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### (54) Pressure sensitive record material

Druckempfindliches Aufzeichnungsmaterial

Matériau d'enregistrement sensible à la pression

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**Description**

The invention relates to paper for carbonless copy paper sets and to copy paper sets made up using it.

5 **BACKGROUND**

Carbonless copy paper sets consist of a top sheet known as the CB (coated back) sheet, a back sheet known as the CF (coated front) sheet, and optionally one or more intermediate sheets known as CFB (coated front and back) sheets. The coatings of the back of the CB sheet, of the front and back of the CFB sheets if any, and of the front of the 10 CF sheet contain materials that when brought into association with each other develop a coloured image.

When the front of the CB sheet is typed on or otherwise pressure imaged, material is transferred between the back of one sheet and the front of the next through the set to give rise to the copies required. Usually, a solution of a dye precursor or "colour former" carried on the sheet as isolated droplets each confined within a pressure rupturable barrier is transferred from the back of one sheet to the front of the next after rupture of the barrier by the applied pressure, and 15 interacts with a "colour developer" present to give the image.

All of this is very well known and requires no detailed description and is disclosed, for example, in EP-A 8 161.

**PIGMENT IN CB-SHEET FRONT COATINGS**

20 The present invention has arisen from a requirement, in the highest grade products, for a pigment-containing coating on the front face of CB sheets, improving them in appearance and in printability.

**THE INVENTION**

25 In one aspect the invention lies in record material comprising a paper CB sheet having on its front a printable pigment coating and on its back isolated droplets of colour former solution each confined within a pressure rupturable barrier, wherein the pigment coating comprises a binder for the pigment together with a synthetic reactive sizing agent and optionally also a coating structure agent.

The sizing agent is for example an alkyl ketene dimer alkenyl succinic anhydride, or other neutral reactive size. 30 Another example is a polyurethane size. The coating structure agent is for example a carboxy methyl cellulose, a soya or other protein, an alginate, or other hydrophilic polymer. The relative amounts of components in the coating are desirably by weight 60 - 95 parts pigment, 10 - 30 parts binder, 0.5 - 10 parts size and 0.5 - 5 parts coating structure agent where present. In options within these ranges, pigment, binder and size are respectively 60 - 95 parts, 16 - 22 parts and 0.5 - 10 parts, or pigment, binder and coating structure agent are respectively 75 - 85 parts, 12 - 22 parts and 0.5 to 5 35 parts, with in the latter case 1 - 5 parts size being present also.

The invention further provides

40 A. Multiple form sets fannable apart without separation of the sheets within the sets each comprising a CB sheet, a CF sheet and optionally one or more CFB sheets, and carrying an age adding adhesive to join the sheets within the sets and the sets to each other, wherein the CB sheet is of the record material above.

B. A method of making a record material comprising a paper sheet having on its front a printable pigment coating and on its back isolated droplets of colour former solution each confined within a pressure rupturable barrier, wherein or the purpose of allowing high speed application of the CB coating subsequent to the application of the 45 pigmented coating the paper sheet is coated with a mix containing a binder for the pigment together with a coating structure agent, a synthetic reactive sizing agent being present also, in an aqueous medium at 25 - 75% advantageously 50 - 65% solids by weight of the mix; is dried to give a coated sheet of Bendtsen porosity 25 to 30 ml/min or more; and is coated on the back at 400 to 450 m/min or more with a colour former coating formulation to give 50 said record material.

The binder is present to hold the pigment in a non-dusting, printable coating, and to enable enough binder to be used for that purpose it must be a material that when tested at 40 weight % in water gives a fluid preparation mixable with pigment to give a coatable dispersion. Normally it will be a latex binder but for example hydroxyalkyl ether derivatives of starches are suitable. Auxiliary binder materials may also be included.

55 The size, as discussed further below, is used to hold off latex-based or other edge-padding adhesives to allow form sets to be fanned.

The coating structure agent, as also discussed further below, is a hydrophilic polymer that provides a Bendtsen porosity of the finished i.e. CB coated sheet of not less than 25 ml/min, preferably more. Such porosities reflect porosities before CB coating of around 30 ml/min or more allowing economic application of the CB coating. Suitable materials

are believed to act by gelling the pigment coating in the course of drying, preventing it from compacting into an impermeable layer, and all are materials that when tested in water at 25 weight % or more give a gel-like preparation not mixable with pigment to give a coatable dispersion.

It will be understood that as the intention is to improve appearance as well as printability, the pigment coating should not have any significant colour developing properties. Such properties would give rise to edge staining after sifting or sheeting, and possibly other marking arising from capsule rupture and release of colour former solution.

#### EDGE PADDING

10 A well known use of copy paper sets is in the production of multiple sets or "form sets" as disclosed, for example, in EP-A 8 161. In these, repeats of the sequence of sheets, CB, optionally one or more CFB and CF, that constitute an individual set are made up as a stack. An adhesive, known as an edge padding adhesive, is applied down one side of the stack, its characteristic being that it is attracted to the coating of the back of the CB (and any CFB) sheets, or to the coating of the front of the CF (and any CFB) sheets, or to both, to a greater extent than to what are, conventionally, 15 uncoated faces of the sheets in the stack, which are the fronts of the CB sheets and the backs of the CF sheets. Thus there is only a weak bond between CB sheets and adjacent CF sheets above them and individual sets can be separated from each other by "fanning" without the sheets within the sets coming apart from each other.

However a CB front face pigment coating would be thought of as incompatible with edge padding, the coating attracting the edge padding adhesive in the same way as the coatings within the sets. The invention overcomes such 20 problems. While of course the use of sizes in paper generally is known, and so is pigment coating and the use of binders to retain the pigment on the paper, there has been no reason to size a pigment coating as such. Indeed a pigment would normally be thought of as incompatible with size, using a lot of it to no purpose, and the success of the combination is surprising.

25 USE OF HIGH PIGMENT COAT WEIGHTS

Separate from questions of edge padding is a desirability of high pigment coat weights for the best properties of printability and appearance.

The requirement however conflicts with ready application of CB coatings. These, containing colour former in relatively fragile (usually encapsulated) form, must in practice be applied after the coating of the front of the sheet. Application involves use of driving rolls run at high speed with the paper tensioned over them and if air is not to be entrained between paper and roll the paper must have enough permeability for the air to escape. Without it the paper is liable to "hover" on a layer of air over the roll with loss of control of the process and variation in the product. Running the coater at a lower speed to avoid the problem is unacceptable for production efficiency. Increasing the tension to exclude the 35 air is possible in theory but risks damage to the product, e.g. by more frequent breaks and/or curing or inferior aspect.

In conventional pigment coated printing paper, the pigment coating is typically highly consolidated to give a smooth surface. The use of these highly consolidated coatings means that the sheet porosity of the paper is very low. We have however surprisingly found both good binding and permeability, even though the invention uses a high content of binder such as would in itself be expected to give an entirely impermeable coating. The adverse effects of this high content of 40 binder are overcome by the presence in the coating mix of the coating structure agent, sufficient permeability for successful subsequent application of CB coatings being obtained.

The inclusion of the coating structure agent in the coating mix promotes the generation of a relatively porous coating. We believe that this arises because as the coating mix dries, the coating structure agent helps the mix to set or gel before all the water is removed, and that the set or gelled structure is, at least in part, preserved through drying to give 45 a relatively bulky and thus porous coating. That this effect generates a porous coating even at the high binder levels typically used in this invention is very surprising as such binder levels would ordinarily be expected to "blind" the coating.

The reason for the success of the invention appears, though such theory is not to be taken as a limitation of the invention itself, to lie in a microporosity arising from early setting or gelling of the coating as referred to above, without excessive loss of binder into the paper, followed by drying out of the water content of the coating without loss of the structure. It does not appear to arise by a multiple micro-cracking of the coating such as is seen in the colour-developer 50 clay coatings used in CF sheets or the CF face of CFB sheets.

#### PIGMENTS

55 The pigments are, generally, conventional paper coating pigments, in particular inorganic or mineral-derived particulate materials. Calcium carbonate especially is economic and suitable, giving good whiteness and purity and having good printing characteristics. It may be supplemented with coating clays such as china clay (kaolin), although with large amounts of clay care will be necessary in formulation to achieve satisfactory rheology and stability for successful coat-

ing, as will be appreciated by those skilled in the art.

Other suitable pigments besides china clay include calcined clays, titanium dioxide, finely divided silica and talc.

A mixture of calcium carbonate and china clay, particularly calcined china clay, is preferred. Calcium carbonate contributes good whiteness and brightness, and high print definition, but on its own tends to give dusting on the surface and 5 may not good good ink receptivity. Clay or talc contribute to a good surface finish and give good ink receptivity without dusting but give a less white appearance. Ground calcite as the calcium carbonate has high purity (to give whiteness etc. as compared with ground limestone or chalk) without the very high surface of precipitated carbonates, which can be used but are not preferred because of high binder demand arising from small particle size.

It will be understood that the pigment in the coatings is not such as to have colour developing properties. To this 10 end the inclusion as pigments of specific colour developer materials, such as the clays that are used as the active constituents of many CF coatings, will be avoided. Kaolin has been mentioned in the literature as a colour developer but in unmodified form is not so used or suitable, and papercoating grades are essentially non-colour developing. The use of high levels of binder reduces even further or eliminates any minor residual colour developing activity of the raw material.

The particle size of the pigment is important. The finer the particles are the more effective the pigment is in terms 15 of brightness but, equally, the more the coating is consolidated (thus reducing porosity) and also the more difficult sizing is; a balance is desirable and the range of 1 to 10 microns, advantageously 2 to 5  $\mu\text{m}$  is preferred.

Such particle sizes are as measured by a laser particle sizer such as the standard Malvern 3600 E Type. For particles of broadly the same dimensions in any direction, such as those of calcium carbonate, such sizes approximate 20 actual sizes; for flat or elongated particles such as those of coating clays the particles sizes as measured are nominal. The laser instrument assesses particle size by measuring the interference pattern arising from diffraction of the laser light illuminating a sample suspension e.g. in water, of the particles. The pattern is manipulated by a computer to give results as particle size by volume, e.g. the volume itself or the diameter of spheres of equal volume.

Amounts of pigment are given earlier. Small quantities say up to 10% of specialist pigments, for example  $\text{TiO}_2$  whitener, can conveniently be included.

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## BINDERS

Within the constraints above, the binder may be selected from among those conventional in themselves in paper 30 coating technology. In particular it may be a synthetic rubber latex such as styrene butadiene latex (normally a carboxylated grade to give good dispersibility and stability in water) or styrene acrylic latex. It is also however possible for it to be for example an ether derivative of starch, as already mentioned, and these are not conventional in the sense of being in wide use.

## SIZING AGENTS

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The size will typically be a neutral reactive size such as an alkyl ketene dimer or alkenyl succinic anhydride with the alkyl or alkenyl groups from  $\text{C}_8$  upwards, generally from  $\text{C}_{12}$  upwards, with  $\text{C}_{15}$  -  $\text{C}_{18}$  typical and the upper limit determined, for example  $\text{C}_{24}$ , by mix workability and suitability of the final coating for printing. Such sizes, in which "neutral" 40 connotes effectiveness as sizes at neutral coating mix pH, are effective in small quantities and readily provide acceptable rheology in the coating process, for example blade, roll or slot (extrusion) coating as known *per se*. Other synthetic sizes such as polyurethane sizes may however be used. Amounts within the ranges given earlier are typically 1 to 5% dry weight of the coating but more usually 1 to 2% will be used.

Suitability of sizes will be in terms of water repellency of the coating in an edge padding context. The water repellency of the coating is defined in terms of the contact angle taken up by a water droplet on the surface of the coated 45 paper, measured within the drop, which for a size to be suitable is above  $70^\circ$  and advantageously above  $90^\circ$  or  $100^\circ$ .

A convenient method of determining the contact angle depends on measurement of the observed height and contact width of a droplet of known volume applied to the paper, in particular in a Lorentzen & Wettre No. 28 surface wetability tester. The method is as follows:-

50 i) A drop of water (initial diameter 4 mm volume ca. 3.35 microlitres) is placed on a test strip of paper  
 ii) The drop height ( $h$ ) and width of contact of the drop on the paper ( $w$ ) are measured on a projected image of the drop using a graticule  
 iii) The contact angle is calculated as

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$$\theta = 2 \tan^{-1} (2h/w)$$

Since the paper will absorb the water slowly the contact angle is taken as that measured 2 seconds after the drop is placed on the paper.

COATING STRUCTURE AGENTS

The coating structure agents that are suitable include in particular carboxy methyl cellulose such as is used in coating technology as a dewatering control. Other suitable materials are proteins, such as soya protein, and alginates such as sodium alginate, their essential characteristic being to provide the desired porous mating structure at the low amounts specified. The amounts used, within the overall range, depend on the nature of the material, enough to be effective but not so much as to increase viscosity or modify the rheology to make the mix uncoatable.

5 Amounts are typically, weight % on coating:

Amounts are typically, weight % on coating:		
Carboxy methyl cellulose	high mol.wt.	0.5-1.5%
	medium mol.wt.	1-2%
	low mol.wt.	2-3%
Sodium alginate		0.7-1.5%
Soya protein		1.5-4%

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OTHER COMPONENTS

25 Other agents, known in themselves may also be present in the mix, for example sodium hydroxide or other alkalis such as potassium hydroxide or ammonia for pH adjustment, and further components of the final coating such as optical brightening agents, dispersants for the pigments, lubricants (e.g. calcium stearate) or antifoams.

COAT WEIGHTS

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Coat weights may conveniently be 2 to 20 g/m<sup>2</sup>, advantageously 3 to 15 g/m<sup>2</sup>. Papers of reduced substance compared to normal, in terms of fibre weight per square metre, may be used compensating in part for the extra cost of the coatings.

35 POROSITY

40 For high speed, high quality (good curl : good aspect) CB coating the Bendtsen porosity of the final product is not less than 25 ml/min and preferably not less than 30 ml/min with (for this product) a typical range of 35 - 50 ml/min. "High speed" is ca.500 m/min or above and a preferred lower limit 400/450 m/min. A typical range is ca. 600 - 900 m/min and higher speeds e.g. up to 1500 m/min are possible.

SOLIDS OF TOPCOAT MIX

45 Widest convenient range 25 - 75% solids, more usual 30 - 70%, advantageously 50 - 65%. Lower solids give a wetter mix and greater drying requirement which restricts machine speed; higher solids may give mix viscosity/rheology problems.

DETAILED PREFERENCES

50 The invention is described broadly above, but most desirably provides a CB sheet with a printable front coat at 2 - 20g/m<sup>2</sup> comprising an inorganic or mineral derived pigment and a latex-derived binder together with a sizing agent, the sizing agent being an alkyl ketene dimer or alkenyl succinic anhydride or other reactive neutral size giving a contact angle of 90° or more. Preferred proportions of components by weight are pigment 60 - 95 parts, binder 5 - 30 advantageously 16 - 22 and size 0.5 - 10 parts.

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EXAMPLES

The invention is illustrated in the following, except Examples 1 and 2 which show the use of coating structure agent in the absence of size, the size being added in Examples 3 and 4.

Example 1

A coating material was prepared from the following components 48.2% solids in water, final pH 9.5.

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Mix Procedure

- Place water in a high speed mixing vessel
- Add the dry coating structure agent and stir for 15 minutes at high speed
- Add first batch of NaOH (40% solids)
- Add calcium carbonate and china clay and stir for 30 minutes at high speed
- Check pH and adjust to approximately 10.0 with some of the remaining NaOH
- Reduce the stirring speeds to slow, add the binder and stir for 10 minutes
- Add the optical brightener
- Bring final pH to 9.5 with NaOH

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Materials

- i) The coating structure agent is a medium molecular weight carboxymethyl cellulose.
- ii) The calcium carbonate pigment is a ground calcite, desirable as high-white material economic in cost. Its median particle size is 2.8  $\mu\text{m}$  (2.8 microns).
- iii) The china clay is a fine, white, commercially available coating clay, median particle size 3.3 microns. It acts as a white pigment accordingly, while preserving the advantages of clay coatings generally in terms of coat adhesion and printing characteristics. It gives no unacceptable reduction in the brightness of coating given by the calcium carbonate.
- iv) The binder is a conventional carboxylated styrene-butadiene synthetic latex giving the coating the necessary adhesion as a whole.

The coating mix so prepared was applied using trailing blade metering to standard base paper of 48 g/m<sup>2</sup> substance for 'Idem' (Trade Mark) CB sheet to give coat weights of 3 to 7 g/m<sup>2</sup>. The coated paper was then calendered and its porosity checked and found to be at a suitable figure. It was CB coated at 800 m/min using a 3 roll coater head, solids of the coating mix ca. 24%, constitution of solids:

- 70% capsules conventional gelatin-based capsules, black-copy colour former formulation in solvent, formed by coacervation encapsulation
- 20% stilt cellulose floc, ungelatinised starch particles or mixture
- 10% binder maize starch

and dried to give ca 4.5 g/m<sup>2</sup> coat weight (dry). A steam shower was used to remove/reduce curl otherwise present from paper wetting during coating.

The resulting CB sheets had excellent printing characteristics and improved visual appeal and feel in terms of formation and roughness.

Example 2

Similarity to Example 1, a coating material was prepared from the following components, made up to 3308 Kg with water

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Component	Dry weight (kg)	Approx. % of dry weight
"Dispex" N40 (40% in water) dispersing agent	3.6	0.2
"Hydrocarb" 70 calcium carbonate pigment	1275	64.5
Sodium hydroxide (30% in water)	2.4	0.12
"Alphatex" calcined kaolin (china clay) pigment	300	15.2
Carboxymethyl cellulose coating structure agent	24	1.2
"Revinex" 98 F10 latex (50% solids in water)	360	18.2
"Nopcote" C104 (50% in water) calcium stearate	10	0.5

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Revinex 98 F10 latex is a carboxylated SBR latex ~~ex~~ Doverstrand Limited. 'Dispex', 'Hydrocarb', 'Alphatex', 'Revinex' and 'Nopcote' are trade marks.

This coating was applied to a conventional CB base paper containing 'Leucophor' (Trade Mark) LN optical brightener which after checking porosity was given a CB coating as before. A CB paper of excellent printability as given without problems in the CB coating process.

Examples 3 and 4

Examples 1 and 2 were repeated with respectively 2 parts by weight and 24 Kg of 'Aquapel' (Trade Mark) 360  $\times$  3 neutral C<sub>16</sub> alkyl ketene dimer size (the level used being such as to give a final coating contact angle of 110° Papers of excellent printability and, further, edge paddable with 100% fanning were obtained.

Examples 5 and 6

Those are further Examples with coating structure agent and size together, mixes as below, with water to total 3630 parts, i.e. solids of mix = 55%

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Component	Example 5			Example 6		
	Wet Parts	Dry Parts	%	Wet Parts	Dry Parts	%
"Hydrocarb" 70 calcium carbonate	1275	1275	63.8	1259	1259	63.0
"Alphatex" calcined kaolin	300	300	15	300	300	15
"Dispex" N40 dispersing agent	9.1	3.6	0.18	9.1	3.6	0.18
CMC (med mol.wt) coating structure agent	24	24	1.2	40	40	2.0
"Aquapel" 360 X 3 size	322.5	24	1.2	322.5	24	1.2
"Revinex" 98F10 latex binder	720	360	18	-	-	-
Dow 620 latex binder	-	-	-	720	360	18
"Nopcote" C104 calcium stearate	20	10	0.5	20	10	0.5

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Procedures for preparation of the coating mix and its application are as in Examples 1 and 2. Measured porosities (Bendtsen) are:

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	Ex. 5	Ex. 6
Before CB coat	40.2	ca. 40
After	35.4	ca. 35

and, generally, similarly successful results to Examples 1 and 2 are obtained.

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#### Example 7

The following is again of the use of a coating structure agent and size together, and is in effect six examples in one (three mixes each coated at two levels).

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The formulations were made and coated as in Example 1, the calcium carbonate being of 4 microns median particle size, at 3 and 6 g/m<sup>2</sup>, on the rougher side of 'Idem' base paper as used in Example 1.

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	Material	Dry parts	
25	Mix 1	Calcium carbonate	100 Total
		Binder	22 55% solids
		Coating structure agent	1 pH 9.5
	Mix 2	Size	2.5
		Optical brightener	1
		Calcium carbonate	75 Total
30		China clay	25 50% solids
		Binder	20 pH 9.5
		Coating structure agent	1
	Mix 3	Size	2.5
		Optical brightener	1
		Calcium carbonate	50 Total
35		China clay	50 47% solids
		Binder	20 pH 9.5
		Coating structure agent	1
		Size	3.7
		Optical brightener	1

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The pairs of samples, all of which showed satisfactory porosities, were subjected to physical testing, in comparison to the uncoated base itself, on a number of criteria significant to CB sheet performance.

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a) Roughness Lower values (of rate of passage of air) indicate improved smoothness

Base 220 ml/min  
3 g/m<sup>2</sup> samples 170 ml/min  
6 g/m<sup>2</sup> samples 140 ml/min

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b) Contact Angle

Base 118°  
Mix 1, both samples 117°

Mix 2, both samples 116°

Mix 3, both samples 111°

These are all very good values of above 110° and, it may be noted, do not vary with the coating weight.

5 Base 19.0 g/m<sup>2</sup>/min  
 Other samples 15.5-17.0 g/m<sup>2</sup>/min

10 d) Whiteness/Brightness A. Eirepho

15 Values calculated using filters 9, 10, 11, the brightness being given by the filter 11 value.

Brightness	Lightness	a	b
Base 87.3	96.96	15.85	-8.81
Coatings 88.5 to 89.1	96.24	16.16 to 16.42	-9.29 to -9.83
+a = redder -a = greener	+b = yellower -b = bluer		

20 B. Macbeth IC System.

25 Results were taken with the U.V. in. Significant improvement was seen in reflectance at 440 nm.

Sample	Coat weight g/m	440 nm Reflectance	L D65	a D65	b D65
Base	-	88.95	95.54	-0.50	0.32
Run 1	3	91.19	95.19	0.24	-0.67
Run 2	6	92.64	95.60	0.39	-0.74
Run 3	3	91.43	95.31	0.19	-0.65
Run 4	6	92.14	95.61	0.32	-0.52
Run 5	3	91.03	95.85	0.20	0.27
Run 6	6	91.30	95.78	0.29	0.11

45 e) I G T Pick

Using Spring A (35 Kgf) and medium oil. Mix 1 and Mix 2 show improvements on the base and Mix 3 approximately equal values to the base, all satisfactory.

50 In a printing trial, mix 1, 2 and 3 papers, which had been CB coated with production black copy formulation with control samples from normal production CB, were printed on a Muller-Martini web offset printing machine using 'Irlam T11392' (Trade Mark) black ink and a speed of 670 rpm (250 m/min). The Mix 1, 2 and 3 papers all showed low dust, with good ink density/intensity, very little set off, and IGT pick very low or not visible.

55 In an edge padding trial, form sets were made up using a latex-based adhesive with CB, 2 x CFB, and CF sheets, the CFB and CF sheets being standard 'Idem' production and the CB sheets being either standard 'Idem' production base, for comparison, or the Mix 1, 2 and 3 papers above. All sets fanned apart 100%. Bonding strengths within sets, on a subjective 1 to 5 scale (too weak, slightly weak, optimum, slightly strong, too strong) were acceptable throughout, the CB-CF bond in particular, though a little less strong with the Mix 1, 2 and 3 papers than with the base, giving no problem through the presence of the front coating.

Example 8

In a further multi-part example the formulation below was made up as before, first as shown (Example 8-C) then with the following changes, substitutions being weight for weight:-

5 Example 8-2 Mistron Vapour 3 P (Trade Mark) talc as pigment replacing the kaolin clay  
 Example 8-5 Solfarex A 55 (Trade Mark) starch hydroxyalkyl ether as binder replacing latex  
 Example 8-7 Cyclopal A (Trade Mark) anionic modified polyurethane as size replacing the 'Aquapel'  
 Example 8-10 CMC coating structure agent omitted  
 10 Example 8-11 Procote 400 (Trade Mark) soy protein as coating structure agent replacing the CMC

Formulation Example 8-C

Components are given in the order, pigment, binder, other components, not the order of addition used in mix preparation.

Material	Description	% (w/w)
20 Hydrocarb 70	Calcium carbonate pigment	63.9
Alphatex	Calcined kaolin clay pigment	15.0
Dow 620	Styrene butadiene latex binder	18.0
25 Aquapel 360X	Alkyl ketene dimer size	1.2
Fifix 5	Carboxy methyl cellulose coating structure agent	1.2
Nopcote C104	Calcium stearate lubricant	0.5
Dispex N40	Sodium polyacrylate dispersing agent	0.18
30 Sodium Hydroxide	-	0.04
Leucophor LN	Optical brightening agent	-
Solids = 55%		

35 The formulations were coated onto base paper as in Example 1, the machine speed being 400 m/min, and measurements made of important properties. The following table shows the mix viscosity of the coating mix, together with porosity before and after application of the CB coat, contact angle, and Bendtsen roughness.

Test Results - Example 8					
Example	Coat Mix Viscosity (cPs)	Porosity before CB (ml/min)	Porosity after CB (ml/min)	Contact Angle (Degrees after 2 seconds)	Roughness (Bendtsen)
45 8-C	520	31.5	25.0	77.6	119.0
8-2	505	38.3	13.0	79.0	100.0
8-5	800	25.2	26.0	108.9	125.0
50 8-7	525	27.3	26.5	79.1	132.0
8-10	195	55.2	60.4	89.8	150.0
8-11	102	25.0	23.0	95.8	146.0

55 In addition to the above tests edge padding trials were carried out as before, with bond strengths found normal or slightly low (but still within-specification) CB-CFB and CFB-CF and 100% fan apart. Printing trials, again carried out as before, gave good results, the ink on this occasion being Bonsfield Constat Black 30862 (Trade Mark). Ink density was

good (slightly light in the absence of the coating structure agent), piling was absent, dusting acceptable throughout and in the mix with starch ether binder exceptionally low.

Example 9

5 In a further example a coat mix was made up as an Example 8-C but with the Aquapel 360X replaced by 3.6 parts by weight of 'Fibran 71' (Trade Mark) from National Starch & Chemical Co., which is an alkenyl succinic anhydride size, the other components being in relative parts by weight as shown there, and coated as before. A satisfactory coating was given, the measured contact angle in particular being 104°, well suited to edge padding.

10 **Claims**

1. Record material comprising a paper CB sheet having on its front a printable pigment coating and on its back isolated droplets of colour former solution each confined within a pressure rupturable barrier, wherein the pigment coating comprises a binder for the pigment together with a synthetic reactive sizing agent and optionally also a coating structure agent.
2. Record material of claim 1, wherein the sizing agent is an alkyl ketene dimer, alkenyl succinic anhydride or other neutral reactive size.
3. Record material of claim 1, wherein the sizing agent is a polyurethane size.
4. Record material claimed in any preceding claim wherein the water repellency of the pigment coating, in terms of the contact angle taken up by a water droplet on the surface of the coated paper, is above 90° and advantageously above 100°.
5. Record material claimed in any preceding claim wherein the coating structure agent is present and is a carboxy methyl cellulose, a soya or other protein, an alginate, or other hydrophilic polymer.
6. Record material claimed in any preceding claim wherein the binder is a synthetic rubber latex binder advantageously a styrene butadiene or styrene acrylic latex.
7. Record material claimed in any one of claims 1 to 5 wherein the binder is a hydroxy alkyl ether starch derivative.
8. Record material claimed in any preceding claim wherein the relative amounts of components are by weight 60 - 95 parts pigment, 10 - 30 parts binder, 0.5 - 10 parts size and 0.5 - 5 parts coating structure agent where present.
9. Record material claimed in claim 8 wherein the relative amounts of pigment, binder and size are respectively 60 - 95 parts, 16 - 22 parts and 0.5 - 10 parts.
10. Record material claimed in claim 8 wherein the coating structure agent is present and the relative amounts of pigment, binder, size and coating structure agent are respectively 75 - 85 parts, 12 - 22 parts 1 - 5 parts and 0.5 to 5 parts.
11. Record material claimed in any preceding claim, wherein the coat weight of the front coating is 2 to 20 g/m<sup>2</sup> advantageously 3 to 15 g/m<sup>2</sup>.
12. Record material claimed in any preceding claim, wherein the pigment comprises an inorganic or mineral-derived particulate material, advantageously calcium carbonate.
13. Record material claimed in any preceding claim, wherein the particle size of the pigment is in the range of 1 to 10 microns, advantageously 2 to 5 microns.
14. Record material claimed in any preceding claim, wherein the size is an alkyl ketene dimer or alkenyl succinic anhydride with the alkyl or alkenyl groups from C<sub>8</sub> upwards advantageously from C<sub>12</sub> upwards, and with a maximum of C<sub>24</sub>.
15. Multiple form sets fannable apart without separation of the sheets within the sets each comprising a CB sheet, a CF sheet and optionally one or more CFB sheets, and carrying an edge padding adhesive to join the sheets within

the sets and the sets to each other, wherein the CB sheet is of the record material of any of claims 1 to 14.

16. A method of making a record material comprising a paper sheet having on its front a printable pigment coating and on its back isolated droplets of colour former solution each confined within a pressure rupturable barrier, wherein for the purpose of allowing high speed application of the CB coating subsequent to the application of the pigmented coating the paper sheet is coated with a mix containing a binder for the pigment together with a coating structure agent, a synthetic reactive sizing agent being present also, in an aqueous medium at 25 - 75% advantageously 50 - 65% solids by weight of the mix; is dried to give a coated sheet or Bendtsen porosity 25 to 30 ml/min or more; and is coated on the back at 400 to 450 m/min or more with a colour former coating formulation to give said record material.

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17. A method according to claim 16, wherein the components of the pigment coating are such as to give a record material according to any of claims 2 to 14.

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## Patentansprüche

1. Aufzeichnungsmaterial umfassend ein Papier-CB-Blatt mit einer druckfähigen Pigmentbeschichtung auf seiner Vorderseite und isolierten Tröpfchen einer Farbbildnerlösung auf seiner Rückseite, jeweils angeordnet innerhalb einer durch Druck zerbrechlichen Barriere, worin die Pigmentbeschichtung ein Bindemittel für das Pigment zusammen mit einem synthetischen reaktiven Leimungsmittel und gegebenenfalls einem Beschichtungsstrukturmittel umfaßt.
2. Aufzeichnungsmaterial nach Anspruch 1, worin das Leimungsmittel ein Alkylketendimer, Alkenylsuccinanhidrid oder ein anderer neutraler reaktiver Leim ist.
- 25 3. Aufzeichnungsmaterial nach Anspruch 1, worin das Leimungsmittel ein Polyurethan-Leim ist.
4. Aufzeichnungsmaterial nach einem der vorhergehenden Ansprüche, enthaltend ein Leimungsmittel, worin die Wasserabstoßung der Pigmentbeschichtung, ausgedrückt als Kontaktwinkel eingenommen von einem Wassertropfen auf der Oberfläche des beschichteten Papiers, mehr als 90° und vorteilhaft oberhalb 100° liegt.
- 30 5. Aufzeichnungsmaterial nach einem der vorhergehenden Ansprüche, worin das Beschichtungsstrukturmittel eine Carboxymethylcellulose, ein Soja- oder anderes Protein, ein Alginat oder ein anderes hydrophiles Polymer ist.
- 35 6. Aufzeichnungsmaterial nach einem der vorhergehenden Ansprüche, worin das Bindemittel ein synthetisches Gummitatexbindemittel, vorzugsweise ein Styrolbutadien- oder Styrolacryllatex ist.
7. Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 5, worin das Bindemittel ein Hydroxylalkylether-Stärke-Derivat ist.
- 40 8. Aufzeichnungsmaterial nach einem der vorhergehenden Ansprüche, worin die relativen Mengen der Komponenten bezogen auf das Gewicht 60 bis 95 Teile Pigment, 10 bis 30 Teile Bindemittel, 0,5 bis 10 Teile Leim und 0,5 bis 5 Teile Beschichtungsstrukturmittel, wo vorhanden, sind.
- 45 9. Aufzeichnungsmaterial nach Anspruch 8, worin die relativen Mengen von Pigment, Bindemittel und Leim respektive 60 bis 95 Teile, 16 bis 22 Teile und 0,5 bis 10 Teile sind.
10. Aufzeichnungsmaterial nach Anspruch 8, worin das Beschichtungsstrukturmittel vorhanden ist und die relativen Mengen von Pigment, Bindemittel, Leim und Beschichtungsstrukturmittel respektive 75 bis 85 Teile, 12 bis 22 Teile, 1 bis 5 Teile und 0,5 bis 5 Teile sind.
- 50 11. Aufzeichnungsmaterial nach einem der vorhergehenden Ansprüche, worin das Schichtgewicht der Vorderseitenbeschichtung 2 bis 20 g/m<sup>2</sup>, bevorzugt 3 bis 15 g/m<sup>2</sup> ist.
12. Aufzeichnungsmaterial nach einem der vorhergehenden Ansprüche, worin das Pigment ein anorganisches oder Mineral-abgeleitetes teilchenförmiges Material, bevorzugt Calciumcarbonat umfaßt.
- 55 13. Aufzeichnungsmaterial nach einem der vorhergehenden Ansprüche, worin die Teilchengröße des Pigments im Bereich zwischen 1 und 10 µm, bevorzugt 2 und 5 µm liegt.

14. Aufzeichnungsmaterial nach einem der vorhergehenden Ansprüche, worin der Leim ein Alkylketendimer oder Alkenylsuccinanhidrid mit Alkyl oder Alkenylgruppen von C<sub>8</sub> aufwärts, bevorzugt von C<sub>12</sub> aufwärts und mit einem Maximum von C<sub>24</sub> ist.

5 15. Sets mit verschiedener Form, die jeweils ein CB-Blatt, ein CF-Blatt und gegebenenfalls ein oder mehrere CFB-Blätter enthalten und ein Kantenpolsteradhäsiv (edge padding adhesive) tragen, um die Blätter in den Sets und die Sets miteinander zu verbinden, worin das CB-Blatt aus dem Aufzeichnungsmaterial nach einem der vorhergehenden Ansprüche ist, wobei das Leimungsmittel vorhanden ist, um zu ermöglichen, daß die Sets ohne Trennung der Blätter in den Sets aufgefächert werden können.

10 16. Verfahren zur Herstellung eines Aufzeichnungsmaterials, umfassend ein Papierblatt mit einer druckfähigen Pigmentbeschichtung auf seiner Vorderseite und isolierten Tröpfchen einer Farbbildnerlösung auf seiner Rückseite, jeweils angeordnet innerhalb einer durch Druck zerbrechlichen Barriere, wobei zum Zweck einer Hochgeschwindigkeitsaufbringung der CB-Beschichtung anschließend an die Aufbringung der pigmentierten Beschichtung man das Papierblatt mit einer Mischung, enthaltend ein Bindemittel für das Pigment zusammen mit einem Beschichtungsstrukturmittel, wobei auch ein synthetisches reaktives Leimungsmittel anwesend ist, in einem wässrigen Medium mit 25 bis 75 %, vorzugsweise 50 bis 65 % Feststoffen, bezogen auf das Gewicht der Mischung, beschichtet, trocknet, um ein beschichtetes Blatt mit einer Bendtsen-Porosität von 25 bis 30 ml/min oder mehr zu erhalten, und auf der Rückseite bei 400 bis 450 m/min oder mehr mit einer Farbbildner-Beschichtungsformulierung beschichtet, um das Aufzeichnungsmaterial zu erhalten.

15 17. Verfahren nach Anspruch 16, worin die Komponenten der Pigmentbeschichtung derart sind, daß sie ein Aufzeichnungsmaterial nach einem der Ansprüche 2 bis 14 ergeben.

20 25 **Revendications**

1. Matériau d'enregistrement comprenant une feuille de papier CB (revêtue à l'envers) comportant à l'endroit un revêtement de pigments imprimables et à l'envers, des gouttelettes isolées d'une solution formatrice de couleur, retenues chacune à l'intérieur d'une barrière pouvant être brisée par pression, dans lequel le revêtement de pigments comprend un liant pour le pigment, avec un agent d'apprêt réactif synthétique et éventuellement en outre un agent de structure de revêtement.

2. Matériau d'enregistrement selon la revendication 1, dans lequel l'agent d'apprêt est un dimère d'alkylcétène, un anhydride alcénysuccinique ou un autre produit d'apprêt réactif neutre.

3. Matériau d'enregistrement selon la revendication 1, dans lequel l'agent d'apprêt est du type polyuréthane.

4. Matériau d'enregistrement selon l'une quelconque des revendications précédentes, dans lequel la capacité de répulsion d'eau du revêtement de pigments, en terme d'angle de contact formé par une gouttelette d'eau à la surface du papier enduit, est supérieur à 90° et de préférence supérieur à 100°.

5. Matériau d'enregistrement selon l'une quelconque des revendications précédentes, dans lequel un agent de structure de revêtement est présent et est la carboxyméthylcellulose, une protéine de soja ou une autre protéine, un alginat ou un autre polymère hydrophile.

6. Matériau d'enregistrement selon l'une quelconque des revendications précédentes, dans lequel le liant est un liant latex en caoutchouc synthétique, avantageusement un latex styrène-butadiène ou un latex styrène-acrylique.

7. Matériau d'enregistrement selon l'une quelconque des revendications 1 à 5, dans lequel le liant est un dérivé d'amidon hydroxyalkyléther.

8. Matériau d'enregistrement selon l'une quelconque des revendications précédentes, dans lequel les quantités relatives des composants sont, en poids, de 60-95 parties de pigments, de 10-30 parties de liant, de 0,5-10 parties d'apprêt et de 0,5-5 parties d'agent de structure de revêtement lorsqu'il est présent.

9. Matériau d'enregistrement selon la revendication 8, dans lequel les quantités relatives de pigments, du liant et de l'apprêt sont respectivement de 60-95 parties, de 16-22 parties et de 0,5-10 parties.

10. Matériau d'enregistrement selon la revendication 8, dans lequel les quantités relatives de pigments, du liant, de

l'apprêt et de l'agent de structure de revêtement sont respectivement de 75-85 parties, de 12-22 parties, de 1-5 parties et de 0,5-5 parties.

- 5 11. Matériau d'enregistrement selon l'une quelconque des revendications précédentes, dans lequel le poids du revêtement sur l'endroit de la feuille est de 2 à 20 g/m<sup>2</sup>, de préférence 3 à 15 g/m<sup>2</sup>.
- 10 12. Matériau d'enregistrement selon l'une quelconque des revendications précédentes, dans lequel le pigment comprend un matériau particulaire inorganique ou dérivé d'un composé minéral, de préférence le carbonate de calcium.
- 15 13. Matériau d'enregistrement selon l'une quelconque des revendications précédentes, dans lequel la taille des particules du pigment est comprise entre 1 à 10 microns, de préférence entre 2 à 5 microns.
- 20 14. Matériau d'enregistrement selon l'une quelconque des revendications précédentes, dans lequel l'agent d'apprêt est un dimère d'alkylcétène ou un anhydride alcénylsuccinique, les groupes alkyles et alcényles étant en C<sub>8</sub> ou plus, de préférence en C<sub>12</sub> ou plus, et au maximum en C<sub>24</sub>.
- 25 15. Liasses à feuilles multiples déployables, sans séparation des feuilles des liasses, comprenant chacune une feuille CB (revêtue à l'envers), une feuille CF (revêtue à l'endroit) et éventuellement une ou plusieurs feuilles CFB (revêtues à l'endroit et à l'envers) et portant un adhésif d'assemblage de bord pour relier les feuilles à l'intérieur des liasses et les liasses entre elles, dans lesquelles la feuille CB est en un matériau d'enregistrement selon l'une quelconque des revendications 1 à 14.
- 30 16. Procédé de préparation d'un matériau d'enregistrement comprenant une feuille de papier comportant à l'endroit un revêtement de pigments imprimables et à l'envers, des gouttelettes isolées d'une solution formatrice de couleur, retenues chacune à l'intérieur d'une barrière pouvant être brisée par pression, procédé dans lequel pour permettre une application à vitesse élevée du revêtement CB à la suite de l'application du revêtement de pigments, la feuille de papier est revêtue d'un mélange contenant un liant pour le pigment, avec un agent de structure de revêtement, un agent d'apprêt réactif synthétique étant également présent dans un milieu aqueux à 25-75 % en poids, et de préférence 50-65 % en poids de matières solides par rapport au mélange ; la feuille est ensuite séchée pour fournir une feuille revêtue de porosité Bendtsen de 25 à 30 ml/min ou plus ; et elle est alors revêtue à l'envers à 400 à 450 m/min ou plus, avec une composition de revêtement formatrice de couleur pour donner ledit matériau d'enregistrement.
- 35 17. Procédé selon la revendication 16, dans lequel les composants du revêtement de pigments sont tels qu'ils conduisent à un matériau d'enregistrement selon l'une des revendications 2 à 14.

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