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(54) Title: YELLOW PRINTING INK COMPOSITION WITH REDUCED TACK

(57) Abstract: The present invention relates to a reduced tack heat-set offset printing ink comprising at least one yellow pigment, petrolatum for reducing the tack, and a mixture of at least two solvents boiling in the range of from 200 to 270°C.

Yellow printing ink composition with reduced tack

The present invention relates to a yellow printing ink composition with reduced tack. Preferably the printing ink composition is formulated as heat-set offset printing ink.

According to preferred embodiments the present invention relates to a set of heat-set offset printing inks, wherein the tack of the yellow coloured printing ink has been reduced when compared to the further printing inks being present in the set. The term "yellow coloured printing ink" or "yellow printing ink" means to include a printing ink comprising a yellow pigment.

The present invention still further refers to a heat-set offset printing process, including but not limited to a heat-set web offset (HSWO) printing process making use of the yellow printing ink according to the invention with the reduced tack for reducing the back-trapping problem. According to preferred processes also fluting is considerably reduced.

The terms "reduced fluting, non-fluting or considerably less fluting" in the sense of this invention are used synonymously and are to be understood as reduction of the AFT value of the printed substrate, which includes but in not limited to a paper, is at least 30% smaller than the value of a respective printed paper comprising standard heat-set offset printing inks. The analytical method and apparatus applied for AFT value determination are described below. Preferably, the AFT value of the printed substrate is below 0.05%, more preferred even below 0.03%.

The expression "heat-set (web) offset printing" in the context of the present invention refers to a printing processes making use of fount solutions that are water-based.

In terms of the invention "reduced tack" with regard to the yellow printing ink is to be understood as a tack being at least 10% lower, preferably more than 15% lower and most preferred even 20% lower than the respective tack for the further printing inks (black, cyan, magenta) present in the set of printing inks.

One should note that also the black, cyan, magenta coloured printing inks described herein have a reduced tack when compared to heat set printing inks described in the art, for example, but not limited to printing inks described in EP 1 602 696.

The printing inks described herein are in particular suitable to be printed on substrates, including but not limited to paper, having a surface with a particular porosity. According to preferred embodiments a substrate with a porosity of the surface being below 0.07 ml/g, as determined by the mercury porosimetry method, and a substrate with a porosity of the surface being such that the Gurley-Hill air permeability value of the substrate is above 7000 s/100 ml are particular suited substrates.

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.

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.

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.

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.

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

According to the prior art, new paper products are suggested, as for example described in Jpn Tappi J., (2003) vol. 57, no. 1, Jan. 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.

Also, coatings capable of avoiding fluting are suggested in the art. In Tappi J., (2000) vol. 83, no. 4, Apr. 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.

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

During the 2002 (69th) Pulp and paper research conference, Tokyo, Japan, 17-18 June 2002 and in the respective report (P-06, pp 166-171 [Tokyo, Japan: Japan TAPPI, 2002, 186pp]) 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.

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

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

According to J. Pulp Pap. Sci., (Sept. 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.

US 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 HSWO 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. Experience with such devices, however, do not show the indicated advantages.

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.

US 5,713,990 and US 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 US 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 US 6,206,960 are as high as 149°C. US 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. US 5,427,615 introduces fatty acid ester solvents with high flash points, decomposing only at temperatures above 350°C.

US 4,357,164 disclose a printing ink comprising low boiling solvents. However, US 4,357,164 relates to a waterless lithographic printing process, which does not comprise the use of a fount solution, i.e. does not give rise to the fluting problem at all.

WO 2005/118728 discloses a printing ink formulation trying to avoid the fluting problem. However, the invention described in this document suffers the drawback of back-trapping.

The term back-trapping means that black printing ink is drawn into the container of the yellow printing ink, thus leading to an unclean printing result during heat-set offset printing. It is very time consuming to clean the printing press after back-trapping has occurred. Printing large green areas for "cleaning" is undesirable, time consuming and costly, too.

Ink compositions being formulated as heat-set offset printing ink compositions which still further have non-fluting properties are very difficult to compose. The printing ink vehicle and its evaporation properties have high impact on the fluting effect. As the printing ink vehicle is also a main factor as far as tack is concerned, it is difficult for the person skilled in the art to compose a heat-set offset printing ink composition that on the one hand has non-fluting properties and on the other hand is suited to solve the back-trapping problem.

Hence, there is a strong need for printing ink compositions formulated as heat-set offset printing inks that avoid the fluting problem and simultaneously reduce back-trapping.

The object of the invention is solved by the subject-matter as described in the patent claims.

It has now surprisingly been found that a particular yellow printing ink composition, preferably having non-fluting properties and having a reduced tack (if compared to the tacks of the remaining black, cyan and magenta colored printing

inks) is suited to reduce back-trapping during a heat-set offset printing process for producing a printed substrate.

The yellow printing ink with reduced tack comprises from 1.5% by weight to 6 % by weight, preferably from more than 1.5 % by weight up to less than 6 % by weight, based on the printing ink composition, petrolatum. More preferred 3% by weight to 5 % by weight, and most preferred 4 % by weight of petrolatum are present within the yellow printing ink, based on the ready-to-use printing ink.

In particular the present invention refers to a printing ink composition being formulated as heat-set offset printing ink with reduced tack comprising at least one yellow pigment, petrolatum for reducing the tack, and a mixture of at least two solvents boiling in the range of from 200 to 270°C. Preferably at least one solvent boils in the range of from 210 to 230°C and a further solvent boils in the range of from 240 to 270°C. According to preferred embodiments the printing ink composition according to the invention comprises a mixture of at least two solvents having different aromatic contents.

Within the printing ink composition according to the invention the yellow pigment is added in the form of a pigment paste.

According to preferred embodiments the printing ink composition according to the invention comprises at least one solvent with an aromatic content of 1% by weight, based on the solvent, and at least a second solvent having an aromatic content of 12% by weight, based on the solvent.

Preferably at least one solvent is a mineral oil solvent and can be present in amounts of at least 1% by weight of the printing ink composition.

Most preferred all solvents present in the printing ink composition are mineral oil solvents.

The printing ink composition according to the invention may comprise a varnish in an amount of from 15 to 30% by weight based on the ready-to-use printing ink composition. and the varnish may comprises at least one vegetable oil, being for example but not limited to stand oil.

The printing ink composition according to the invention may include a varnish comprising at least one self-structured resin, being for example but not limited a self-structured rosin resin with a viscosity of 30 Pas (35% in 6/9AR blend) and good compatibility. The varnish additionally may comprise 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).

According to the present invention the printing ink compositions being formulated as heat-set offset printing ink compositions with different colours than yellow fulfill the above mentioned criteria, however, are substantially free of petrolatum, i.e. have a higher tack than the yellow printing ink composition described herein. In terms of the invention "substantially free" is to be understood in such a manner that the respective compound has not been purposefully added to the composition.

The present invention also relates to a set of printing ink compositions wherein the tack of the yellow printing ink has been reduced as compared to the remaining printing inks. The set of printing ink compositions is formulated as heat-set offset printing inks.

The present invention also refers to the use of a yellow printing ink composition as defined herein in a heat-set offset printing process together with further printing inks having higher tack than the yellow printing ink for avoiding back trapping. The further printing inks are either black, cyan of magenta colored and are substantially free of petrolatum.

With the use described herein it is possible to achieve AFT value of a resulting printed substrate, including a printed paper, of below 0.05%.

Said AFT value is measured on a piece of printed substrate in the dimensions of 27cm x 5cm at standard conditions with an AFT-meter.

The invention also is directed to a heat-set offset printing process comprising applying to a substrate a set of printing inks comprising a yellow printing ink with reduced tack as defined above for reducing back trapping. According to the process furthermore an AFT value of the printed substrate of below 0.05% can be achieved.

According to the process described herein the web temperatures in the last zone of the heat-set dryer are between 85°C and 120°C.

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.

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).

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."

One definition mentioned in the ASTM standard for tack measurement D 4361-97: is "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."

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.

Fig. 3 shows a schematic drawing of a three-roller-tackmeter.

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.

Operation principle of tack measurement instruments:

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.

Additionally, the present invention refers to the use of petrolatum for lowering the tack of yellow printing ink composition being useful within a set of heat-set offset printing inks.

The mineral oil solvents used in this invention are characterized by their boiling ranges, their aromatic contents and their aniline points. The boiling or distillation range [in °C] is determined by distillation according to DIN ISO 3405 or ASTM D86. 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

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).

The standard test procedure to test the cloudpoint of natural or synthetic resins for the production of printing inks is as follows: Two grams of resin and 18 grams of test oil are weighted into a glass test tube into which a magnetic stirrer rod has been inserted. Under controlled heating and stirring conditions the sample is completely dissolved in the test oil. This clear and homogeneous solution is then cooled down until the cloudpoint temperature is reached. At the end of the test the measured value is printed on paper with a test report by an integrated data printer. CP = cloud point (the lower, the better soluble).

The aromatic content of the first mineral oil is preferably 1% and the aromatic content of the second mineral oil is preferably 12%.

The present invention also describes printing ink compositions comprising varnishes that allow for superior printing performance as far as fluting and tack are concerned. An example for a varnish is called 7131.

The mixture of both mineral oils present in the described varnishes has an aromatic content of preferably 6% to 10%, more preferably 7% to 9% and most preferably of 8% by weight.

The varnishes further comprise vegetable oil, preferably stand oil.

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

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.

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.

The printing ink compositions comprise pigment pastes 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.

Varnishes are present within the non-fluting heat-set printing ink composition described herein in amounts of between 15% and 50% preferably in an amount of from 15% to 30% by weight of the printing ink composition.

Preparation Example (Varnish "7131"):

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 (25mm diameter) and a plate at 23°C. The gap between cone and plate must be 0.05mm. The viscosity is measured at a shear rate of $25s^{-1}$.

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 6/9*) 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.

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

Preparation Example 2:

Description of "1/3 varnish":

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

The "1/3 varnish" comprises a mineral oil with a very low boiling range: 210 to 230°C (aromatic content <1%), vegetable oil (wood oil) and a plasticizer (Di-Acid-di-Ester). 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 6/9*) and gel reactivity. The varnish is gelled with an aluminium chelate complex.

The resins are diluted in solvent and additives, heated to 160°C and stirred for 30 min. Then the gelling agent (diluted in 3.8% of the 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.

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

	„1/3 varnish"	
Component		wt. %
Mineral oil C	Bp 210-240°C, C_{ar} < 1%, AP = 84°C	33.8
Vegetable oil	Wood oil	5.0
Plasticizer	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	Polymeric aluminum chelate complex	0.9
Antioxidant	MTBHQ solution	1.5

Example 1:

Ink Series 16001 is based on "1/3 varnish" and varnish 7131.

The printing ink composition comprises pigment paste (pigment level 30%). Mineral oil solvents with low boiling range (Boiling point (bp) = 210-230°C, Aromatic content (C_{ar}) < 1%, Aniline Point (AP) = 84°C) were chosen for improved drying. Mineral oil solvents with high boiling range (bp = 280-310°C, C_{ar} = 12%, AP = 82°C) were chosen for improved roller stability. A high pigment level allows

thin printing ink films on the printing press which speeds up drying. For improved rub resistance and good slip of the paper sheets PTFE wax paste was used. In order to avoid back-trapping problems, the tack of the yellow printing ink was reduced by using petrolatum.

Composition of printing ink Series 16001:

Component	**Yellow**	**Magenta**	**Cyan**	**Black**
Yellow pigment paste	38	-	-	-
Magenta pigment paste	-	40	-	-
Cyan pigment paste	-	-	39	-
Black pigment paste	-	-	-	45
Toner paste	0.6	-	-	-
Varnish 7131	20	11	15	17
1/3 varnish	18	11	13	15
Extender paste	10	10	10	10
Petrolatum	2	-	-	2
PTFE wax paste	2	2	2	2
Antioxidant solution	1	1	1	1
Mineral oil B	3.4	14	4.5	6
Mineral oil C	5	2	4.5	1
Total (wt. %)	100.0	100.0	100.0	100.0

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

Example 2:

Ink Series 16004 is based on "1/3 varnish" and varnish "7131".

The printing ink composition comprises pigment paste (pigment level 30%). Mineral oil solvents with low boiling range (210-230°C) were chosen for improved drying. Mineral oil solvents with medium boiling range (240-270°C) were chosen. A high pigment level allows thin printing ink films on printing press which speeds up drying. For improved rub resistance and good slip of the paper sheets PTFE wax paste was used. In order to solve the back-trapping problem, the tack of the yellow printing ink was reduced by using petrolatum.

Composition of printing ink Series 16004:

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	5	5	5	5
Petrolatum	4			
Varnish 7131	29	17	20	25.5
1/3 varnish	10	14	18	15.5

PTFE wax paste	2	2	2	2
Antioxidant solution	1	1	1	1
Mineral oil B	5.9	11	11	6
Mineral oil C	4.5	5	4	-
Total (wt. %)	100.0	100.0	100.0	100.0

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

Analytical method for the determination of AFT values

The above-mentioned varnishes, printing ink compositions and the described process are suited to obtain printed paper that shows significantly less fluting when compared to printed paper comprising standard heat-set offset printing inks. The non-fluting heat-set offset printing ink compositions, varnishes and the respective process are capable of reducing the fluting phenomenon by at least 30% when measured according to the below described analytical method.

Figure 1 illustrates principle of AFT measurement. Figure 2 shows an apparatus for AFT measurement.

The AFT device as shown in Figure 2 is used by insertion of a sample of printed substrate 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 paper is stretched until it becomes totally flat, i.e. when the shadow pattern caused by fluting has disappeared. The elongation of the strip by stretching is measured and is the length B – length A. The AFT value is the elongation in mm divided by 250 mm (length of the initial sample between the clamps into stretching direction) expressed in percent. For this method the following further parameter were set:

Sample preparation for AFT measurement:

- printed paper was obtained by HSWO printing
- Fluting was measured on a green area printed on both sides.
- Yellow optical density was 1.2 and cyan optical density was1.5 in the printed green area.
- Dimension of printed green area are 20 cm * 20 cm (MD * CD)[1]. The printed area was surrounded by unprinted white paper.
- 27 cm * 5 cm (CD*MD)[1] sample is cut over the printed green area.

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

Typical AFT values of commercial heat-set offset printed papers are 0.07-0.11 % (see comparative example). 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%.

Claims

1. A reduced tack heat-set offset printing ink comprising at least one yellow pigment, petrolatum for reducing the tack, and a mixture of at least two solvents boiling in the range of from 200 to 270°C.

2. The printing ink composition according to claim 1, wherein at least one solvent boils in the range of from 210 to 230°C.

3. The printing ink composition according to claim 1 or 2, wherein at least one solvent boils in the range of from 240 to 270°C.

4. The printing ink composition according to one or more of the preceding claims, comprising petrolatum in an amount of from more than 1.5 % by weight based on the ready-to-use printing ink composition.

5. The printing ink composition according to one or more of the preceding claims, comprising petrolatum in an amount of up to 6 % by weight based on the ready-to-use printing ink composition.

6. The printing ink composition according to one or more of the preceding claims, comprising petrolatum in an amount of from more than 1.5 % by weight based on the ready-to-use printing ink composition and up to less than 6 % by weight based on the ready-to-use printing ink composition.

7. The printing ink composition according to one or more of the preceding claims, wherein the mixture of the at least two solvents comprise solvents having different aromatic contents.

8. The printing ink composition according to one or more of the preceding claims, wherein the yellow pigment is added in the form of a pigment paste.

9. The printing ink composition according to one or more of the preceding claims, wherein at least one solvent has an aromatic content of 1% by weight, based on the solvent, and at least a second solvent has an aromatic content of 12% by weight, based on the solvent.

10. The printing ink composition according to one or more of the preceding claims, wherein at least one solvent is a mineral oil solvent.

11. The printing ink composition according to one or more of the preceding claims, wherein the solvent is present in amounts of at least 1% by weight of the printing ink composition.

12. The printing ink composition according to one or more of the preceding claims, wherein all solvents present in the printing ink composition are mineral oil solvents.

13. The printing ink composition according to one or more of the preceding claims further comprising a varnish in an amount of from 15 to 30% by weight based on the ready-to-use printing ink composition.

14. The printing ink composition according to claim 13, wherein the varnish comprises at least one vegetable oil.

15. The printing ink composition according to claim 14, wherein the vegetable oil comprises stand oil.

16. The printing ink composition according to one or more of claims 13 to 15, wherein the varnish comprises at least one self-structured resin.

17. The printing ink composition according to one or more of claims 13 to 16, wherein the varnish comprises at least one self-structured rosin resin with a viscosity of 30 Pas (35% in 6/9AR blend) and good compatibility.

18. The printing ink composition according to one or more of claims 13 to 17, wherein the varnish additionally comprises 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).

19. A heat-set offset set of printing inks wherein the tack of the yellow printing ink in the set has been reduced as compared to the remaining printing inks in the set.

20. The set of printing ink compositions according to claim 19 being formulated as heat-set offset printing inks.

21. Use of a reduced tack yellow printing ink composition as defined in one or more of the preceding claims as part of a set of heat-set offset printing inks for avoiding back trapping on a printed substrate during printing.

22. Use according to claim 21, wherein the non-yellow printing inks in the set are either black, cyan or magenta colored and are substantially free of petrolatum.

23. Use according to claims 21 or 22 for achieving an AFT value of the resulting printed substrate of below 0.05%.

24. A heat-set offset printing process having reduced back trapping on a printed substrate comprising applying to a substrate a set of heat-set offset printing inks comprised of a yellow printing ink of reduced tack as defined in one or more of the preceding claims.

25. The process according to claim 24, for achieving an AFT value of the resulting printed substrate of below 0.05%.

26. The process according to claims 24 or 25, wherein the web temperatures in the last zone of the heat-set dryer of the printing process are between 85°C and 120°C.

27. A heat-set offset printing process having reduced back trapping on a printed substrate comprising applying to a substrate selected from a substrate with a porosity of the surface being below 0.07 ml/g as determined by the mercury porosimetry method and a substrate with a porosity of the surface being such that the Gurley-Hill air permeability value of the substrate is above 7000 s/100 ml a set of heat-set offset printing inks comprised of a yellow printing ink of reduced tack and containing at least two solvents boiling in the range of from 200 to 270°C.

28. The process according to claim 27, for achieving an AFT value of the resulting printed substrate of below 0.05%.

29. The process according to claims 27 or 28, wherein the web temperatures in the last zone of the heat-set dryer of the printing process are between 85°C and 120°C.

30. 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%.

31. The method according to claim 30, wherein the substrate is selected from a substrate with a porosity of the surface being below 0.07 ml/g as determined by the mercury porosimetry method or from a substrate with a porosity of the surface being such that the Gurley-Hill air permeability value of the substrate is above 7000 s/100 ml.

32. 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.

33. The method according to claim 32, wherein the substrate is selected from a substrate with a porosity of the surface being below 0.07 ml/g as determined by the mercury porosimetry method or from a substrate with a porosity of

the surface being such that the Gurley-Hill air permeability value of the substrate is above 7000 s/100 ml.

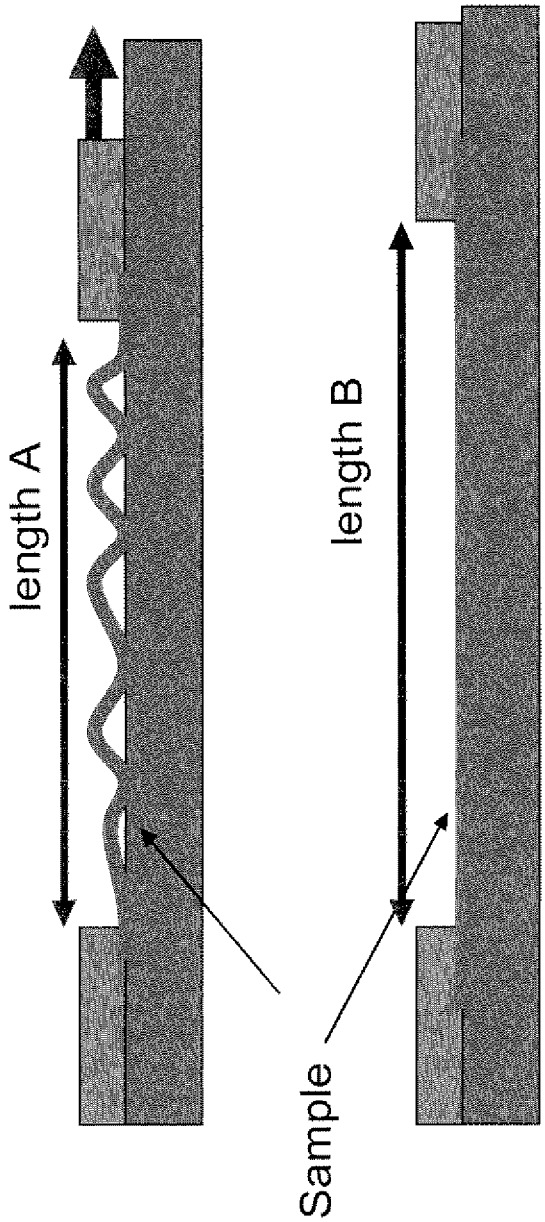

Fig. 1

The Idea of AFT Measurement

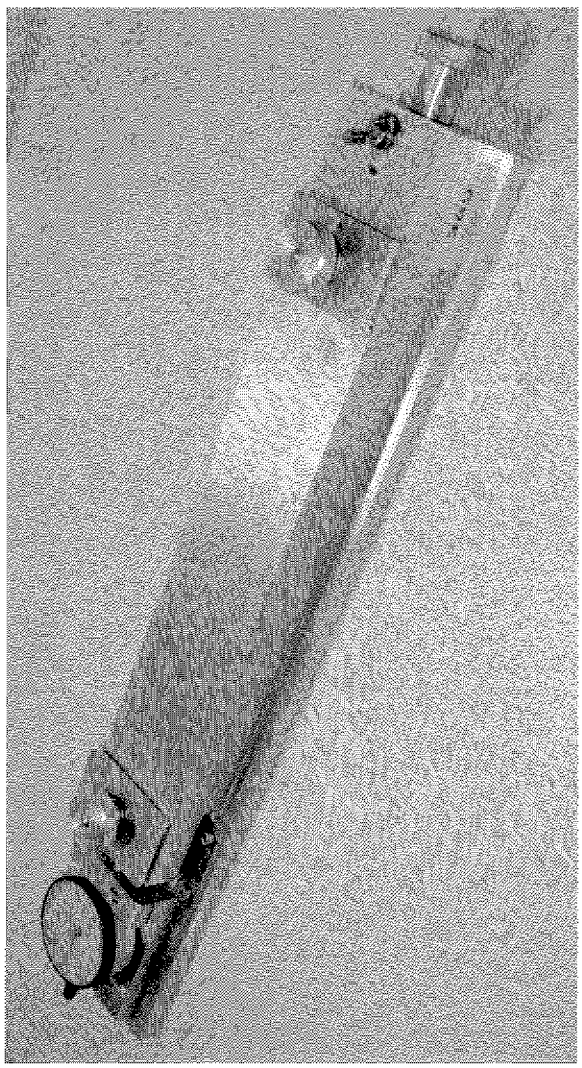

Fig. 2

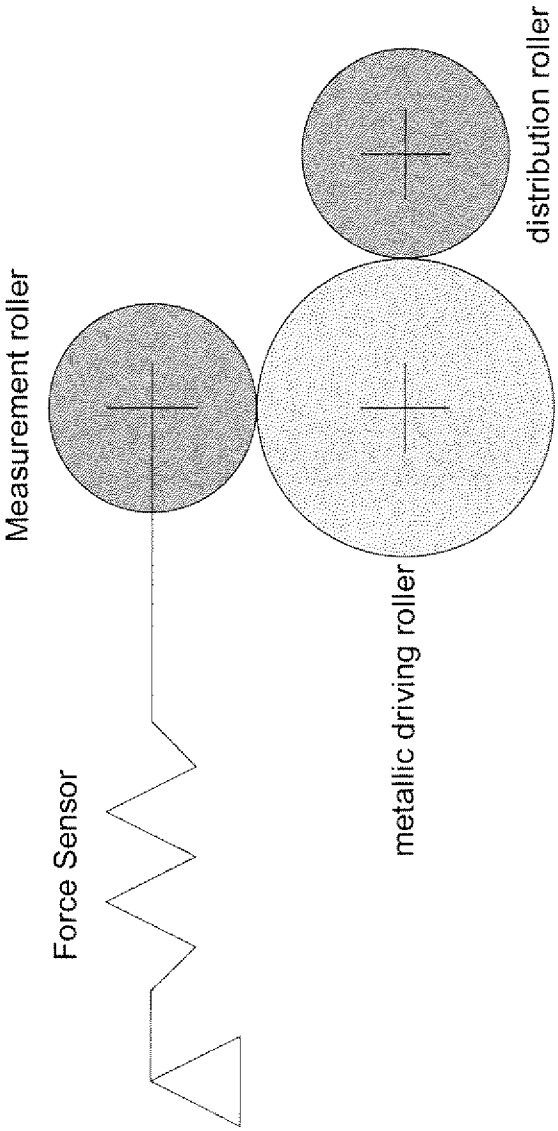
Measurement roller
distribution roller
Force Sensor
metallic driving roller

Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/055121

A. CLASSIFICATION OF SUBJECT MATTER
INV. B41F23/00 B41F23/04 C09D11/02 C09D11/06 C09D11/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B41F C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2005/191469 A1 (ANTTILA MIKA [FI] ET AL) 1 September 2005 (2005-09-01)	31,33
A	paragraphs [0026] - [0028], [0034], [0180], [0189] - [0193]; claims 1-18; example 1; tables 1,3	31,33
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Y	EP 0 633 299 A (MERCK PATENT GMBH [DE]) 11 January 1995 (1995-01-11)	13-18
Y	example 6	13-18

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 September 2008	26/09/2008

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Feldmann, Gabriele

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/055121

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 445 671 A (HERGET GERHARD [DE] ET AL) 29 August 1995 (1995-08-29)	13-18
Y	example 6	13-18
Y	WO 98/30597 A (ARIZONA CHEM [US]) 16 July 1998 (1998-07-16)	13-18
Y	page 10, lines 13-28; claims 1-32; examples 1,2,5,7,8; tables 5,6 page 8, line 20 - page 9, line 9	13-18
A	page 19, lines 15-25	1-24
A	WO 2005/113694 A (NOVEON IP HOLDINGS CORP [US]; MULLAY JOHN J [US]; LARSEN JOHN H [US];) 1 December 2005 (2005-12-01)	1-33
A	paragraph [0046]	1-33

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2008/055121

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [X] Claims Nos.: 19-29
because they relate to subject matter not required to be searched by this Authority, namely:

A non specified use of a substrate and a printing ink is claimed. Therefore, the requirements of Art. 6 PCT are not fulfilled.

2. [X] Claims Nos.: 33-39
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

see FURTHER INFORMATION sheet PCT/ISA/210

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. [ ] As all required additional search fees were timely paid by the applicant, this international search report covers allsearchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this international search reportcovers only those claims for which fees were paid, specifically claims Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

[ ] The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

[ ] No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.1

Claims Nos.: 19-29

A non specified use of a substrate and a printing ink is claimed. Therefore, the requirements of Art. 6 PCT are not fulfilled.

Continuation of Box II.2

Claims Nos.: 33-39

A non specified use of a substrate and a printing ink is claimed. Therefore, the requirements of Art. 6 PCT are not fulfilled.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2)PCT declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2008/055121

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