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(71) Applicant: **The British Ceramic Research Association Limited**
Queens Road Penkhull
Stoke-on-Trent Staffordshire(GB)

(72) Inventor: **Birtles, John Frederick**
15 Asbourne Drive Silverdale
Newcastle under Lyme Staffordshire(GB)

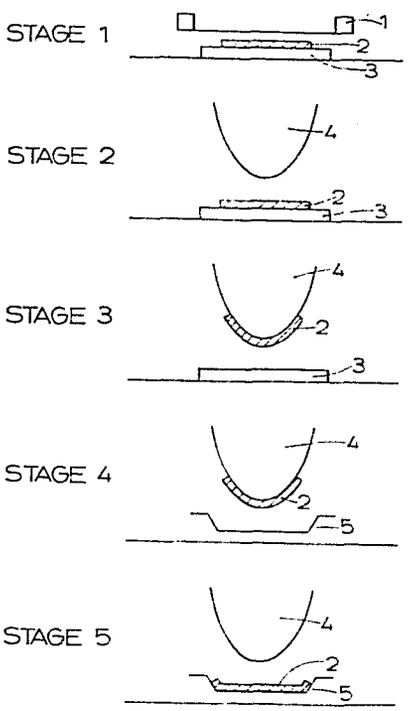
(72) Inventor: **Brett, Robert Dennis**
14 Meliden Way Penkhull
Stoke-on-Trent Staffordshire(GB)

(72) Inventor: **Roberts, Wilfred**
43 Naples Drive Westlands
Newcastle under Lyme Staffordshire(GB)

(74) Representative: **Lomas, Geoffrey Michael et al,**
BARKER, BRETTELL & DUNCAN 138 Hagley Road
Edgbaston
Birmingham B16 9PW(GB)

(54) Off-set printing.

(57) An ink design (2) is silk screened onto an intermediate surface (3) and is then transferred to an article (5) by a deformable pad (4). In order to provide a large difference in the ink affinities of the intermediate surface and pad these are made of silicone rubbers in which different catalysts are used in the curing of the rubbers. Dibutyltindilaurate as catalyst provides an intermediate surface of low ink affinity which can enable 100% transfer of ink from the intermediate surface to the pad when a stannous octoate calysed, condensation cured rubber, or a suitable addition cured rubber, is used for the pad. The screen is heated to a greater temperature than that of the intermediate surface.



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OFF-SET PRINTING

This invention relates to repetitive off-set printing processes of the kind in which a deformable pad is employed to transfer an ink design to an article.

Off-set transfer pad processes for printing onto complex shapes are well established in the ceramic, plastics, toy and packaging industries. The majority of these processes use a deformable gelatine or silicone rubber pad to transfer an ink design from an intaglio metal plate to the items to be decorated or marked. The metal plate can be engraved or etched.

The cost of these metal plates can be high, particularly if hand engraved. U.K. Patent Specification 737 461 has proposed replacing the intaglio metal plate by a silk screen and an intermediate flat surface. The ink design is applied to the intermediate flat surface by screen printing and then transferred to the item to be marked or decorated by means of the deformable pad. It was suggested that the intermediate surface can be any non-absorbent material, and examples of metal or glass were given. However, it was found in practice that the ink film on the intermediate surface split on removal of the deformable pad from the intermediate surface. The result was that the design ink spread with successive prints and there was a loss of definition.

In U.K. Patent Specification No. 1 602 225 it was stated that to overcome the above problem and to remove the risk of excessive build up of ink on the intermediate surface, it was found necessary to ensure that, at each silk screen operation, the intermediate surface was free from residual colour remaining from the previous print. To achieve this, the intermediate surface may be doctored

between successive prints, or half-sized paper fed from a roll, such that a fresh area of paper is presented for each screening operation.

When doctoring is employed the efficiency of doctoring is crucial, and care has to be exercised to prevent scratching of the intermediate surface. Failure to doctor efficiently, or to prevent scratching, immediately leads to spoiled prints.

With all of the known processes the ink film is split at each transfer operation with the further disadvantage that only some of the ink is transferred to the work piece. Particularly in the case of ceramics there is a need to be able to print heavy blocks or bands of colours, and with such ink splitting processes this is difficult to achieve.

The present invention stems from attempts to provide an improved off-set printing process, where the ink design on the intermediate surface is transferred substantially completely to the item to be marked or decorated by the deformable pad.

U.K. Patent Specification No. 804 751 suggests that the transfer of the design in its entirety from an intermediate surface to the ware to be printed can be effected by coating both the intermediate surface and the resilient pad with an adhesive layer. The fact that this proposal appears never to have been exploited commercially casts doubts on the effectiveness of that method.

The basis for the present invention lies in our discovery that the relative affinity of an ink for the intermediate surface, deformable pad and work piece can be controlled by the use of two dissimilar silicone

rubbers for pad and intermediate surface, the silicone rubbers differing in the catalysts that are employed in curing of the rubbers.

U.S. Specification No. 4,261,749 is concerned with a thermoplastic ink formulation for use in an off-set process in which an ink design is applied to a silicone elastomer intermediate surface and is then transferred to the ware by a further silicone elastomer. It is stated at lines 47 to 51 of column 4 that 'it is highly desirable to have as great a difference in surface energy as possible between the two silicone surfaces in order to facilitate ink release from one to the other', but no details are given of what rubbers are to be employed. It would appear that it was contemplated to provide different surface energies by employing different compositions of rubber, such as by varying the phenyl/methyl ratio as was previously known.

It is further stated at lines 54 to 58 of column 4 that 'the inventive materials can result in less frequent replacement of the silicone rolls or pads than is required for other presently-available thermoplastic ink formulations' and at lines 50 to 52 of column 4 that 'it has been found that the surface energy of the silicone surface increases with repeated release cycles'.

Thus, U.S. Specification No. 4 261 749 is concerned with devising an ink formulation to accommodate changes in ink affinity of the silicone rubber surfaces which occur in use, whereas the present invention is concerned with providing substantially stable ink affinities of the two surfaces, so that the silicone rubber surfaces rarely, if ever, require replacement to alter ink affinity.

According to one aspect of the invention we provide a repetitive off-set printing process in which an ink design is first applied to an intermediate surface from which it is then transferred to an article by a deformable pad, the intermediate surface and the pad being formed of first and second silicone rubbers respectively, the first and second rubbers employing different catalysts in the curing thereof, and the catalysts being chosen such that the affinity of the first silicone rubber for the ink is substantially less than the affinity of the second silicone rubber for the ink.

The intermediate surface is preferably flat.

Appropriate choice of the catalysts employed in curing the silicone rubbers and control of the visco-elastic properties of the inks as described in detail hereafter enable the ink design to be transferred 100% from the intermediate surface to the work piece. There is then no need for doctoring of the intermediate surface, with the result that the printing apparatus can be made much simpler and reliable.

The ink design may be applied to the intermediate surface by any suitable method. Preferably silk screening will be employed, but other stencilling operations may be used.

We have found that condensation type silicone rubbers having a wide range of ink affinities can be produced by employing as catalysts the carboxylic acid salts of various metals such as Pb, Zn, Zr, Sb, Fe, Cd, Sn, Ba, Ca, and Mn.

In particular, we have found that a range of ink affinities is provided by the following list of salts: metal naphthenates, octoates, hexoates, laurates and acetates, the ink affinity generally reducing through the list.

In theory it would appear best to use a metal acetate in curing the first rubber, and a metal naphthenate in curing the second rubber, taking the extremes from the list. In practice, however, partly for the reason of availability we prefer to use a metal laurate for the first rubber and a metal octoate for the second rubber, when both rubbers are of the condensation type. We have tried using certain acetates for the first rubber but the resulting rubbers tended to be slightly unstable thereby restricting their commercial potential.

On this scale of ink affinities addition cured rubbers are at the high end of the scale.

It has been discovered that silicone rubbers of the condensation type, and using dibutyltindilaurate as the catalyst in the curing process, have much less affinity for ink than condensation cure rubbers using most other catalysts in the curing process or addition cure rubbers.

We prefer to use stannous octoate catalysed, condensation cured rubber for the pad when a dibutyltindilaurate catalysed, condensation cured rubber is used for the intermediate surface, but addition cured rubbers for the pad can also enable the process to operate effectively.

Also, it has been found preferable to heat treat the dibutyltindilaurate silicone rubber after cure, in order

to stabilise its ink affinity properties relative to other silicone rubbers.

Because of its lesser affinity for ink, a stabilised dibutyltindilaurate catalysed silicone rubber provides an ideal material for the intermediate surface. It is able to accept ink from the silk screen to form a design of high definition but then, on subsequent pressure contact from a deformable pad of a suitably dissimilar silicone rubber, due to differences in ink affinity, it gives up the ink design 100% to the pad.

When screen printing of the design onto the intermediate surface is employed it is preferable to arrange a change in the visco-elastic properties of the ink between the screen printing stage and the ink design transfer stage. The need for this change is that the visco-elastic properties of the ink required for screen printing are different from those desirable for good transfer. An ink of the correct viscosity is the prime consideration for quality screen printing whilst the tack properties of the ink can be of importance at transfer. This change in emphasis from viscosity at screen printing to tack at transfer is preferably effected by the use of heat.

An electrically heated metal screen is conveniently used, but an externally heated screen may be employed.

Additionally the ink should be compatible with the silicone rubber of both transfer pad and intermediate surface and not induce significant deterioration in either during the period of printing. It has been found that inks meeting all the above criteria are preferably composed of a solid resin, a liquid resin, a wax and a ceramic pigment. The wax should have a melting point

below the desired silk-screen temperature and the solid resin a melting point above this temperature. Viscosity control at the silk screen is effected by adjustment to the solid/liquid resin ratio and tack at the transfer stage by the wax to total resin ratio.

According to a second aspect of the invention an off-set printing machine suitable for use in printing onto the curved surface of an article comprises an intermediate surface, means for applying an ink design to the intermediate surface, a deformable pad, means for bringing the deformable pad into register with the intermediate surface to pick up the ink design, and means for bringing the pad carrying the ink design into register with the article to transfer the ink design to the article, the intermediate surface and the pad being formed of first and second silicone rubbers respectively, the first and second rubbers employing different catalysts in the curing thereof, and the catalysts being chosen such that the affinity of the first silicone rubber for ink is substantially less than the affinity of the second silicone rubber for the ink.

In a preferred embodiment of the invention an electrically heated metal screen and an ink formulation are employed such that, at the temperature of the screen, the ink viscosity is correct for screen printing. The ink in the form of the required design is screened onto the intermediate surface of stabilised dibutyltindilaurate catalysed silicone rubber which is heated to a lower temperature than the screen, such that after screening the tack properties of the ink dominate. A deformable pad of dissimilar silicone rubber, for example addition cured or octoate-catalysed condensation cured, is used to pick up the ink design 100% from the intermediate surface. In the final stage of the operation the

pad transfers the ink design 100% to the work piece. The process is illustrated diagrammatically in the accompanying single Figure in which the reference numeral 1 designates the heated silk screen, 2 designates the ink design, 3 designates the heated intermediate surface, 4 designates the deformable pad, and 5 designates the work piece.

As an illustration of the process there now follows examples of formulations for the silicone rubbers and ink together with details of operating temperatures for screen and intermediate surface. The examples selected are to demonstrate the principles of the invention and do not imply any limitation.

Silicone rubber transfer pads

(A1) Addition cure*:

	Parts weight
rubber polymer	40 - 60
50 cst silicone fluid	60 - 40
manufacturers cross linker and catalyst on the basis of 11.1% of the polymer	4.4 - 6.6

*Based on rubber polymer ME 622 supplied by

Wacker Chemicals (UK) Ltd.,
The Clock Tower,
Mount Felix
Bridgest
Walton-on-Thames, Surrey KT12 1AS

(A2) Condensation cure*:

	Parts Weight
rubber Polymer	60 - 90
50 cst silicone fluid	40 - 10
ethyl silicate on the basis of 0.5 to 2% of the polymer	0.3 - 1.8
stannous octoate on the basis of 0.3 to 2% of the polymer	0.18 - 1.8

*Based on rubber polymer 573A supplied by

Rhodia (UK) Ltd.
Hulton House
161-166 Fleet Street
LONDON EC4 2DP

Silicone rubber intermediate surface examples

(B1) Based on rubber polymer silicoset 105 supplied by

ICI Ltd.
Organics Division
Blackley
MANCHESTER.

	Parts Weight
rubber polymer	60 - 100
50 cst silicone fluid	40 - 0
dibutyltindilaurate and cross linker on the basis of 0.1 to 3% of the polymer	0.06 - 3

(B2) Based on rubber polymer 573A supplied by

Rhodia (UK) Ltd.
Hulton House
161-166 Fleet Street
LONDON EC4 2DP

	Parts Weight
rubber polymer	80 - 100
50 cst silicone fluid	20 - 0
dibutyltindilaurate and cross linker on the basis of 0.5 to 3% of the polymer	0.4 - 3

The rubber of Example (B1) or (B2) is produced as a thin uniform layer, 0.5 to 5 mms in thickness, on a metal backing. Following fabrication and cure the rubber is stabilised by heat treating for 4 h. at 110°C.

Example of ink formulation

(C)	Parts Weight
Staybelite Ester Resin 3	64.8
Staybelite Ester Resin 10	17.6
Polyethylene Glycol 1500	17.6
Pigment	200.0

The ink is produced by intimate mixing either by bead or triple roll mill.

Staybelite resins are supplied by

Hercules Ltd.
20, Red Lion Street
LONDON WC1R 4PB

Typical Operating Temperatures

Silk-screen	60 - 100°C
Intermediate surface	30 - 45°C

CLAIMS

1. A repetitive off-set printing process in which an ink design (2) is first applied to an intermediate surface (3) from which it is then transferred to an article (5) by a deformable pad (4), the intermediate surface and the pad being formed of first and second silicone rubbers respectively, characterised in that the first and second rubbers employ different catalysts in the curing thereof, and the catalysts are chosen such that the affinity of the first silicone rubber for the ink is substantially less than the affinity of the second silicone rubber for the ink.

2. A process as claimed in claim 1 in which the first silicone rubber is of the condensation type, and the catalyst employed in curing that rubber is a carboxylic acid salt of a metal.

3. A process as claimed in claim 2 in which the salt is a metal laurate.

4. A process as claimed in claim 3 in which the salt is a dibutyl metal dilaurate.

5. A process as claimed in claim 4 in which the salt is dibutyltindilaurate.

6. A process as claimed in any of the preceding claims in which the second silicone rubber is an addition cured rubber.

7. A process as claimed in any of claims 1 to 5 in which the second silicone rubber is of the condensation type, and the catalyst employed in curing that rubber is a carboxylic acid salt of a metal.

8. A process as claimed in any of claims 3 to 5 in which the second silicone rubber is of the condensation type, and the catalyst employed in curing that rubber is a metal octoate.

9. A process as claimed in claim 8 in which the metal octoate is stannous octoate.

10. A process as claimed in any of the preceding claims in which the first silicone rubber was heat treated after curing so as substantially to stabilise its ink affinity properties.

11. A process as claimed in any of the preceding claims in which the ink design is applied to the intermediate surface by a silk screening method.

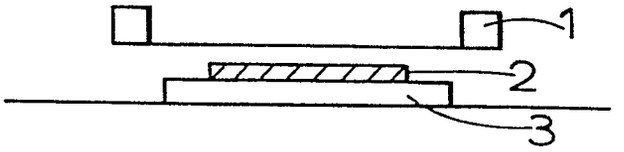
12. A process as claimed in claim 11 in which the silk screen and the intermediate surfaces are maintained at temperatures greater than the ambient temperature, the temperature of the silk screen being greater than that of the intermediate surface.

13. A process as claimed in claim 12 in which the silk screen is maintained at a temperature in the range 60° to 100°C, and the intermediate surface is maintained at a temperature in the range 30° to 45°C.

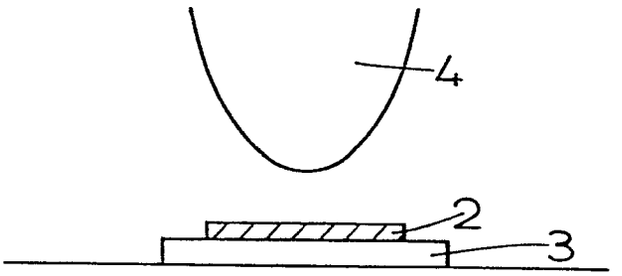
14. An off-set machine suitable for use in printing onto the curved surface of an article comprising an intermediate surface, means for applying an ink design to the intermediate surface, a deformable pad, means for bringing the deformable pad into register with the intermediate surface to pick up the ink design, and means for bringing the pad carrying the ink design into register with the article to transfer the ink design to

the article, characterised in that the intermediate surface and the pad are formed of first and second silicone rubbers respectively, the first and second rubbers employ different catalysts in the curing thereof, and the catalysts are chosen such that the affinity of the first silicone rubber for ink is substantially less than the affinity of the second silicone rubber for the ink.

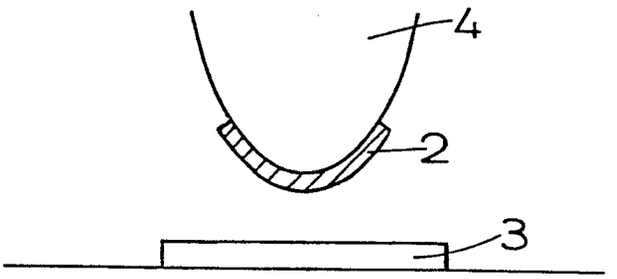
STAGE 1



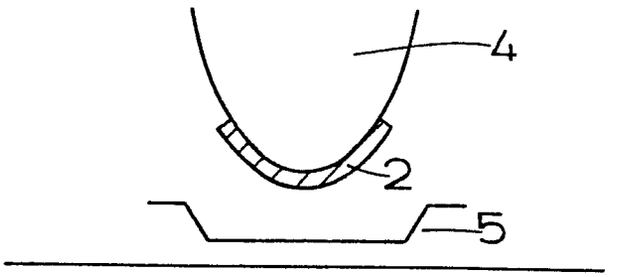
STAGE 2



STAGE 3



STAGE 4



STAGE 5