

①⑫

EUROPEAN PATENT SPECIFICATION

④⑤ Date of publication of patent specification: **22.01.86**

⑤① Int. Cl.⁴: **D 21 H 5/00, B 05 C 11/04**

②① Application number: **82301149.9**

②② Date of filing: **05.03.82**

⑤④ **Improvements in coating methods.**

③③ Priority: **11.03.81 GB 8107711**

④③ Date of publication of application:
15.09.82 Bulletin 82/37

④⑤ Publication of the grant of the patent:
22.01.86 Bulletin 86/04

③④ Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

⑤⑥ References cited:
GB-A-1 339 082
GB-A-2 014 481
GB-A-2 052 588
US-A-3 897 578

⑦③ Proprietor: **DRG (UK) LIMITED**
1 Redcliffe Street
Bristol, BS99 7QY (GB)

⑦② Inventor: **Jones, Nicholas J.B.**
43 Lakeside Road
Kirkcaldy Fife (GB)

⑦④ Representative: **Pattullo, Norman et al**
Ian G. Murgitroyd and Company 49 Bath Street
Glasgow G2 2DL Scotland (GB)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Description

This invention relates to a method of coating a support with microcapsules, especially but not exclusively in the preparation of pressure-sensitive recording papers.

In recent years there has been a considerable increase in the use of pressure-sensitive recording papers which act by virtue of a coating of microcapsules, containing a colour former such as crystal violet lactone, on one face of a first sheet of the paper, and a coating of a colour developer such as clay on a face of a second sheet. The colour former and developer are reactive to form a coloured product. Rupture of the microcapsules when the two coated faces are in contact releases the colour former for reaction with the developer, producing a coloured area on the second sheet in the area of rupture.

Many techniques have been proposed for applying the microcapsule coating, but in each case it has been considered essential to avoid excessive shear being applied to the microcapsules themselves, and it has therefore been advocated to use an air-knife technique. In this a suspension of the microcapsules in water is applied in excess to the paper as it passes in continuous form through a coating machine, and the excess is then removed by passing the paper with its applied suspension past a fine blast of air. The air blast is controlled at a velocity sufficient to remove all but a predetermined thickness of the suspension from the paper.

The air-knife technique is very reliable and accurately controllable, and avoids mechanical damage of the microcapsules. However, a disadvantage is that the suspension must be of low solids content otherwise the air blast is insufficient to remove the excess accurately. The coated paper emerging from the air-knife is therefore very wet, and this leads to swelling of the paper. As a result the image on the copies can be of poor definition and it is necessary to provide large drying apparatus. These coating machines therefore occupy considerable areas, primarily due to the amount of drying needed. Further, the coating applied by the air-knife technique is relatively rough in surface finish, and the coated paper has to be calendered to provide an acceptable smoothness. This can be done when the coating is the colour developer, but the calendering process ruptures microcapsules and cannot therefore be performed on the sheet coated with colour former. The colour former-coated sheet has had to remain rough.

It has previously been proposed in, for example, production of magazine-quality paper, to coat the paper on each side with starch by application of a blade-coating technique. Blade coating has been found to produce a much smoother surface finish than air-knife coating, but such a technique has never before been used industrially in the application of a microcapsule coating in view of the much greater mechanical forces applied by the blade to the paper and

coating material. Blade coating has therefore been regarded as necessarily resulting in rupture of the microcapsules and has not been considered to be a practical proposition. This has been emphasised by the use of gelatin-walled microcapsules; gelatin is hydrophilic and swells on absorption of water, thus weakening the integrity of the microcapsules when wet and making them more likely to rupture under blade coating.

Advances have been made in recent years in the manufacture of microcapsules, for example as described in UK Patent Nos. 1,292,939 and 1,319,123 of Fuji Photo Film Co. Ltd., whereby the capsule wall material is a synthetic polymer produced *in situ* rather than the conventional gelatin. The synthetic polymer wall is hydrophobic and therefore less likely than gelatin to swell when wet. As a result it has now surprisingly been discovered that a coating of such hydrophobic synthetic polymer-walled microcapsules can be applied to paper successfully by techniques other than the air-knife method.

US Patent No. 3,897,578 describes a method of applying to a paper support a dispersion of microcapsules having a solids content of from 20 to 80%, and optionally containing cellulose flocks to increase the anti-wear property of the microcapsule coating. An excess of the dispersion is applied and the support is then passed below a blade to remove the excess at a speed of 90 to 120 metres per minute.

According to the present invention there is provided a method of providing a sheet support with a coating of microcapsules, comprising providing in a carrier liquid a dispersion of microcapsules having hydrophobic walls and particulate material of greater particle size than the microcapsules, the dispersion having a solids content in excess of 40 per cent by weight, applying the dispersion in the form of a continuous liquid to the sheet support, passing the support with the applied dispersion past a blade in contact with the dispersion on the support at a speed of at least 600 metres per minute to remove excess of the dispersion, and drying the coated support.

The microcapsules are typically 10—90 per cent by weight of the solids in the coating material, and the balance may be made up of "stilt" and other material. "Stilt" comprises the particles of greater size than the microcapsules so that in use they extend further from the support and protect the microcapsules from accidental rupture during transit and storage of the coated support. Starch is a typical stilt material, although others such as glass beads and polymer granules can be used. A further factor of considerable importance in the use of particulate stilt material in the method of this invention is that the stilt protects the microcapsules during the coating procedure. As the particles are larger than the microcapsules they are struck by the blade in preference to the microcapsules which thus pass below the blade

with the minimum of physical contact. In the prior art it has been suggested to use cellulose fibres as the stilt material when air-knife coating, but fibrous material is not recommended in the present invention as it tends to clog the blade by the fibre becoming entangled and causing a build-up. This also tends to cause scoring of the support paper. The particulate material used in the present invention such as starch, does not suffer from this disadvantage.

The support may be paper and the microcapsules may contain a colourless colour former.

The concentration of coating material in the dispersion is preferably selected to make the solids content in the dispersion as high as possible to minimise the required amount of drying) while still allowing the blade to produce a reasonably smooth coating on the substrate. A solids content of 40—60 per cent has been found to be effective in this.

The blade is preferably flexible so as to "spread" the dispersion on the substrate; flexible blades are also to be recommended as they cause less mechanical damage to the microcapsules than do rigid blades and spread the dispersion more evenly over the substrate surface.

In order that the specified concentration of microcapsule-containing coating material can be achieved without the microcapsules being ruptured by the blade, they should be synthetic polymer-walled rather than gelatin-walled, and the polymer preferably provides physical strength greater than that provided by the conventional gelatin wall. Examples of suitable materials for producing such a polymer wall are polyurea, polyamide, urea-formaldehyde, melamine-formaldehyde and polyurethane, all of which are hydrophobic.

The hydrophobic walls of the microcapsules used in the present invention resist swelling and weakening when wet, and therefore provide a medium which can be passed through a blade coater without rupture and which allow a sharp image to be achieved in use. The hydrophobic property of the wall material therefore allows the coated support, which may for example be pressure-sensitive recording paper, to retain its microcapsule walls intact, with the result that when the microcapsules contain colourless colour former the colour former does not escape during the coating procedure and undesirable background colouration of the paper is absent when it comes into contact with a sheet containing colour developer.

The blade coating technique provides a considerably smoother surface finish to the coated support than does the conventional air-knife technique and, as paper coated with microcapsules cannot be calendered for fear of rupturing the microcapsules, this allows a superior product to be obtained. The smooth finish enhances not only the feel and appearance of the coated paper, making it a more commercially-acceptable product, but also the sharpness of the image obtained on rupture of the

microcapsules in view of the more even microcapsule coating.

As well as producing a superior product, the method of this invention allows considerable manufacturing advantages to be gained over conventional and commonly-used coating methods, especially in the saving of space and power for the drying stages. The coating operation can also be conducted at much higher speeds than previously, thus producing an increase in output and greater capacity for the coating machinery. The blade-type coating machinery used in the method of this invention can operate at speeds in excess of 1000 metres of continuous paper sheet per minute, and the reduced drying requirement allows such coating speeds to be coped with without an overall increase in the size of the machine as compared with conventional air-knife machinery. Thus the present method allows great savings to be made both in capital cost of machinery and in running costs.

A further advantage in the use of the present method is in the ease of controlling and maintaining the equipment used. In conventional air-knife coating it is necessary to make fine adjustments to the velocity of the air blasts and to ensure that the air jets remain clear, otherwise the uniformity of the coating suffers. With blade coating however much less maintenance is required as the blade is a fixed mechanical entity, set at a predetermined pressure against the support, and adjustment after initial setting is rarely needed.

An embodiment of the invention will now be described by way of example with reference to the accompanying drawings, in which:

Fig. 1 is a schematic view of a part of a coating machine for performing the method of this invention; and

Fig. 2 is a side view of the blade portion of the machine of Fig. 1.

Referring to the drawings, a continuous length of paper 1 is fed to calendering rollers 2 and passes between them to receive a smooth surface. From the rollers 2 the paper 1 passes round a guide roller 3 and thence downwards past a horizontally-disposed slot, orifice 4 through which a dispersion of hydrophobic-walled microcapsules in water is fed onto one face of the paper 1. The paper with its applied dispersion then passes between a flexible steel blade 5 and a driven roller 6, the blade 5 being biased towards the roller 6 on the coated side of the paper 1 so that as the paper passes between them the blade 5 allows only a predetermined depth of dispersion to remain on the paper 1, the excess dispersion remaining in a pool 7 above the blade line of contact between the blade 5 and paper 1 and flowing from the ends of the blade 5 into a receiving vessel (not shown) for feeding back to the orifice 4.

The blade 5 is set at an acute angle to the paper 1 where it contacts the roller 6 so that, as the paper passes, the microcapsule coating is spread

and smoothed over the surface of the paper. The blade is of similar length to the width of the paper 1 and is about 80 mm wide and 0.5 mm thick.

After passing the blade 5 the paper coated with the dispersion passes through a drying tunnel 10 until the coating is dry, round heated conditioning rollers 8 and then wound onto a spool 9.

The invention will be further illustrated in the following Examples which describe embodiments of the invention, in which the machine shown in the drawings was used for coating.

Example 1

Polyurethane-walled microcapsules were prepared as described in Example 1 of U.K. Patent No. 1,292,939, and a dispersion of the following components was made up in water:

microcapsules	100 parts by weight
granular starch	25 parts by weight
polyvinyl alcohol binder	10 parts by weight

The solids content of the dispersion was 45% by weight.

The resulting dispersion was applied to one face of 40 g/m² support paper 1 by applying from the slot orifice 4 an excess of the dispersion continuously onto the paper face as the paper in strip form was run at 1000 metres per minute through the coating machine. After being sprayed the paper passed between the flexible blade 5 and roller 6 which spread the dispersion evenly over the paper face to a constant depth and removed the excess. The coated paper then passed over the drying rollers 8 to remove the water from the dispersion and leave the microcapsules evenly coated on the paper face.

Because of the high percentage of solids in the dispersion and despite the high feed rate of the paper, no additional drying apparatus was needed; thus increased output was obtained at no additional capital cost and greatly reduced heating costs for the drying apparatus.

Example 2

The method of Example 1 was followed, with the exception that the feed rate of the paper was 700 metres per minute, and the coating dispersion had 50% solids content. The number of drying rollers 8 was correspondingly reduced. The dispersion contained the following components in water:

microcapsules having urea-formaldehyde walls	100 parts by weight
glass beads	15 parts by weight
acrylic latex binder	15 parts by weight, calculated as dry weight

Example 3

The method of Example 1 was followed with

the exception that the paper feed rate was 600 metres per minute and the coating dispersion had a solids content of 50%. The amount of drying was even less than in Example 2. The dispersion contained the following components in water:

microcapsules having polyurethane walls	100 parts by weight
starch granules	30 parts by weight
acrylic latex binder	10 parts by weight, calculated as dry weight

Example 4

The method of Example 1 was followed with the exception that the paper feed rate was 950 metres per minute and the coating dispersion had a solids content of 60% by weight. The dispersion contained the following components in water:

microcapsules having polyurea walls	100 parts by weight
granular starch	40 parts by weight
polyvinyl alcohol binder	30 parts by weight

In these Examples the microcapsules contained colourless colour-forming material and the coated paper was useful as pressure-sensitive recording paper when in contact with paper coated with colour developer such as activated bentonite clay.

Claims

1. A method of providing a sheet support with a coating of microcapsules, comprising providing in a carrier liquid a dispersion of microcapsules having hydrophobic walls and having a solids content in excess of 40 per cent by weight, applying the dispersion in the form of a continuous liquid to the sheet support, passing the support with the applied dispersion past a blade in contact with the dispersion on the support to remove excess of the dispersion, and drying the coated support, characterised in that the dispersion contains particulate material of greater particle size than the microcapsules and the support with the applied dispersion passes the blade at a speed of at least 600 metres per minute.

2. A method according to Claim 1, wherein the particulate material is starch.

3. A method according to Claim 1 or 2, wherein the microcapsules have synthetic walls selected from the group consisting of polyurea, polyamide, urea-formaldehyde, melamine-formaldehyde and polyurethane.

4. A method according to any one of the preceding Claims wherein the solid content of the dispersion does not exceed 60 per cent.

5. A method according to any one of the preceding Claims, wherein the blade is flexible.

6. A method according to Claim 7, wherein the blade is biased against a roller and the support with the applied dispersion passes between the blade and the roller.

7. A method according to any one of the preceding Claims, wherein the sheet support is paper.

8. A method according to any one of the preceding Claims, wherein the microcapsules form from 10 to 90 per cent by weight of solids in the dispersion.

9. A method according to any one of the preceding Claims, wherein the support is paper and the microcapsules contain a colourless colour former.

Revendications

1. Procédé pour l'application sur une feuille support d'un revêtement de microcapsules, consistant à préparer dans un liquide porteur une dispersion de microcapsules à parois hydrophobes et ayant une concentration en solides supérieure à 40% en poids, à appliquer la dispersion sous la forme d'un liquide continu à la feuille support, à déplacer le support sur lequel est appliquée la dispersion devant une lame de râclage en contact avec la dispersion sur le support, de manière à enlever la dispersion en excès, et à sécher le support revêtu, caractérisé en ce que la dispersion contient une matière en particules de grosseur supérieure à celle des microcapsules et en ce que le support sur lequel est appliquée la dispersion passe devant la lame à une vitesse d'au moins 600 mètres par minute.

2. Procédé suivant la revendication 1, dans lequel la matière en particules est de l'amidon.

3. Procédé suivant la revendication 1 ou 2, dans lequel les microcapsules ont des parois en résine synthétique choisie parmi l'ensemble comprenant les polyurée, polyamide, uréeformaldéhyde, mélamine-formaldéhyde et polyuréthane.

4. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la concentration en solides de la dispersion ne dépasse pas 60%.

5. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la lame de râclage est flexible.

6. Procédé suivant la revendication 5, dans lequel la lame est rappelée contre un rouleau et le support sur lequel est appliquée la dispersion passe entre la lame et le rouleau.

7. Procédé suivant l'une quelconque des reven-

dications précédentes, dans lequel la feuille support est un papier.

8. Procédé suivant l'une quelconque des revendications précédentes, dans lequel les microcapsules constituent de 10 à 90% en poids des solides dans la dispersion.

9. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le support est un papier et les microcapsules contiennent une substance incolore de formation de couleur.

Patentansprüche

1. Verfahren zur Beschichtung einer Trägerbahn mit Mikrokapseln, bei dem man eine Trägerflüssigkeit mit einer Dispersion von Mikrokapseln mit hydrophoben Wänden und einem Feststoffgehalt von über 40 Gewichtsprozent vorsieht, die Dispersion in Form einer kontinuierlichen Flüssigkeit auf die Trägerbahn aufbringt, die Bahn mit der aufgetragenen Dispersion hinter ein Rakelmesser führt, das die Dispersion auf der Bahn berührt, um Dispersionsüberschuß abzustreichen und bei dem man die beschichtete Trägerbahn trocknet, dadurch gekennzeichnet, daß die Dispersion teilchenförmiges Material enthält, dessen Teilchen größer als die Mikrokapseln sind und daß die Bahn mit der aufgetragenen Dispersion das Rakelmesser mit einer Geschwindigkeit von mindestens 600 Meter pro Minute passiert.

2. Verfahren nach Anspruch 1, bei dem das teilchenförmige Material Stärke ist.

3. Verfahren nach Anspruch 1 oder 2, bei dem die Mikrokapseln synthetische Wände haben, die aus der aus Polyharnstoff, Polyamid, Harnstoff-Formaldehyd, Melamin-Formaldehyd und Polyurethan bestehenden Gruppe ausgewählt sind.

4. Verfahren nach einem der vorangegangenen Ansprüche, bei dem der Feststoffgehalt der Dispersion 60% nicht übersteigt.

5. Verfahren nach einem der vorangegangenen Ansprüche, bei dem das Rakelmesser flexibel ist.

6. Verfahren nach Anspruch 7, bei dem das Rakelmesser gegen eine Walze vorgespannt ist und die Bahn mit der aufgetragenen Dispersion zwischen dem Rakelmesser und der Walze hindurch verläuft.

7. Verfahren nach einem der vorangegangenen Ansprüche, bei dem die Trägerbahn Papier ist.

8. Verfahren nach einem der vorangegangenen Ansprüche, bei dem die Mikrokapseln von 10 bis 90 Gewichtsprozent des Feststoffanteils in der Dispersion bilden.

9. Verfahren nach einem der vorangegangenen Ansprüche, bei dem die Trägerbahn Papier ist und die Mikrokapseln einen farblosen Farbbildner enthalten.

FIG1

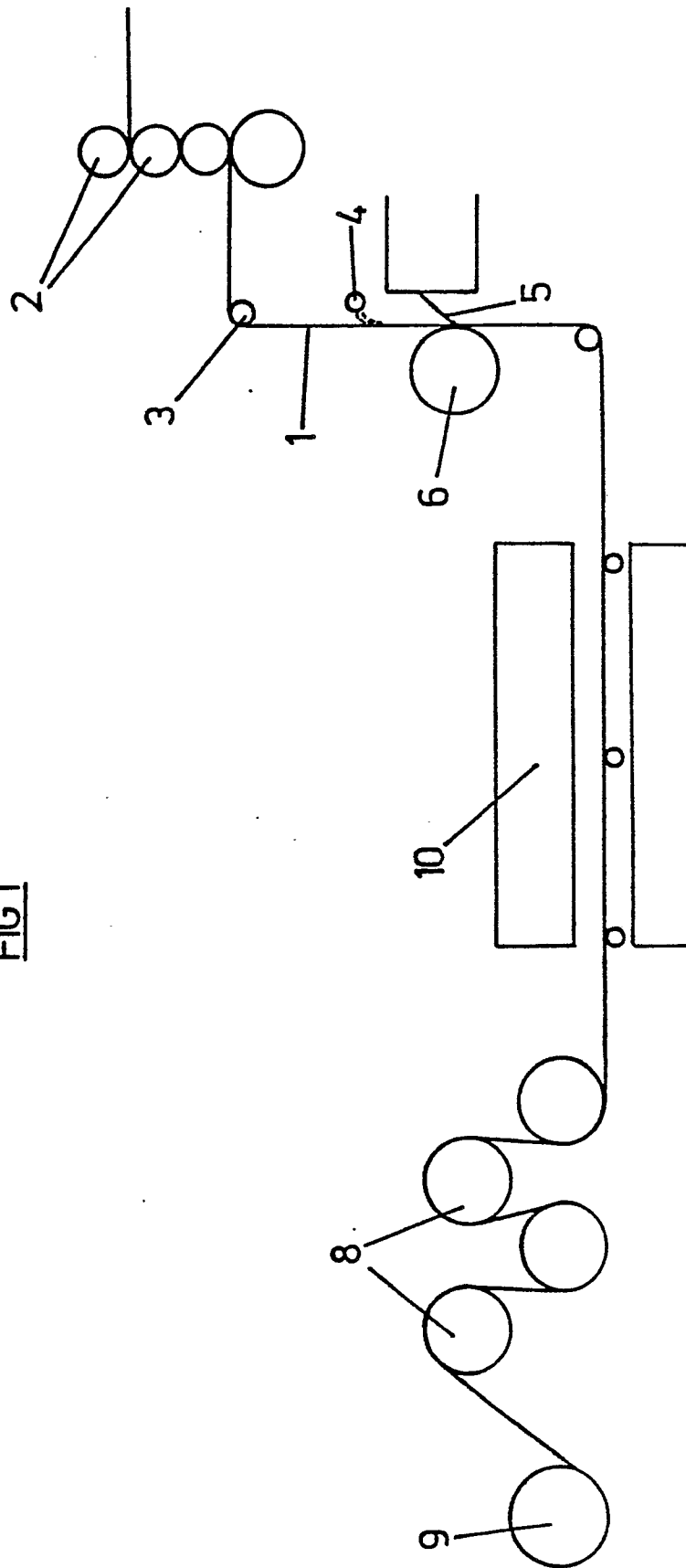


FIG 2

