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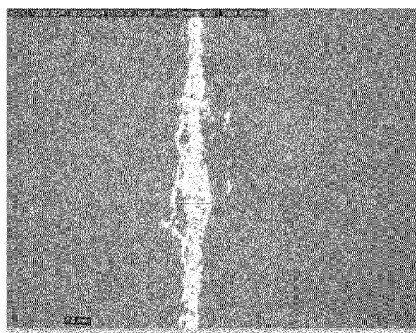
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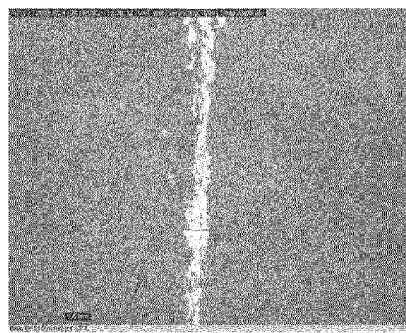
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(54) Title: TONER COMPOSITION



(A)



(B)

Fig. 3

(57) Abstract: The present invention relates to a colored toner composition that shows improved fusing behavior. The toner composition comprises a small amount of iron oxide. The invention further relates to the use of between 0.1 and 4 wt% of iron oxide in a colored toner composition for said purpose.



TONER COMPOSITION

5 FIELD OF THE INVENTION

The present invention relates to a toner composition, in particular to a colored toner composition.

BACKGROUND ART

10 Toner powders for (photo) electrographic printing have been known for a long time in the art. It is also known from the prior art to use iron oxide in black toner compositions, in order to provide (electrically) conductive properties to the toner compositions.

In US 2012/0270146 a magnetic toner composition comprising spherical barium iron oxide particles are disclosed. In EP2592478 a black toner composition comprising iron
15 oxide as a magnetic pigment is disclosed. EP1178360 discloses dry a toner for electrophotography comprising colored resin particles. In general iron oxide is not used in colored toner compositions (e.g. cyan, magenta, yellow, red, green, blue, etc), because iron oxide has a negative influence on the color of such toner compositions.

20 It is known in the art that once a toner image has been formed on a printing substrate (e.g. paper), the image needs to be fixated to the printing substrate. This step is also termed fusing. After fusing the toner has been immobilized and fixated to the printing substrate and the image shows certain robustness (i.e. resistance to removal of the toner image from the printing substrate). For example, if a printed image is folded,
25 forces are exerted to the toner image and the image may partly separate from the substrate. The larger the part of the image that separates, the lower the robustness is.

It is seen in the art that, in particular in the case of colored toner compositions, there is room for improvement of the fusing properties of a toner composition in order to enable
30 to produce prints with improved robustness characteristics.

It is therefore an object of the present invention to provide a colored toner composition having improved fusing properties that enable the production of prints with improved robustness.

SUMMARY OF THE INVENTION

The object is at least in part achieved by providing a colored toner composition comprising:

- a resin;
- 5 • a colorant;
- iron oxide in an amount of between 0.1 wt% and 4 wt% relative to the total toner composition.

It is stated that in the context of the present invention the colorant does not include iron oxide and that the iron oxide is present in addition to a colorant.

Therefore the present invention relates to a colored toner composition comprising:

- a resin;
- a colorant, with the proviso that iron oxide is excluded as a colorant;
- 15 • iron oxide in an amount of between 0.1 wt% and 4 wt% relative to the total toner composition.

Inventors have surprisingly found that by adding a small amount of iron oxide to a colored toner composition, the robustness of the prints produced with that toner can be significantly improved.

Using iron oxide in a colored toner composition is not an obvious choice, because iron oxide also significantly influences the color of the toner. Therefore, the amount of iron oxide in a toner composition according to the present invention should be small, but large enough to obtain the intended robustness improvement effect.

In an embodiment, the iron oxide is present in an amount of between 0.2 wt% and 2 wt%, preferably between 0.25 wt% and 1 wt%, more preferably between 0.3 wt% and 0.6 wt%.

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In an embodiment, the colorant is a pigment.

In an embodiment, the colorant is a mixture comprising at least one pigment

35 In an embodiment, the colorant is a mixture comprising at least one pigment and at least

one dye.

In an embodiment, the resin is a polyester resin.

- 5 In an embodiment, the toner composition comprises a mixture of resins, preferably a mixture of polyester resins.

In an embodiment, the toner composition further comprises at least one component selected from a wax, a flow additive, a charging agent, a coating and a whitener.

- 10 In another aspect the present invention relates to the use of between 0.1 wt% and 4 wt%, preferably between 0.2 wt% and 2 wt%, more preferably between 0.25 wt% and 1 wt%, and even more preferably between 0.3 wt% and 0.6 wt% of iron oxide in a (colored) toner composition for improving robustness properties of a printed object comprising such toner.

- 15 The above disclosed preferred concentration ranges also apply to this particular use.

In an embodiment, the robustness properties are represented by a folding resistance wherein a printed full density area of a print sample is folded in a standardized manner, e.g. by using a Kirchner roll and the folding resistance is calculated with equation 1

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$$\text{Alpha} = \frac{1 - 10^{-\text{ODKfold}}}{1 - 10^{-\text{ODKref}}} \quad \text{Equation 1.}$$

wherein:

Alpha [-] is a measure for folding resistance;

- 25 ODKfold is the optical density of an unfolded part of the full density area;

OKDref is the optical density of a folded part of the full density area.

In an embodiment, Alpha is above 0.92, preferably above 0.95.

- 30 BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will become more fully understood from the detailed description given herein below and accompanying schematical drawings which are given by way of illustration only and are not limitative of the invention, and wherein:

Fig. 1 shows a print medium and a print zone in the middle of the print medium and two print zones located at the edges of the print medium (the frame)

Fig. 2 shows a schematic presentation of the Kirchner roll, the folding apparatus used in the experiments.

Fig. 3 shows pictures of folded prints made with A) a toner according to the prior art (no iron oxide) and B) a toner according to the present invention, comprising a small amount of iron oxide.

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DETAILED DESCRIPTION

Toner composition

The toner composition according to the present invention comprises at least a (binder) resin, a colorant (pigment and/or dye) and iron oxide.

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Binder resins

The binder resins used in a toner in accordance with the present invention are not limited to any kind. The toner comprises at least one binder resin, for example a thermoplastic polymer or a pressure-sensitive polymer. Common binder resins are styrene polymers, styrene copolymers such as styrene acrylates, styrene-butadiene copolymers and styrene maleic acid copolymers, cellulose resins, polyamides, polyethylenes, polypropylenes, polyesters, polyurethanes, polyvinyl chlorides, epoxy resins and so on. The resin binders in the toner may be a single component or a mixture of various binder resins. Preferably, the binder resin has a weight-averaged molecular weight of between 200 and 100,000, for example a weight-averaged molecular weight of between 500 and 50,000, more preferably a weight-averaged molecular weight of between 1000 and 30,000. This molecular weight may, for example, be adapted to the required mechanical properties of the image or to the intrinsic properties of the image-forming process. The glass transition temperature of the binder resin is in the range 40 °C to 85 °C, more preferably in the range 45 °C to 75°C, or alternatively, in the range 50 °C to 65 °C.

Suitable epoxy resins, for example, are the Epikote resins (Shell), such as Epikote 828, Epikote 838 and Epikote 1001. In addition, many other epoxy resins may be used which contain one or more epoxy groups per molecule. These epoxy resins may be

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saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic, and may be substituted with substituents such as halogen atoms, hydroxyl groups, alkyl, aryl or alkaryl groups, alkoxy groups and the like. The phenol compounds suitable in the toner powder according to the invention are those compounds which have at least one hydroxyl group bonded to an aromatic nucleus. Mainly etherification takes place on reaction between the epoxy resin and the phenol compound, thereby forming the epoxy resin. However, not all epoxy groups present may react with a phenol compound, resulting in the presence of unreacted epoxy groups within the resin. It may be desirable to control the amount of free epoxy groups present within the resin, for example because of the HSE effects of epoxy functional groups, or because of the reactivity of the resin towards other components present in the toner. The amount of free epoxy groups may be suitably controlled by adding a blocking agent. A blocking agent is a compound, which reacts with the epoxy group, such that the epoxy group is converted into another functional group, for example an ether functional group. Thereby, the epoxy group is prevented from reacting further. For example, a phenol compound having one hydroxyl group bonded to an aromatic nucleus may be used for as blocking agent in a blocking reaction of the epoxy resin.

Examples of suitable phenols as blocking agent are phenol, p-cumylphenol, o-tert.butylphenol, p-sec. butylphenol, octylphenol, p-cyclohexylphenol and -naphthol. Other blocking agents, for example, monofunctional carboxylic acids, are also suitable. Examples of suitable carboxylic acids are phenylacetic acid, diphenylacetic acid and p-tert.butylbenzoic acid.

The selection of a specific polyester resin depends on the required use of the toner powder. Suitable diols are, inter alia, etherified bisphenols, such as polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)-propane, polyoxypropylene(3)-2,2-bis(4-hydroxyphenyl)-propane, polyoxypropylene(3)-bis(4-hydroxyphenyl)-sulphone, polyoxyethylene(2)-bis(4-hydroxyphenyl)-sulphone, polyoxypropylene(2)-bis(4-hydroxyphenyl)-thioether and polyoxypropylene(2)-2,2-bis(4-hydroxyphenyl)-propane or mixtures of these diols, in which a plurality of oxyalkylene groups per molecule of bisphenol may be present. This number is preferably between 2 and 3 on average. It is also possible to use mixtures of etherified bisphenols and (etherified) aliphatic diols, triols, etc. Examples of suitable carboxylic acids are phthalic acid, terephthalic acid, isophthalic acid, cyclohexane dicarboxylic acid, fumaric acid, maleic acid, malonic acid, succinic acid, glutaric acid, adipic acid and anhydrides of these acids. Furthermore esters, e.g. methyl esters of

these carboxylic acids, are suitable.

In a further embodiment the polyester resin has a number-averaged molecular weight of at least 2500, for example 2500 - 250 000, preferably 3000 - 100 000, more preferably
5 5000 - 50 000. The epoxy resin has a number-averaged molecular weight of less than 1200, for example 100 -1200, preferably 200-500 and the epoxy groups of the epoxy resin are blocked for at least 60% by a monofunctional phenol compound, for example 60% - 100%, preferably 65% - 95%, more preferably 70% - 90%.

10 Particularly preferred is a toner powder whose polyester resin is mainly a reaction product of ethoxylated 2,2-bis(4-hydroxyphenyl)propane, a phthalic acid and adipine acid. More preferably the phthalic acid is terephthalic acid or isophthalic acid. A toner powder of this kind has a sufficiently high glass transition temperature and also a surprisingly low
15 lower fusing limit, so that the energy required to fixate a toner image prepared with this toner powder is relatively low.

Colorants

The toner according the invention comprises at least one colorant, which may be a pigment or a dye or any combination thereof. Preferably a pigment is used, possibly in
20 combination with a dye. The toner may be of any color, for example: Cyan, Magenta or Yellow (for a CMYK toner set) or Red, Green, Blue (for a RGB toner set) and any other color. In a particular embodiment, for a specific application, a blue toner is preferred.

Pigments and dyes that are suitable to be used in toner compositions are not limited to any kind as long as they are compatible or made compatible (e.g. by surface treatment
25 known in the art) with the other components of the toner composition. Such pigments and dyes are well known in the art. In the context of the present invention iron oxide is not considered to be a colorant.

Iron oxide

30 The toner according to the present invention comprises iron oxide, which is not particularly limited to a certain kind or to a certain supplier. Iron oxide suitable for use in a toner composition according to the present invention comprises iron(II)oxide, iron(III)oxide or mixtures thereof. A known mixture is also indicated with chemical formula Fe_3O_4 , indicated with CAS number 1317-61-9 and with synonyms: magnetic
35 iron oxide nanocrystals or magnetite.

EXPERIMENTS

MaterialsToner components:

- 5 Polyester resins obtained from KAO
Pigment blue 15:3 (Copper(II) phthalocyanine) obtained from Clariant
Iron oxide (CAS number 1317-61-9) obtained from Huntsman Corp. (formerly Rockwood)
TiO₂ obtained from Kronos
- 10 Silica (as flow additive) obtained from Degussa
Dye obtained from Clariant

- Carrier: the toner is charged against a carrier particle in a similar way as is performed for black toner (e.g. in the Océ PlotWave 750 printing process). Carrier particles are
- 15 similar as for black toner and basically comprise coated cores of ferrite or magnetite. Typical toner concentration varies between 2 wt%-6 wt%, more preferably between 3 wt%-5 wt% with respect to the developer compositions (i.e. toner and carrier). The carrier is obtained from Océ

- 20 Print substrate:
Océ Red label 75 gr/m² containing about 6,9% moist.

Methods

Conditioning of print substrate

Prior to printing, the print substrate is subjected to conditioning for at least 24 hours 23 ± 2 °C and a relative humidity (RH) of $50 \pm 5\%$.

5

Printing of the test samples

Test samples are produced on an Océ PlotWave 750 equipped with radiant fusing technology and under the constant and reproducible conditions: 22°C and 60% RH.

Said printer comprises a photo-conductor roller, which is charged by scorotron (corona) charging. In a next step a latent image is written on photo conductor by an optical printhead. Toner is charged by carrier in a developer unit. In a next step a toner image is developed by application of a developer composition (i.e. toner and carrier) from development unit to the photo-conductor roller. Next, the formed toner image is transferred from the photo-conductor roller to a receiving substrate (e.g. paper) by electrical transfer. Finally the transferred toner image is fused to the printing substrate by heating the print substrate comprising the transferred toner image by radiant fusing.

A full density area (i.e. 100% coverage) is printed on the print substrate 1 in Fig. 1 as a frame 2 and 2' in Fig. 1 and in the middle 3 in Fig. 1 of print substrate, the printed full density area covering at least 45 mm * 195 mm.

Sample preparation

Test samples of 45 mm *195 mm are cut from the printed full density areas.

Both 45 mm wide ends of the test sample are bent together such that the toner image is folded inwardly. The folded test sample 23 with the end to be folded on the inclined surface 21 of the folding device 20 (a Kirchner roll), shown in Fig. 2 against the roll. The handle 22 of the folding device 20, which causes the test piece to be folded. The folded test sample is opened and the detached toner is removed by using a soft brush.

Optical Density (OD) Measurement

The optical density of the test sample is measured using a Gretag type D19C OD meter. An unprinted white part is used as a reference ($\text{OD}=0$). Then the OD's of an unfolded full density area is measured (OD_{Kref}) and of the folded area (OD_{Kfold}) are measured.

30

Folding resistance

The folding resistance of the image, which is a measure for the adhesion of the tested toner to the used print substrate (and hence of the fuse quality or the print robustness) is expressed as Alpha and determined with the Murray Davies equation (i.e. equation 1 given below).

$$\text{Alpha} = \frac{1 - 10^{-\text{ODKfold}}}{1 - 10^{-\text{ODKref}}} \quad \text{Equation 1.}$$

The closer Alpha is to 1, the better the fuse quality is.

Remark: Sample preparation and measurement are performed under constant and reproducible conditions, which are 23 ± 2 °C and $50 \pm 5\%$ RH.

Examples15 Comparative example A: preparation of a (blue) toner *without* iron oxide

Table 1 provides the compositions of toners that were prepared by combining the ingredients and tumbling and mixing the components for 10 minutes. The resulting mixture was melt mixed in a Buss single screw extruder (model MDK-46-15D). The resulting extruded material were milled and classified to a median size of about 11 micron. Agglomerates were removed by performing a sieve step which results in the toner product. Developer is made by mixing the toner with carrier.

The prepared developer (binary system of toner and carrier, i.e. so called binary toner) was printed, test samples were prepared, OD measurements were performed and fuse quality was determined (Alpha) in accordance with the above methods. For the toner according to Comparative example A, Alpha was 0.92. The sample after folding is shown in Fig 3A.

Example 1: preparation of a blue toner *with* iron oxide

30 Comparative example A was repeated with iron oxide present as an ingredient (see Table 1).

Again the prepared developer was printed, test samples were prepared, OD measurements were performed and fuse quality was determined (Alpha) in accordance

with the above methods. For the toner according to Comparative example A, Alpha was 0.96. The sample after folding is shown in Fig 3B.

Comparative Examples B and C: preparation of blue toners *without* iron oxide

- 5 Comparative example A was repeated with the components as shown in column B and C of Table 1, respectively.

Examples 2-4: preparation of blue toners *with* iron oxide

- 10 Example 1 was repeated with the components as shown in column 2, 3 and 4 of Table 1, respectively.

Table 1: prepared toner compositions

Component	(Comparative) Example (amounts in wt% relative to the total composition)						
	A	1	B	2	C	3	4
Polyester resin	97	96.6	97	96,5	95	92	82
Pigment Blue 15:3)	1.75	1.75	2	2	4	4	4
dye	0.25	0.25	-	-	-		
Iron oxide	-	0.4	-	0.5	-	3	3
TiO ₂ (whitener)	-	-	-	-	-		10
Flow and charging additives (e.g. silica)	1.0	1.0	1.0	1.0	1,0	1,0	1,0

- 15 Figure 3A shows a photograph of a folded sample, prepared according to the methods disclosed above and made with toner composition according to comparative example A. The value of Alpha as calculated according to equation 1 was 0.92. Figure 3B shows a photograph of a folded sample made with toner composition according to example 1. The value of Alpha was 0.96. It can therefore be concluded that by adding a small amount of iron oxide to the toner composition provides improved fuse quality to the
- 20

prints reproducibly made with said toner (and all other conditions and parameters constant).

Similar differences in fuse quality (print robustness, toner adhesion) were seen in toner compositions without a dye present in the composition (Comparative Example B and
5 Example 2) and with an increased amount of iron oxide (Comparative Example C and Example 3) even when a significant amount of whitener is added in order to compensate for the color shift caused by the larger amount of iron oxide (Example 4). Photographs of the folded print samples looked similar to the respective photographs shown in Figures 3A and 3B. The values of Alpha were also similar for the toners with
10 and without iron oxide respectively.

CLAIMS

1. A colored toner composition comprising:
 - a resin;
 - 5 • a colorant;
 - iron oxide in an amount of between 0.1 wt% and 4 wt% relative to the total toner composition.
2. The toner composition according to claim 1, wherein the iron oxide is present in
10 an amount of between 0.2 and 2 wt%.
3. The toner composition according to any one of claims 1-2, wherein the colorant is a pigment.
- 15 4. The toner composition according to claim 3, wherein the pigment is Pigment Blue 15:3.
- 5 The toner composition according to any one of the preceding claims, wherein the colorant is a mixture comprising at least one pigment.
20
6. The toner composition according to any one of the preceding claims, wherein the colorant is a mixture comprising at least one pigment and at least one dye.
7. The toner composition according to any one of the preceding claims, wherein the
25 resin is a polyester resin.
8. The toner composition according to any one of the preceding claims, wherein the toner composition comprises a mixture of resins.
- 30 9. The toner composition according to any one of the preceding claims, wherein, the toner composition further comprises at least one component selected from a wax, a flow additive, a charging agent, a coating and a whitener.
10. Use of between 0.1 wt% and 4 wt% of iron oxide in a colored toner composition
35 for improving robustness properties of a printed object comprising such toner.

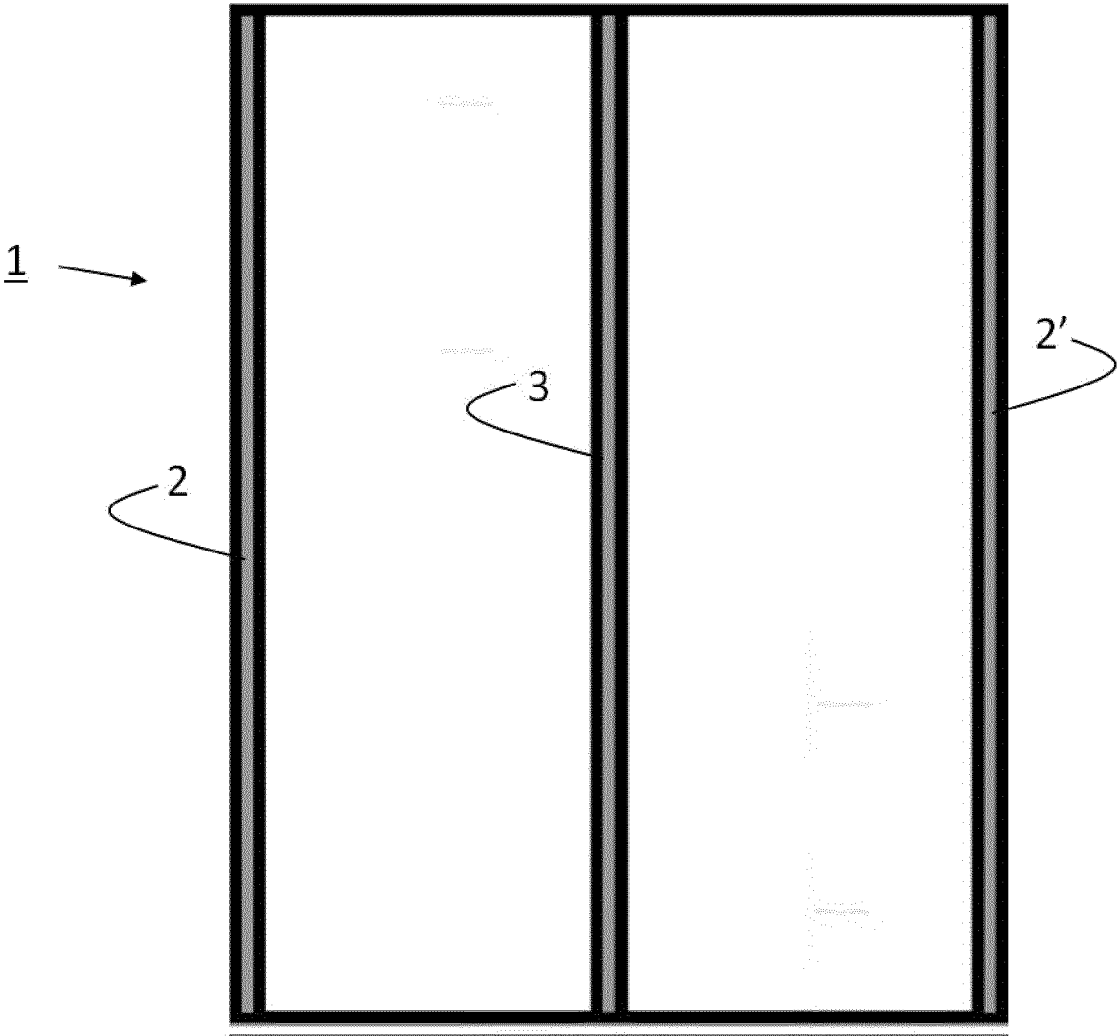


Fig. 1

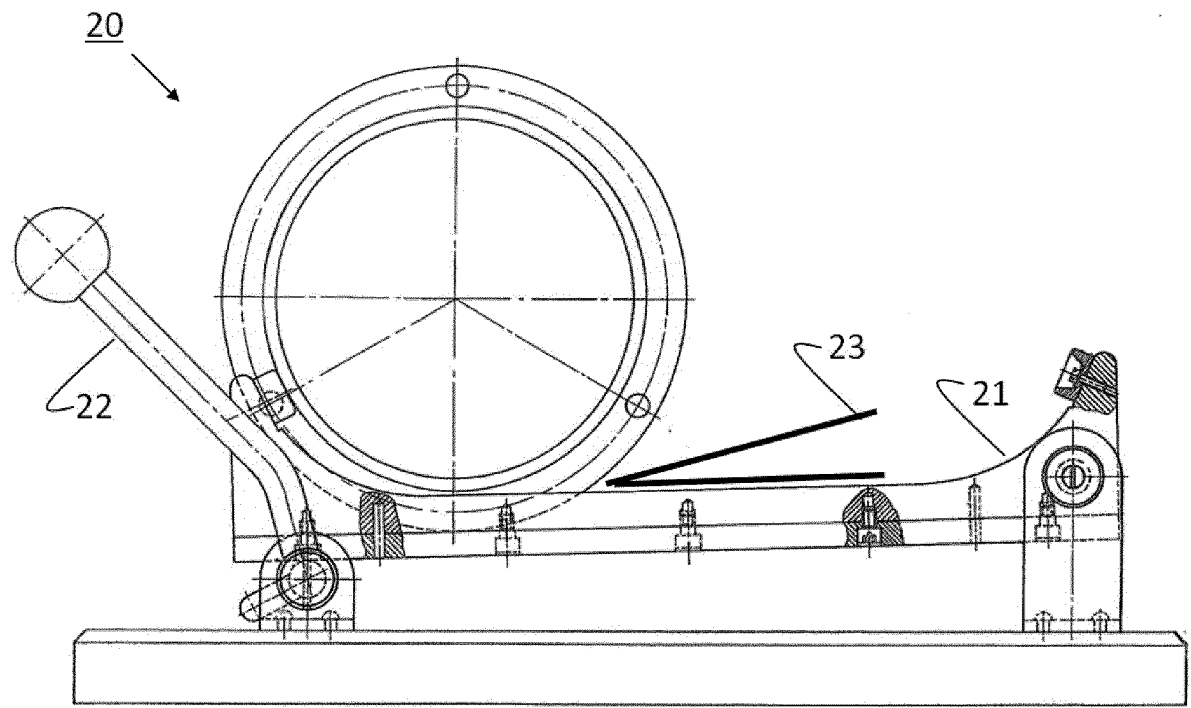
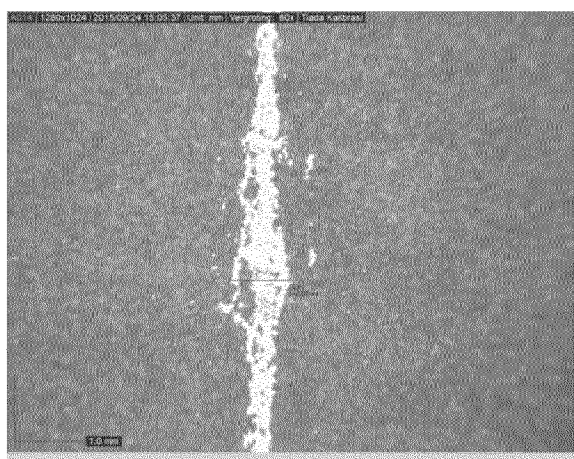
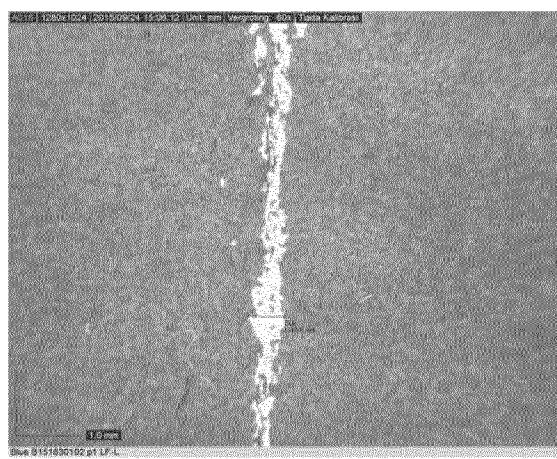


Fig. 2

3/3



(A)



(B)

Fig. 3