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(54) IMPROVEMENTS IN OR RELATING TO A RAPID-DRYING PRINTING INK AND A PRINTING PROCESS USING SAME

(71) We, O+R INKTCHEMIE N.V. a limited liability Company, organised and existing under the laws of the Netherlands, of Oostzijde 253, Zaandam, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a rapid drying printing ink and printing process using same.

In modern printing techniques a rapid drying of the applied ink is of extreme importance, because otherwise the still wet ink is transferred to the reverse side of the following printed sheet and moreover the further processing, including printing the reverse side of the material, is considerably delayed.

In order to avoid the above problems resulting from the still wet condition of the applied printing ink, in the sheet-fed offset process and in relief printing process the still wet ink layer is sprayed with a powder on the basis of starch, as a result of which a protective layer is formed. However, this technique has several drawbacks, such as pollution of the working-space and the printing machines, as a result of which extra maintenance has to be carried out, and the obtention of a qualitatively inferior final product.

In the rotary offset process powder is not used but several so-called cold and hot processes are applied to accelerate the drying of the ink layer. These processes do not lead to the desired effect, at least not to a sufficient extent, or have the drawbacks that the printed paper is deformed, the energy consumption is high, and great quantities of solvent of the printing ink find their way into the atmosphere.

There has now been found a printing ink which very rapidly dries under the influence of heat, in particular from infra-red radiation, so that the above-described drawbacks of the prior art techniques can simply be avoided. The rapid-drying printing ink according to the invention comprises:

- a non-polar solvent,
- a phenol- or cresol formaldehyde resin modified with colophony,
- a crosslinkable unsaturated polyester,
- a peroxide catalyst for said polyester, and
- a pigment.

In the printing ink the resin and the polyester, together forming the binder, are both present in dissolved state. In fact the polyester keeps the resin in solution, because it sees to it that the threshold concentration of binder is passed, below which the resin is not soluble in the non-polar solvent. By the influence of the heat, in particular from infra-red radiation, on the wet ink layer the peroxide catalyst is activated, as a result of which free radicals are produced which initiate a rapid crosslinking of the unsaturated polyester. The crosslinked polyester is not soluble in the non-polar solvent, so that said threshold concentration is no longer reached and the resin expels the non-polar solvent, which is subsequently absorbed by printed substrate. By means of this particularly rapid process an effective drying of the ink layer is obtained in a simple manner. In practice excellent results are obtained when the weight ratio of the resin and polyester together to the non-polar solvent is greater than 1/1, while the weight ratio of the resin only to the non-polar solvent is smaller than 1/1.

The non-polar solvent used according to the invention usually is a hydrocarbon

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11 mixture conventional in printing inks, such as a paraffinic oil having an aliphatic nature obtained by distillation of petroleum, but which may contain minor amounts of aromatics or naphthenes.

5 The modified phenol or cresol formaldehyde resin used in the printing ink is modified with colophony and preferably subsequently further esterified with a
10 polyhydric alcohol, such as glycerol, pentaerythritol or sorbitol. These resins are only compatible with non-polar organic solvents when the total quantity of binder passes a specific minimum concentration (threshold concentration). Below this
15 concentration expulsion takes place.

The crosslinkable unsaturated polyester is preferably composed of three types of components, namely units derived from a
20 polyhydric alcohol, such as glycerol, pentaerythritol, manitol or sorbitol, units derived from a phthalic acid, preferably isophthalic acid, and units derived from an unsaturated aliphatic acid, most preferably
25 linoleic acid and/or linolenic acid, which latter units mostly constitute the greatest part by weight of the polyester.

The peroxide catalyst may be composed of a conventional organic peroxide or
30 hydroperoxide and a siccative. The peroxide or hydroperoxide is preferably used in an amount of 1 to 5 wt.%, calculated on the total binder (resin plus polyester). As suitable compounds may be
35 mentioned cumene hydroperoxide and cyclohexanone peroxide.

Siccatives, which are used in combination with the conventional organic peroxide or hydroperoxide, are the likewise
40 conventional siccatives. As such can be used soaps of a trivalent metal, e.g. trivalent vanadium, iron, manganese or cobalt. Cobalt soaps are preferred, such as cobalt naphthenate, cobalt resinate, cobalt
45 stearate or cobalt octoate. The siccative is usually added in an amount of 0.2 to 2 wt.%, calculated on the total binder.

According to this invention the conventional organic peroxide or
50 hydroperoxide may not be added to the rest of the printing ink too long before printing. At a normal temperature of about 20°C the storage time of the mixed ink is about 24 hours. However, taking this into account, it
55 will be possible to obtain a smoothly going printing process and a very rapid drying of the ink layer by the influence of heat, preferably originating from infra-red radiation. This latter to a very high extent
60 activates the influence of the siccative on the peroxide or hydroperoxide, so that rapidly free radicals are formed which immediately initiate the crosslinking of the unsaturated polyester, which results in a

rapid drying of the ink layer as earlier described. 65

However, the peroxide catalyst preferably is an organic peroxide which is decomposed at a temperature between 70 and 80°C with formation of free radicals
70 initiating the crosslinking of the polyester. The required decomposition temperature is obtained by the influence of heat, preferably originating from infra-red
75 radiation. Below a temperature of 70°C the thermally decomposable organic peroxides are particularly stable, so that the ink ready for printing can be stored for a long time, namely for about six months at a
80 temperature of about 20°C. This is an important advantage, since this renders it possible to prepare a ready ink, to market same and to keep same in stock. Suitable thermally decomposable organic peroxides
85 are inter alia isobutyl peroxide, dibenzoyl peroxide and tert. butylperoxy-2-ethyl hexoate, which all decomposes at a temperature of 70°C. These organic peroxides are mostly added in an amount of
90 1 to 6 wt.%, calculated on the total binder. An ink prepared with these thermally decomposable peroxides has excellent properties on the printing press; it causes
95 practically no deposition of solid material on the rollers and ensures a rapid and effective drying of the applied ink layer upon heating, most preferably by means of infra-red radiation.

When a thermally decomposable peroxide is used no siccative need be used,
100 which is the case, though, when there are used the earlier described conventional organic peroxides or hydroperoxides. However, the drying can be accelerated by also adding to the printing ink an activator
105 for the thermally decomposable peroxide. This may be useful when a thick ink film is printed. Particularly effective activators are tertiary amines, e.g. dimethyl-p-toluidine, which may be added in a very small
110 amount, namely an amount of 0.05 to 0.4%. As a result of the presence of these activators the storage life of the ready printing ink is reduced somewhat.

The present printing ink can be prepared
115 according to techniques conventional to one skilled in the art. Usually, the resin and the polyester are first dissolved in the non-polar solvent under heating. After cooling, the other components, namely a pigment,
120 siccative, if any, thermally decomposable organic peroxide, activator and other additives used in some cases, such as fillers, are added to the obtained solution, and the mixture is milled in a conventional
125 apparatus, such as a three-roller mill or a ball mill, to form a homogeneous printing ink. This can be brought into cans and as such be supplied to printing works. Only

when a conventional organic peroxide or hydroperoxide is used together with a siccative, does the peroxide have to be added afterwards, as has already been described above.

A particularly interesting additive for the present printing ink is fine granules of a modified starch or a starch derivative having a limited swelling power (as herein defined) under the influence of water, or of another natural or synthetic substance having similar properties. Such granules make an extra contribution towards the prevention of damage and the transfer of the freshly printed ink layer, in particular when a printed sheet "lands" on the previously printed sheet in a sheet-fed printing process.

As used herein the term "limited swelling power" means that the swelling power of the granules is so limited that they do not burst open and, as a result, lose their granular form.

Before and/or during printing said fine granules take up a little water, which is always present somewhere in their surroundings and which need therefore not be specially supplied. For example, the water may originate from the printing ink itself, from the ambient air, from the printing plate and/or from the material to be printed. As a result of the absorption of water, which is even accelerated by the infra-red radiation, the fine granules swell somewhat but their swelling power is limited owing to the use of a suitable modified starch or a suitable starch derivative, so that in fact globules are produced which slightly project above the printed ink layer and constitute bearing faces on which the following printed sheet "lands". Thus, during said "landing", damage to and part transfer of the still fresh ink layer of the previous sheet to the reverse side of the "landing" sheet is prevented. The swelling of the granules may by no means be such that they burst open and pass into a sort of colloidal state, because then the contemplated effect can no longer be obtained.

The globules formed have the additional advantage that the freshly printed ink layer feels less sticky and that the printed sheets in a stack less easily stick together.

Preferably, the fine granules for use in the printing ink according to the invention in dry state have an average size of about $10\ \mu$. The desired granular size can be obtained by screening the starch powder concerned. Particularly suitable starches for use according to the invention are tapioca, wheat starch and in particular corn starch.

In the printing ink the fine granules have

an average granular size of, for example, not more than $20\ \mu$.

The swelling power of the fine granules used has to be limited, as was described above. In the printing ink the granules may occur in a somewhat swollen condition, but the swelling may not be too much, so that the average size of the swollen granules or globules does not exceed a value of about $20\ \mu$. Larger granules or globules cause troubles, such as sagging and sticking together, during the printing process. In order to attain the required limited swelling power of the granules, the starch is suitably modified or converted to a suitable starch derivative.

The modification can be carried out by treating the starch in a known manner with a preferably concentrated acid or with enzymes in order to effect a limited hydrolytic degradation, as a result of which there can, for example, be obtained a modified starch having a fluidity (determined by an American testing method) of 50 to 60, which is particularly suitable for the object of the invention. Another known method to so modify starch to obtain a product suitable for the present invention consists in a controlled oxidizing treatment with oxidizing substances, such as a hypochlorite, hydrogen peroxide or a periodate. Particularly suitable is an oxidizing treatment with 3% active chlorine, originating from an alkali metal hypochlorite, in a neutral or weakly alkaline medium.

Suitable starch derivatives for use according to the present invention are esterification and etherification products of starch, for example of native starch having a high swelling degree, as a result of which a certain swelling-inhibitory effect is obtained. As starch esters may be mentioned acetyl starch and haloacetyl starch products. Hydroxyethyl starch, hydroxypropyl starch, carboxymethyl starch and cyanoalkyl starch products are suitable as starch ethers.

The fine granules of a modified starch or a starch derivative are usually added to the printing ink in an amount of 0.1 to 2.0 wt.%, preferably 0.2 to 1.2 wt.%, calculated on the total ink. The optimum quantity to be used in a specific case of course depends on a number of factors, in particular the nature of the starch product used, the rest of the composition of the printing ink, as well as the manner of printing and the nature of the material to be printed, and can easily be determined by way of experiment.

According to a particularly suitable method to process the fine granules into he printing ink there is prepared beforehand a paste of said granules, and this paste is then

mixed uniformly with the ink. Such a paste usually contains 15 to 40 wt. % fine granules of the modified starch or of the starch derivative and for the rest may be composed of a carrier liquid, for example water or an organic liquid such as hydrocarbon mixture, a binder, for example a known varnish for printing ink, and possibly aids such as waxes and surfactants. In this paste the fine granules may already be slightly swollen, so that the granular size lies between 10 and 15 μ .

The present printing ink may also be a so-called emulsion ink, in which a water phase has been emulsified in the organic phase. The water phase then constitutes preferably not more than about 20 wt. % of the total ink and may contain all sorts of useful additives, such as buffering agents, waxes, e.g. polyethylene wax, oxidizing agents, accelerators and gums or other binding agents, for example in latex form. When fine granules of a modified starch or for a starch derivative are used in the printing ink, as has been described above, then the water phase promotes the swelling of said granules and therefore the contemplated effect. On account of the vigorous heat treatment of the freshly printed ink layer the use of an emulsion ink in the present case does not lead to degradation of the printing properties, in particular loss of gloss and strength of the printed layer.

The printing ink according to the present invention can be successfully employed in various printing processes. However, it is extremely suitable for relief printing (letterpress printing) or planographic printing, such as sheet-fed offset or rotary offset, it being possible to carry out both single-colour and multicolour printing, for example four-colour printing. Any conventional material, such as paper, cardboard or synthetic material, can be printed; it being important, however, that the printed surface is at least somewhat porous, so that it is capable of at least partially absorbing the expelled non-polar solvent. When a totally non-porous material, such as tin, is printed, it will only be possible to obtain a rapid drying if the present printing technique (ink plus heat, e.g. infra-red radiation) is combined with known techniques of accelerated drying.

In practice infrared irradiation is usually used for carrying out the heat treatment and, in this case, infra-red lamps or elements are so arranged that they irradiate the still wet ink layer of the freshly printed material.

For several reasons there are preferably used infra-red lamps which substantially, for example for more than 75%, radiate in the near infra-red, i.e. in the spectral range between 0.75 and 3 microns. Such lamps

have the advantage that the supplied heat is substantially absorbed by the printed areas which have the highest optical density, while the non-printed, mostly white, areas for the greater part reflect the heat rays, so that the risk of excess heating and deformation of the printed material is avoided. Moreover, with this type of lamp the heating and cooling time are very short (only a few seconds), so that, when the printing machine is stopped, the paper remaining in front of the lamps cannot catch fire. Suitable infrared lamps emitting in the near infra-red are the IRK-lamps having a power of 1000 or 2000 W of Philips N.V., Eindhoven (Netherlands).

A very rapid drying of the ink is also attained by means of infra-red lamps particularly emitting in the deep infra-red, i.e. in the spectral range between 3 and 10 microns. Elstein ("Elstein" is a Trade Mark) elements of 1000 W are an example of such lamps. However, they have the drawback that deformation of the printed paper easily occurs, because the non-printed areas also absorb great quantities of heat, and that the heating time (about 15 minutes) and the cooling time about 10 minutes) are very long. The long afterglow can even set the stationary paper on fire.

The infra-red lamps are mostly arranged in a blowing-air cooled battery which extends over the total width of the printing machine. The power of the infra-red lamps together varies of course as a function of several factors, such as the width of the printing machine, the distance to the printed material, the nature thereof, the composition of the printing ink etc. For the purpose of orientation it may be stated that, for example, in a four-colour rotary offset press having a paper web width of 1 m excellent drying results are obtained when the total power of the infra-red lamps lies between 25 and 35 kW. The time of irradiation is at most some tenths of a second.

In addition to the advantages already discussed above the invention offers a number of other advantages over the prior art printing inks and printing techniques. For example, the printed ink layer has a higher colour density, as a result of which a considerable saving of ink can be obtained. Furthermore there is observed an improvement of the print definition, and the dry ink layer has a considerably higher gloss as well as a much higher resistance to abrasion, so that the application of a final glossy protective layer can be omitted. Finally, the vapours liberated during drying can easily and efficiently be removed via a central discharge system, so that nuisance caused by smell is avoided. Also the still warm stack of freshly printed material can

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be connected to the discharge system, for example, via a plastics cover and a tube.

The invention will now be further illustrated by way of the following examples.

Example I

At 200°C there was prepared a solution (varnish) having the following composition:

	parts by weight
10 Krumbhaar Resin K 1400* (Lawter Chemicals, Chicago, U.S.A.)	40
15 Trionol 7** (Lawter Chemicals)	15
20 paraffin oil (petroleum distillate being 100% aliphatic in nature and having a boiling range of 260—290°C)	45

* a phenol formaldehyde resin modified with colophony and subsequently esterified with pentaerythritol (acid number <20; melting point Ring and Ball 160°C; compatible with mineral oils having a Kb-value of about 27 in an amount of at least 1/1);

** a crosslinkable unsaturated polyester comprising substantially linoleic acid (74%) and for the rest of isophthalic acid and pentaerythritol (acid number maximally 10; viscosity 20°C 700 Poise; in all ratios compatible with mineral oils having a Kb-value of about 27).

There was prepared a red ink for four-colour sheet-fed offset printing having the following composition:

	parts by weight
40 varnish (prepared as described above)	80.0
pigment red 57 (CI 15,850)	17.8
cobalt octoate (10% cobalt)	0.4

45 The resulting mixture was milled in a three-roller mill to form a homogeneous dispersion, after which the ink could be brought into cans. A short time before printing 1.8 parts of cyclohexanone peroxide were added.

50 After printing with the thus prepared ink there was obtained a highly effective and rapid drying of the ink layer by irradiating same for 0.1 to 0.2 seconds with IRK-lamps of 1000 W (about 85% of the radiation lies in the range of 0.75 to 3 microns).

Example II

60 There was prepared a red ink for relief or letterpress printing having the following composition:

	parts by weight
varnish (prepared as described in Example I)	76
aluminum hydroxide	4.8
pigment red 57	17.0
cobalt octoate (10% cobalt)	0.4

The resulting mixture was milled and further treated as indicated in Example I. Shortly before printing 1.8 parts by weight of cyclohexanone peroxide were added.

After printing followed by infra-red irradiation, as in Example I, there was obtained an excellent and rapid drying.

Example III

A red ink for rotary offset printing was prepared by milling a mixture consisting of 60.9 parts by weight of varnish, as described in Example I, and 12.0 parts by weight of pigment red 57 in a three-roller mill, and adding to the thus obtained homogeneous dispersion 26.0 parts by weight of paraffin oil (see Example I) and 0.2 parts by weight of cobalt octoate. The printing ink could subsequently be brought into cans. Shortly before use there was added 1.0 part by weight of cyclohexanone peroxide.

After printing followed by infra-red irradiation, as in Example I, there was obtained an excellent and rapid drying.

Example IV

A red ink for four-colour sheet-fed offset printing was prepared by mixing 17.8 parts by weight of pigment red 57 with 80.4 parts by weight of varnish, as described in Example I, milling said mixture in a three-roller mill, adding, at a temperature below 40°C, 1.8 parts by weight of dibenzoyl peroxide, and properly mixing same.

The thus prepared ink was ready for use and could easily be stored for 3 to 4 months at room temperature without a decrease of the good drying properties.

After printing and drying, as in Example I, the same favourable drying result was obtained.

Example V

A red ink for relief or letterpress printing was prepared by mixing 4.3 parts by weight of aluminum hydroxide and 17.0 parts by weight of pigment red 57 with 77.0 parts by weight of varnish, as described in Example I, milling the mixture in a three-roller mill, adding, at a temperature below 40°C, 1.7 parts by weight of isobutyl peroxide, and properly mixing same.

The thus prepared ink was ready for use and could be stored for a long time.

After printing and drying, as in Example II, the same favourable drying result was obtained.

Example VI

A red ink for rotary offset printing was prepared by mixing 12.0 parts by weight of pigment red 57 with 61.0 parts by weight of varnish, as described in Example I, milling the mixture in a three-roller mill, adding 26.0 parts by weight of paraffin oil (see Example I), once again properly mixing same, and finally adding, at a temperature below 40°C, 1.0 part by weight of isobutyl peroxide.

The thus prepared ink was ready for use and could be stored for a long time.

After printing and drying, as in Example III, the same favourable drying result was obtained.

Example VII

A paste was prepared by intimately mixing together the following components:

	parts by weight
varnish (prepared as described in Example I)	1400
modified starch***	700
polyethylene wax	100
water	250
tridecyl alcohol	50

*** Corn starch having a granular size of about 10 μ , which at 20°C under stirring is treated with concentrated hydrochloric acid until a fluidity of about 55 is reached, after which the hydrolytic degradation is topped by addition of sodium carbonate.

From a mixture of the following composition:

	parts by weight
varnish (prepared as described in Example I)	79.0
40 pigment red 57	17.8
paste (prepared as described above)	1.0
cobalt octoate (10% cobalt)	0.4

was prepared a red ink for four-colour sheet-fed offset printing as described in Example I. Shortly before printing were added 1.8 parts by weight of cyclohexanone peroxide.

After printing and drying, as in Example I, the same favourable drying result was obtained, while during "landing" of the successive printed sheets no transfer of the still fresh ink layer took place.

Example VIII

A red ink for relief or letterpress printing was prepared having the following composition:

	parts by weight	
varnish (prepared as described in Example I)	74	60
aluminum hydroxide	4.8	
5 pigment red 57	17.0	
paste (prepared as described in Example VII)	2.0	
10 cobalt octoate (10% cobalt)	0.4	

The resulting mixture was milled and further treated as indicated in Example I. Shortly before printing were added 1.8 parts by weight of cyclohexanone peroxide.

After printing and drying, as in Example II, the same favourable drying result was obtained without transfer of the ink layer during "landing" of the printed sheets.

Example IX

A red ink for four-colour sheet-fed offset printing was prepared by mixing 17.4 parts by weight of pigment red 57 with 79.4 parts by weight of varnish, as described in Example I, and 1.4 parts by weight of paste as described in Example VII, milling the mixture in a three-roller mill, adding at a temperature below 40°C 1.8 parts by weight of dibenzoyl peroxide, and properly mixing same.

The thus prepared ink was ready for use and could easily be stored for 3 to 4 months at room temperature without a decrease of the good drying properties.

After printing and drying, as in Example I, the same favourable drying result was obtained, while practically no transfer of the ink layer took place during "landing".

Example X

A red ink for relief or letterpress printing was prepared by mixing 4.3 parts by weight of aluminum hydroxide and 16.6 parts by weight of pigment red 57 with 75.8 parts by weight of varnish, as described in Example I, and 1.6 parts by weight of paste as described in Example VII, milling the mixture in a three-roller mill, adding, at a temperature below 40°C, 1.7 parts by weight of isobutyl peroxide, and properly mixing same.

The thus prepared ink was ready for use and could be stored for a long time.

After printing and drying, as in Example II, the same favourable drying result was obtained, while also transfer during "landing" of the printed sheets was prevented.

WHAT WE CLAIM IS:—

1. A printing ink which rapidly dries under the influence of heat and which comprises:

—a non-polar solvent,

Example VI

A red ink for rotary offset printing was prepared by mixing 12.0 parts by weight of pigment red 57 with 61.0 parts by weight of varnish, as described in Example I, milling the mixture in a three-roller mill, adding 26.0 parts by weight of paraffin oil (see Example I), once again properly mixing same, and finally adding, at a temperature below 40°C, 1.0 part by weight of isobutyl peroxide.

The thus prepared ink was ready for use and could be stored for a long time.

After printing and drying, as in Example III, the same favourable drying result was obtained.

Example VII

A paste was prepared by intimately mixing together the following components:

	parts by weight
varnish (prepared as described in Example I)	1400
modified starch***	700
polyethylene wax	100
water	250
tridecyl alcohol	50

*** Corn starch having a granular size of about 10 μ , which at 20°C under stirring is treated with concentrated hydrochloric acid until a fluidity of about 55 is reached, after which the hydrolytic degradation is topped by addition of sodium carbonate.

From a mixture of the following composition:

	parts by weight
varnish (prepared as described in Example I)	79.0
40 pigment red 57	17.8
paste (prepared as described above)	1.0
cobalt octoate (10% cobalt)	0.4

was prepared a red ink for four-colour sheet-fed offset printing as described in Example I. Shortly before printing were added 1.8 parts by weight of cyclohexanone peroxide.

After printing and drying, as in Example I, the same favourable drying result was obtained, while during "landing" of the successive printed sheets no transfer of the still fresh ink layer took place.

Example VIII

A red ink for relief or letterpress printing was prepared having the following composition:

	parts by weight	
varnish (prepared as described in Example I)	74	60
aluminum hydroxide	4.8	
pigment red 57	17.0	
paste (prepared as described in Example VII)	2.0	
cobalt octoate (10% cobalt)	0.4	

The resulting mixture was milled and further treated as indicated in Example I. Shortly before printing were added 1.8 parts by weight of cyclohexanone peroxide.

After printing and drying, as in Example II, the same favourable drying result was obtained without transfer of the ink layer during "landing" of the printed sheets.

Example IX

A red ink for four-colour sheet-fed offset printing was prepared by mixing 17.4 parts by weight of pigment red 57 with 79.4 parts by weight of varnish, as described in Example I, and 1.4 parts by weight of paste as described in Example VII, milling the mixture in a three-roller mill, adding at a temperature below 40°C 1.8 parts by weight of dibenzoyl peroxide, and properly mixing same.

The thus prepared ink was ready for use and could easily be stored for 3 to 4 months at room temperature without a decrease of the good drying properties.

After printing and drying, as in Example I, the same favourable drying result was obtained, while practically no transfer of the ink layer took place during "landing".

Example X

A red ink for relief or letterpress printing was prepared by mixing 4.3 parts by weight of aluminum hydroxide and 16.6 parts by weight of pigment red 57 with 75.8 parts by weight of varnish, as described in Example I, and 1.6 parts by weight of paste as described in Example VII, milling the mixture in a three-roller mill, adding, at a temperature below 40°C, 1.7 parts by weight of isobutyl peroxide, and properly mixing same.

The thus prepared ink was ready for use and could be stored for a long time.

After printing and drying, as in Example II, the same favourable drying result was obtained, while also transfer during "landing" of the printed sheets was prevented.

WHAT WE CLAIM IS:—

1. A printing ink which rapidly dries under the influence of heat and which comprises:

—a non-polar solvent,



- a phenol- or cresol formaldehyde resin modified with colophony,
- a crosslinkable unsaturated polyester,
- a peroxide catalyst for said polyester, and
- a pigment.
2. A printing ink as claimed in claim 1, in which the non-polar solvent is a hydrocarbon mixture conventional in printing inks.
3. A printing ink as claimed in claim 1 or claim 2, in which the resin is a colophony modified phenol formaldehyde resin and is further esterified with a polyhydric alcohol.
4. A printing ink as claimed in any one of claims 1 to 3, in which the unsaturated polyester comprises a polyhydric alcohol, a phthalic acid component and an unsaturated aliphatic carboxylic acid.
5. A printing ink as claimed in any one of claims 1 to 4, in which the peroxide catalyst is an organic peroxide which decomposes at a temperature between 70 and 80°C with formation of free radicals.
6. A printing ink as claimed in claim 5, in which the organic peroxide is isobutyl peroxide.
7. A printing ink as claimed in claim 5, in which the organic peroxide is dibenzoyl peroxide.
8. A printing ink as claimed in claim 5, in which the organic peroxide is tert. butylperoxy-2-ethyl hexoate.
9. A printing ink as claimed in any one of claims 1 to 8, in which the weight ratio of the solvent, the resin and the polyester is such that the two latter components are present in dissolved state, but the resin is no longer soluble after the polyester has been crosslinked, and as a result has become insoluble and has disappeared from the solution.
10. A printing ink as claimed in claim 9, in which the weight ratio of the resin and polyester together to the solvent is greater than 1/1, while the weight ratio of the resin only to the solvent is smaller than 1/1.
11. A printing ink as claimed in any one of claims 1 to 10, in which the heat is from infra-red radiation.
12. A printing ink as claimed in any one of claims 1 to 11 in which the ink contains, as additive, fine granules of a modified starch or a starch derivative having a limited swelling power (as herein defined) under the influence of water.
13. A printing ink as claimed in claim 12, in which the fine granules have an average granular size of not more than 20 μ .
14. A printing ink as claimed in either claim 12 or claim 13, in which the additive is a starch modified by treatment with an acid or with enzymes.
15. A printing ink as claimed in either claim 12 or claim 13 in which the additive is an oxidized starch.
16. A printing ink as claimed in either claim 12 or claim 13, in which the additive is a starch ether or a starch ester.
17. A printing ink as claimed in any one of claims 12 to 16, in which the additive is a modified corn starch or a corn starch derivative.
18. A printing ink as claimed in any one of claims 12 to 17, in which the additive is present in an amount of 0.1 to 2.0 wt. % calculated on the total ink.
19. A printing ink as claimed in claim 18, in which the additive is present in an amount of 0.2 to 1.2 wt. % calculated on the total ink.
20. A printing ink as claimed in any one of claims 1 to 11, in which the ink is an emulsion ink, in which in the organic phase has been emulsified a water phase which, if necessary, contains additives.
21. A printing ink as claimed in any one of claims 12 to 19 in which the ink is an emulsion ink, in which in the organic phase has been emulsified a water phase which, if necessary, contains additives.
22. A printing ink substantially as hereinbefore described and with particular reference to any one of Examples I to VI.
23. A printing ink substantially as hereinbefore described and with particular reference to any one of Examples VII to X.
24. A printing process, in which is employed a printing ink as claimed in any one of claims 1 to 10 or 20 for printing a material which is capable of absorbing the solvent of the printing ink, and the printed material is exposed to the influence of heat.
25. A printing process as claimed in claim 24, in which the heat is from infra-red radiation which substantially lies in the near infra-red.
26. A printing process as claimed in claim 24 or claim 25 which is a planographic printing or relief printing process.
27. A printing process, in which is employed a printing ink as claimed in any 11 or claim 22 for printing a material which is capable of absorbing the solvent of the printing ink, and the printed material is exposed to the influence of heat.
28. A printing process as claimed in claim 27, in which the heat is from infra-red radiation which substantially lies in the near infra-red.
29. A printing process as claimed in claim 27 or claim 28 in which is a planographic or relief printing process.
30. A printing process, in which is employed as a printing ink as claimed in any one of claims 12 to 19, 21 or 23 for printing a material which is capable of absorbing the solvent of the printing ink, the printing is carried out in the presence of a sufficient



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amount of water for effecting a limited swelling of the fine granules used as the additive, and the printed material is exposed to the influence of heat.

5 31. A printing process as claimed in claim 30, in which the heat is from infra-red radiation which substantially lies in the near infra-red.

10 32. A printing process as claimed in claim 30 or claim 31 which is a sheet-fed planographic printing or relief printing process.

15 33. A printing process substantially as hereinbefore described with particular reference to any one of Examples I to VI.

34. A printing process substantially as

hereinbefore described with particular reference to any one of Examples VII to X.

35. Printed material whenever obtained by a process as claimed in any one of claims 24 to 26. 20

36. Printed material whenever obtained by a process as claimed in any one of claims 27 to 29 or 33. 25

37. Printed material whenever obtained by a process as claimed in any one of claims 30 to 32.

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