
(12) **UK Patent Application** (19) **GB** (11) **2 039 934 A**

(21) Application No **7943388**

(22) Date of filing **17 Dec 1979**

(30) Priority data

(31) **365U**

45768U

(32) **29 Dec 1978**

5 Jun 1979

(33) **United States of America**
(US)

(43) Application published

20 Aug 1980

(51) **INT CL³**

B41M 5/22 5/16

(52) Domestic classification

C4A C12E C14 C15 C16

C17 C19 C2 C4 C6A C6B

C6C C7

D2B 40C1 40C2 40C4B3

40C4D2 40C4D3 40F1

(56) Documents cited

GB 1337924

US 3775424A

(58) Field of search

C4A

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(54) **Record receiving sheet**

(57)

A record receiving sheet for use in a pressure-sensitive copying system has a coating of a water-insoluble, substantially chemically-neutral pigment (e.g. CaCO₃) with 7-(1-ethyl-2-methylindol-3-yl)-7-(4-diethylamino-2-ethoxyphenyl)-5,7-dihydrofuro (3,4-b) pyridin-5-one and/or 5-(1-ethyl-2-methylindol-3-yl)-5-(4-diethylamino-2-ethoxyphenyl)-5,7-dihydrofuro (3,4-b)pyridin-7-one adsorbed thereon.

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SPECIFICATION

Record receiving sheet

5 This invention principally relates to a record receiving sheet, a process for its preparation, and to a pressure-sensitive manifold set containing it. 5

The colour forming systems used in pressure - sensitive record material generally employ a substantially colourless chromogenic material, a colour developer capable of reacting with the chromogenic material to generate a colour, and also a solvent in which the colour forming reaction can take place. The reactive components of the colour forming system are kept apart until the time of use and this is normally achieved by microencapsulating a solvent solution of one of them. At the time of use, the application of pressure causes rupture of those microcapsules that are subject to such pressure and consequential release of the solvent solution. This then allows both colour forming components to be brought into reactive contact and to generate a coloured image which exactly corresponds to the pattern of applied pressure. In this way, pressure-sensitive record material can be used to provide copies without the need for any carbon paper. 15

The reactive colour forming components and the solvent can be arranged on record material in a number of ways. In one arrangement, referred to as a transfer system, a micro-encapsulated solution of one of the colour forming components is coated onto a side of a sheet (the CB sheet), and the second of the colour forming components is coated onto a side of another sheet (the CF sheet). The pair of sheets are then assembled into a manifold set with their coatings in continuous relationship so that, on the application of pressure to the uncoated side of the CB sheet, the solution is released and transferred to the record receiving CF sheet for the colour forming reaction to take place thereon. The manifold set may additionally include one or more intermediate sheets (CFB sheets) which have a coating of the microencapsulated solution on one side and a coating of the second of the colour forming components on the other side. In this way, further copies can be obtained as long as the sheets are appropriately arranged for the solution to be transferred to the record receiving CF or CFB sheets. 20 25

In another arrangement, referred to as a self-contained system, a microencapsulated solution of one of the colour forming components and the second of the colour forming components are admixed and incorporated within, or coated onto the same side of, a sheet. On application of pressure to the record receiving sheet, the solution is released and reacts with the second of the colour forming components to generate a coloured image on the sheet in correspondence with the pattern of applied pressure. 30

In both the transfer and the self-contained systems, the colour forming component which is microencapsulated as a solution is normally the chromogenic material since this is usually more susceptible to atmospheric deterioration than the colour developer. However, there has recently been described in British patent 1337924 a record receiving sheet i.e. a sheet upon which the colour forming reaction takes place, having a coating of a water-insoluble substantially chemically-neutral pigment on which is adsorbed a substantially colourless basic chromogenic material capable of forming a colour when reacted with a colour developer. Adsorption on to the pigment substantially stabilizes the chromogenic material against atmospheric deterioration and thus enables the sheet to be used in a reverse system in which the colour developer, and not the chromogenic material, is microencapsulated as a solvent solution. 35 40

Although others are mentioned, the only chromogenic material actually employed in the record receiving sheet of British patent 1337924 is crystal violet lactone (3,3- bis - (p-dimethylaminophenyl) - 6 - dimethylaminophthalide). The use of this material affords a sheet which is eminently suitable for use in a reverse system but which has a number of properties that still require improvement. Such properties include the intensity of the developed coloured image (image intensity), the ability of the image to resist fading (fade resistance), and the ability of the adsorbed chromogenic material to resist atmospheric deterioration. 45

It is an object of the present invention to provide a record receiving sheet for use in a reverse system and which contains an improvement in the above-mentioned properties.

The present invention provides a record receiving sheet having on one side a coating of water-insoluble substantially chemically-neutral pigment with pyridyl blue adsorbed on the pigment. 50

The use of pyridyl blue imparts to the record receiving sheet of the present invention an improvement in its resistance to atmospheric deterioration and an ability to produce an image of improved intensity and fade resistance, whilst retaining all the advantages of a record receiving sheet for use in a reverse system.

Pyridyl blue itself is a novel chromogenic material which has the following formula:-

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65

5-(1-Ethyl-2-methylindol-3-yl)-5-(4-diethylamino-2-ethoxyphenyl)-5,7-dihydrofuro (3,4-b)

5 pyridin-7-one

7-(1-Ethyl-2-methylindol-3-yl)-7-(4-diethylamino-2-ethoxyphenyl)-5,7-dihydrofuro (3,4-b)

pyridin-5-one

5

10 Either of these two isomers can be used as the chromogenic material although the pyridin-5-one isomer is the more effective. However, the processes which can be used to synthesise pyridyl blue (for example see British patent 1367567 and U.S. patent 3775424) usually produce a mixture of isomers and separation of one isomer from the mixture by conventional techniques (e.g. chromatography) is difficult, time-consuming, and costly on a commercial basis. It is therefore more convenient to use a mixture and to use for its preparation a synthetic process in which the conditions have been selected to favour formation of the pyridin-5-one isomer. In this way, a mixture can be obtained for use in the record receiving sheet, and in which the more effective pyridin-5-one isomer predominates. When it is reacted with a colour developer, pyridyl blue

15 generates a blue colour.

Examples of water-insoluble substantially chemically-neutral pigments include calcium carbonate, zinc oxide, barium sulphate, titanium dioxide, barium carbonate magnesium carbonate, calcium oxide, magnesium titanate and zinc sulphide. Calcium carbonate is however preferred.

20 For a transfer system, the record receiving sheet is used as such as a CF sheet or is coated on the other side with a pressure rupturable microencapsulated solution of a colour developer to provide a CFB sheet.

For a self-contained system, a pressure-rupturable micro-encapsulated solution of a colour developer is coated on the same side of, or distributed within, the sheet, preferably within its coating.

The record receiving sheet of the invention has a plastic on preferably a paper base.

25 The present invention also provides a process for the preparation of a record receiving sheet which comprises adsorbing pyridyl blue on to a water-insoluble substantially chemically-neutral pigment and then coating a formulation containing the resulting pigment on to a sheet.

30 The method of effecting adsorption of the pyridyl blue on to the pigment is not critical to the invention - the only requirement being that pyridyl blue be adsorbed in a colourless state on the pigment. Methods which can be used include passing a solution of pyridyl blue through a bed of the pigment as in chromatographic processes, and precipitation of pyridyl blue from solution in the presence of the pigment by any of the many precipitation inducing techniques known in the chemical art. Examples of such techniques include dilution of the pyridyl blue solution with a solution-miscible non-solvent for pyridyl blue, chemical neutralization of an acidic aqueous solution of pyridyl blue, cooling a hot solution of pyridyl blue, and evaporation of the solvent from a solution of pyridyl blue. Any of these methods provides a water-insoluble substantially

35 chemically-neutral pigment having pyridyl blue adsorbed thereon and such a pigment represents a further aspect of the present invention.

40 A formulation containing the pigment with pyridyl blue adsorbed thereon, which formulation represents another aspect of the present invention, is coated on to the sheet by any one of the well known coating methods used in the pressure-sensitive record material art. For example a Mayer rod or air-knife coating method can be used.

The formulation itself is normally aqueous and contains a suitable binder, such as a styrene-butadiene latex and/or starch. In addition, it may contain small amounts of conventional paper coating ingredients, for example wetting agents and defoamers.

45 Further information concerning coating formulations and coating methods for use in the process of the present invention can be obtained from U.S. Patents 3627581, 3775424 and 3853869.

50 However, in applying the teaching of these patents to the present process, due allowance should be made for the fact that, when the record receiving sheet is to be used in a transfer system, the formulation containing the pigment with pyridyl blue adsorbed thereon should be coated on the CF sheet or the CF side of a CFB sheet. And the microencapsulated solvent solution of the colour developer should be coated on the CB sheet or the CB side of a CFB sheet. As mentioned previously, this is a reverse arrangement to that normally encountered in the pressure-sensitive record material art.

If the record receiving sheet is to be used in a self-contained system in which both colour forming components are contained in the coating, then the coating formulation should also contain the microencapsulated solvent solution of a colour developer.

55 The colour developer may be any of those known in the pressure-sensitive record material art but it must of course be capable of being dissolved in a solvent and of developing the colour of pyridyl blue. Suitable examples of such colour developers include acidic novolak resins, such as p-phenylphenol-formaldehyde resin or p-octyl phenol-formaldehyde resin.

60 The solvent for the acidic resin colour developer again may be any of those known in the pressure-sensitive record material art. Preferred examples include dibenzyl ether; Magnaflux oil (which is a saturated hydrocarbon oil having been distilled within the temperature range of from 370° to 500°F); benzyl benzoate; 2,2,4-trimethyl-1,3-pentanediol di-i-butyrate (TX1B; U.S. patent 4027065); dibutyl phthalate; 1,2,4-trimethyl benzene; ethyldiphenyl methane (U.S. Patent 3 996 405); C₁₁ - C₁₂ alkylbenzene; and i-propyl biphenyl (U.S. Patent 3 627 581). However, the most preferred is a mixed solvent of dibenzyl ether and

65 Magnaflux oil.

65

The microcapsules for the solvent solution of an acidic resin colour developer can be prepared from gelatin, as described in U.S. Patent 3 041 289, from a urea-formaldehyde polymer, as described in U.S. Patent 4 001 140, from resorcinol-formaldehyde filled polyvinyl alcohol wall capsules, as described in U.S. Patent 3 755 190, or from various melamine-formaldehyde polymers, as described in U.S. Patent 4 100 103.

5 The present invention further provides a pressure-sensitive manifold set which includes a record receiving sheet as described herein before. 5

The present invention will now be described with reference to a number of examples thereof which do not however limit the scope of the invention.

10 *Example 1 - Preparation of Pyridyl Blue* 10

Quinolinic anhydride (0.21 mol) and 1-ethyl-2-methylindole (0.33 mol) were mixed together in a reaction flask at 65 - 70°C for 3 hours. The reaction mixture was then cooled and washed with benzene (or chlorobenzene) to provide (1-ethyl-2-methylindol-3-yl) (3-carboxypyridin-2-yl) ketone and its isomer (0.19 mol).

15 (1-Ethyl-2-methylindol-3-yl) (3-carboxypyridin-2-yl) ketone and its isomer (together 58.0g; 0.188 mol) were stirred for two hours at 60-65°C with N, N-diethyl-m-phenetidine (35.3 g; 0.188 mol) and acetic anhydride (250ml). The reaction mixture was poured into water (500 ml) and the acetic anhydride hydrolyzed by slowly adding 29% ammonium hydroxide (450 ml). After stirring for two hours, the resulting solid was filtered and washed with water, 40% methanol/water (200 ml) and petroleum ether (b.p. 60-110°C; 50 ml). The solid was 20

then dried to constant weight in an oven at 75°C to give a mixture (9:1 respectively) of 7-(1-ethyl-2-methylindol-3-yl)-7-(4-diethylamino-2-ethoxyphenyl)-5, 7-dihydrofuro (3,4-b) pyridin-5-one and 5-(1-ethyl-2-methyl-indol-3-yl) -5-(4-diethylamino-2-ethoxyphenyl)-5, 7- dihydrofuro (3,4-b) pyridin-7- one (80.5g, 90%, m.p.~134-137°C). 20

25 *Example 2 - Preparation of Pyridyl Blue CF Record Receiving Sheet* 25

(a) Pyridyl blue (1g) was dissolved in acetone (150 ml). Precipitated calcium carbonate (70g), Cabolite 100 urea - formaldehyde resin pigment (20g; U.S. patent 3988522), and zinc oxide (10g; Green Seal 8 from New Jersey Zinc Co., U.S.A.) were then blended in the above solution and the resulting dispersion allowed to dry in a hood.

30 (b) The product of stage (a) was then made up into a coating formulation with the following ingredients and proportions: 30

	Parts by Weight		Dry Weight %	
	Wet	Dry		
35 Stage (a) product	84	84	83.4	35
Penford Gum 260 (modified corn starch)	100	10	9.9	
Dow Latex 620 (carboxylated styrene - butadiene latex)	12	6	6.0	40
40 Tamol 731 (25% solution of the sodium salt of a poly-meric carboxylic acid, supplied by Roh m & Haas)	3	0.75	0.7	45
45 Water	250			
	449	100.75	100	50

(c) The resulting formulation was coated on 34 pound (15.42 kg) bond sheet paper with a No. 12 Mayer rod, and subsequently dried. The dry coating weight was about 4.5 pounds (2.04 kg) per ream of 500 sheets, measuring 25 by 38 inches (63.5 × 96.5 cm).

55 *Example 3 - Preparation of CVL CF Record Receiving Sheet* 55

The procedures of stages (a), (b) and (c) of example 2 were repeated except with the replacement of pyridyl blue by crystal violet lactone.

60 *Example 4 - Alternative Preparation of Pyridyl Blue CF Record Receiving Sheet* 60

(a) Pyridyl blue (300 g), calcium carbonate (600 g), 10% solids Penford Gum 230 (modified corn starch; 300g), 25% solids Tamol 731 (30 g), and water (1200g) were ground in an attritor for 45 minutes together with a few drops of octanol to reduce foaming.

(b) The product of stage (a) was then made up into a coating formulation with the following ingredients and proportions: 65

	Wet	Parts by Weight Dry	Dry Weight %	
Stage (a) product	6.3	2.0	3.0	
5 Calcium carbonate	43.4	43.4	65.8	5
Ansilex clay (U.S. patent 3586523)	9.9	9.9	15.0	
Penford Gum 230	68.0	6.6	10.0	
Dow Latex 620	8.0	4.0	6.0	
10 Calgon T	0.1	0.1	0.1	10
(fused sodium - zinc phosphate glass powder composition)				
Water	110.3			
15	244.0	66.0	99.9	15
Coating solids		27%		
Viscosity		58 cps		

20 (c) The resulting formulation was coated on 34 pound (15.42 kg) base sheet paper with an air knife coater, and subsequently dried. The dry coating weight was about 4.5 pounds (2.04 kg) per ream of 500 sheets, measuring 25 by 38 inches, (63.5 × 96.5 cm). 20

25 *Example 5 - Alternative Preparation of CVL CF Record Receiving Sheet* 25

The procedures of stages (a), (b) and (c) of example 4 were repeated except with the replacement of pyridyl blue by crystal violet lactone and also the replacement of 300 g of calcium carbonate in stage (a) by 300 g of zinc resinate.

The coating solids and viscosity of the formulation were 27% and 57 cps respectively.

30 *Example 6 - Preparation of Acidic Resin CB and CFB Sheets* 30

(a) p-Phenylphenol resin (1200 g; PPP resin) was dissolved in dibenzyl ether (3200g) and Magnaflux oil (1600g) with heat and agitation. EMA 31 (ethylene - maleic anhydride copolymer with a molecular weight range of from 75,000 to 90,000; 200g) was dissolved in deionized water (1800g) with heat and agitation. 35 The resulting EMA solution was diluted with deionized water (6000g) and the pH adjusted to 4.0 with 20% sodium hydroxide solution. The oil solution of PPP resin was then emulsified in the EMA solution with a Cowles Dissolver at 25°C. Emulsification was continued until an average oil drop size of approximately 2 microns was attained with the total drop size distribution ranging from about 0.5 to 15 microns. The resulting emulsion was then transferred to a water bath controlled at 55°C and, with rapid agitation, 80% Resloom 714 40 (etherified methylol melamine. 1000g) diluted with deionized water (1000g) was added. the resulting mixture was kept at 55°C for 2 hours under constant agitation to effect capsule formation. After 2 hours, the temperature was allowed to equilibrate slowly with the ambient temperature. Agitation was continued for an additional 16 hours.

(b) The microencapsulated solvent solution of PPP was then made up into a coating formulation with the 45 following ingredients and proportions: 45

	Wet	Parts by Weight Dry	Dry Weight %	
50 Stage (a) capsules	26.60	12.50	71.4	50
Stilt starch	3.20	3.12	17.9	
Stayco S Starch	6.30	0.63	3.6	
Dow Latex 638	2.50	1.25	7.1	
(carboxylated styrene- butadiene latex)				
55 Water	26.40			55
	65.00	17.50	100.00	
Coating solids		27%		
60 Viscosity		68 cps		60

(c) The resulting formulation was coated on 34 pound (15.42 kg) base sheet paper with an air knife coater, and subsequently dried. The dry coating weight was about 3.75 lbs (1.7 kg) per ream of 500 sheets, 65 measuring 25 by 38 inches (63.5 × 96.5 cm). In addition the formulation was coated on to the back side of the 65

record receiving sheets prepared in accordance with the procedure of examples 4 and 5 in order to make CFB sheets.

Example 7 - Preparation of Alternative Acidic Resin CB Sheet

- 5 (a) An oil solution of p-octylphenol resin (1400g; POP) in dibenzyl ether (3200g) and Magnaflux oil (1600g) was prepared using sufficient heat and agitation to effect dissolution. The oil solution was then microencapsulated using the procedure described for stage (a) of example 6. 5
- (b) and (c) The procedures according to stages (b) and (c) of example 6 were repeated except that 27.30 (instead of 26.60) parts by weight (wet) of the POP stage (a) capsules were used and that the formulation was used only to prepare CB sheets. 10

Example 8 - Comparison of Pyridyl Blue and CVL Record Receiving Sheets

Pyridyl blue and Crystal Violet Lactone record receiving sheets were subjected to the Typewriter Intensity test in which a standard pattern is typed on a manifold set comprising a CF and a CB sheet and optionally an intermediate CFB sheet. A coloured print image corresponding to the pattern is thus produced on the CF sheet or the CF side of a CFB sheet, and the intensity of the image is determined with the aid of an opacimeter. 15

The intensity is a measure of colour development and is the ratio of the reflectance of the print image to that of the unimaged area (I/I₀) expressed as a percentage. A high value indicates little colour development and a low value indicates high colour development. 20

For the comparison of pyridyl blue and CVL record receiving sheets, the following intensities were determined:

- A - The original intensity, i.e. the intensity of a print image 24 hours after its initial development
- B - The intensity of an image after it had been exposed: 25
- (i) to fluorescent light, 25
- (ii) to natural sunlight,
- (iii) to ambient conditions, or,
- (iv) within an oven,
- C - The intensity of an image produced on a sheet which had previously been exposed: 30
- (i) to fluorescent light, 30
- (ii) to natural sunlight,
- (iii) to ambient conditions, or,
- (iv) within an oven.

The device for the fluorescent light tests comprised a light box containing a bank of 18 daylight fluorescent lamps (21 inches (53.3cm) long, 13 nominal lamp watts) vertically mounted on 1 inch central supports. The sheets with or without the image were placed 1 to 1.5 inches (2.5 to 3.8 cm) from the lamps for 48 hours. Imaging was done with an IBM Executive Typewriter using a 4-bar cross hatch character. 35

Exposure of the sheets with or without the image to natural sunlight was carried out by placing them for 48 hours in a south-facing window. Imaging was done with an IBM Memory Typewriter using an "X" character. 40

Exposure of the sheets with or without the image to ambient conditions was carried out by hanging them on a laboratory wall for seven and nine weeks during which time the sheets were subjected to air, natural and fluorescent room light, air temperature and moisture content. Imaging was done with an IBM Selectric Typewriter using a solid block character. 40

Exposure of the sheets within the oven was carried out for 3 weeks at a temperature of 140°F (60°C). Imaging was done with an IBM Executive Typewriter using a 4-bar cross hatch character. 45

The results obtained were as follows:

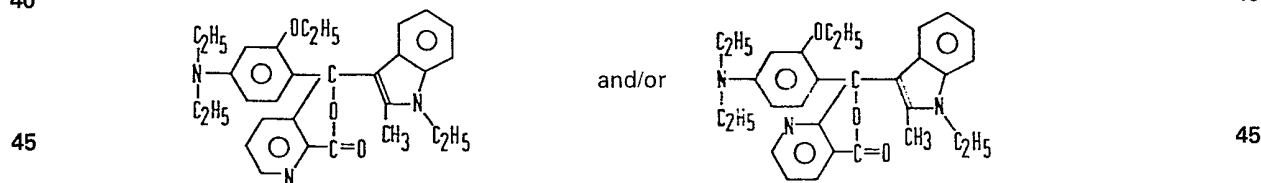
	Acidic Resin Sheet	Record Sheet	A	B(i)	C(i)	
50	Example 6-CB	Example 4-CF	38	48	55	50
	Example 6-CB	Example 5-CF	51	74	78	
	Example 6 and	Example 6 and				
	Example 4-CFB	Example 4-CFB	49	51	56	
55	Example 6 and	Example 6 and				
	Example 5-CFB	Example 5-CFB	52	68	75	55
			A	B(ii)	C(ii)	
60	Example 6-CB	Example 2-CF	40	41	65	60
	Example 7-CB	Example 2-CF	52	53	75	
	Example 6-CB	Example 3-CF	40	52	88	
	Example 7-CB	Example 3-CF	56	74	96	

		A	B(iii)	C(iii)	
				7 Weeks	
5	Example 6-CB	Example 4-CF	33	38	48
	Example 7-CB	Example 4-CF	44	56	54
	Example 6-CB	Example 5-CF	34	45	72
	Example 7-CB	Example 5-CF	57	73	89
10			A	B(iii)	C(iii)
					9 Weeks
	Example 6-CB	Example 4-CF	32	42	44
	Example 6-CB	Example 5-CF	34	54	76
15	Example 6 and	Example 6 and	33	42	45
	Example 4-CFB	Example 4-CFB			
	Example 6 and	Example 6 and	35	55	76
	Example 5-CFB	Example 5-CFB			
20			A	B(iv)	C(iv)
	Example 6-CB	Example 4-CF	40	49	52
	Example 6-CB	Example 5-CF	48	49	75
25	Example 6 and	Example 6 and	48	45	51
	Example 4-CFB	Example 4-CFB			
	Example 6 and	Example 6 and	51	51	68
	Example 5-CFB	Example 5-CFB			

30 From the foregoing results, it can be clearly seen that the record receiving sheet of the present invention is a substantial improvement over the known record receiving sheet utilizing crystal violet lactone at the same concentration. In particular, there is an improved resistance to degradation including atmospheric deterioration and an ability to produce an image of improved intensity and fade resistance.

35 CLAIMS

40 1. A record receiving sheet having on one side a coating of a water-insoluble substantially chemically-neutral pigment and, adsorbed on the pigment, a chromogenic material of formula,



50 2. A record receiving sheet according to claim 1, wherein the pigment is calcium carbonate.
3. A record receiving sheet according to either of claims 1 or 2, wherein the other side of the sheet has a coating of a pressure-rupturable microencapsulated solution of a colour developer.

55 4. A record receiving sheet according to either of claims 1 or 2, wherein a pressure-rupturable microencapsulated solution of a colour developer is coated on the same side of, or distributed within, the sheet.

5. A record receiving sheet according to either of claims 3 or 4, wherein the colour developer is an acidic novolak resin.

6. A record receiving sheet according to claim 5, wherein the resin is a p-phenylphenol-formaldehyde resin or a p-octylphenol-formaldehyde resin.

7. A record receiving sheet according to any one of preceding claims, wherein the sheet has a paper base.

60 8. A process for the preparation of a record receiving sheet which comprises adsorbing a chromogenic material, as defined in claim, 1 on to a water-insoluble substantially chemically-neutral pigment and then coating a formulation containing the resulting pigment on to a sheet.

9. A process according to claim 8, wherein coating is carried out with a Mayer rod or air-knife.

10. A process according to either of claims 8 or 9, wherein the formulation contains a binder.

65 11. A process according to claim 10, wherein the binder is starch.

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12. A process according to claim 10, wherein the binder is styrene-butadiene latex.
13. A pressure-sensitive manifold set which includes a record receiving sheet, as defined in any one of claims 1 to 7.
14. A water-insoluble substantially chemically-neutral pigment having a chromogenic material, as defined in claim 1, adsorbed thereon. 5
15. A coating formulation which contains a water-insoluble substantially chemically-neutral pigment having a chromogenic material, as defined in claim 1, adsorbed thereon.
16. A record receiving sheet substantially as described hereinbefore with reference to any one of the examples.
- 10 17. A process for the preparation of a record receiving sheet substantially as described hereinbefore with reference to any one of the examples. 10
18. A pressure-sensitive manifold set substantially as described hereinbefore with reference to any one of the examples.
- 15 19. A water-insoluble substantially chemically-neutral pigment having a chromogenic material, as defined in claim 1, adsorbed thereon substantially as described hereinbefore with reference to any one of the examples. 15
20. A coating formulation substantially as described hereinbefore with reference to any one of the examples.