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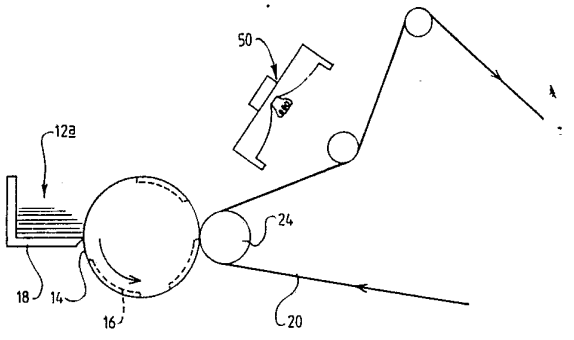
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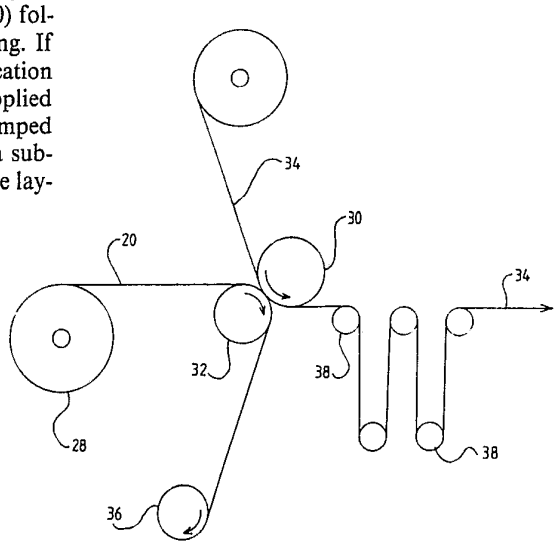
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(54) Title: PRINTING INKS, AND METHODS OF PRINTING

(57) Abstract

A printing ink is utilised, comprising a polyvinylchloride copolymer, plasticiser, antioxidant, stabiliser and pigment, and is applied to a transfer sheet (20) by a gravure roller (14). Successive layers of the printing ink are applied to the transfer sheet (20), and a desired pattern is transferred onto textile (34) by the use of heated pressure rollers (30, 32), at which the applied pattern becomes detached from the transfer sheet (20), and retains adhered to the textile sheet. The ink may be in the form of a powder at room temperature, being melted and applied in molten form to the gravure roller (14) or may be paste or liquid at room temperature, being heated by a lamp (50) following its application to the transfer sheet (20), to initiate curing. If desired, the transfer sheet (20) may be flocked, and after application of the ink to the flocked transfer sheet, a powder adhesive is applied to the ink, enabling (e.g.) a decorative motive or pattern to be stamped from the transfer sheet (20), for the subsequent application to a substrate by the use of heat and pressure, prior to removal of the base layer of the transfert sheet (20), exposing the decorated flocking.





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Description of the Invention

Title: "Printing inks, and methods of printing"

This invention is concerned with improvements relating to printing inks, particularly for use with methods of printing decorative patterns, for example onto textile.

Conventional printing techniques for printing onto textile involve the use of inks which are highly viscous and slow to print, requiring long curing times, and this causes a substantial production delay, particularly where several different colours are to be printed to produce a desired pattern.

Additionally many conventionally used inks, particularly those applied by a sublimation process, produce noxious effluent which require to be removed from the working area and treated to reduce environmental pollution.

Further many conventional inks have restricted colour capability, inasmuch as it is difficult to print successfully, with high resolution, certain colours, particularly onto textile which is darker than the colour or colours to be applied.

Problems are also encountered in producing a printed pattern which is non-toxic to the user of the product, specifically where the product is a textile article, such as may be used by children, and which additionally retains its structural integrity (particularly in relation to cracking) over a significant period of wear, and/or over a number of washing or cleaning cycles.

It is one of the various of this invention to reduce these and other problems encountered in the printing of textile or fabric material: it is however to be appreciated that the invention has applicability in other fields where similar or analogous problems arise, for example in the printing of certain types of wall covering.

It is to be appreciated that the term "ink" is used herein generically as including compositions and materials which may be applied to sheet material, including but not limited to fabric or textile material in sheet form, generally.

According to this invention there is provided a printing ink comprising

[a] a polymeric carrier material;

[b] a plasticiser;

[c] stabiliser; and

[d] pigment.

Preferably the polymeric material is present in a quantity (excluding the pigment) are between 25% and 45%. Advantageously the polymeric material is afforded by a surface coating resin containing hydroxyl groups, and preferably comprises polyvinyl chloride (PVC). Advantageously the carrier material is in the form of a copolymer, conveniently a copolymer of PVC and acrylic acid ester or polyvinyl acetate (PVA).

Advantageously the polymeric material comprises a mixture of copolymers for example in proportions between 60:40 and 40:60.

Advantageously the plasticiser is utilised in a quantity significantly greater than would normally be used, and is preferably present in, in relation to the carrier material, in proportions between 60:40 and 40:60.

Thus the effect of the plasticiser is significantly to reduce the viscosity of the printing ink, particularly where the printing ink is one which is solid at room temperature.

Advantageously there is used as plasticiser a constituent comprising a material selected from the group consisting of adipates, phthalates, sebacates, citrates and phosphates.

Advantageously however the plasticiser comprises a second plasticising component, conveniently selected from the group consisting of polyurethane-based polymeric plasticisers.

In this manner, by the use of two plasticising materials, one may have the effect of reducing the viscosity of the ink during application, particularly where the ink is applied whilst molten, the second being to reduce the hardness of the ink when it has been applied.

By the use of a polyurethane-based plasticiser, some resistance to extraction by common solvents is provided.

Preferably ink comprises an antioxidant, such as a sterically hindered phenolic antioxidant which protects the carrier material against thermo-oxidative degradation.

As stabiliser, preferably an organotin stabiliser of the octyltin mercaptide type is utilised.

Preferably the ink comprises a wax, preferably in an amount (excluding pigment)

at less than 4%, conveniently afforded by a polyethylene wax, preferably a partially-oxidised polyethylene wax. By this means, due to its limited compatibility with PVC, there is produced a pronounced external lubricating action to produce an antisticking effect, reducing the tendency of the ink, particularly when applied in molten form, to the printing roller.

Advantageously the ink comprises a lubricant, conveniently an epoxidised soya bean oil. The effect of such a lubricant is to counter the negative effect of the stabiliser, which can cause the compound to stick to the engraved etch in the printing roller, producing an unlevel print. Additionally, such a lubricant has some secondary heat stabilisation effect.

Advantageously the printing ink comprises a thixotropic agent, conveniently one based on calcium, such as a partially hydrated mixed carbonate of magnesium and calcium. The effect of such an agent is to reduce the viscosity of the formulation under shear, allowing easier application of the ink, but to retain the definition of a design applied by the printing roller.

As pigment many types of organic and inorganic pigment have been found to be suitable for use.

According to this invention there is also provided a method of applying a pattern involving the use of an ink according to Claim 1, and the steps:

[a] applying the ink in fluid condition to a first printing roller;

[b] applying the ink from the said printing roll to a transfer sheet;

[c] applying ink in fluid condition to one or more subsequent printing rolls;

[d] applying ink from each such printing roll to the transfer sheet.

In this manner patterns consisting of inks of a plurality of different colours may be applied to transfer sheet for subsequent application.

Conveniently the transfer sheet may be in the form of a continuance web conveniently paper.

Where the invention is to be utilised in the provision of wall covering, the paper may be of heavy duty, being capable of being applied directly to a surface to be decorated.

Alternatively, where the invention is to be utilised to apply a decorative pattern to textiles, a paper of lighter weight may be utilised.

Preferably the ink is in the form of a powder at room temperature, and is melted prior to application by way of the printing roll to the transfer sheet.

Alternatively the ink may be fluid at room temperature, e.g. liquid or paste, and under these conditions preferably subsequent to each application of ink onto the transfer sheet, the sheet is passed through a heating station to initiate curing of the ink on the carrier, e.g. by the use of IR radiation.

Under these conditions, preferably the ink is applied in reverse order of light absorbency, so that the lighter colours of ink are applied first, and the darker colours are applied last.

The transfer sheet may be flocked, and the ink applied to the flocked transfer sheet so as to penetrate the flocking. Advantageously, immediately subsequent to the application of the ink, the exposed surface of the coated flocking is coated with an adhesive material, by spraying, dusting, roller application or the like. In this manner, when the printing operation has been concluded, the flocked carrier may be cut into pieces, and the pieces individually applied as a decoration by the application of pressure and heat between the receiving material and the transfer sheet, so that the exposed (adhesive-coated) surface is adhered to the receiving material, and the decorative pattern appears on the reverse side of the flocking when the transfer sheet has been peeled away.

However, the method may include the further step of transferring the pattern to sheet textile by the use of heat and pressure applied between the transfer sheet and the textile.

Alternatively a completed pattern, produced as described above, may be transferred directly to a flocked material.

There will now be given detailed descriptions, to be read with reference to the accompanying drawings, of two formulations which have been selected for the purposes of illustrating the invention by way of example, and three methods of printing involving the use of these formulation, which are also illustrative of certain aspects of the invention.

FORMULA 1

Formula 1 consists of the following compositions, in the following approximate amounts:

Polymeric carrier material	39%
Plasticiser	37.5%
Wax	4%
Antioxidant	0.5%
Stabiliser	1.5%
Lubricant	2.5%
Thixotropic Agent	15%

POLYMERIC CARRIER MATERIAL

As polymeric carrier material, preferably are used surface coating resins containing hydroxyl groups based on copolymers of vinyl chloride and acrylic acid ester or vinyl acetate. In Formula 1 blend of two copolymers is used, specifically Vinnol E/40a and E15/48a, supplied by Wacker-Chemie GMBH, of Germany. The materials are provided in the form of white powders, having a particle size of less than 4 mm, and a packing density of approximately 0.4 gram per centimetre cube. The physical specification of these materials are as follows:

Vinnol		E15/40A	E15/48A
K-value (DIN 53276)		39+/-1	48+/-1
Vinyl Chloride content (Wacker method)	% w/w	84+/-1	82.4+/-1
Hydroxyl group content (Wacker method)	% w/w	1.8+/-0.2	1.8+/-0.2
Vicat softening point (DIN 53460)	oC	appr. 0.64	0.67
Viscosity 20% w/w in MEK, dissolved at 50°C (122°F)			

DIN 53015 Hoppler	mPa.s	20+/-5	55+/-10
DIN 53211 4mm cup	s	appr. 0.14	appr. 0.23
DIN ISO 2431 4mm cup	s	appr. 0.22	appr. 0.47

Alternative to the use of vinnol, other polymeric materials, particularly vinyl acetate/vinylchloride copolymers may be used, such as VYHH, VYHD, VYLF, VAGH, VAGD, VROH, VMCH, VMCC, VMCA, as supplied by Union Carbide (UK) Limited of England.

PLASTICISER

As plasticiser preferably Unimoll 66 is utilised, a dicyclohexyl phthalate plasticiser manufactured by Bayer AG, Germany. Unimoll 66 is supplied as a white crystalline material, and has only limited compatibility with PVC.

Other plasticisers which could be used include adipates, phthalates. sebacates, citrates, phosphates and other monomeric and polymeric materials when manufactured in a dry PVC carrier system. For example, REOMOL TPP as manufactured by Ciba-Geigy may be utilised.

PLASTICISER-SECOND CONSTITUENT

As a second constituent of the plasticiser, Ultramoll PU is utilised, as manufactured by Bayer AG. Ultramoll PU is a highly flexible polyurethane based polymeric plasticiser in the form of colourless and odourless powder and incorporates a small proportion of PVC as powdering agent. This product is especially designed for combination with PVC at any ratio, also allowing incorporation of monomeric plasticiser and other polymeric plasticiser. Additionally however, the use of Ultramoll PU affords resistance to extraction by most common solvents, including perchloro and trichloroethylene.

WAX CONSTITUENT

A wax constituent, preferably used Irgawax 371, manufactured by Ciba-Geigy Marienberg GMBH of Germany. This material is partially oxidised polyethylene wax, and due to its limited capability with PVC it exhibits a pronounced external lubricating action. Concentrations above 0.2 phr it has a noticeable antisticking effect, reducing the sticking tendency of the melt onto the hot metal parts of the printing roller.

However other wax-type release agents may be utilised, including Epolene C10P manufactured by Eastman Chemical Corporation, and Hoechst-wachs PED 521, manufactured by Hoechst AG.

ANTIOXIDANT

As antioxidant it is preferred to use Irganox 1076, manufactured by Ciba-Geigy Marienberg GMBH, of Germany. Irganox 1076 is a sterically hindered phenolic antioxidant which protects the substrates into which it is incorporated against thermo-oxidative degradation. The chemical structure is believed to be octadecyle 3-(3,5-di-tert.butyle-4-hydroxyphenyl)-propionate.

Of course alternative antioxidants may be used, such as Irganox 1010, or Hostanox DAR 24, manufactured by Hoechst A.G.

STABILISER

Preferably an organotin stabiliser of the octyltin mercaptide type is utilised, preferably Irgastab 17 MOK, manufactured by Ciba-Geigy Marienberg GMBH. The use of Irgastab 17 MOK allows the melted compound to be processed for longer or at higher temperature without discolouration or degradation. This prolongs the life of the melted ink, preventing discolouration from occurring and also ensuring colour consistency from batch to batch of compound produced.

However other octyltin PVC stabilisers can be used, such as Hostastab SNS 10, manufactured by Hoechst AG, or Tinstab ZT 903, supplied by Haagen Chemie b.v. of Holland.

LUBRICANT

As lubricant preferably Reoplast 392, manufactured by Ciba-Geigy Marienberge GMBH is used, being a grade of epoxidised soya bean oil designed for use as an internal lubricant for PVC. The Reoplast 392 counters the negative effects of the octyltin stabiliser, which can cause the compound to stick into the engraved etch of the impression rollers, thus producing an unlevel print onto the paper. It acts not only as an internal lubricant but also as a secondary heat stabiliser, thus reinforcing the advantages of the primary heat stabiliser.

Alternatively however, other epoxy soya bean oil products can be used.

THIXOTROPIC COMPONENT

As thixotropic component it is preferred to use Ultracarb U5,

manufactured by Microfine Minerals & Chemicals Limited, of England. The material is a natural carbonate filler, additionally having flame retardant properties.

The use of Ultracarb US introduces a thixotropic effect to the formulation of the melted compound, to reduce the viscosity of the ink under shear, and to retain a high viscosity after transfer, to retain the definition of the transfer design.

However many other similar filler types can be utilised.

PIGMENT

Many types or organic or inorganic pigment have been found to be suitable for use within the system, although products from the following two ranges of organic pigments have been shown to be superior with regard to brightness of tone, light fastness, heat stability, toxicity, low dusting and ease of compounding: Hostaprint, manufactured by Hoechst AG, and Microlith C-K manufactured by Ciba-Geigy.

Additionally, to produce "metallic effects", a useful pigment is Silvet EX 592 & 972, manufactured by Silberlene Limited, of Scotland.

To produce "fluorescent effects", it is possible to use various Radglow formulations manufactured by Ciba-Geigy, in particular P-18, PS-10, R-18 and R-19.

Whilst in Formula 1 all the preferred materials are available in powder form, if desired, and in particular in relation to the pigmentary material, and/or the wax, and/or the lubricant, these may be provided in liquid form, although preferably being encapsulated in PVC-compatible solid state material, so that mixing of the constituents of the formula may be carried out in dry state.

FORMULA 2

Polymeric Carrier Material	40%
Plasticiser	34%
Wax	2%
Antioxidant/Lubricant	11.5%
Stabiliser	1%
Thixotropic Agent	11.5%

The preferred materials utilised in Formula 2 are as follows:

POLYMERIC CARRIER MATERIAL

As polymeric carrier material Ucar vinyl resin was utilised, manufactured by Union Carbide Corporation. This material is a vinyl chloride/vinyl acetate copolymer, approximately 86%/14%. Coatings based on this product are thermo-plastic, non-oxidising and non-heat reactive, with a notable absence of colour odour and taste. Their physical characteristics are as follows:

VCL/VA	%	86/1d
Inherent Viscosity	(ASTM D-1243)	0.5
Specific Gravity	(ASTM D-792)	1.35
Glass Transition Temperature	°C	72
Average Molecular Weight,	Mn	20,00
Solution Viscosity at 25°C	cP	600
Particle size	98% by wt through 20 mesh	
Bulky density	385-545 kg/m^3	

Alternatively, Vinnol H15/45, H15/50, H14/36, as manufactured by Wacker-Chemie GMBH could be used.

PLASTICISER

As plasticiser Bisoflex DOP is used, manufactured by BP Chemicals Limited of England. Bisoflex DOP is well known as a general purpose plasticiser for PVC, having Molecular Mass of 390, a Refractive index of n20.D of 1.487, a Density at 20°C of 0.983 Kg/L, and a Boiling point of 220°C at 5 mbar.

However other plasticisers could be used, including DINP, DIDP, DIDP, DOA, or DIDA.

Desirably Bisoflex DOP is used in an amount (excluding pigment), of about 24%.

PLASTICISER/SECOND CONSTITUENT

As a second constituent of the plasticiser, desirably about 10% of Perchem MF is used, manufactured by AKZO Chemicals Limited of England. Perchem

MF is a finely divided hydrogenated castor oil that is used generally s a rheological control agent for paints, polyester gel coats, printing inks, cosmetics and the like. In particular, when used in Formula 2, this product imparts a lower melting point and viscosity, allowing a greater percentage of suspended pigment solids. However other grades of hydrogenated castor oil may be used.

ANTIOXIDANT

As antioxidant, preferably Hercolyn D is used, in an amount (excluding pigment) of about 11.5%. Hercolyn D is manufactured by Hercules BV of the Netherlands, and is a hydrogenated methyl ester of rosin, having an acid number of 4-8.

This material also serves as a lubricant, having excellent wetting properties in relation to others of the components.

STABILISER

Preferably an Organotin stabiliser is utilised, preferably that specified in Formula 1, namely Irgastab 17 MOK. However as will be appreciated, other stabilisers may be used.

WAX CONSTITUENT

A wax constituent, totalling about 2% by weight is used, preferably comprising a mixture in general equal proportions, of Epolene C10P and Irgawax 371, described in more detail in relation to Formula 1.

THIXOTROPIC COMPONENT

As thixotropic component, Ultracarb U5 is preferred, in an amount of about 40% by weight.

PIGMENT

Similar pigments may be used in formula 2 as are described in formula 1, but excellent results have been obtained by use of PV and PV fast, manufactured by Hoechst AG, and Cromopthal and Irgalite manufactured by Ciba-Geigy.

Whilst in Formula 1 the materials are mixed in solid state, in Formula 2 the materials are mixed together at an elevated temperature at which they form a paste, allowing the material when thoroughly mixed to be applied as hereinafter described. Preferably however in the preparation of Formula 2 for application, heat is introduced, to assist thorough mixing and subsequent curing.

Descriptions of the use of the two formulas above described, in relation

to the production of a printed pattern on sheet material, particularly textile, will now be described with reference to the accompanying drawings:

Figure 1 illustrates schematically a machine for applying the first formula, in carrying out a method which is illustrative of certain aspects of this invention, having similarly being selected for the purposes of illustrating the invention by way of example.

In the machine illustrated in of Figure 1, a plurality of stations are shown, the number depending upon the number of colours to be applied. In Figure 1, four stations A, B, C and D are illustrated, although it will be appreciated that the number of stations used will be dependent upon the pattern it is desired to print.

Each of the stations A, B, C and D comprises a mixing station, (better shown in Figure 2) comprising twin calendar rolls 6, 8 into the nip of which the mixed constituents of formula 1 are added, to be calendered to thoroughly mix and melt the constituents. A take-off zone 10 is provided to remove the melted ink, and to transfer it to a heated gravure roller 14, allowing molten ink to be transferred to the patterned recesses 16 of the roller (having a depth of approximately 1.5 mm) in conventional manner. A doctor blade 18, engaging against the gravure roller over the full length thereof, ensures that the non-engraved portions of the roller 14 are retained free of molten ink.

Transfer material, conveniently in the form of a continuous web 10 of paper, is pulled from a supply roll 22 thereof and fed between the gravure roller 14 and a pressure-applying roller 24, bringing the transfer sheet into contact with the gravure roller, and causing ink from the gravure impressions 16 to be applied to the transfer sheet as it passes between the rollers 14 and 24. With the formula used, it has been found that a wholly acceptable transfer onto a transfer sheet of conventional paper weighing 28 grams/metre 2 is successful.

The transfer sheet is similarly applied to the gravure roller of successive stations 14b, 14c and 14d at which further colours are applied to the transfer sheet, to build up a desired pattern of a composite of colours, prior to the sheet being rolled onto a roller 28, where it may be stored until required.

When required to be used, the transfer sheet 20 is drawn from the roll 28 and passed between heated rollers 30 and 32, at which the transfer sheet is brought

into contact with a web 34 of textile material, (Figure 3) which picks up the ink image from the transfer sheet. In this manner the patterns which have been applied to the transfer sheet on its passage through the stations A, B, C and D may successfully be applied to the textile material, allowing scrap transfer sheet to be roller in on a collecting roller 36.

The printed textile 34 may then be passed over a series of idler rollers 38, prior to being taken off.

The machine illustrated in Figure 4 is similar to that illustrated in Figure 1, and will be described hereinafter only insofar as it differs from the machine previously described. For simplicity, only a single station has been shown.

The machine of Figure 2 is suitable for use with the formula No. 2, which when heated is in paste-form, or in the form of a highly viscous liquid. The ink is loaded into a trough 12a, at which it is applied to the gravure roller 14, surplus material being removed by the doctor blade 18. Ink from the gravure 16 is applied to the transfer sheet 20, by the use of a heated roller 24, and the applied coating is passed beneath a high powered IR lamp 50, which heats the surface of the applied coating and initiates curing and setting thereof. Similarly, after passage of the transfer sheet 20 through each of the stations B, C and D, further radiation will be applied to the sheet 20 and the ink deposited thereon, to ensure sufficient curing to minimise any tendency for the pattern being built up onto the transfer sheet to become blurred as it passes through successive rollers.

Figure 5 illustrates schematically the use of the invention in the preparation of decorative items such as for "Applique" work.

As is shown in Figure 5, a flocked transfer sheet 20b, comprising a base 21a of paper or the like material and a coating 21b of flocking, is passed between a heated gravure roller 14 and a pressure roller 24 to apply ink to the flocked layer 21b, generally similar to the manner described in relation to Figures 1, 2 and 3.

After each application station, the surface of the applied ink is coated with a polyester adhesive, such as Turbitrans Elastomelt 95F, manufactured by CHT of Germany, conveniently by the application of the adhesive in powder form, so that the powder adhere to the hot plastics of the ink. Thus on conclusion of the printing process, the flocked sheet is provided with patterns, as desired, on the exterior surfaces of which

a coating of adhesive is provided.

Applique items may then be stamped from the flocked sheet, and these may be applied as desired to (e.g.) textile items by laying the adhesive-coated side against the textile item, and applying heat and pressure against the paper layer 21a, sufficient to activate the adhesive and cause the flocking to adhere to the textile. On setting of the adhesive, the paper backing 20b may be peeled off.

Alternatively, a completely-formed pattern may be applied to the flocked surface, by the use of a transfer sheet 20 as described in relation to Figures 1 to 4, so that an entire series of patterns is provided to the flocked coating at one time, the ink penetrating the fibres 21b of the flocking down to the base layer 21a, and being provided with a coating of hot melt adhesive on completion of printing. At a subsequent stage, applique items may be stamped out of the flocked sheet, and applied by the use of heat and pressure, prior to peeling off of the back layer 21a.

By the use of this invention, printed textile may be obtained in a variety of colours and patterns, which have the advantages of colour fastness and durability, particularly being durable under conditions of cleaning processes, are soft to the touch and are non-toxic.

The following is an acknowledgement of Trade Marks used in this specification:

VINNOL (Wacker-Chemie GMBH)
UNIMOLL (Bayer AG)
REOMOL (Ciba-Geigy)
ULTRAMOLL (Bayer AG)
IRGAWAX (Ciba-Geigy Marienberg GMBH)
EPOLENE (Eastman Chemical Corporation)
IRGANOX (Ciba-Geigy Marienberg GMBH)
IRGASTAB (Ciba-Geigy Marienberg GMCH)
HOSTASTAB (Hoechst AG)
TINSTAB (Haagen Chemie b.v.)
REOPLAST (Ciba-Geigy Marienberg)
ULTRACARB (Microfine Minerals & Chemicals Limited)
HOSTAPRINT (Hoechst A.G.)

MICROLITH (Ciba-Geigy)

SILVET (Silberlene Limited)

RADGLOW (Ciba-Geigy)

UCAR (Union Carbide Corporation)

BISOFLEX (BP Chemicals Limited)

PERCHEM (AKZO Chemicals Limited)

HERCOLYN D (Hercules BV)

CROMOPTHAL (Ciba-Geigy)

IRGALITE (Ciba-Geigy)

FASTINOX (Hoechst AG)

The features disclosed in the foregoing description, or the following claims, or the accompanying drawings, expressed in their specific forms or in the terms or means for performing the desired function, or a method or process for attaining the disclosed result, may, separately or in any combination of such features, be utilised for realising the invention in diverse forms thereof.

CLAIMS:

1. A printing ink comprising

[a] a polymeric carrier material;

[b] a plasticiser;

[c] stabiliser; and

[d] pigment.

2. A printing ink according to Claim 1 wherein the polymeric material is present in a quantity (excluding the pigment) of between 25% and 45%.

3. An ink according to Claim 1 wherein the polymeric material comprises PVC.

4. An ink according to Claim 1 wherein the polymeric material comprises a copolyester of PVC and an acrylic acid ester.

5. An ink according to Claim 1 wherein the polymeric material comprises a copolyester of PVC and polyvinyl acetate.

6. An ink according to Claim 12 wherein the polymeric material comprises a mixture of copolymers in proportions between 80:20 and 20:80.

7. An ink according to Claim 1 wherein the plasticiser is utilised in a quantity significantly greater than would normally be used.

8. An ink according to Claim 7 wherein the plasticiser is present in relation to the carrier material in proportions between 60:40 and 40:60.

9. An ink according to Claim 1 wherein the plasticiser comprises two plasticising materials, a first of said plasticising materials being effective reduce the viscosity of the ink during application, the second being to reduce the hardness of the ink

when it has been applied.

10. An ink according to Claim 1 wherein the plasticiser comprises a material selected from the group consisting of adipates, phthalates, sebacates, citrates and phosphates.

11. An ink according to Claim 1 wherein the plasticiser comprises polyethylene-based polymeric plasticiser.

12. An ink according to Claim 1 comprising an antioxidant.

13. An ink according to Claim 1 wherein the stabiliser is an organotin stabiliser.

14. An ink according to Claim 13 wherein the stabiliser is an octyltin mercaptide.

15. An ink according to Claim 1 comprising also a wax.

16. An ink according to Claim 15 wherein the wax is a polyethylene wax.

17. An ink according to Claim 1 comprising also a lubricant.

18. An ink according to Claim 17 wherein the lubricant is an epoxidised soya bean oil.

19. An ink according to Claim 1 comprising also a thixotropic agent.

20. An ink according to Claim 19 wherein the thixotropic agent comprises a carbonate of magnesium.

21. An ink according to Claim 19 wherein, excluding the pigment, the thixotropic agent is present in a quantity of between 10% and 20%.

22. An ink according to Claim 1 wherein all the constituents are in powder form a room temperature.

23. A method of applying a pattern to an article involving the use of an ink according to Claim 1, and the steps:

[a] applying ink in fluid condition to a first printing roll;

[b] applying ink from the said printing roll to a transfer sheet;

[c] applying ink in fluid condition to one or more subsequent printing rolls;

[d] applying ink from each such printing roll to a transfer sheet.

24. A method according to Claim 23 wherein the transfer sheet is in the form of a continuous web.

25. A method according to Claim 24 wherein the transfer sheet is paper.

26. A method according to Claim 23 wherein the ink is in the form of a powder at room temperature, and is melted prior to application by way of the printing roll to the transfer sheet.

27. A method according to Claim 23 wherein the ink is in fluid form at room temperature, and subsequent to the application of ink to the transfer sheet, the sheet is passed through a heating station to initiate curing of the ink on the transfer sheet.

28. A method according to Claim 23 wherein the transfer sheet is flocked, and the ink is applied to the flocked transfer sheet to penetrate the flocking.

29. A method according to Claim 28 wherein, subsequent to the

application of ink to the flocking, an adhesive is applied to the exposed surface of the applied ink.

30. A method according to Claim 23 involving the further step of transferring the pattern to textile by the use of heat and pressure applied between the transfer sheet and the textile.

31. An ink substantially as hereinbefore described with reference to either of the formulas.

32. A method of applying a pattern to a textile article, when carried out substantially as hereinbefore described with reference to the accompanying drawings.

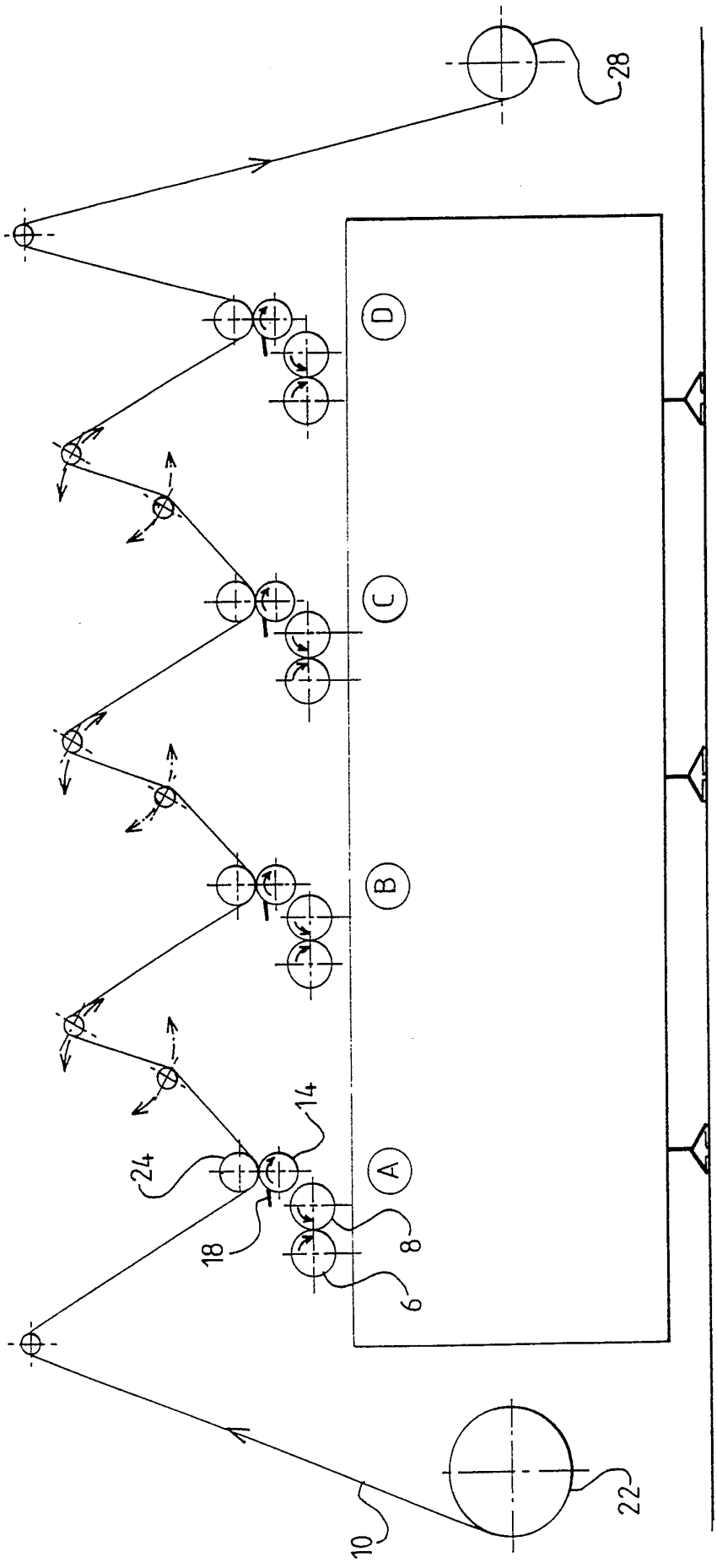


FIG 1

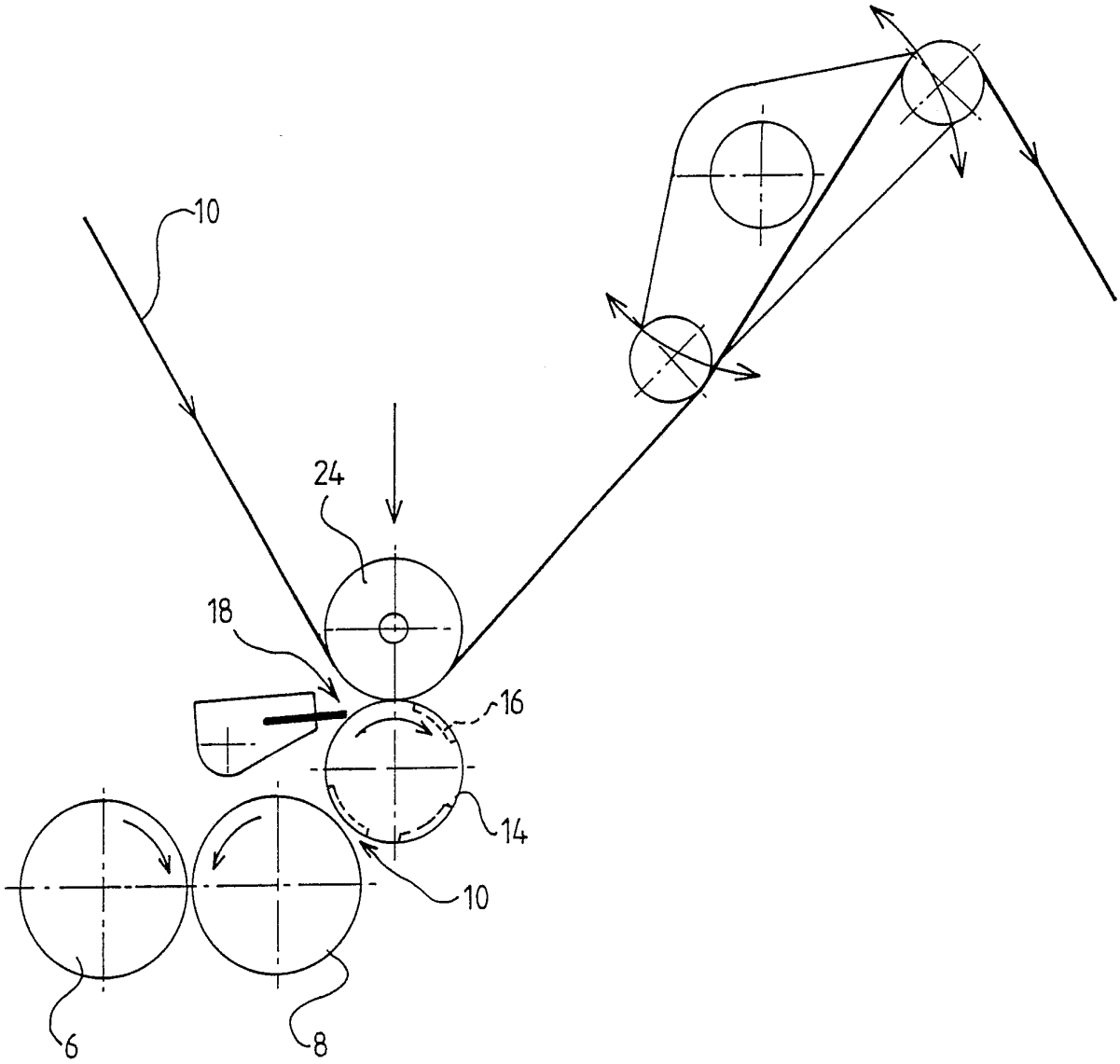


FIG 2

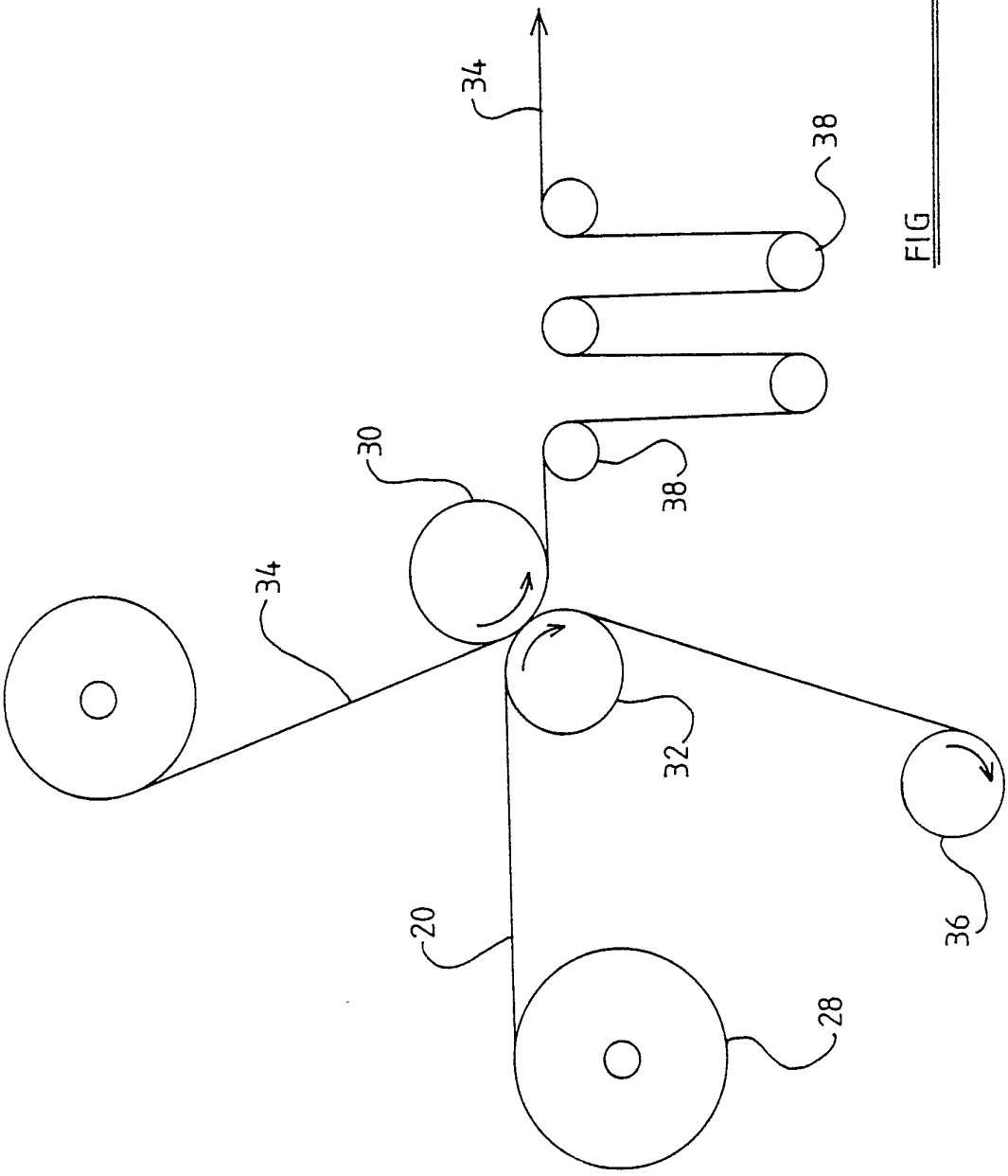


FIG 3

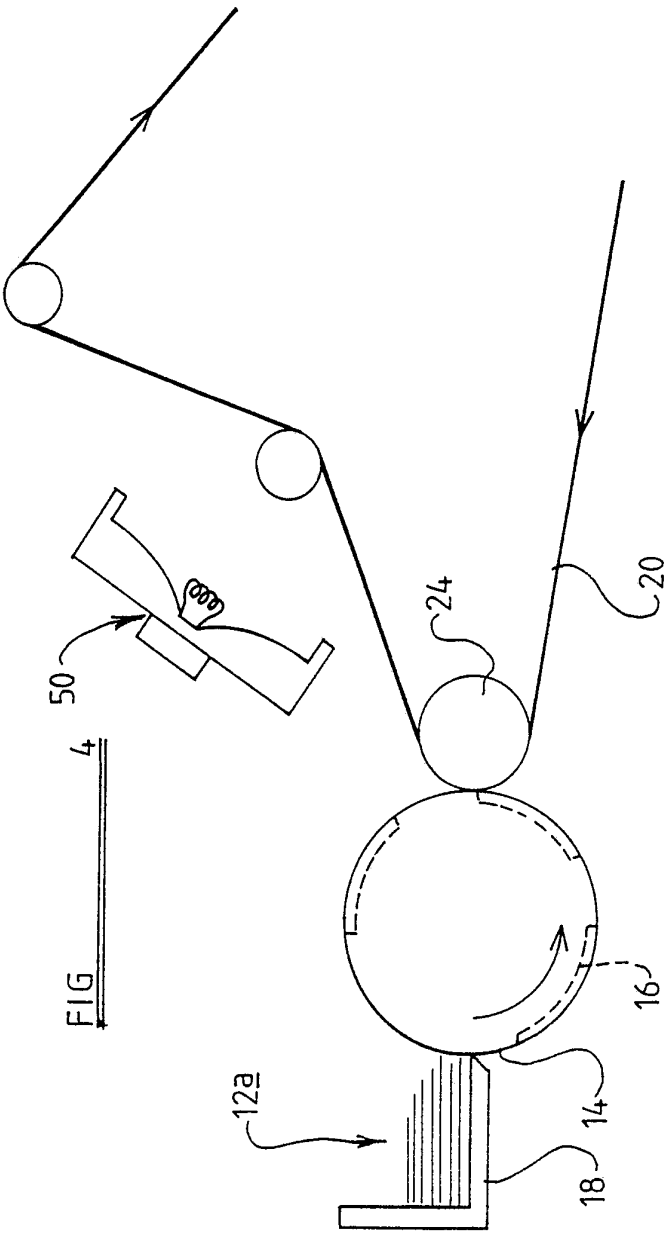


FIG 4

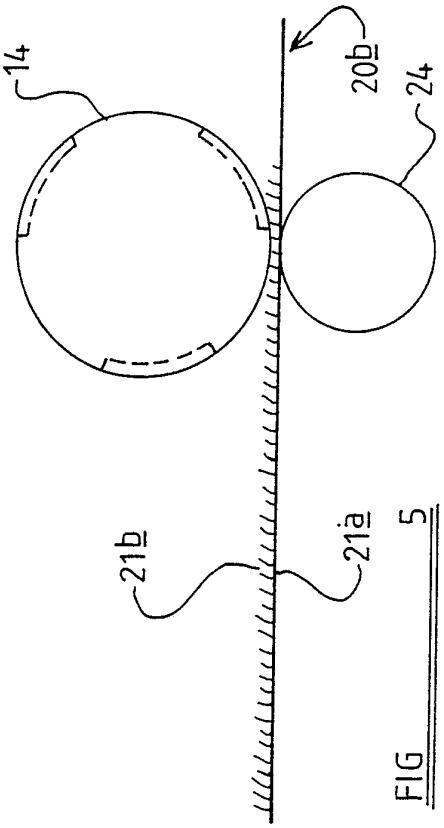


FIG 5

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 91/00686

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 D06P5/00 ; C09D11/10

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	D06P

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	DATABASE WPIL, no 87-076488 Derwent Publications Ltd, London, G.B., & JP-A-62030077(SHACHIHATA KOGYO KK)(09-02-1987) see the whole abstract	1-22
A	WO,A,8 701 334 (TARKETT, INC) March 12, 1987 see page 9, line 23 - page 12, line 9	1-22
A	DE,A,2 847 642 (ADOLF SIEBERT GMBH & CO) May 8, 1980 see the whole document	1-22

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
02 SEPTEMBER 1991	13.09.91
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	J-F. DELZANT

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

GB 9100686
SA 47170

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

02/09/91

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-8701334	12-03-87	AU-A- 6406886	24-03-87
		EP-A- 0236478	16-09-87
		US-A- 5015516	14-05-91
DE-A-2847642	08-05-80	None	