19. The printed substrate according to claim **14**, wherein the particle size distribution of the coating pigment is such that at least 40% by weight of the coating pigment particles are smaller than 2 μm.

20. The printed substrate according to claim **14**, wherein the particle size distribution of the coating pigment is such that at least 25% by weight of the coating pigment particles are smaller than 1 μm.

21. The printed substrate according to claim **14**, wherein the particle size distribution of the coating pigment is such that at least 10% by weight of the coating pigment particles are smaller than 0 5 μm.

22. The printed substrate according to claim **14** wherein the AFT value of the printed substrate is below 0.05%.

23. The printed substrate according to claim **14**, wherein the Gurley-Hill air permeability value is above 10000 s/100 ml.

24. The printed substrate according to claim **14**, wherein the Gurley-Hill air permeability value is above 12000 s/100 ml.

25. A heat-set offset printing process comprising

applying to a substrate that has a surface with a porosity such that the Gurley-Hill air permeability value of the substrate is above 7000 s/100 ml a heat-set offset printing ink with reduced tack comprising at least one pigment and a mixture of at least two solvents boiling in the range of from 200° C. to 270° C. and

achieving an AFT value of the printed substrate of below 0.05%.

26. The process according to claim **25**, wherein the surface of the substrate is coated with at least two layers, at least one of which is said printing ink.

27. The process according to claim **25**, wherein the printing ink solvent mixture comprising solvents having different aromatic contents.

28. The process according to claim **25**, wherein at least one solvent present has an aromatic content of 1% by weight, based on the solvent, and at least a second solvent present has an aromatic content of 12% by weight, based on the solvent.

29. The process according to claim **25**, wherein the surface of the substrate having said porosity is a coated surface.

30. The process according to claim **29**, wherein the coating comprises a coating colour comprising a coating pigment, at least one bonding agent or both.

31-35. (canceled)

36. A method for reducing fluting of a heat-set offset printed substrate comprising applying a heat-set offset printing ink to a coated substrate and thereby achieving an AFT value of the printed substrate below 0.05%.

37. The method according to claim **36**, wherein the substrate has a porosity of the surface being such that the Gurley-Hill air permeability value of the substrate is above 7000 s/100 ml.

38. A method for reducing the web temperature in the last zone of a heat-set dryer in a heat-set offset printing process comprising applying a heat-set offset printing ink with low boiling solvent to a coated substrate.

39. The method according to claim **38**, wherein the substrate has a porosity of the surface being such that the Gurley-Hill air permeability value of the substrate is above 7000 s/100 ml.

40. The printed substrate according to claim **1**, wherein the heat-set offset printing ink comprises at least one low boiling solvent in an amount of from 1 to 5% by weight based on the printing ink composition.

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