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(54) Title: A PRINTING INK

(57) Abstract: This invention relates to a printing ink and in particular inks for use in screen printing that are cured using ultraviolet radiation and are formulated to provide a high film weight. The ink comprises a passive thermoplastic vinyl resin; tetrahydrofurfuryl acrylate; one or more UV-curable multifunctional oligomers; one or more photoinitiators; and one or more colouring agents.

A Printing Ink

This invention relates to a printing ink and in particular inks for use in screen printing that are cured using ultraviolet radiation and are formulated to provide a high film weight.

In screen printing, an ink forming an image is supported on a mesh stretched across a frame. The ink is forced through openings in the mesh and onto the substrate by the action of squeegee which is drawn across the mesh. Once the ink has been transferred to the substrate it must dry within a reasonable amount of time which is dependent on the application. Inks suitable for application to a substrate using screen-printing typically have a viscosity of 0.1 to 10 Pas (1 to 100 poise) at 25°C when measured under shear conditions encountered during the printing process.

The screen printing technique is suitable for many different types of drying processes. Screen-printing inks are commonly formulated to contain a large proportion of a mobile liquid vehicle or solvent and the ink dries by the evaporation of the liquid vehicle or solvent. Unfortunately, inks that include a large proportion of water or solvent cannot be handled after printing until the inks have dried, either by evaporation of the solvent or its absorption into the substrate. This drying process is often slow and in many cases (for example, when printing on to a heat-sensitive substrate such as paper) cannot be accelerated.

Another type of ink contains unsaturated organic compounds, termed monomers, which polymerise by irradiation, typically UV radiation, in the presence of a photoinitiator. This type of ink has the advantage that it is not necessary to evaporate the liquid phase to dry the print; instead the print is exposed to radiation to cure or harden it, a process which is more rapid than evaporation of solvent at moderate temperatures.

However, difficulties arise in formulating inks which polymerise by irradiation but which are also suitable for forming thick films on the substrate. The provision of UV-cured thick films is difficult because as the film becomes thicker the UV light which penetrates the film decreases in intensity resulting in a film which is cured at the

surface but essentially uncured at the substrate/coating interface. The resulting stresses within the coating tend to show as a wrinkling of the surface that is easily removed, leaving still fluid material below.

The attenuation of light energy as it passes into, or through any material, is described by Beer-Lambert's Law:

$$I_a = \frac{I_o(1 - 10^{-A})}{d}$$

where I_o is the intensity of incident energy, I_a is the intensity of the energy at a given depth, A is the absorbance of a coating at a given wavelength, and d is the depth from the surface.

The light intensity decrease becomes even more difficult with pigmented systems due to the light-filtering effect of the pigment.

Ideally, in order to minimise the stress in curing thick sections, the coating should be formulated to cure throughout the thickness at a relatively uniform rate as opposed to curing from the surface down. There remains a need in the art for such inks.

Accordingly, the present invention provides an ink comprising a passive thermoplastic vinyl resin; tetrahydrofurfuryl acrylate; one or more UV-curable multifunctional oligomers; one or more photoinitiators; and one or more colouring agents.

The ink of the present invention dries primarily by curing, i.e. by the polymerisation of the monomers present, as discussed hereinabove, and hence is a curable ink. The ink does not, therefore, require the presence of water or a volatile organic solvent to effect drying of the ink, although the presence of such components may be tolerated. Preferably, however, the ink of the present invention is substantially free of water and volatile organic solvents.

Passive resins are resins which do not enter into the UV curing process, i.e. the resin is substantially free of functional groups which polymerise under the curing conditions to which the ink is exposed. Such resins are useful for modifying the properties of an ink as well as acting as acting as a UV transparent filler in the system. The ink of the present invention incorporates a passive thermoplastic vinyl resin which was found to provide a good balance between toughness, adhesion and flexibility. The vinyl resin is preferably a copolymer comprising vinyl chloride and vinyl acetate. The vinyl acetate reduces the softening temperature of the polymer and helps the polymer to dissolve in the monomer. The vinyl acetate also imparts toughness and flexibility to the ink. The ratio of vinyl chloride to vinyl acetate will depend on the substrate and the balance of toughness and flexibility required. Preferably the resin is predominantly vinyl chloride, more preferably contains 60-90 wt%, most preferably 85% of vinyl chloride, and 10-40 wt%, more preferably 15 wt% of vinyl acetate. Other co-monomers may be included in the resin, such as dicarboxylic acids or dicarboxylic acid esters, e.g. maleate and fumarate. Preferably the resin contains 0-15 wt% of other co-monomers.

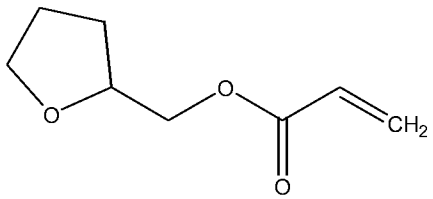
The K-value of the passive vinyl resin is preferably 35-80, more preferably 40-50 and most preferably about 45. The K-value is a measure of the molecular weight of the passive vinyl resin based on measurements of viscosity of a solution of the resin and is a standard term in the art. The K-value may be measured according to ISO 1628-2:1998 for resins fulfilling the criteria of this standard (resin in powder form, predominantly vinyl chloride, a volatile monomer content not in excess of 0.5±0.1% when determined in accordance with ISO 1269, resin entirely soluble in cyclohexanone) and otherwise by ISO 1628-1:1998. A low K-value implies low molecular weight, which makes the resin easier to dissolve in the monomer and enables a beneficial resin content to be achieved at a screen-printable viscosity. A particularly preferred resin has a K-value of about 48.

The ink preferably contains 3 to 30 wt%, more preferably 5 to 20 wt%, and most preferably 7 to 15 wt% of passive vinyl resin based on the total weight of the ink.

One of the disadvantages of vinyl resins is that they are difficult to dissolve in UV-curable monomers which are typically used in ink formulations and usually only a low

vinyl content can be achieved in an ink without an unacceptably large increase in the viscosity of the ink. It has been found that tetrahydrofurfuryl acrylate will dissolve the vinyl resin in a sufficient amount whilst maintaining a workable solution viscosity. In addition, tetrahydrofurfuryl acrylate cures to provide a tough film with adhesion to plastics substrates without embrittling them, as well as low shrinkage in thick films.

Tetrahydrofurfuryl ("THF") acrylate has the following formula:



THF acrylate is monofunctional and has a relatively slow curing rate and hence in order to speed up the curing rate of the ink, a radiation-curable oligomer is also incorporated into the ink to provide cross-linking.

The ink preferably contains 40-60 wt% of THF acrylate based on the total weight of the ink.

The ink also contains a UV-curable oligomer. The oligomer is preferably a UV-curable (meth)acrylate having a molecular weight of from 500 to 5,000. The degree of functionality of the oligomer determines the degree of crosslinking and hence the properties of the cured ink, particularly a balance between hardness and flexibility. The oligomer is multifunctional meaning that it contains more than one UV-reactive functional group per molecule. The degree of functionality is preferably from 2 to 6.

UV-curable oligomers of this type are well known in the art. The ink of the present invention is preferably a blend of urethane, amine and polyester oligomers. Each oligomer may advantageously have a different functionality. A blend of a difunctional aliphatic urethane and a hexafunctional polyester acrylate is particularly preferred.

The ink preferably contains 5 to 50 wt% and most preferably 10 to 30 % wt% of UV-curable oligomers based on the total weight of the ink.

In addition to the components described hereinabove, the ink includes a photoinitiator which, under UV irradiation, initiates the polymerisation of the monomers and oligomers. Preferred are photoinitiators which produce free radicals on irradiation (free radical photoinitiators), such as benzophenone, 1-hydroxycyclohexyl phenyl ketone, 2-benzyl-2-dimethylamino-(4-morpholinophenyl)butan-1-one, benzil dimethylketal, bis(2,6-dimethylbenzoyl)-2,4,4-trimethylpentylphosphine oxide or mixtures thereof. Such photoinitiators are known and commercially available such as, for example, under the trade names Irgacure, Darocur (from Ciba) and Lucerin (from BASF). Evaluation of UV initiators showed that an acylphosphineoxide initiator is the most effective for through cure together with small amount of another initiator to give surface cure.

The wavelength of the UV radiation and the nature of the photoinitiator system used must coincide. Longer wavelength UV radiation has greater transmission through semi-transparent materials and hence is preferred. The photoinitiator acylphosphineoxide is preferred with longer wavelength UV radiation. By longer radiation is meant UVA radiation which is typically considered to be 320-400 nm.

Preferably the photoinitiator is present from 1 to 20% by weight, preferably from 2 to 10% by weight, more preferably from 3 to 7% by weight of the ink.

The ink of the present invention also includes a colouring agent, which may be either dissolved or dispersed in the liquid medium of the ink. Preferably the colouring agent is a dispersible pigment, of the types known in the art and commercially available such as, for example, under the trade-names Paliotol (available from BASF plc), Cinquasia, Irgalite (both available from Ciba Speciality Chemicals) and Hostaperm (available from Clariant UK). The pigment may be of any desired colour such as, for example, Pigment Yellow 13, Pigment Yellow 83, Pigment Red 9, Pigment Red 184, Pigment Blue 15:3, Pigment Green 7, Pigment Violet 19, Pigment Black 7. Especially useful are black and the colours required for trichromatic process printing. Mixtures of pigments may be used.

The total proportion of pigment present is preferably from 0.5 to 15% by weight, more preferably from 1 to 5% by weight.

It is possible to modify further the film properties of the inks by inclusion of multifunctional monomers. Examples of the multifunctional acrylate monomers which may be included in the ink formulation include hexanediol diacrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate, polyethyleneglycol diacrylate, for example, tetraethyleneglycol diacrylate), dipropyleneglycol diacrylate, tri(propylene glycol) triacrylate, neopentylglycol diacrylate, bis(pentaerythritol) hexa-acrylate, and the acrylate esters of ethoxylated or propoxylated glycols and polyols, for example, propoxylated neopentyl glycol diacrylate, ethoxylated trimethylolpropane triacrylate, and mixtures thereof. Particularly preferred are difunctional acrylates with a molecular weight greater than 200. In addition, suitable multifunctional acrylate monomers include esters of methacrylic acid (i.e. methacrylates), such as hexanediol dimethacrylate, trimethylolpropane trimacrylate, triethyleneglycol dimethacrylate, diethyleneglycol dimethacylate, ethyleneglycol dimethacrylate, 1,4-butanediol dimethacrylate. Mixtures of (meth)acrylates may also be used.

Although the ink of the present invention cures by a free radical mechanism, the ink of the present invention may also be a so-called "hybrid" ink which cures by a radical and cationic mechanism. The ink of the present invention, in one embodiment, therefore further comprises at least one cationically curable monomer, such as a vinyl ether, and at least one cationic photoinitiator, such as an iodonium or sulfonium salt, e.g. diphenyliodonium fluoride and triphenylsulfonium hexafluophosphate. Suitable cationic photoinitiators are be sold under the Trade names of Irgacure 184, Irgacure 500, Darocure 1173, Irgacure 907, ITX, Lucerin TPO, Irgacure 369, Irgacure 1700, Darocure 4265, Irgacure 651, Irgacure 819, Irgacure 1000, Irgacure 1300, Esacure KT046, Esacure KIP150, Esacure KT37, Esacure EDB, H-Nu 470 and H-Nu 470X.

Other components of types known in the art may be present in the ink to improve the properties or performance. These components may be, for example, surfactants, defoamers, dispersants, synergists for the photoinitiator, stabilisers against

deterioration by heat or light, reodorants, flow or slip aids, biocides and identifying tracers.

The present invention also provides a method of printing using the above-described ink and a substrate having the cured ink thereon at a weight (thickness) of 100 to 200 microns, preferably about 150 microns. The ink of the present invention is particularly suited for printing on to a PVC or polyester substrate.

The ink of the present invention preferably has a viscosity of 0.1 to 10 Pas (1 to 100 poise) at 25°C. Viscosity may be determined by an ICI Rotothinner which operates with a fixed spindle and fixed speed.

(Meth)acrylate is intended herein to have its standard meaning, i.e. acrylate and/or methacrylate. Mono and multifunctional are also intended to have their standard meanings, i.e. one and two or more groups, respectively, which take part in the polymerisation reaction on curing.

The inks of the invention may be prepared by known methods such as, for example, stirring with a high-speed water-cooled stirrer, or milling on a horizontal bead-mill.

Example

The invention will now be described, by way of example, with reference to the following example (parts given are by weight).

Example 1

An ink formulation of the present invention was prepared by combining the following components:

Terpolymer of vinyl chloride, vinyl acetate and a dicarboxylic acid, K value 48, chlorine content = 48% (Passive vinyl resin)	10.50
Difunctional aliphatic urethane acrylate, 30% in TPGDA, viscosity 85,000 mPas at 25°C (oligomer)	9.60
Hexafunctional polyester acrylate, viscosity 45,000 mPas at 25°C (oligomer)	9.30
Difunctional amine acrylate, viscosity = 3,000-5,000 mPas at 25°C (oligomer)	2.00
Tetrahydrofurfuryl acrylate	47.45
Acylphosphineoxide initiator	10.00
2-methyl-1(methylthio)-2-morpholinopropan-1-one	1.00
Titanium dioxide	6.00
Pigment	0.15
Silicone flow aid	1.00
Amorphous fumed silica	2.00
Stabiliser	1.00
Total	**100.00**

Viscosity at 25°C by ICI Rotothinner = 5 Pas (50 poise).

The ink was screen-printed through a 34.100 mesh onto a 220 micron PVC substrate. The resulting film was cured using a mercury vapour UV lamp providing a radiation dose of 300 mJ/cm^2. The resulting coating was both tough and flexible.

Claims

1. An ink comprising a passive thermoplastic vinyl resin; tetrahydrofurfuryl acrylate; one or more UV-curable multifunctional oligomers; one or more photoinitiators; and one or more colouring agents.

2. An ink as claimed in claim 1, wherein the passive thermoplastic vinyl resin comprises vinyl chloride and vinyl acetate co-monomers.

3. An ink as claimed in claim 2, wherein the passive thermoplastic vinyl resin further comprises a dicarboxylic acid or dicarboxylic acid ester co-monomer.

4. An ink as claimed in claim 3, wherein the passive thermoplastic vinyl resin has a K-value of 35-80.

5. An ink as claimed in any preceding claim, wherein the one or more UV-curable multifunctional oligomers have a degree of functionality of from 2 to 6.

6. An ink as claimed in any preceding claim, wherein the ink comprises a plurality of UV-curable multifunctional oligomers two or more having a different degree of functionality.

7. An ink as claimed in any preceding claim, wherein the one or more photoinitiators comprise an acylphosphineoxide photoinitiator and at least one other photoinitiator.

8. A method of printing, comprising printing the ink as claimed in any preceding claim on to a substrate and curing the ink.

9. A method as claimed in claim 8, wherein the printing method is screen printing.

10. A method as claimed in claim 8 or 9, wherein the substrate is a PVC or polyester substrate.

11. A substrate having the ink as claimed in any of claims 1 to 11 printed thereon at a weight of 100 to 200 microns.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2007/050445

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D11/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	WO 03/027162 A (3M INNOVATIVE PROPERTIES CO [US]; CARLSON JAMES G [US]; LEE JENNIFER L) 3 April 2003 (2003-04-03) examples 1,comp.ex.1	1-11
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X	WO 03/010249 A (3M INNOVATIVE PROPERTIES CO [US]) 6 February 2003 (2003-02-06) examples	1-11

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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

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"P" document published prior to the international filing date but later than the priority date claimed

"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02/38688 A (3M INNOVATIVE PROPERTIES CO [US]) 16 May 2002 (2002-05-16) examples -----	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

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