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(54) **Process for the preparation of polymer laminated base paper and polymer laminated photographic base paper obtainable by said process**

(57) The invention is directed to a process for the preparation of polymer laminated base paper, said process comprising laminating a base paper web on at least

one side thereof with at least one polymer layer by extrusion-coating at a coating speed of 300 m/min or more, wherein the said base paper web is heated prior to laminating.

Description

[0001] The invention is directed to the preparation of polymer laminated base paper and more in particular to the preparation of polymer laminated photographic base paper.

[0002] Polymer laminated base paper for photographic printing paper is conventionally prepared from a base paper that is laminated with at least one polymer resin layer, usually a titanium dioxide filled polyethylene, polypropylene or a polymethylene-methacrylate resin, by extrusion-coating (or co-extrusion-coating) of a polymer melt onto the surface of the base paper.

[0003] In JP-A 57-102622 a process is described for the extrusion-coating of a base paper with polyethylene, in which process the base paper is subjected to a corona treatment, followed by heating to a temperature of at least 80°C. This process aims at improving the adhesion between base paper and polymer coating.

[0004] An important aspect of the quality of polymer resin laminated base paper is the resin surface appearance, which should not have a large number of crater-like defects (or pits) after extrusion-coating of the polymer resin on the base paper.

[0005] Further important aspects of photographic base paper are the speed of production and the thickness of the polymer layers. Both aspects are important in view of the economy of the process of producing photographic print paper. The formation of pits has turned out to be strongly dependent on those aspects.

[0006] It has been attempted to suppress the number of pits by increasing the thickness of the polymer resin layer. At high extrusion-coating speeds, such as over 300 m/min this is not sufficiently effective, unless very large amounts of polymer are used. Furthermore, it has economical disadvantages as the polymer resin is an important cost factor in the production of photographic print paper.

[0007] At extrusion-coating speeds of the polymer resin of 300 m/min or more it has been found to be much more difficult to reduce the number of pits.

[0008] In the art of providing polymer laminated photographic base paper there is a need for high speed production, especially during the extrusion-coating of the paper with the polymer resin, whereby the amount of pits remains at a sufficiently low value.

[0009] Accordingly it is an object of the present invention to provide a process for the preparation of a polymer laminated base paper, more in particular a polymer laminated photographic base paper, wherein the number of pits is decreased, especially at higher extrusion-coating speeds.

[0010] It is a further object of the invention to provide a process for the preparation of a polymer laminated base paper, more in particular a polymer laminated photographic base paper, wherein the number of pits is decreased, at higher extrusion-coating speeds, without the need to increase the polymer weight.

[0011] The present invention is based thereon, that the coated paper shows less pits in case the base paper web is heated, preferably by infrared radiation, prior to the extrusion-coating with the polymer resin.

[0012] Accordingly the present invention is directed to a process for the preparation of polymer laminated base paper, said process comprising laminating a base paper web on at least one side thereof with at least one polymer layer, by extrusion-coating at a coating speed of 300 m/min or more, wherein the said base paper web is heated prior to laminating.

[0013] Surprisingly it has been found that with this process the number of pits can be reduced, even at high extrusion-coating speeds, such as extrusion-coating speeds in excess of 300m/min. The advantages of the invention become apparent already at extrusion speeds of 300 m/min or over. It is preferred to use a speed of at least 350 m/min, more in particular at least 400 m/min. Presently an upper limit of 700 m/min is considered acceptable.

[0014] In the broadest sense the present invention resides therein that the paper web is heated just prior to the (co-) extrusion-coating. This heating can be done by the application of heated air, heated rollers and/or by radiation. More in particular, preference is given to the use of radiation in the Near Infra Red (NIR) region. In particular, it is to be noted that the NIR radiation can be emitted at radiation temperatures of over 2500 K, preferably over 2900 K, most preferred over 3000 K. Generally, the upper limit for the emission temperature is 3500 K.

[0015] It has been found that surprisingly the use of NIR radiation provides good results in terms of product properties. Further, it has been found that in terms of heating rate the use of NIR has advantages.

[0016] The advantages of the treatment of the web by infra-red radiation, with wavelength ranges between 0.8 µm and 1 mm, results in the increase of the web temperature in an extremely short treatment period, usually less than 1 second. With the use of conventional heating technologies this is less easy to achieve. The fastest temperature increase can be realised with NIR radiation of a wavelength between 0.8 and 1.5 µm. Advantages of this method are that it is contactless, eliminating the risk of mechanical damage as in case of the use of heated rollers and is highly flexible as the heating power can continuously and immediately be adapted to process needs, such as varying laminating speed, with temperature controlling devices which control the surface temperature.

[0017] In the heating step prior to the extrusion-coating the temperature of the paper is preferably raised to a value of at least 30°C, preferably to a value between 30 and 125°C. More in particular the upper limit of the temperature of

the web is 90°C. In case energy consumption is a consideration, the temperature may be kept at a value of less than 80°C without negative effects.

[0018] The extrusion-coating can be done with one layer of polymer or with a combination of polymer layers by co-extrusion. The paper web can be coated on one side or on both sides, the latter embodiment having preference. The polymers to be used for the extrusion-coating are the conventional polymers used in paper coating, more in particular in the preparation of photographic base paper. Examples are polyolefins, polyacrylates or polyesters. More in particular, the coating is done using low-density polyethylene, high density polyethylene and blends thereof. The amount of polymer coating depends on the required properties of the laminated base paper, such as stiffness, gloss, number of pits and the like. More in particular the amount is preferably not more than 50 g/m², more preferably between 25 and 50 g/m².

[0019] The heating step can be incorporated in an extrusion-coating line for paper. It is to be noted that in case of the use of more than one layer of polymer resin it is possible to use co-extrusion. The term 'extrusion' is therefor intended to include also co-extrusion.

[0020] In the extrusion line also other treatments of the paper web can be used such as corona treatment, ozone treatment, flame-treatment and plasma treatment, which treatments all aim at improving the adhesion of the polymer melt to the base paper web.

[0021] The invention is now elucidated on the basis of the attached figure. In this figure an extrusion-coating line has been shown. The base-paper web is fed, via a number of rollers, past a corona treatment, via the nip-roll to the nip-zone. The polymer melt and the base paper web come together in the nip. The polymer melt is then cooled on the chill-roll and is released from the chill-roll at the release-roll, from where it is transported further.

[0022] Between the corona treatment and the nip-roll, NIR radiation equipment is installed. In order to get a very good efficiency, the infra-red radiation is provided from one side and a radiation mirror is provided on the other side. It is also possible to install the NIR-radiation equipment before the corona treatment.

[0023] It is to be noted that the present figure shows lamination on only one side of the paper web. In case lamination on both sides has to be provided, the partly laminated paper web can be laminated on the other side in a comparable co-extrusion line. It is also possible to include a second extruder and, if necessary, suitable radiation equipment in this line.

[0024] The invention is now elucidated on the basis of the Example.

Example

[0025] Two paper substrates were used for testing. These substrates, or base papers, represent a range of base paper qualities as can be found in the market. Paper substrate '1' represents a good quality in relation to the number of pits. Paper substrate '2' represents a lower quality.

[0026] The web width of the substrates was 47 cm. The substrates were first extrusion coated with 21.0 g/m² transparent polyolefin resin film on the backside at a line speed of 200 m/min.

[0027] Before extrusion-coating of the topside, the substrate was pretreated with corona and subsequently preheated with NIR radiation up to a temperature of 39°C or 83°C. The treating width of the NIR-equipment covered 24 cm in the centre of the total web width of 47 cm. For the pretreatment two NIR-units were used. After the online pretreatments (Corona and preheating) the substrate was extrusion coated at the topside with a polyolefin resin LDPE of 28 g/m² (containing metaloxide, dyes, coloured pigments, optical brighteners and the like) at a speed of 400 m/min. The hotmelt (temperature 326°C) was nipped (pressure 6 bar) between the substrate and a cooling chill-roll. Because of the NIR-pretreatment the crater like defects or so-called pits defects decreased in comparison to the samples which received no heat pretreatment (remaining at room temperature). The NIR-pretreatment shows no disadvantage in the number of releasing defects, when the extrusion coated web releases from the cooling chill-roll.

[0028] The following test results are obtained which shows the effectivity of the heat pretreatment in order to reduce the number of pits defects:

	Paper type 1		Paper type 2		
	Number of pits per 4mm ²		Number of pits per 4mm ²		
	(800-1200 μm^2)	(>1200 μm^2)	(800-1200 μm^2)	(>1200 μm^2)	
5	No NIR treatment(23°C)	9.3	2.3	22.3	9.3
10	NIR treatment (39°C)	1.7	0.3	14.3	5.0
15	NIR treatment (83°C)	2.0	1.3	9.7	1.3

20 In the example the following methods were used to determine the various parameters:

Pits: Olympus microscope; measure area of 4 mm²

Web temperature: Minolta Land temperature meter.

25 [0029] These results show that for the lower quality base paper type, a significant reduction of the number of pits can be realised, even at temperatures as high as 83°C. With a good quality of base paper also a significant reduction of the number of pits is realised.

30 Claims

1. Process for the preparation of polymer laminated base paper, said process comprising laminating a base paper web on at least one side thereof with at least one polymer layer by extrusion-coating at a coating speed of 300 m/min or more, wherein the said base paper web is heated prior to laminating.
2. Process according to claim 1, wherein the coating speed is at least 350, preferably at least 400 m/min, more in particular not more than 700 m/min.
3. Process according to claim 1 or 2, wherein the said heating is done by use of heated air, heated roller(s) and/or radiation.
4. Process according to claim 3, wherein the said radiation is near-infrared radiation.
5. Process according to claim 4, wherein the said infrared radiation is emitted at temperatures of over 2500 K.
6. Process according to claims 1-5, wherein the base paper web is extrusion-coated on both sides.
7. Process according to claims 1-6, wherein the said polymer is a polyolefin, a polyacrylate or a polyester.
8. Process according to claims 1-7, wherein the said base paper web is preheated to a temperature of between 30 and 125°C.
9. Process according to claim 8, wherein the temperature is not more than 90°C.
- 55 10. Process according to claims 1-9, wherein the base paper web is subjected to one or more additional other treatments, prior to extrusion-coating.
11. Process according to claim 10, wherein the said other treatment comprises at least one of corona treatment, ozone

treatment, flame treatment and plasma treatment.

12. Process according to claims 1-11, wherein the laminated base paper is a polymer laminated photographic base paper.

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13. Process according to claim 12, wherein the polymer laminated photographic base paper is provided with at least one layer of a photographic emulsion.

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14. Process according to claim 13, wherein the polymer laminated photographic base paper is provided with at least one layer of a gelatin sublayer between the polymer coating and the photographic emulsion.

15. Polymer laminated photographic base paper or print paper obtainable by the process of claims 12-14.

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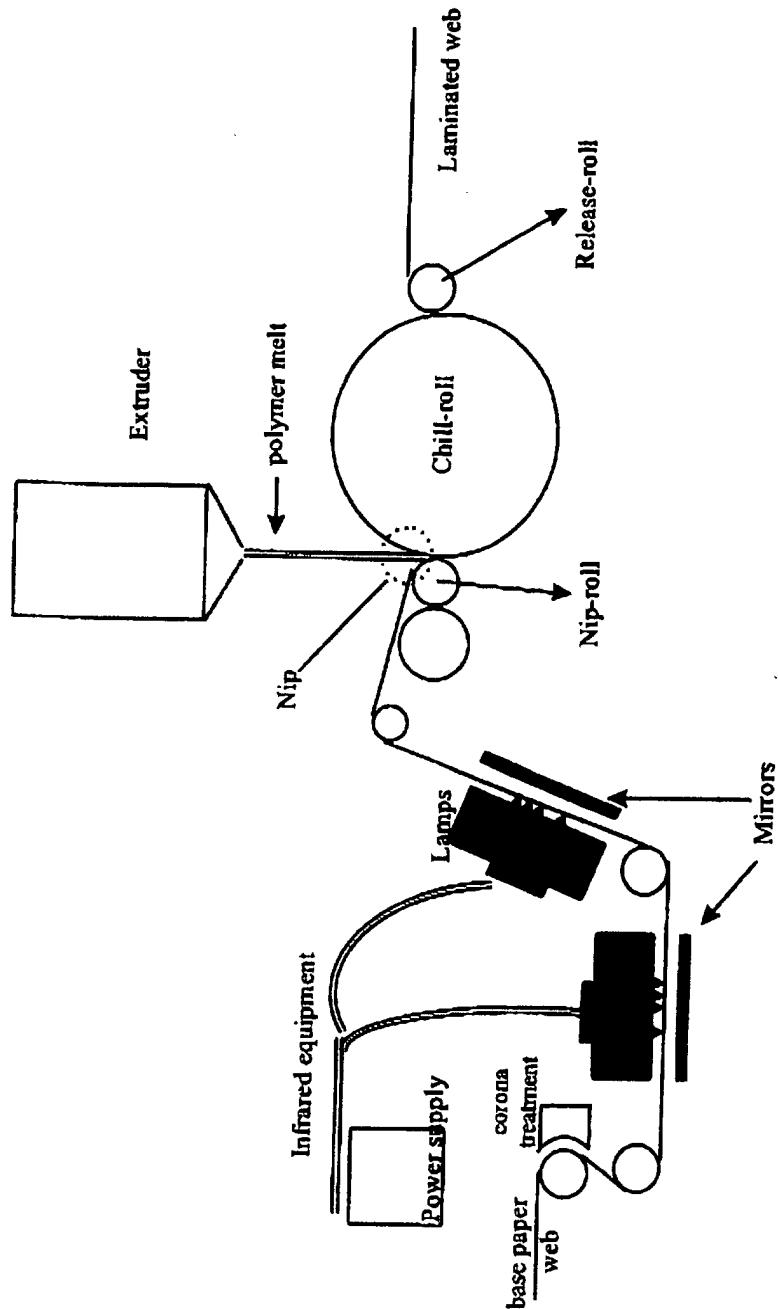
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D, Y	JP 57 102622 A (MITSUBISHI) 25 June 1982 (1982-06-25) * page 2, right-hand column, line 11 – line 16 * * page 2, right-hand column, line 35 – line 38 * * page 3, right-hand column, line 30 – line 39 * * page 4, left-hand column, line 4 – line 15; claims 1,4 *	1-15	G03C1/79 D21H23/30 D21H23/46
Y	EP 0 704 753 A (KODAK) 3 April 1996 (1996-04-03) * page 2, line 13 – line 16 * * page 2, line 30 – line 31 * * page 4, line 51 – line 52 * * page 6, line 16 – line 30 *	1-15	
Y	US 6 030 742 A (BOURDELAIS ET AL.) 29 February 2000 (2000-02-29) * column 1, line 19 – line 22 * * column 4, line 54 – line 61 * * column 14, line 25 – line 28 * * column 14, line 57 – line 67 *	1-15	
Y	EP 0 952 483 A (FUJI) 27 October 1999 (1999-10-27) * page 2, line 11 – line 32 * * page 4, line 29 – line 40; claim 24 *	1-15	
Y	EP 0 573 753 A (FELIX SCHÖLLER) 15 December 1993 (1993-12-15) * page 2, line 2 – line 6 * * page 3, line 1 – line 3 * * page 5, line 1 – line 57; claims 1,2,7 *	6	
		-/-	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search		Examiner
THE HAGUE	22 March 2001		Magrizos, S
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
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EUROPEAN SEARCH REPORT

Application Number
EP 01 20 0764

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Y	DE 198 21 446 A (VOITH SULZER) 18 November 1999 (1999-11-18) * column 3, line 5 - line 31; claims 1,3; figure 1 *	6	
Y	US 5 182 161 A (NODA ET AL.) 26 January 1993 (1993-01-26) * column 8, line 33 - line 38 * * column 9, line 40 - line 45 * * column 10, line 11 - line 18 * * column 12, line 51 - line 55 *	14	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)			

<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search		Examiner
THE HAGUE	22 March 2001		Magrizos, S
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 20 0764

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

22-03-2001

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
JP 57102622	A	25-06-1982		JP 1024291 B JP 1622861 C	11-05-1989 25-10-1991
EP 704753	A	03-04-1996		US 5503968 A DE 69501609 D DE 69501609 T JP 8190171 A	02-04-1996 19-03-1998 17-09-1998 23-07-1996
US 6030742	A	29-02-2000		CN 1257222 A EP 1004932 A JP 2000162734 A	21-06-2000 31-05-2000 16-06-2000
EP 952483	A	27-10-1999		JP 11338105 A	10-12-1999
EP 573753	A	15-12-1993		DE 4219194 C JP 6208197 A US 5455073 A	16-12-1993 26-07-1994 03-10-1995
DE 19821446	A	18-11-1999		NONE	
US 5182161	A	26-01-1993		JP 2899078 B JP 4069648 A JP 2871817 B JP 4080743 A	02-06-1999 04-03-1992 17-03-1999 13-03-1992