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Description

This invention relates to a process for forming fixed images on image receiving material, in which by means of toner powder comprising thermoplastic resin, an image is applied to a medium whose surface consists of material having a lower affinity for the softened toner powder than the image receiving material, and the toner powder is transferred by pressure to the image receiving material, the toner powder being softened by heat before and/or during passage through the pressure zone.

A process of this kind is described *inter alia* in GB—A—1 245 426 and US—A—3 554 836 and US—A—3 893 761. In these processes, a powder image formed, for example, on a photoconductive or magnetisable image recording material is transferred by pressure to a medium, the surface of which consists of a material having a low affinity for the softened powder, e.g. silicone rubber. The powder image is then transferred to image receiving material, again by application of pressure, the powder being softened by heat before and/or during passage through the pressure zone, so that it acquires viscous properties such that, as a result of the pressure exerted on it, it forms a cohesive layer which, preferably at least partially, penetrates into the image receiving material. After cooling, the image is permanently bonded to the image receiving material. The powder is heated by heating the medium on which the powder image is situated before transfer to the image receiving material, and possibly by heating the image receiving material itself. In doing so the temperature is so controlled that the powder softens sufficiently to be capable of deforming and being pressed into the image receiving material at a relatively low pressure, but does not soften to such an extent that the cohesion in the powder is so reduced that powder splitting occurs upon separation of the medium and the image receiving material and some of the powder image remains on the medium.

The toner powders hitherto proposed for use in the process according to the preamble comprise epoxy resin or polystyrene as thermoplastic resin. With such toner powders it is possible to obtain working systems but it has been found that these systems have shortcomings in practice.

In a system in which only the medium is heated to soften the toner powder, a high medium temperature of at least 130°C is required to heat the toner powder in a relatively short time to a temperature within its working range. The working range is the temperature range within which the temperature of the toner powder must lie to enable this powder to be transferred completely and with good adhesion from the medium to the image receiving material. This working range is limited at the bottom by the temperature at which complete transfer and good adhesion of the powder melt are still just obtained, while it is limited at the top by the temperature at which splitting of the powder melt still just does not take place.

The disadvantage of the high medium temperature required is that the image recording material (e.g. the photoconductive element) with which the hot medium is repeatedly brought into pressure contact, is subjected to a high thermal load, which has an adverse effect on the life of the image recording material.

Another disadvantage of this system is that the working range becomes increasingly smaller, probably as a result of thermal degradation of the medium, and after some tens of thousands of loads of the medium a situation is reached in which there is no practical working range any more.

It is possible to reduce the medium temperature to 100—105°C if the image receiving material is also heated to about 80°C before it is brought into pressure contact with the medium. However, this system has the disadvantage of a much higher energy consumption and it restricts the choice of image receiving material.

Image receiving material comprising thermoplastic substance e.g. highly sized paper and paper pre-printed with ink comprising thermoplastic resin, cannot be processed in this system because the resin in the paper is softened and the softened resin is partly transferred via the medium to the image recording material so that the latter becomes unsuitable for further use. In this system too, the working range gradually decreases although the speed at which this takes place is lower than in the system in which only the medium is heated in order to soften the powder image.

The invention provides a process as described in the preamble characterised in that the image is applied by means of toner powder comprising as thermoplastic resin crystalline polyester having a melting point between 50 and 100°C.

The process according to the invention gives an adequately wide working range at much lower temperatures than hitherto established for such processes using the previously proposed toner powders. The result is a much lower energy consumption and a longer life for that medium.

When the process according to the invention is employed in an electrophotographic copying process, another effect is that the load on the photo-conductive image recording material is reduced, thus benefiting the life of this material.

In an attractive embodiment of the process according to the invention, only the medium on which the toner powder is applied imagewise is heated in order to soften the toner powder. In most cases the working range is then 20°C to 30°C, while its bottom limit will usually be at a medium temperature which is little higher than the melting point of the crystalline polyester being present in the toner powder.

The process according to the invention can also be performed by applying the heat required to soften the toner powder exclusively or substantially to the image receiving material. In this embodiment too there is a wide working range of usually at least 20°C.

The exact position and size of the working range are determined, not only by the properties of the toner powder itself, but also by the geometry of the device in which the process according to the invention is performed, the speed at which the device operates, the composition and hardness of the medium to which the toner powder is applied imagewise, the way in which the powder image is softened and the pressure with which the softened toner powder is transferred to the image receiving material. The contact time, in particular, between the medium bearing the powder image and the image receiving material is a factor which considerably governs the working range.

The working range can readily be determined for a specific device by measuring the temperature range within which complete transfer and good adhesion of the powder image to the image receiving material are obtained. A reasonable indication of the position and size of the working range of a specific toner powder can be obtained by measuring the visco-elastic properties of the toner powder. Generally speaking, the working range of the toner powder corresponds to the temperature range within which the loss compliance (J″) of the toner powder, measured at a frequency equal to 0.5 times the reciprocal of the contact time in the device used for performing the process according to the invention, is between 10^{-4} and $10^{-6} m^2/N$. The visco-elastic properties of the toner powder are measured in a rheometer, the moduli G′ and G″ being determined as a function of the frequency at a number of different temperatures. The curves found are then reduced to one temperature, the reference temperature.

From this reduced curve the loss compliance (J″) is calculated as a function of the frequency. The displacement factors of the bottom and top limit temperatures ($J'' = 10^{-6}$ and 10^{-4} m^2/N respectively) of the working range can then be read off from the loss compliance-frequency-curve. The bottom and top limit temperatures of the working range can then be calculated by means of the WLF equation compiled from the displacement factors found during the measurements at different temperatures.

The toner powder used in the process according to the invention comprises crystalline polyester having a melting point between 50 and 100°C and preferably between 60 and 85°C. The melting point of the crystalline polyester is determined by melting the polyester, then cooling the melt to 20°C at a cooling rate of 10°C per minute and immediately thereafter re-heating the solid mass at a heating rate of 10°C per minute. During the second heating step the melting point is recorded as being the temperature at which the maximum endothermic heat effect is observed. The number-average molecular weight of the crystalline polyester amounts preferably at least 5,000 and most preferably is between 8,000 and 45,000.

When the process according to the invention is performed in a device in which a relatively short contact time is used for the transfer of the powder image from the medium to the image receiving material, then the powder image preferably is formed by means of toner powder comprising crystalline polyester having a number-average molecular weight betwen 8,000 and 25,000. In a device of this kind, the medium, for example, consists of a roller having a diameter of from 20 to 40 mm, which roller has been provided with a silicone rubber covering some tenths of a millimetre thick, and the transfer of the powder image from the medium to the image receiving material is carried out in the nip between this roller and a similar roller which presses against the medium at a force of about 80—100 N/cm.

The number-average molecular weight of the polyester is determined by GPC measurement with a low angular laser-light scattering detector.

Examples of suitable crystalline polyesters are: polycaprolactone (Tm ± 60°C), poly(hexamethylene sebacate) (Tm ± 65°C), poly(hexamethylene adipate) (Tm ± 55°C), poly(hexamethylene oxalate) (Tm ± 65°C), poly(ethylene adipate) (Tm ± 60°C), poly(decamethylene azelate) (Tm ± 70°C), poly(decamethylene sebacate) (Tm ± 76°C), poly(tetramethylene suberate) (Tm ± 56°C), poly(ethylene(methyl)terephthalate) (Tm ± 70°C), poly(tetramethylene sebacate) (Tm ± 61°C), poly(ethylene suberate) (Tm ± 65°C), poly(ethylene sebacate) (Tm ± 76°C), poly(decamethylene oxalate) (Tm ± 80°C), poly(decamethylene adipate) (Tm ± 78°C), poly(decamethylene dodecanedioate) (Tm ± 82°C), poly(decamethylene octadecanedioate) (Tm ± 93°C), poly(hexamethylene dodecanedioate) (Tm ± 76°C), poly(hexamethylene-decamethylene sebacate) (Tm ± 64°C), poly(decamethylene-sebacate-terephthalate) (Tm ± 71°C) and poly-(decamethylene-2-methyl-1,3-propanediol-dodecanedioate) (Tm ± 72°C).

In addition to crystalline polyester, the toner powder used in the process according to the invention also comprises colouring material, which may consist of carbon black or of inorganic or organic pigment or dye. The toner powder may also comprise other additives, the nature of which depends on the way in which the image is applied by means of the toner powder.

Thus toner powder for developing latent magnetic images, or toner powder fed, by magnetic conveying means, to an electrostatic image to be developed, will also have to comprise magnetically attractable material, usually in a quantity of between 40 and 70% by weight. Toner powders used for developing electrostatic images may also be made electrically conductive in manner known *per se* by finely distributing electrically conductive material in a suitable quantity into the powder particles, or depositing it on the surface of the powder particles. If, for the development of electrostatic images, the toner powder is used in a so-called two-component developer, the powder particles may also comprise a charge control agent that causes the powder particles, upon tribo-electric charging, to accept a charge of polarity opposite to that of the electrostatic image to be developed. The known materials can be used as magnetically attractable material, electrically conductive material or charge control agent.

The result of including fillers, such as magnetically attractable pigment or carbon black, in the toner resin is that the loss compliance of the toner powder is reduced in comparison with that of corresponding toner resin without fillers. Particularly when the toner powder for use in the process according to the invention comprises crystalline polyester having a relatively low number-average molecular weight of, for example, 5000—15000, it may be necessary to include fillers in the toner powder in order to bring the loss compliance of the toner powder to the required level. If the toner powder need not also be magnetically attractable and/or electrically conductive, then inert fillers, such as talc, silica, clay, titanium dioxide and zinc oxide may also be included in the toner powder instead of magnetically attractable and/or electrically conductive fillers. An electrically conductive filler which has a clear influence on the loss compliance and the electrical conductivity of the toner powder even when relatively small quantities are used from 5 to 15% by weight, is carbon black having a specific area of at least 750 m^2/g and an oil absorption between 250 and 400 ml/100 g.

The toner powder can be prepared in known manner by melting the crystalline polyester, finely distributing the colouring material and any other additives in the melt, cooling the melt to a solid mass, and grinding the solid mass into particles of the required particle size, which is generally 8—30 micrometers.

If, in the preferred embodiment of the process according to the invention in which the toner powder is softened by heating only the medium, the toner powder is applied to said medium by pressure transfer from a photoconductive or magnetic image recording material, the top limit of the working range may possibly be limited not by the temperature at which splitting of the powder melt occurs, but by the temperature at which the toner powder is already softened during the pressure transfer from the image recording material to the medium and partly adheres to the image recording material. It has been found that in this case the top limit of the working range can frequently be raised by storing the toner powder for some time, e.g. 2—7 days, at elevated temperature, but below the softening temperature of the toner powder, e.g. at about 50°C. During storage at elevated temperature the percentage of crystalline polyester resin in the toner powder increases but it is not clear whether the increase of the percentage of crystallisation is responsible for raising the top limit of the working range.

The process according to the invention can be performed in the devices known for this purpose, as described, for example in GB—A—1 245 426, US Patents 3 554 836, 3 893 761 and 4 068 937 and EP—A—0045102. It is preferred to heat only the medium on which the powder image is formed before transfer to the image receiving material.

As already stated, the working range is wide and is on a much lower level than the working range of the known toner powders based on polystyrene or epoxy resins.

The invention will be explained in detail with reference to the following examples.

Example 1

2,500 g of polycaprolactone having a number-average molecular weight of about 21,000 were melted and 2,500 g of magnetically attractable pigment (Bayferrox 318M made by Bayer A.G., West Germany) were finely distributed in the melt. The melt was then cooled to room temperature and the solid mass was ground to particles having a particle size between 10 and 30 micrometers. The resulting toner powder was used in an electrophotographic copying machine as described in EP—A—0045102. The medium to which the powder image formed on the photoconductive image recording material was applied by pressure transfer consisted of a metal roller having a diameter of 25 mm, which roller has been provided with a first covering of pigmented RTV silicone rubber (RTV 200/201 made by Messrs. Possehl, West Germany) in a thickness of about 500 micrometers, and a second covering thereon consisting of a non-pigmented RTV silicone rubber about 70 micrometers thick obtained by cross-linking an α-ω-hydroxy-polydimethylsiloxane with a tetra-ethyl silicate under the influence of dibutyl tin dilaurate.

To soften the powder image only the medium was heated. Océ plain paper was used as image receiving material. The working range was at a medium temperature of 65 to 85°C. If the toner powder was stored for 5 days at 50°C before use the working range was 70—100°C.

The working range had become scarcely smaller after 80,000 copies had been made.

Using the toner powder described just above, the process according to the invention was also carried out by softening the powder image by heating both the medium and the image receiving material. The working range was now at a medium temperature of between 40 and 45°C and a temperature of the image receiving material between 70 and 100°C.

Example 2

A toner powder of the following composition was produced in the manner described in Example 1:

50% by weight of polycaprolactone having a number-average molecular weight of about 15,000
50% by weight of magnetically attractable pigment (Bayferrox 318M).

1500 g of this toner power were dispersed in a dispersion containing:

24 g of carbon having a particle size between 10 and 250 nanometer
12 g of hydrophobic silica
10 g of polyvinyl alcohol
3000 ml of ethanol
7000 ml of water.

The dispersion was heated to approximately 65°C with continuous stirring and held at this temperature for about 10 minutes. It was then cooled to room temperature and the toner particles now covered with carbon were separated from the liquid. The resulting toner powder had a resistivity of 7.10^4 ohm.m.

The toner powder was used in the electrophotographic copying machine referred to in Example 1. The working range was at a medium temperature of about 70—125°C.

Example 3

A toner powder was prepared in the manner described in Example 1 containing:
50% by weight of polycaprolactone having a number-average molecular weight of about 43,000
50% by weight of magnetically attractable pigment (Bayferrox 318M).

The toner powder was used for the magnetic brush development of electrostatic images formed on a photoconductive image recording material the photoconductive layers of which were made up as described in Example 5 of Netherlands Patent Application No. 7808418 and the support of which consisted of a plastic film covered with a layer of aluminium screened as described in European Patent Application No. 0037193. The electrostatic images were formed by electrostatically charging the image recording material, projecting the image of an original onto the photosensitive side of the material, and also exposing the material via its support. The powder images formed on the image recording material were transferred to unheated Océ plain paper in a transfer-fixing device as used in an Océ 1900 copier. The working range was at a medium temperature of 70—95°C.

Example 4

The process of Example 1, in which only the medium was heated to soften the powder image, was repeated using a toner powder of the following composition:
42.5% by weight of polycaprolactone having a number-average molecular weight of about 9,200
50% by weight of magnetically attractable pigment (Bayferrox 318M)
7.5% by weight of carbon black having an average particle size of about 30 nanometer, a specific area of about 100 m^2/g and an oil absorption of about 340 ml/100 g.

The working range was now at a medium temperature of 75 to 95°C. Substantially the same result as described above was obtained using a toner powder of the composition just described, in which however the thermoplastic resin was polycaprolactone having a number-average molecular weight of 5,200.

Example 5

The following toner powders A up to F inclusive of the composition following hereafter were prepared in the manner described in Example 1:

A. 42.5% by weight of poly(hexamethylene sebacate) having a number-average molecular weight of about 18,000
50% by weight of magnetically attractable pigment (Bayferrox 318M)
7.5% by weight of carbon black having the specifications given in Example 4.

B. 42.5% by weight of poly(hexamethylene adipate) having a number-average molecular weight of about 17,000
50% by weight of magnetically attractable pigment (Bayferrox 318M)
7.5% by weight of carbon black having the specifications given in Example 4.

C. 50% by weight of poly(hexamethylene dodecanedioate) having a number-average molecular weight of about 18,000
50% by weight of magnetically attractable pigment (Bayferrox 318M).

D. 43% by weight of poly(hexamethylene-decamethylene-sebacate) having a number-average molecular weight of about 22,250
50% by weight of magnetically attractable pigment (Bayferrox 318M)
7% by weight of carbon black having the specifications given in Example 4.

E. 50% by weight of poly(decamethylene dodecanedioate) having a number-average molecular weight of about 22,000
50% by weight of magnetically attractable pigment (Bayferrox 318M).

F. 50% by weight of poly(ethylene suberate) having a number-average molecular weight of about 22,000
50% by weight of magnetically attractable pigment (Bayferrox 318M).

The powder images formed with these toner powders on a photoconductive image recording material were transferred to unheated Océ plain paper in a transfer-fixing device as used in an Océ 1900 copier.

The working range for the different toner powders was appointed to be at the following medium temperatures:

Powder A: ± 85 — ± 110°C
Powder B: ± 65 — ± 85°C
Powder C: ± 85 — ± 115°C
Powder D: ± 75 — ± 100°C
Powder E: ± 90 — ± 115°C
Powder F: ± 85 — ± 105°C

Claims

1. A process for forming fixed images on image receiving material, in which by means of toner powder

comprising thermoplastic resin, an image is applied to a medium whose surface consists of material having a lower affinity for the softened toner powder than the image receiving material, and the toner powder is transferred by pressure to the image receiving material, the toner powder being softened by heat before and/or during passage through the pressure zone, characterised in that the image is applied by means of toner powder comprising as thermoplastic resin crystalline polyester having a melting point between 50 and 100°C.

2. A process according to claim 1, characterised in that the image is formed with toner powder comprising crystalline polyester having a melting point between 60 and 85°C.

3. A process according to claim 1, characterised in that the image is applied with toner powder comprising crystalline polyester having a number-average molecular weight of at least 5,000.

4. A process according to claim 2, characterised in that the image is applied with toner powder comprising crystalline polyester having a number-average molecular weight between 8,000 and 45,000.

5. A process according to any of the preceding claims, characterised in that the toner image is softened by heating only the medium upon which the image is applied.

Patentansprüche

1. Verfahren zum Erzeugen von fixierten Bildern auf einem Bildempfangsmaterial, bei dem mit Hilfe eines thermoplastisches Harz enthaltenden Tonerpulvers ein Bild auf ein Medium aufgebracht wird, dessen Oberfläche aus einem Material besteht, das eine geringere Affinität zu dem aufgeweichten Tonerpulver aufweist als das Bildempfangsmaterial, und bei dem das Tonerpulver durch Druck auf das Bildempfangsmaterial übertragen wird, wobei das Tonerpulver vor und/oder während des Durchgangs durch die Druckzone thermisch aufgewicht wird, dadurch gekennzeichnet, dass das Bild mit Hilfe eines Tonerpulvers aufgebracht wird, das als thermoplastisches Harz kristallinen Polyester mit einem Schmelzpunkt zwischen 50 und 100°C enthält.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass das Bild mit einem Tonerpulver aufgebracht wird, das kristallinen Polyester mit einem Schmelzpunkt zwischen 60 und 85°C enthält.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass das Bild mit einem Tonerpulver aufgebracht wird, as kristallinen Polyester mit einem zahlenmittleren Molekulargewicht von wenigstens 5000 enthält.

4. Verfahren nach Anpruch 2, dadurch gekennzeichnet, dass das Bild mit einem Tonerpulver aufgebracht wird, das kristallinen Polyester mit einem zahlenmittleren Molekulargewicht zwischen 8000 und 45000 enthält.

5. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass das Tonerbild dadurch aufgewicht wird, dass nur das Medium beheizt wird, auf das das Bild aufgebracht wird.

Revendications

1. Procédé permettant de former des images fixées sur un matériau récepteur d'image, selon lequel, à l'aide d'une poudre de toner comprenant une résine thermoplastique, on applique une image sur un support dont la surface est constituée d'un matériau présentant une affinité pour la poudre de toner ramollie plus faible que le matériau récepteur d'image, et on transfère par pression la poudre de toner au matériau récepteur d'image, cette poudre de toner étant ramollie par la chaleur ayant et/ou pendant le passage à travers la zone de pression, caractérisé en ce qu'on applique l'image à l'aide d'une poudre de toner comprenant, en tant que résine thermoplastique, un polyester cristallin ayant un point de fusion compris entre 50 et 100°C.

2. Procédé selon la revendication 1, caractérisé en ce qu'on forme l'image avec une poudre de toner comprenant un polyester cristallin ayant un point de fusion compris entre 60 et 85°C.

3. Procédé selon la revendication 1, caractérisé en ce qu'on applique l'image à l'aide d'une poudre de toner comprenant un polyester cristallin ayant un poids moléculaire moyen d'au moins 5.000.

4. Procédé selon la revendication 2, caractérisé en ce qu'on applique l'image à l'aide d'une poudre de toner comprenant un polyester cristallin ayant un poids moléculaire moyen compris entre 8.000 et 45.000.

5. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce qu'on ramollit l'image de toner en ne faisant chauffer que le support sur lequel l'image est appliquée.