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HOT-STAMPING GLASS, CERAMICS AND OTHER SUBSTRATES

This invention relates to the application of decorative coatings to glass, ceramics and perhaps other substrates, by a procedure akin to that known as hot-stamping, and is an important development of our earlier invention as described and claimed in our previous European Patent Application No. 93 3 04160.0, now EPA 0 626 354.

The well-established hot-stamping procedure involves applying both heat and pressure by means of a heated die or roller (hereinafter for convenience referred to generically as a "hot compress") to a so-called hot-stamping foil, consisting of a pigmented colour or metallized surface film borne on a usually-polyester carrier, so as by means of the hot compress to force it into contact with a thermoplastic substrate, and thereby soften the thermoplastic substrate and also activate the film-coating on the foil, thereby enabling it to form a strong physico-chemical bond with the underlying thermoplastic substrate wherever heat and pressure have been applied to the foil, but not elsewhere. When subsequently the foil is pulled away, just the areas of the film which have been subjected to the hot-stamping remain affixed to the plastic substrate, and the remainder peels away.

In order to carry out this hot-stamping operation one normally employs either a vertical stamping machine or a roll-on machine. The vertical stamping machine contains a heated compress of die of brass, steel or silicone rubber, performed to define the deserved design, which compress serves to apply both heat and pressure and thus to transfer the desired design defined by the die (whatever that design may be - thus decorative areas and/or writing or other printed

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information) from the film onto the thermoplastic substrate, as each part is positioned beneath the compress. Roll-on methods utilize a silicone rubber roller or an arcuate die as the hot compress to transfer the desired design from the foil onto the thermoplastic substrate, in either a continuous or batch process.

Hot-stamping is an efficient and inexpensive way to apply decoration to thermoplastic substrates. Unfortunately however hot-stamping of this nature cannot be used with glass, because glass melts at a much higher temperature than most thermoplastic materials. Consequently decoration in the form of gold leaf, colour design or printing etc. is generally applied to glass containers by a glazing process similar to that used with ceramics. Thus for example in gold-leafing the gold decoration is applied to the glass container by a variety of methods such as silk-screen printing, etc. The glass container is then subjected to extremely high kiln temperatures, and in essence the decoration is baked on. Unfortunately this process is however time-consuming, expensive, energy-intensive and raises safety considerations due to the high temperatures that have to be employed and the nature of the gases which are evolved in the operation of the kilns.

There has thus been a considerable and long-standing need for a simple, economical and ultra-safe procedure for applying decoration to glass substrates, quite unfulfilled until we devised the method for achieving these objectives described in our above-mentioned EPA 0,626,354, which is akin to the known hot-stamping process but operable on glass and ceramics.

However, the problems with the recently-devised procedure, as set out in our EPA 0,626,354, is that the



inks do not always adhere to the glass to the degree required for commercial decorating purposes.

We have therefore carried out extensive investigations, directed to the search for an ink with
5 excellent bond strength to glass and which at the same time is capable of adhering hot stamping foil. It has been thus discovered that the key to the achievement of commercially-acceptable decorating lies in the use of one particular, previously-unconsidered, class of
10 cationically radiation-curable cycloaliphatic epoxides.

According to the present invention there is provided a method for applying a decorative coating to a glass, ceramic or indeed other substrate, which comprises the steps of:

15 a) applying a desired design to the substrate with a curable adhesive ink composition containing a cationically radiation-curable cycloaliphatic epoxide;

20 b) curing the adhesive ink on the substrate by exposing it to the radiation by which it is curable, thereby to bond the cured ink to the substrate;

25 c) compressing a hot-stamping foil bearing a film of decorative material against the substrate with a hot compress defining a desired design and heated to a temperature sufficient to cause the film to adhere to the cured ink pattern but not to
30 the ink-free areas of the substrate; and

d) removing the compress, thereby leaving the decorative film from the hot-stamping foil adhering to the adhesive ink pattern only.

35 A wide variety of glass or ceramic articles may be provided with a decorative coating by means of the



method of this invention, and so far as we are aware there is no limit on the kind of glass or ceramics that may thus be decorated. Thus the term "substrate" as used herein embraces all kinds of glass and ceramic
5 (including china) substrates and indeed also others, provided only that they require decoration..and that there is no equally effective and cheaper way of achieving the same objective, as for instance there is with thermoplastic substrates. In short, this
10 technique will work with a thermoplastic substrate, but there is no need to employ it since conventional hot-stamping is fully effective on thermoplastic substrates and tends to be cheaper.

Such substrates may for instance take the form of
15 containers e.g. bottles, dishes, cups and glasses, as well as also purely decorative objects eg. figurines, vases, windows, tiles and so on.

In the first step of the decorative method of this invention the desired decorative or other pattern is
20 essentially "painted" onto the glass utilizing an adhesive ink composition as the "paint". The "painting" may be accomplished by silk-screening, screen-printing, offset-printing, stencilling, actual painting (with a brush) or any other of the wide
25 variety of available methods.

Generally-speaking we currently prefer to apply the desired pattern of adhesive ink by silk-screening it onto the glass container, utilizing the traditional screen and squeegee well known to those skilled in the
30 art, because it is adaptable to on-line production. However the ink may be applied by means of hand-held applicators such as paintbrushes or the like, especially where the ink is to be applied to a substrate in the form of a figurine or other like
35 highly-decorative article which is not readily amenable to screen-printing.



The curable adhesive ink composition used in the present invention must be one based upon a cationically radiation-cured cycloaliphatic epoxide. The term "cationically radiation-curable" is here used in the sense that it has become accepted in the radiation curing art, and roughly-speaking means that the radiation curing takes place in air - as contrasted with anionic curing, which must take place under anaerobic conditions.

The cycloaliphatic epoxide employed will preferably be one having at least two epoxy groups per molecule. Polymeric cycloaliphatic epoxides are however also suitable, such as those formed as the reaction products between epichlorohydrin and phenol or a phenolformaldehyde resin, diepoxy resin, epoxidized oils and epoxidized polyolefins. Such epoxides include novolac epoxides, glycidyl ethers of various types including diglycidyl ethers of bisphenol, diglycidyl ethers of butanediol, and the like. Also suitable are homopolymers and copolymers that contain pendant epoxide groups such as those made from glycidyl acrylate and/or methacrylate with or without other ethylenically unsaturated monomers. Cycloaliphatic epoxides are however also suitable, such as those set forth in U.S. Patents Nos. 3,027,357, 3,890,194, 2,890,197, 3,031,434, 3,125,592, 3,201,360 and 5,204,930 (the disclosure of all of which are incorporated herein by cross-reference). Preferred are 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, bis-(3,4-epoxy-cyclohexylmethyl)-adipate, vinylcyclohexene diepoxide, bis(2,3-epoxycyclophenyl)ether, epoxidized butadiene, 2,3-epoxy-2-methylcyclohexylmethyl-3,4-epoxy-2-methylcyclohexane carboxylate, or mixtures thereof.

The preferred cycloaliphatic epoxides are the cationically UV-cured cycloaliphatic epoxides sold



under the tradename CYRACURE by Union Carbide Chemicals and Plastics Company, Danbury, Connecticut, USA., such as CYRACURE UVR 6110, 6379, 6351 and 5200.

5 The proportion of the cationically UV-cured cycloaliphatic epoxide to be employed in the ink composition is not highly critical, but we recommend the use of from about 10% to about 90% thereof, by weight of the composition, and preferably 35-90%.

10 If the ink composition is to be cured with actinic radiation (including UV light) rather than with an electron beam, it is then very desirable, indeed almost a necessity that the ink composition should also contain a photoinitiator, which will catalyze the polymerization of the cycloaliphatic epoxide. If an
15 electron beam is used, such a photoinitiator is not necessary. However, since preparing the composition one cannot always be sure how it will subsequently be cured, it is an advisable precaution always to include a photoinitiator therein.

20 Especially suitable photoinitiators are carbonyl compounds such as ketones and derivatives thereof, for example methyl ethyl ketone, benzophenone, benzyl dimethyl ketal, 1-hydroxycyclohexylphenylketone, 2,1-dimethoxy-2-phenylacetophenone, diethoxyacetophenone
25 and 2-methyl-1-(methylethylphenyl)-2-(4-morpholinyl)-1-propanone.

Other photosensitive onium salts are particularly good UV activated photoinitiators. The use of photosensitive onium salts to promote the curing of
30 epoxides when exposed to UV radiation is described in U.S. Patents Nos. 4,058,401, 4,138,255 and 4,161,478, the disclosure of which is incorporated herein by cross-reference. The photosensitive onium salts mentioned in these Patents are good UV-light
35 photoinitiators. These preferred photoinitiators are triaryl sulphonium salts sold by Union Carbide under



the tradename CYRACURE UVI 6974.

The proportion of photoinitiator needed is not critical, but we recommend the use from about 0.5% to 20%, by weight of the composition, and preferably 3-15%
5 by weight.

The ink composition may also advantageously include an ester-containing polyol having a molecular weight of less than 850 and a viscosity of less than 0.6 Pa s (60 poise), which serves the purpose of
10 controlling its viscosity.

Such ester-containing polyols are oligomers prepared by methods well known in the esterification or alkyd resin arts. Suitable polyols are for instance described in U.S. Patent No. 3,994,851, the disclosure
15 of which is hereby incorporated by cross-reference. The ester-containing polyols are the reaction product of polycarboxylic acids (such as adipic, azeleic, malic, fumaric, succinic or glutaric acids) with a polyol (such as ethylene glycol, neopentyl glycol,
20 diethylene glycol, trimethylolpropane monoallyl ether, 1,6-hexandiol, etc.).

The preferred ester-containing polyols are the polycaprolactone polyols sold under the tradename "TONE Polyols" by Union Carbide, particularly TONE Polyol 310
25 or trimethylolpropane caprolactone.

The proportion of the ester-containing polyol to be used is not critical, but we recommend the use of from about 1% to about 20% by weight of the composition, and preferably 3-15%, of the ester-
30 containing polyol.

The curable adhesive ink composition may also desirably contain an adhesion-promotor, thus an agent that serves to increase the adhesion of the cycloaliphatic epoxide to the substrate. If the
35 substrate is glass, silanes are excellent coupling agents with glass, and will promote adhesion of the ink



to the substrate. Suitable acryloxy-functional silanes are described in U.S. Patent No. 5,221,560, the disclosure of which is hereby incorporated by cross-reference.

5 Such acryloxy-functional silanes include:

- 3-methacryloxypropyltrimethoxysilane,
- 3-acryloxypropyl-trimethoxysilane,
- 2-methacryloxyethyltrimethoxysilane,
- 2-acryloxyethyltrimethoxysilane,
- 10 3-methacryloxypropyltriethoxysilane,
- 3-acryloxypropyltrimethoxysilane,
- 3-acryloxypropyltriethoxysilane,
- 2-methacryloxyethyltriethoxysilane,
- 3-acryloxypropyltriethoxysilane,
- 15 2-methacryloxyethyltriethoxysilane, and
- 2-methacryloxyethyltriethoxysilane, etc.

Glycidoxy-functional silanes may also be suitable. Such glycidoxysilanes include 3-glycidoxypropyltrimethoxysilane, 2-glycidoxyethyltrimethoxysilane,

20 3-glycid-oxypropyltriethoxysilane,

2-glycidoxyethyltriethoxysilane,

3-glycidoxypropyltrimethylsilane and so on.

The glycidoxy silanes are preferred, in particular 3-glycidoxypropyltrimethylsilane. We recommend the use

25 of from about 1% to about 10%, by weight of the composition, of an adhesion promotor, which can usually be relied upon to cause improved adhesion of the ink to the substrate.

It is generally desirable that the curable

30 adhesive ink composition should also include a defoaming agent, because it promotes smooth, even application of the ink onto the substrate, eliminating bubbles and distortions.

A variety of defoaming agents are suitable, but

35 those which we currently prefer are polyalkyl acrylics, such as the polyvinyl butyl ether in Stoddard solvent



[this is a petroleum distillate, widely used as a dry-cleaning solvent, with a minimum flash point of 35°C (100°F) and a distillation range range of from not less than 50% over at 177°C (350°F) up to an end point not higher than 210°C (410°F)] as sold under the tradenames BYK-052 and BYK-053 by BYK - Chemie.

The proportion of defoaming agent to be employed is not critical, but we generally recommend the use of from about 1 to 20%, by weight of the composition and preferably 3-15%.

It is of course permissible, and for some purposes it may be advantageous, to incorporate other ingredients in the curable adhesive ink composition, including for instance stabilizers, inert fillers, wetting agents, levelling agents and so on. If present, these ingredients can be in the range of from about 1 to about 15% by weight of the total composition.

In the second step of the decorative method of this invention, thus after the curable adhesive ink composition has been applied to the substrate, the cationically radiation-curable cycloaliphatic epoxide (and thus the ink composition as a whole) must be cured by exposure to the radiation by which it is curable. We have found that the cycloaliphatic epoxide may be cured by an electron beam without further assistance, but actinic radiation (including ultra-violet radiation) will also serve to cure the epoxide (especially if assisted by the presence of a photoinitiator) and is to be preferred over an electron beam.

Therefore, especially if it is for use with actinic radiation, the curable adhesive ink composition will very preferably include a photo-initiator, which catalyzes the polymerization of the cycloaliphatic epoxide.



For the avoidance of doubt it is perhaps desirable to observe that the terms "actinic radiation" and "ultra-violet radiation" are here used in their normal sense, that is to say :

5

the term "actinic radiation" in general means light in the violet and ultra-violet regions which will bring about chemical changes, and may be regarded as corresponding to wavelengths of from 4 to 600 nm; and

10

the term "ultra-violet (or UV) radiation" refers to the non-visible part of actinic radiation, and may be regarded as corresponding to wavelengths of from 4 to 400nm., and preferably (for present purposes) 325-365nm.

15

The substrate bearing the decorative pattern of ink composition is exposed to UV light (or other radiation) for a time sufficient to effect polymerization of the epoxide and the polyol, usually for a period of from 1 to 30 minutes, and preferably for from 2 to 25 minutes, depending on how thickly the ink has been applied to the substrate.

This exposure may be conveniently accomplished by use of so-called UV-conveyers, which consist of a conveyor belt situated beneath an ultraviolet lamp, such as those manufactured by Fusion Systems. When the substrate is placed on the conveyor belt it is moved along and is irradiated by the lamp. Obviously, where longer cure times are needed, the substrate can be passed successively through several conveyors in line, or several times through the same conveyor. The conveyor system is set up so that the substrate passes through the UV-light for the total amount of time appropriate to cure the ink composition and adhere to the substrate.

35



In the third step of the decorative method of this invention, thus after the ink composition has been cured and is thus fully adhered to the substrate, the substrate must be stamped with hot-stamping foil, that is say a foil bearing a film of decorative material is compressed against the substrate with a compress heated to a sufficient temperature to cause the film on the hot-stamping foil to adhere to the cured ink design, but not to the ink-free areas of the glass.

The duration of the compression and the temperature of the compress are interdependent, and the optimum conditions for both can and will be determined by competent operatives in each individual case. By way of general guidance it can however be said that we have found that the compress should usually be heated to a temperature in the range of 395K-478K (250-400°F) preferably 395K-450K (250-350°F) to achieve adherence of the foil to the cured ink design. The compress must of course be pressed tightly against the substrate, and the period of such compression will range from fractions of a second up to several minutes, depending on the nature of the compress used, its temperature and the specific cycloaliphatic epoxide.

The term "hot-stamping foil" means, in general, a laminate comprised of a carrier material (often polyester, cellulose acetate, or another similar material capable of release), a release film, and a decorative or colour coat, in that order. The decorative coat is usually colour or metallized coat. The metallized coat can be actual gold, silver, or aluminium which is coloured to look like gold or silver, or have holographic properties. The coloured layer is most often applied by vacuum metallization.

More specifically, hot-stamping foil can be defined as a multilayer web comprising a backing film-carrier, a release coating, one or more protective top



coatings, one or more colour coatings, and a hot-melt adhesive, in that order.

Generally, the hot-melt adhesive layer of the foil is compressed against the substrate with a heated die.
5 The hot-melt adhesive layer adheres to the substrate, and the application of heat also causes the release layer to release the backing film carrier from the protective top-coat layer, leaving the protective top-coat layer exposed on the surface of the substrate.

10 The release coating is either wax (or a wax-like material) or a thermoplastic material, which melts upon application of heat to release the protective top-coat layer from the backing for release layers include ethylene vinyl acetate (EVA). acrylics,
15 polyvinylchlorides (PVC), polyamides, or similar thermoplastic materials as set forth in U.S. Patent No. 5,104,719, the disclosure of which is hereby incorporated by cross-reference.

The protective top-coat is usually a lacquer of
20 some type, which is capable of protecting the colour or metallized layer.

The final layer is a hot-melt adhesive, which can be a wide variety of substances, and is selected so that it is capable, upon application of heat, of
25 adhering to the substrate to which it is applied. Suitable hot-melt adhesives generally are thermoplastic materials, such as EVA, PVC and the like.

In the fourth step of the decorative method of this invention, the hot compress is removed and along
30 with it the foil, leaving a portion of the foil adhering to the substrate.

Thus, a portion of the hot-stamping foil, in particular the hot-melt adhesive layer and the metallized or colour layer, as well as the protective
35 top-coat if present (in that order) remain affixed to the cured ink design such that the hot-melt adhesive



adheres to the cured ink design, followed by the coloured coating layer and the protective top-coat layer on the surface of the container. The protective top-coat may or may not contain part of the release coat layer, which is designed to release the carrier layer from the protective top coat.

The decoration which is applied to the substrate is extremely durable and capable of withstanding conditions found in normal handling operations.

According to another aspect of the invention there is also provided an adhesive ink composition for use in the method herein disclosed, which adhesive ink composition is or includes a radiation-curable polymer composition comprising:

- from 10 to 90% of a cationically radiation-curable,

cycloaliphatic epoxide,

- from 1 to 20% of an ester-containing polyol, and

- from 1 to 20% of a defoaming agent,

as well as optionally other ingredients.

In addition, the preferred composition contains from 3 to 15% of a photoinitiator, and it may also contain from 1 to 10% of a silane.

According to a still further feature of this invention there are also provided containers, having an inner surface and an outer surface, in which:

- a) the outer surface has bonded thereto a partial coating of a cured ink which is a cationically radiation-cured cycloaliphatic epoxide, in a design that covers less than the whole of the said outer surface; and

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- b) the ink design is entirely overlaid by a multilayer web comprising (i) a hot-melt adhesive, (ii) a colour coating and (iii) a protective top-coat (in that order from the ink design outwards) said web being
5 adherent to the cured adhesive ink and covering only said ink and not extending to the ink-free areas of the said outer surface.

10 While the invention extends to containers of all kinds, even thermoplastic ones, that bear an outer coating of this type it fulfills its potential when the container is, as preferred, either glass or ceramic.

In order that the invention may be well understood
15 it will now be described in more detail, though only by way of illustration, with reference to the following examples:

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Example 1

A clear adhesive ink composition was made up as follows:

		grams
5	w/w%	
	Cycloaliphatic epoxide (CYRACURE UVR 6110)	50
	72.73	
10	Trimethylolpropane caprolactone (TONE Polyol 310)	6.25
	9.10	
15	Triaryl sulphonium salts(s) (CYRACURE UVI 6974)	5.00
	7.27	
	Polyvinyl butyl ether defoamer (BYK-053)	7.5
20		
	10.90	

These ingredients were mixed until dissolved, and were then ready for use as described in subsequent examples.

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Example 2

The ink composition of Example 1 was silk-screened onto a glass makeup container using a 255 line screen (having about 50 fibres per square centimetre, or (255 fibres per square inch) imprinted with a decorative design.

The glass container was passed through a 300 watt/9.2 metres (30 feet) per minute UV-conveyor for a total of 5 minutes to effect curing of the ink.

Gold hot-stamping foil (Crown Royal Leaf, Paterson, New Jersey, USA) was compressed against the container with a die heated to 395K (250°F) for several seconds.

The die was then removed, leaving a portion of foil adhered only to the ink design, and on peeling off the foil a gold metallic decorative design identical in appearance to gold leaf was left on the surface of the glass makeup container.

Example 3

The ink composition of Example 1 was used to hand-paint a simple design onto the side of a ceramic bowl, using a fine-tipped sable brush.

The bowl was subjected to UV-radiation by passing it through a 300 watt/9.2 metres (30 feet) per minute UV-conveyor for about 4 minutes.

Silver holographic hot-stamping foil was compressed against the cured ink design with a die heated to 288K (300°F) for several seconds.

Then the die was removed, leaving a portion of the hot-stamping foil adhered to the cured ink design, resulting in a metallic silver decoration.

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CLAIMS

1. A method for applying a decorative coating to a glass, ceramic or other substrate with hot-stamping foil which comprises the steps of:

5 a) applying a desired design to the substrate with a curable adhesive ink composition containing a cationically radiation-curable cycloaliphatic epoxide;

10 b) curing the adhesive ink on the substrate by exposing it to the radiation by which it is curable, thereby to bond the cured ink composition to the substrate;

15 c) compressing a hot-stamping foil bearing a film of decorative material against the substrate with a hot compress defining a desired design and heated to a temperature sufficient to cause the film to adhere to the cured ink pattern but not to the ink-free areas of the substrate; and

20

d) removing the compress, thereby leaving the decorative film from the hot-stamping foil adhering to the adhesive ink pattern only.

25 2. A method as claimed in claim 1, in which the ink is applied to the substrate by silk-screening.

30 3. A method as claimed in claim 1 or claim 2, in which the cationically radiation-curable cycloaliphatic epoxide is one having at least two epoxide groups per molecule.

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4. A method as claimed in any of the preceding claims in which the cationically radiation-curable cycloaliphatic epoxide is one or a mixture of more than one of the following, namely 3,4-epoxycyclohexylmethyl-
5 3,4-epoxycyclohexane carboxylate, bis-(3,4-epoxycyclohexylmethyl)-adipate, vinylcyclohexene diepoxide, bis(2,3-epoxycyclophenyl)ether, epoxidized butadiene and 2,3-epoxy-2-methylcyclohexylmethyl-3,4-epoxy-2-methylcyclohexane carboxylate.
- 10 5. A method as claimed in any of the preceding claims, in which the ink composition further comprises from 1 to 20% of an ester-containing polyol.
- 15 6. A method as claimed in claim 5, in which the ester-containing polyol is the reaction product of a polycarboxylic acid with a polyol.
- 20 7. A method as claimed in claim 5 or claim 6, in which the ester-containing polyol has a molecular weight of less than 850, and a viscosity of less than 60 Pa s (60 poise).
- 25 8. A method as claimed in any of claims 5 to 7, in which the ester-containing polyol is a polycaprolactone polyol.
- 30 9. A method as claimed in any of the previous claims, in which the ink composition also comprises from 1 to 10% of a defoaming agent.
10. A method as claimed in claim 9, in which the defoaming agent is polyvinylbutylether.
- 35 11. A method as claimed in any of the preceding claims, in which the cycloaliphatic epoxide is cured by





exposure to ultraviolet radiation.

12. A method as claimed in any of the preceding
5 claims, in which the hot-stamping foil comprises a
carrier material, a release film and a decorative
coating, in that order.

13. A method as claimed in any of the preceding
10 claims, in which the hot-stamping foil comprises a
multilayer web consisting essentially of a backing film
carrier, a release coating, a protective coating, a
colour coating and a hot-melt adhesive, in that order.

14. A method as claimed any of the preceding claims,
15 in which the compress is heated to a temperature of at
least 395K (250°F).

15. A radiation-curable polymer composition
20 comprising:

- from 10 to 90% of a cationically radiation-
curable cycloaliphatic epoxide,
- 25 - from 1 to 20% of an ester-containing polyol, and
- from 1 to 20% of a defoaming agent.

16. A composition as claimed in claim 15, in which
30 the cationically radiation-curable cycloaliphatic
epoxide is one having at least two epoxide groups per
molecule.

17. A composition as claimed in claim 15 or claim
35 16, in which the cationically radiation-curable
cycloaliphatic epoxide is one or a mixture of more than
one of the following, namely 3,4-epoxycyclohexylmethyl-





3,4-epoxycyclohexane carboxylate, bis-(3,4-epoxycyclohexylmethyl)-adipate, vinylcyclohexene diepoxide, bis(2,3-epoxycyclophenyl)ether, epoxidized
5 butadiene and 2,3-epoxy-2-methylcyclohexylmethyl-3,4-epoxy-2-methylcyclohexane carboxylate.

18. A composition as claimed in any of claims 15 to 17, which further comprises from 1 to 50% of pigment.

10

19. A container, having an inner surface and an outer surface, in which:

- a) the outer surface has bonded thereto a partial
15 coating of a cured ink which is a cationically radiation-cured cycloaliphatic epoxide, in a design that covers less than the whole of the said outer surface; and

20 - b) the ink design is entirely overlaid by a multilayer web comprising (i) a hot-melt adhesive, (ii) a colour coating and (iii) a protective top-coat (in that order from the ink design outwards) said web being adherent to the cured adhesive ink and covering
25 only said ink and not extending to the ink-free areas of the said outer surface.

20. A container as claimed in claim 19, which is glass.

30

21. A container as claimed in claim 19, which is ceramic.

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ABSTRACT OF DISCLOSURE

"HOT-STAMPING GLASS, CERAMIC AND OTHER SUBSTRATES"

A method for decorating a substrate with hot-stamping foil comprising of the steps of:

- 5 a) applying an ink composition comprising a cationically radiation-curable cycloaliphatic epoxide to the substrate in a predetermined design, said ink being operable when cured to bond to the substrate,
- 10 b) curing the ink on the substrate by exposure to the radiation by which it is curable, thereby bonding the ink composition to the substrate,
- 15 c) pressing a sheet of hot stamping foil against the substrate with a compress heated to a temperature sufficient to cause a portion of the hot stamping foil to adhere to the heated, cured ink design but not to the ink-free areas of the substrate, and
- 20 d) removing the die, thereby leaving behind a portion of the foil adhered to the ink design.

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HOT-STAMPING GLASS, CERAMICS AND OTHER SUBSTRATES

This invention relates to the application of decorative coatings to glass, ceramics and perhaps other substrates, by a procedure akin to that known as hot-stamping, and is an important development of our earlier invention as described and claimed in our previous European Patent Application No. 93 3 04160.0, now EPA 0 626 354.

The well-established hot-stamping procedure involves applying both heat and pressure by means of a heated die or roller (hereinafter for convenience referred to generically as a "hot compress") to a so-called hot-stamping foil, consisting of a pigmented colour or metallized surface film borne on a usually-polyester carrier, so as by means of the hot compress to force it into contact with a thermoplastic substrate, and thereby soften the thermoplastic substrate and also activate the film-coating on the foil, thereby enabling it to form a strong physico-chemical bond with the underlying thermoplastic substrate wherever heat and pressure have been applied to the foil, but not elsewhere. When subsequently the foil is pulled away, just the areas of the film which have been subjected to the hot-stamping remain affixed to the plastic substrate, and the remainder peels away.

In order to carry out this hot-stamping operation one normally employs either a vertical stamping machine or a roll-on machine. The vertical stamping machine contains a heated compress of die of brass, steel or silicone rubber, performed to define the desired design, which compress serves to apply both heat and pressure and thus to transfer the desired design defined by the die (whatever that design may be - thus decorative areas and/or writing or other printed

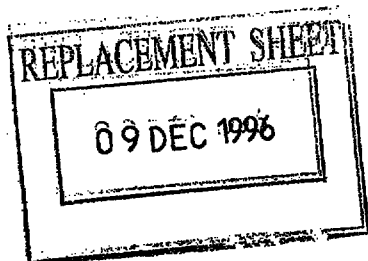
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information) from the film onto the thermoplastic substrate, as each part is positioned beneath the compress. Roll-on methods utilize a silicone rubber roller or an arcuate die as the hot compress to transfer the desired design from the foil onto the thermoplastic substrate, in either a continuous or batch process.

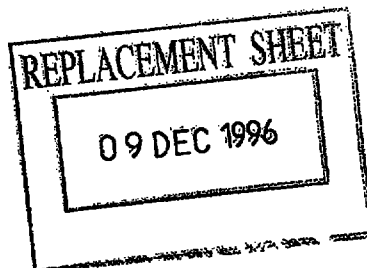
Hot-stamping is an efficient and inexpensive way to apply decoration to thermoplastic substrates. Unfortunately however hot-stamping of this nature cannot be used with glass, because glass melts at a much higher temperature than most thermoplastic materials. Consequently decoration in the form of gold leaf, colour design or printing etc. is generally applied to glass containers by a glazing process similar to that used with ceramics. Thus for example in gold-leafing the gold decoration is applied to the glass container by a variety of methods such as silk-screen printing, etc. The glass container is then subjected to extremely high kiln temperatures, and in essence the decoration is baked on. Unfortunately this process is however time-consuming, expensive, energy-intensive and raises safety considerations due to the high temperatures that have to be employed and the nature of the gases which are evolved in the operation of the kilns.

There has thus been a considerable and long-standing need for a simple, economical and ultra-safe procedure for applying decoration to glass substrates, quite unfulfilled until we devised the method for achieving these objectives described in our above-mentioned EPA 0,626,354, which is akin to the known hot-stamping process but operable on glass and ceramics.

However, the problems with the recently-devised procedure, as set out in our EPA 0,626,354, is that the

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inks do not always adhere to the glass to the degree required for commercial decorating purposes.

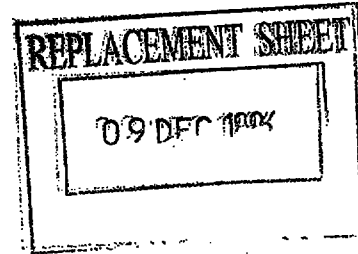
We have therefore carried out extensive investigations, directed to the search for an ink with excellent bond strength to glass and which at the same time is capable of adhering hot stamping foil. It has been thus discovered that the key to the achievement of commercially-acceptable decorating lies in the use of one particular, previously-unconsidered, class of cationically radiation-curable cycloaliphatic epoxides.

According to the present invention there is provided a method for applying a decorative coating to a glass, ceramic or indeed other substrate, which comprises the steps of:

- 15 a) applying a desired design to the substrate with a curable adhesive ink composition containing a cationically radiation-curable cycloaliphatic epoxide;
- 20 b) curing the adhesive ink on the substrate by exposing it to the radiation by which it is curable, thereby to bond the cured ink to the substrate;
- 25 c) compressing a hot-stamping foil bearing a film of decorative material against the substrate with a hot compress defining a desired design and heated to a temperature sufficient to cause the film to adhere to the cured ink pattern but not to the ink-free areas of the substrate; and
- 30 d) removing the compress, thereby leaving the decorative film from the hot-stamping foil adhering to the adhesive ink pattern only.
- 35 A wide variety of glass or ceramic articles may be provided with a decorative coating by means of the

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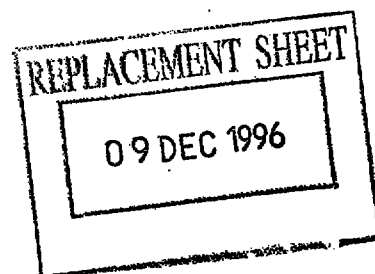
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method of this invention, and so far as we are aware there is no limit on the kind of glass or ceramics that may thus be decorated. Thus the term "substrate" as used herein embraces all kinds of glass and ceramic
5 (including china) substrates and indeed also others, provided only that they require decoration..and that there is no equally effective and cheaper way of achieving the same objective, as for instance there is with thermoplastic substrates. In short, this
10 technique will work with a thermoplastic substrate, but there is no need to employ it since conventional hot-stamping is fully effective on thermoplastic substrates and tends to be cheaper.

Such substrates may for instance take the form of
15 containers e.g. bottles, dishes, cups and glasses, as well as also purely decorative objects eg. figurines, vases, windows, tiles and so on.

In the first step of the decorative method of this invention the desired decorative or other pattern is
20 essentially "painted" onto the glass utilizing an adhesive ink composition as the "paint". The "painting" may be accomplished by silk-screening, screen-printing, offset-printing, stencilling, actual painting (with a brush) or any other of the wide
25 variety of available methods.

Generally-speaking we currently prefer to apply the desired pattern of adhesive ink by silk-screening it onto the glass container, utilizing the traditional screen and squeegee well known to those skilled in the
30 art, because it is adaptable to on-line production. However the ink may be applied by means of hand-held applicators such as paintbrushes or the like, especially where the ink is to be applied to a substrate in the form of a figurine or other like
35 highly-decorative article which is not readily amenable to screen-printing.

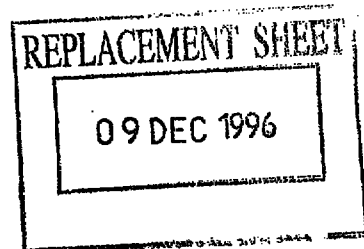


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5 The curable adhesive ink composition used in the present invention must be one based upon a cationically radiation-cured cycloaliphatic epoxide. The term "cationically radiation-curable" is here used in the sense that it has become accepted in the radiation curing art, and roughly-speaking means that the radiation curing takes place in air - as contrasted with anionic curing, which must take place under anaerobic conditions.

10 The cycloaliphatic epoxide employed will preferably be one having at least two epoxy groups per molecule. Polymeric cycloaliphatic epoxides are however also suitable, such as those formed as the reaction products between epichlorohydrin and phenol or
15 a phenolformaldehyde resin, diepoxy resin, epoxidized oils and epoxidized polyolefins. Such epoxides include novolac epoxides, glycidyl ethers of various types including diglycidyl ethers of bisphenol, diglycidyl ethers of butanediol, and the like. Also suitable are
20 homopolymers and copolymers that contain pendant epoxide groups such as those made from glycidyl acrylate and/or methacrylate with or without other ethylenically unsaturated monomers. Cycloaliphatic epoxides are however also suitable, such as those set
25 forth in U.S. Patents Nos. 3,027,357, 3,890,194, 2,890,197, 3,031,434, 3,125,592, 3,201,360 and 5,204,930 (the disclosure of all of which are incorporated herein by cross-reference). Preferred are 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane
30 carboxylate, bis-(3,4-epoxy-cyclohexylmethyl)-adipate, vinylcyclohexene diepoxy, bis(2,3-epoxycyclophenyl)ether, epoxidized butadiene, 2,3-epoxy-2-methylcyclohexylmethyl-3,4-epoxy-2-methylcyclohexane carboxylate, or mixtures thereof.

35 The preferred cycloaliphatic epoxides are the cationically UV-cured cycloaliphatic epoxides sold



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under the tradename CYRACURE by Union Carbide Chemicals and Plastics Company, Danbury, Connecticut, USA., such as CYRACURE UVR 6110, 6379, 6351 and 5200.

5 The proportion of the cationically UV-cured cycloaliphatic epoxide to be employed in the ink composition is not highly critical, but we recommend the use of from about 10% to about 90% thereof, by weight of the composition, and preferably 35-90%.

10 If the ink composition is to be cured with actinic radiation (including UV light) rather than with an electron beam, it is then very desirable, indeed almost a necessity that the ink composition should also contain a photoinitiator, which will catalyze the polymerization of the cycloaliphatic epoxide. If an
15 electron beam is used, such a photoinitiator is not necessary. However, since preparing the composition one cannot always be sure how it will subsequently be cured, it is an advisable precaution always to include a photoinitiator therein.

20 Especially suitable photoinitiators are carbonyl compounds such as ketones and derivatives thereof, for example methyl ethyl ketone, benzophenone, benzyl dimethyl ketal, 1-hydroxycyclohexylphenylketone, 2,1-dimethoxy-2-phenylacetophenone, diethoxyacetophenone
25 and 2-methyl-1-(methylethylphenyl)-2-(4-morpholinyl)-1-propanone.

Other photosensitive onium salts are particularly good UV activated photoinitiators. The use of photosensitive onium salts to promote the curing of
30 epoxides when exposed to UV radiation is described in U.S. Patents Nos. 4,058,401, 4,138,255 and 4,161,478, the disclosure of which is incorporated herein by cross-reference. The photosensitive onium salts mentioned in these Patents are good UV-light
35 photoinitiators. These preferred photoinitiators are triaryl sulphonium salts sold by Union Carbide under

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the tradename CYRACURE UVI 6974.

5 The proportion of photoinitiator needed is not critical, but we recommend the use from about 0.5% to 20%, by weight of the composition, and preferably 3-15% by weight.

10 The ink composition may also advantageously include an ester-containing polyol having a molecular weight of less than 850 and a viscosity of less than 0.6 Pa s (60 poise), which serves the purpose of controlling its viscosity.

15 Such ester-containing polyols are oligomers prepared by methods well known in the esterification or alkyd resin arts. Suitable polyols are for instance described in U.S. Patent No. 3,994,851, the disclosure of which is hereby incorporated by cross-reference. The ester-containing polyols are the reaction product of polycarboxylic acids (such as adipic, azelaic, malic, fumaric, succinic or glutaric acids) with a polyol (such as ethylene glycol, neopentyl glycol, 20 diethylene glycol, trimethylolpropane monoallyl ether, 1,6-hexandiol, etc.).

25 The preferred ester-containing polyols are the polycaprolactone polyols sold under the tradename "TONE Polyols" by Union Carbide, particularly TONE Polyol 310 or trimethylolpropane caprolactone.

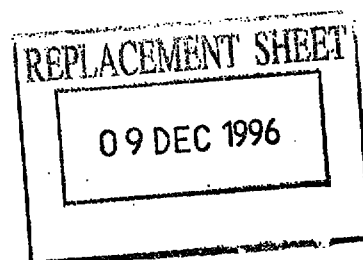
30 The proportion of the ester-containing polyol to be used is not critical, but we recommend the use of from about 1% to about 20% by weight of the composition, and preferably 3-15%, of the ester-containing polyol.

35 The curable adhesive ink composition may also desirably contain an adhesion-promotor, thus an agent that serves to increase the adhesion of the cycloaliphatic epoxide to the substrate. If the substrate is glass, silanes are excellent coupling agents with glass, and will promote adhesion of the ink

to the substrate. Suitable acryloxy-functional silanes are described in U.S. Patent No. 5,221,560, the disclosure of which is hereby incorporated by cross-reference.

5 Such acryloxy-functional silanes include:

- 3-methacryloxypropyltrimethoxysilane,
- 3-acryloxypropyl-trimethoxysilane,
- 2-methacryloxyethyltrimethoxysilane,
- 2-acryloxyethyltrimethoxysilane,
- 10 3-methacryloxypropyltriethoxysilane,
- 3-acryloxypropyltrimethoxysilane,
- 3-acryloxypropyltriethoxysilane,
- 2-methacryloxyethyltriethoxysilane,
- 3-acryloxypropyltriethoxysilane,
- 15 2-methacryloxyethyltriethoxysilane, and
- 2-methacryloxyethyltriethoxysilane, etc.



- Glycidoxy-functional silanes may also be suitable. Such glycidoxysilanes include 3-glycidoxypropyltri-
- methoxysilane,
 - 2-glycidoxyethyltrimethoxysilane,
 - 20 3-glycid-oxypopyltriethoxysilane,
 - 2-glycidoxyethyltriethoxysilane,
 - 3-glycidoxypropyltrimethylsilane and so on.

The glycidoxy silanes are preferred, in particular 3-glycidoxypropyltrimethylsilane. We recommend the use

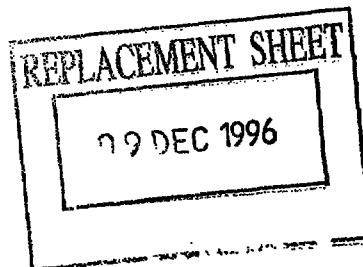
25 of from about 1% to about 10%, by weight of the composition, of an adhesion promotor, which can usually be relied upon to cause improved adhesion of the ink to the substrate.

It is generally desirable that the curable

30 adhesive ink composition should also include a defoaming agent, because it promotes smooth, even application of the ink onto the substrate, eliminating bubbles and distortions.

A variety of defoaming agents are suitable, but

35 those which we currently prefer are polyalkyl acrylics, such as the polyvinyl butyl ether in Stoddard solvent



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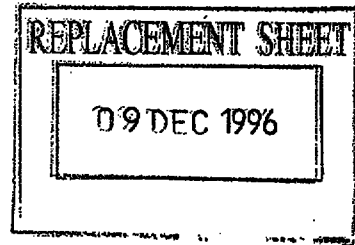
[this is a petroleum distillate, widely used as a dry-cleaning solvent, with a minimum flash point of 35°C (100°F) and a distillation range range of from not less than 50% over at 177°C (350°F) up to an end point not
5 higher than 210°C (410°F)] as sold under the tradenames BYK-052 and BYK-053 by BYK - Chemie.

The proportion of defoaming agent to be employed is not critical, but we generally recommend the use of from about 1 to 20%, by weight of the composition and
10 preferably 3-15%.

It is of course permissible, and for some purposes it may be advantageous, to incorporate other ingredients in the curable adhesive ink composition, including for instance stabilizers, inert fillers,
15 wetting agents, levelling agents and so on. If present, these ingredients can be in the range of from about 1 to about 15% by weight of the total composition.

In the second step of the decorative method of this invention, thus after the curable adhesive ink composition has been applied to the substrate, the cationically radiation-curable cycloaliphatic epoxide (and thus the ink composition as a whole) must be cured by exposure to the radiation by which it is curable.
20 We have found that the cycloaliphatic epoxide may be cured by an electron beam without further assistance, but actinic radiation (including ultra-violet radiation) will also serve to cure the epoxide (especially if assisted by the presence of a
25 photoinitiator) and is to be preferred over an electron beam.

Therefore, especially if it is for use with actinic radiation, the curable adhesive ink composition will very preferably include a photo-initiator, which
35 catalyzes the polymerization of the cycloaliphatic epoxide.



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For the avoidance of doubt it is perhaps desirable to observe that the terms "actinic radiation" and "ultra-violet radiation" are here used in their normal sense, that is to say :

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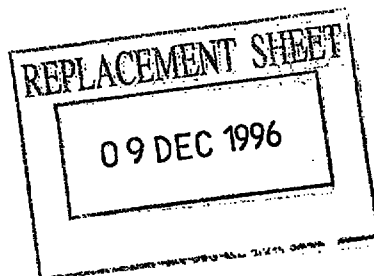
the term "actinic radiation" in general means light in the violet and ultra-violet regions which will bring about chemical changes, and may be regarded as corresponding to wavelengths of from 4 to 600 nm; and

10

the term "ultra-violet (or UV) radiation" refers to the non-visible part of actinic radiation, and may be regarded as corresponding to wavelengths of from 4 to 400nm., and preferably (for present purposes) 325-
15 365nm.

The substrate bearing the decorative pattern of ink composition is exposed to UV light (or other radiation) for a time sufficient to effect
20 polymerization of the epoxide and the polyol, usually for a period of from 1 to 30 minutes, and preferably for from 2 to 25 minutes, depending on how thickly the ink has been applied to the substrate.

This exposure may be conveniently accomplished by
25 use of so-called UV-conveyers, which consist of a conveyor belt situated beneath an ultraviolet lamp, such as those manufactured by Fusion Systems. When the substrate is placed on the conveyor belt it is moved along and is irradiated by the lamp. Obviously, where
30 longer cure times are needed, the substrate can be passed successively through several conveyors in line, or several times through the same conveyor. The conveyor system is set up so that the substrate passes through the UV-light for the total amount of time
35 appropriate to cure the ink composition and adhere to the substrate.

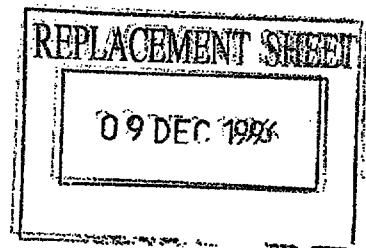


In the third step of the decorative method of this invention, thus after the ink composition has been cured and is thus fully adhered to the substrate, the substrate must be stamped with hot-stamping foil, that is say a foil bearing a film of decorative material is compressed against the substrate with a compress heated to a sufficient temperature to cause the film on the hot-stamping foil to adhere to the cured ink design, but not to the ink-free areas of the glass.

The duration of the compression and the temperature of the compress are interdependent, and the optimum conditions for both can and will be determined by competent operatives in each individual case. By way of general guidance it can however be said that we have found that the compress should usually be heated to a temperature in the range of 395K-478K (250-400°F) preferably 395K-450K (250-350°F) to achieve adherence of the foil to the cured ink design. The compress must of course be pressed tightly against the substrate, and the period of such compression will range from fractions of a second up to several minutes, depending on the nature of the compress used, its temperature and the specific cycloaliphatic epoxide.

The term "hot-stamping foil" means, in general, a laminate comprised of a carrier material (often polyester, cellulose acetate, or another similar material capable of release), a release film, and a decorative or colour coat, in that order. The decorative coat is usually colour or metallized coat. The metallized coat can be actual gold, silver, or aluminium which is coloured to look like gold or silver, or have holographic properties. The coloured layer is most often applied by vacuum metallization.

More specifically, hot-stamping foil can be defined as a multilayer web comprising a backing film-carrier, a release coating, one or more protective top



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coatings, one or more colour coatings, and a hot-melt adhesive, in that order.

Generally, the hot-melt adhesive layer of the foil is compressed against the substrate with a heated die.
5 The hot-melt adhesive layer adheres to the substrate, and the application of heat also causes the release layer to release the backing film carrier from the protective top-coat layer, leaving the protective top-coat layer exposed on the surface of the substrate.

10 The release coating is either wax (or a wax-like material) or a thermoplastic material, which melts upon application of heat to release the protective top-coat layer from the backing for release layers include ethylene vinyl acetate (EVA). acrylics,
15 polyvinylchlorides (PVC), polyamides, or similar thermoplastic materials as set forth in U.S. Patent No. 5,104,719, the disclosure of which is hereby incorporated by cross-reference.

20 The protective top-coat is usually a lacquer of some type, which is capable of protecting the colour or metallized layer.

The final layer is a hot-melt adhesive, which can be a wide variety of substances, and is selected so that it is capable, upon application of heat, of
25 adhering to the substrate to which it is applied. Suitable hot-melt adhesives generally are thermoplastic materials, such as EVA, PVC and the like.

In the fourth step of the decorative method of this invention, the hot compress is removed and along
30 with it the foil, leaving a portion of the foil adhering to the substrate.

Thus, a portion of the hot-stamping foil, in particular the hot-melt adhesive layer and the metallized or colour layer, as well as the protective
35 top-coat if present (in that order) remain affixed to the cured ink design such that the hot-melt adhesive

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adheres to the cured ink design, followed by the coloured coating layer and the protective top-coat layer on the surface of the container. The protective top-coat may or may not contain part of the release coat layer, which is designed to release the carrier layer from the protective top coat.

The decoration which is applied to the substrate is extremely durable and capable of withstanding conditions found in normal handling operations.

According to another aspect of the invention there is also provided an adhesive ink composition for use in the method herein disclosed, which adhesive ink composition is or includes a radiation-curable polymer composition comprising:

- from 10 to 90% of a cationically radiation-curable

cycloaliphatic epoxide,

- from 1 to 20% of an ester-containing polyol, and

- from 1 to 20% of a defoaming agent,

as well as optionally other ingredients.

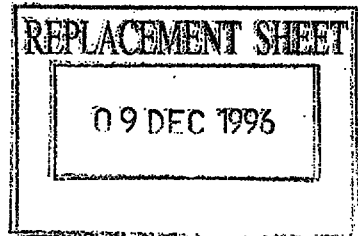
In addition, the preferred composition contains from 3 to 15% of a photoinitiator, and it may also contain from 1 to 10% of a silane.

According to a still further feature of this invention there are also provided containers, having an inner surface and an outer surface, in which:

a) the outer surface has bonded thereto a partial coating of a cured ink which is a cationically radiation-cured cycloaliphatic epoxide, in a design that covers less than the whole of the said outer surface; and

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5 - b) the ink design is entirely overlaid by a multilayer web comprising (i) a hot-melt adhesive, (ii) a colour coating and (iii) a protective top-coat (in that order from the ink design outwards) said web being adherent to the cured adhesive ink and covering only said ink and not extending to the ink-free areas of the said outer surface.

10 While the invention extends to containers of all kinds, even thermoplastic ones, that bear an outer coating of this type it fulfills its potential when the container is, as preferred, either glass or ceramic.

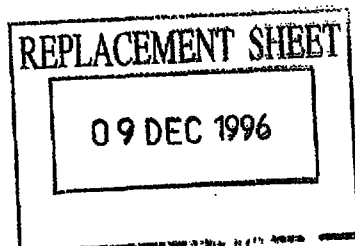
15 In order that the invention may be well understood it will now be described in more detail, though only by way of illustration, with reference to the following examples:

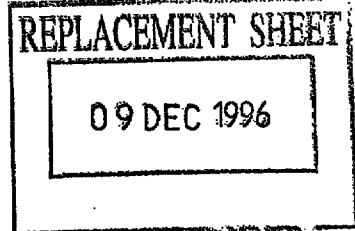
Example 1

A clear adhesive ink composition was made up as follows:

		grams
5	w/w%	
	Cycloaliphatic epoxide (CYRACURE UVR 6110) 72.73	50
10	Trimethylolpropane caprolactone (TONE Polyol 310) 9.10	6.25
15	Triaryl sulphonium salts(s) (CYRACURE UVI 6974) 7.27	5.00
20	Polyvinyl butyl ether defoamer (BYK-053) 10.90	7.5

These ingredients were mixed until dissolved, and were then ready for use as described in subsequent examples.





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Example 2

5 The ink composition of Example 1 was silk-screened onto a glass makeup container using a 255 line screen (having about 50 fibres per square centimetre, or (255 fibres per square inch) imprinted with a decorative design.

The glass container was passed through a 300 watt/9.2 metres (30 feet) per minute UV-conveyor for a total of 5 minutes to effect curing of the ink.

10 Gold hot-stamping foil (Crown Royal Leaf, Paterson, New Jersey, USA) was compressed against the container with a die heated to 395K (250°F) for several seconds.

15 The die was then removed, leaving a portion of foil adhered only to the ink design, and on peeling off the foil a gold metallic decorative design identical in appearance to gold leaf was left on the surface of the glass makeup container.

Example 3

20

The ink composition of Example 1 was used to hand-paint a simple design onto the side of a ceramic bowl, using a fine-tipped sable brush.

25 The bowl was subjected to UV-radiation by passing it through a 300 watt/9.2 metres (30 feet) per minute UV-conveyor for about 4 minutes.

30 Silver holographic hot-stamping foil was compressed against the cured ink design with a die heated to 288K (300°F) for several seconds.

Then the die was removed, leaving a portion of the hot-stamping foil adhered to the cured ink design, resulting in a metallic silver decoration.



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4. A method as claimed in any of the preceding claims in which the cationically radiation-curable cycloaliphatic epoxide is one or a mixture of more than one of the following, namely 3,4-epoxycyclohexylmethyl-
- 5 3,4-epoxycyclohexane carboxylate, bis-(3,4-epoxycyclohexylmethyl)-adipate, vinylcyclohexene diepoxide, bis(2,3-epoxycyclophenyl)ether, epoxidized butadiene and 2,3-epoxy-2-methylcyclohexylmethyl-3,4-epoxy-2-methylcyclohexane carboxylate.
- 10
5. A method as claimed in any of the preceding claims, in which the ink composition further comprises from 1 to 20% of an ester-containing polyol.
- 15 6. A method as claimed in claim 5, in which the ester-containing polyol is the reaction product of a polycarboxylic acid with a polyol.
- 20 7. A method as claimed in claim 5 or claim 6, in which the ester-containing polyol has a molecular weight of less than 850, and a viscosity of less than 60 Pa s (60 poise).
- 25 8. A method as claimed in any of claims 5 to 7, in which the ester-containing polyol is a polycaprolactone polyol.
- 30 9. A method as claimed in any of the previous claims, in which the ink composition also comprises from 1 to 10% of a defoaming agent.
10. A method as claimed in claim 9, in which the defoaming agent is polyvinylbutylether.
- 35 11. A method as claimed in any of the preceding claims, in which the cycloaliphatic epoxide is cured by

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exposure to ultraviolet radiation.

5 12. A method as claimed in any of the preceding claims, in which the hot-stamping foil comprises a carrier material, a release film and a decorative coating, in that order.

10 13. A method as claimed in any of the preceding claims, in which the hot-stamping foil comprises a multilayer web consisting essentially of a backing film carrier, a release coating, a protective coating, a colour coating and a hot-melt adhesive, in that order.

15 14. A method as claimed any of the preceding claims, in which the compress is heated to a temperature of at least 395K (250°F).

20 15. A radiation-curable polymer composition comprising:

- from 10 to 90% of a cationically radiation-curable cycloaliphatic epoxide,
- 25 - from 1 to 20% of an ester-containing polyol, and
- from 1 to 20% of a defoaming agent.

30 16. A composition as claimed in claim 15, in which the cationically radiation-curable cycloaliphatic epoxide is one having at least two epoxide groups per molecule.

35 17. A composition as claimed in claim 15 or claim 16, in which the cationically radiation-curable cycloaliphatic epoxide is one or a mixture of more than one of the following, namely 3,4-epoxycyclohexylmethyl-

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3,4-epoxycyclohexane carboxylate, bis-(3,4-epoxycyclohexylmethyl)-adipate, vinylcyclohexene diepoxide, bis(2,3-epoxycyclophenyl)ether, epoxidized
5 butadiene and 2,3-epoxy-2-methylcyclohexylmethyl-3,4-epoxy-2-methylcyclohexane carboxylate.

18. A composition as claimed in any of claims 15 to 17, which further comprises from 1 to 50% of pigment.

10

19. A container, having an inner surface and an outer surface, in which:

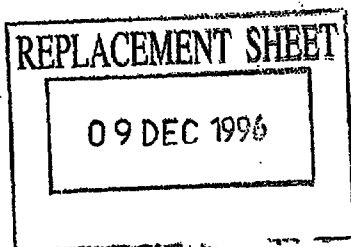
- a) the outer surface has bonded thereto a partial
15 coating of a cured ink which is a cationically radiation-cured cycloaliphatic epoxide, in a design that covers less than the whole of the said outer surface; and

20 - b) the ink design is entirely overlaid by a multilayer web comprising (i) a hot-melt adhesive, (ii) a colour coating and (iii) a protective top-coat (in that order from the ink design outwards) said web being adherent to the cured adhesive ink and covering
25 only said ink and not extending to the ink-free areas of the said outer surface.

20. A container as claimed in claim 19, which is glass.

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21. A container as claimed in claim 19, which is ceramic.



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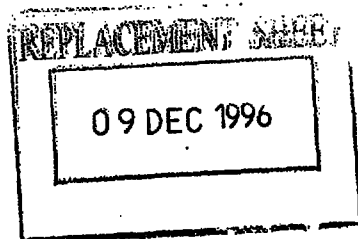


ABSTRACT OF DISCLOSURE

"HOT-STAMPING GLASS, CERAMIC AND OTHER SUBSTRATES"

A method for decorating a substrate with hot-stamping foil comprising of the steps of:

- 5 a) applying an ink composition comprising a cationically radiation-curable cycloaliphatic epoxide to the substrate in a predetermined design, said ink being operable when cured to bond to the substrate,
- 10 b) curing the ink on the substrate by exposure to the radiation by which it is curable, thereby bonding the ink composition to the substrate,
- 15 c) pressing a sheet of hot stamping foil against the substrate with a compress heated to a temperature sufficient to cause a portion of the hot stamping foil to adhere to the heated, cured ink design but not to the ink-free areas of the substrate, and
- 20 d) removing the die, thereby leaving behind a portion of the foil adhered to the ink design.



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HOT-STAMPING GLASS, CERAMICS AND OTHER SUBSTRATES

This invention relates to the application of decorative coatings to glass, ceramics and perhaps other substrates, by a procedure akin to that known as hot-stamping, and is an important development of our earlier invention as described and claimed in our European Patent Application No. 9304160.0, now EPA 0 626 354.

The well-established hot-stamping procedure involves applying both heat and pressure by means of a heated die or roller (hereinafter for convenience referred to generically as a "hot compress") to a so-called hot-stamping foil, consisting of a pigmented colour or metallized surface film borne on a usually-polyester carrier, so as by means of the hot compress to force it into contact with a thermoplastic substrate, and thereby soften the thermoplastic substrate and also activate the film-coating on the foil, thereby enabling it to form a strong physico-chemical bond with the underlying thermoplastic substrate wherever heat and pressure have been applied to the foil, but not elsewhere. When subsequently the foil is pulled away, just the areas of the film which have been subjected to the hot-stamping remain affixed to the plastic substrate, and the remainder peels away.

In order to carry out this hot-stamping operation one normally employs either a vertical stamping machine or a roll-on machine. The vertical stamping machine contains a heated die of brass, steel or silicone rubber, which serves to apply both heat and pressure and thus to transfer the desired pattern defined by the die (whatever that pattern may be - thus decorative areas and/or writing or other printed

REPLACEMENT SHEET

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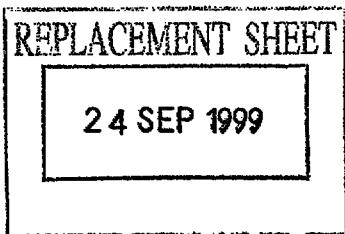
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- ☒ Description : paged 13th to paged 14th
- ☒ Claim(s) : paged 11th to paged 11th
- ☐ Drawing(s) : paged to paged
- ☒ Abstract : paged 2nd to paged 1st

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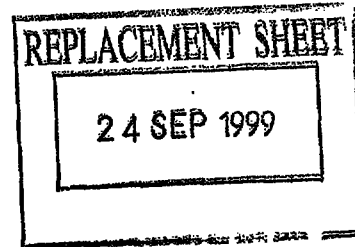


information) from the film onto the thermoplastic substrate, as each part is positioned beneath the compress. Roll-on methods utilize a silicone rubber roller or an arcuate die as the hot compress to transfer the desired design from the foil onto the thermoplastic substrate, in either a continuous or batch process.

Hot-stamping is an efficient and inexpensive way to apply decoration to thermoplastic substrates. Unfortunately however hot-stamping of this nature cannot be used with glass, because glass melts at a much higher temperature than most thermoplastic materials. Consequently decoration in the form of gold leaf, colour design or printing etc. is generally applied to glass containers by a glazing process similar to that used with ceramics. Thus for example in gold-leafing the gold decoration is applied to the glass container by a variety of methods such as silk-screen printing, etc. The glass container is then subjected to extremely high kiln temperatures, and in essence the decoration is baked on. Unfortunately this process is however time-consuming, expensive, energy-intensive and raises safety considerations due to the high temperatures that have to be employed and the nature of the gases which are evolved in the operation of the kilns.

There has thus been a considerable and long-standing need for a simple, economical and ultra-safe procedure for applying decoration to glass substrates, quite unfulfilled until we devised the method for achieving these objectives described in our above-mentioned EPA 0,626,354, which is akin to the known hot-stamping process but operable on glass and ceramics.

EPA 0,626,354 concerns a method of applying a decorative coating to glass using an adhesive ink comprising a monomer, a polymer dissolved in the monomer and a polymerisation-initiating agent. Japanese Laid Open Application 63017075 also describes the application of a decorative pattern to glass using printing ink and



a hot-stamping foil.

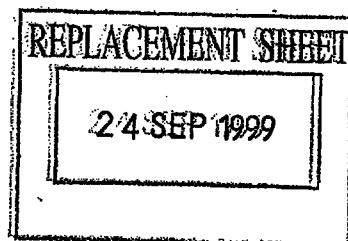
However, the problems with the recently-devised procedure, as set out in our EPA 0,626,354, is that the inks do not always adhere to the glass to the degree required for commercial decorating purposes.

We have therefore carried out extensive investigations, directed to the search for an ink with excellent bond strength to glass and which at the same time is capable of adhering hot-stamping foil. It has been thus discovered that the key to the achievement of commercially-acceptable decorating lies in the use of one particular, previously-unconsidered, class of cationically radiation-curable cycloaliphatic epoxides.

According to the present invention there is provided a method for applying a decorative coating to a glass, ceramic or indeed other substrate, which comprises the steps of:

- (a) applying a desired design to the substrate with a curable adhesive ink composition containing a cationically radiation-curable cycloaliphatic epoxide;
- (b) curing the adhesive ink on the substrate by exposing it to the radiation by which it is curable, thereby to bond the cured ink to the substrate;
- (c) compressing a hot-stamping foil bearing a film of decorative material against the substrate with a hot compress defining a desired design and heated to a temperature sufficient to cause the film to adhere to the cured ink pattern but not to the ink-free areas of the substrate; and
- (d) removing the compress, thereby leaving the film of decorative material from the hot-stamping foil adhering to the cured ink pattern only.

A wide variety of glass or ceramic articles may be provided with a decorative coating by means of the



adheres to the cured ink design, followed by the coloured coating layer and the protective top-coat layer on the surface of the container. The protective top-coat may or may not contain part of the release coat layer, which is designed to release the carrier layer from the protective top coat.

The decoration which is applied to the substrate is extremely durable and capable of withstanding conditions found in normal handling operations.

The adhesive ink composition for use in the method herein disclosed, which adhesive ink composition is or includes a radiation-curable polymer composition therefore suitably comprises:

- from 10 to 90% of a cationically radiation-curable cycloaliphatic epoxide,
- from 1 to 20% of an ester-containing polyol, and
- from 1 to 20% of a defoaming agent,

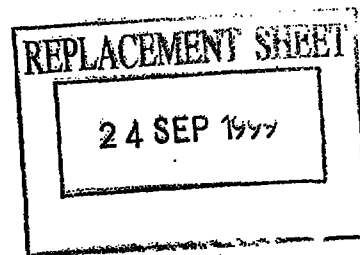
as well as optionally other ingredients.

The ink composition may comprise from 1 to 50% of pigment.

In addition, the preferred composition contains from 3 to 15% of a photoinitiator, and it may also contain from 1 to 10% of a silane.

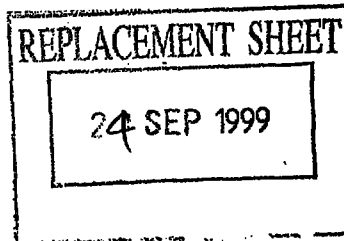
According to a further feature of this invention there are also provided containers, having an inner surface and an outer surface, in which:

- a) the outer surface has bonded thereto a partial coating of a cured adhesive ink which is a cationically radiation-cured cycloaliphatic epoxide, in a design that covers less than the whole of the said outer surface; and

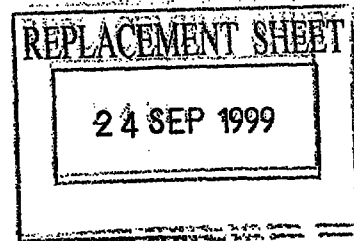


CLAIMS

1. A method for applying a decorative coating to a glass, ceramic or other substrate with hot-stamping foil which comprises the steps of:
 - a) applying a desired design to the substrate with a curable adhesive ink composition containing a cationically radiation-curable cycloaliphatic epoxide;
 - b) curing the adhesive ink on the substrate by exposing it to the radiation by which it is curable, thereby to bond the cured ink composition to the substrate;
 - c) compressing a hot-stamping foil bearing a film of decorative material against the substrate with a hot-compress defining a desired design and heated to a temperature sufficient to cause the film to adhere to the cured ink pattern but not to the ink-free areas of the substrate; and
 - d) removing the compress, thereby leaving the film of decorative material from the hot-stamping foil adhering to the cured ink pattern only.
2. A method as claimed in claim 1, in which the ink is applied to the substrate by silk-screening.
3. A method as claimed in claim 1 or claim 2, in which the cationically radiation-curable cycloaliphatic epoxide is one having at least two epoxide groups per molecule.
4. A method as claimed in any of the preceding claims in which the cationically radiation-curable cycloaliphatic epoxide is one or a mixture of more than one of the following, namely 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, bis-(3,4-epoxycyclohexylmethyl)-adipate, vinylcyclohexene diepoxide, bis(2,3-epoxycyclophenyl)ether, epoxidized butadiene and 2,3-epoxy-2-methylcyclohexylmethyl-3,4-epoxy-2-methylcyclohexane carboxylate.



5. A method as claimed in any of the preceding claims, in which the ink composition further comprises from 1 to 20% of an ester-containing polyol.
6. A method as claimed in claim 5, in which the ester-containing polyol is the reaction product of a polycarboxylic acid with a polyol.
7. A method as claimed in claims 5 or 6, in which the ester-containing polyol has a molecular weight of less than 850, and a viscosity of less than 0.6 Pa.s (60 poise).
8. A method as claimed in any of claims 5 to 7, in which the ester-containing polyol is a polycaprolactone polyol.
9. A method as claimed in any of the previous claims, in which the ink composition also comprises from 1 to 10% of a defoaming agent.
10. A method as claimed in claim 9, in which the defoaming agent is polyvinylbutyl-ether.
11. A method as claimed in any of the preceding claims, in which the ink composition further comprises from 1 to 50% of pigment.
12. A method as claimed in any of the preceding claims, in which the cycloaliphatic epoxide is cured by exposure to ultraviolet radiation.
13. A method as claimed in any of the preceding claims, in which the hot-stamping foil comprises a carrier material, a release film and a decorative coating.
14. A method as claimed in any of the preceding claims, in which the hot-stamping foil is a multilayer web consisting essentially of a backing film carrier, a release coating, a protective coating, a colour coating and a hot-melt adhesive.
15. A method as claimed in any of the preceding claims, in which the compress is heated to a temperature of at least 395K (250°F).
16. A container having an inner surface and an outer surface, in which:
 - a) the outer surface has bonded thereto a partial coating of a cured adhesive ink which is cationically radiation-cured cycloaliphatic epoxide, in a design that covers less than the whole of the said outer surface;



and

- b) the ink design is entirely overlaid by a multilayer web comprising (i) a hot-melt adhesive, (ii) a colour coating and (iii) a protective top-coat in that order from the ink design outwards, said web being adherent to the cured adhesive ink and covering only said ink and not extending to the ink-free areas of the said outer surface.

17. A container as claimed in claim 16, which is glass.

18. A container as claimed in claim 16, which is ceramic.

"HOT-STAMPING GLASS, CERAMIC AND OTHER SUBSTANCES"**ABSTRACT**

A method for decorating a substrate with hot-stamping foil comprising of the steps of:

- a) applying a ink composition comprising a cationically radiation-curable cycloaliphatic epoxide to the substrate in a predetermined design, said ink being operable when cured to bond to the substrate,
- b) curing the ink on the substrate by exposure to the radiation by which it is curable, thereby bonding the ink composition to the substrate,
- c) pressing a sheet of hot stamping foil against the substrate with a compress heated to a temperature sufficient to cause a portion of the hot stamping foil to adhere to the heated, cured ink design but not to the ink-free areas of the substrate, and
- d) removing the die, thereby leaving behind a portion of the foil adhered to the ink design.

