

INK COMPOSITION FOR COSMETIC CONTACT LENSES

Related Applications

This application claims priority to U.S. Patent Application Serial No. 16/987,673, filed August 7, 2020, and U.S. Provisional Patent Application Serial No. 62/899,311, filed September 12, 2019, which is incorporated herein by reference in its entirety.

Field of the Invention

The invention relates to cosmetic contact lenses, more specifically to ink compositions that can be used to make cosmetic contact lenses, such as cosmetic silicone hydrogel lenses.

Background of the Invention

The use of tinted hydrogel contact lenses to alter the natural color of the eye for cosmetic purposes is known. Ink compositions employed to produce tinted hydrogel contact lenses are typically composed of a binding polymer and colorants. Known ink compositions for cosmetic lenses are generally designed for conventional (non-silicone) lenses.

In recent years, contact lenses formed from silicone hydrogels have become popular. These contact lenses have higher oxygen permeability than traditional hydrogels. The improved oxygen permeability has reduced the symptoms of hypoxia in contact lens users wearing them. Unfortunately, processes used to produce traditional hydrogel lenses do not work well to consistently produce silicone hydrogel contact lenses. An example of one such process is the production of cosmetic silicone hydrogel contact lenses.

Ink compositions that provide cosmetic contact lenses, such as cosmetic silicone hydrogel contact lenses, without significant smearing or rub-off of the ink, and that are compatible with the base lens material, would be an advance in the art.

Summary of the Invention

The invention provides ink compositions that contain a colorant, a nonreactive hydrophilic polymer, and optionally a binder polymer. The ink compositions, when used for example with silicone hydrogel contact lenses, provide contact lenses that are round (not distorted) and where the ink, once applied to the lens, does not smear and easily rub-off. The ink compositions, therefore, are well suited for the manufacture of cosmetic contact lenses.

In one aspect, therefore, the invention provides an ink composition for making cosmetic contact lenses. The ink composition comprises: (a) a colorant; and (b) a nonreactive hydrophilic polymer; and optionally (c) a binder polymer. The binder polymer may comprise a polymer formed from at least one hydrophilic monomer comprising functionality selected from the group consisting of hydroxyalkyl, aminoalkyl, and mixtures thereof, at least one silicone-containing macromer; and optionally a silicone-containing monomer.

In another aspect, the invention provides a cosmetic contact lens. The cosmetic contact lens comprises: a contact lens having applied thereon an ink composition as described herein. As is apparent, the cosmetic contact lens may include multiple layers of ink compositions (e.g., 2, 3, or 4 layers) optionally with multiple layers of clear coat, and the compositions of the multiple layers of the ink compositions, including the pigments used, may be the same or different. The cosmetic contact lens may include additional layers thereon, including layers containing pigments but that are free of nonreactive hydrophilic polymer.

In a further aspect, the invention provides a method for making a cosmetic contact lens. The method comprises: (i) applying a clear coat to a lens forming surface of a first lens forming mold; (ii) applying to the clear coat an ink composition as described herein; (iii) optionally repeating step (i), step (ii), or both step (i) and step (ii); (iv) dispensing a lens material to the first lens forming mold; (v) applying a second lens forming mold; and (vi) curing the lens material to form the cosmetic contact lens.

Detailed Description of the Invention

It is to be understood that the invention is not limited to the details of construction or process steps set forth in the following description. The invention is capable of other embodiments and of being practiced or being carried out in various ways using the teaching herein.

As noted above, in one aspect, the invention provides ink compositions. The inventors have discovered that ink compositions as described herein can be used to produce cosmetic contact lenses, such as cosmetic silicone hydrogel contact lenses, with favorable properties. For instance, such lenses exhibit low or no haze, which indicates a favorable compatibility between the materials of the ink composition and the materials of the base lens. In addition, the inks exhibit little or no smearing or rub-off of the ink. Further, the ink compositions do not adversely affect the shape of the lenses. The lenses, therefore, generally retain their round shape.

With respect to the terms used in this disclosure, the following definitions are provided.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention belongs. The polymer definitions are consistent with those disclosed in the Compendium of Polymer Terminology and Nomenclature, IUPAC Recommendations 2008, edited by: Richard G. Jones, Jaroslav Kahovec, Robert Stepto, Edward S. Wilks, Michael Hess, Tatsuki Kitayama, and W. Val Metanomski. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference.

As used herein, the term "(meth)" designates optional methyl substitution. Thus, a term such as "(meth)acrylates" denotes both methacrylates and acrylates.

Unless otherwise indicated, ratios, percentages, parts, and the like are by weight.

Unless otherwise indicated, numeric ranges, for instance as in "from 2 to 10," are inclusive of the numbers defining the range (e.g., 2 and 10).

The term "contact lens" refers to an ophthalmic device that can be placed on the cornea of an individual's eye. The contact lens may provide corrective, cosmetic, or therapeutic benefit, including wound healing, the delivery of drugs or nutraceuticals, diagnostic evaluation or monitoring, ultraviolet light absorbing, visible light or glare reduction, or any combination thereof. A contact lens can be of any appropriate material known in the art and can be a soft lens, a hard lens, or a hybrid lens containing at least two distinct portions with different physical, mechanical, or optical properties, such as modulus, water content, light transmission, or combinations thereof.

Lenses of the present invention may be comprised of silicone hydrogels or conventional hydrogels. Silicone hydrogels typically contain at least one hydrophilic monomer and at least one silicone-containing component that are covalently bound to one another in the cured device.

An ink composition according to the invention comprises: (a) a colorant; and (b) a nonreactive hydrophilic polymer; and optionally (c) a binder polymer.

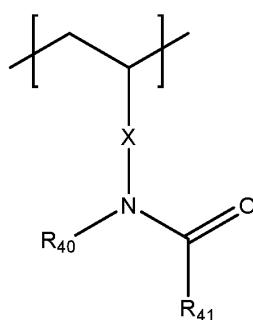
The colorant for use in the ink compositions of the invention may be any organic or inorganic pigment or dye suitable for use in contact lenses, or combinations of such pigments and/or dyes. The opacity may be controlled by varying the concentration of the colorant in the composition, with higher amounts yielding greater opacity. Illustrative colorants include, without limitation, phthalocyanine blue, phthalocyanine green, carbazole violet, vat orange #1, iron oxide

black, iron oxide brown, iron oxide yellow, iron oxide red, titanium dioxide, dichlorotriazine, vinyl sulfone-based dyes, and mixtures of two or more thereof. Useful dyes and pigments are commercially available.

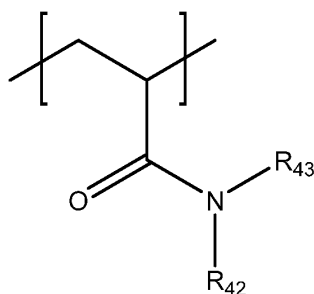
The ink composition of the invention comprises at least one nonreactive hydrophilic polymer. By "nonreactive" is meant that the hydrophilic polymer, when used in the formulation, does not contain free-radical polymerizable groups that are capable of copolymerizing with other constituents in the formulation under the free-radical polymerization conditions described herein. Without wishing to be bound by theory, it is believed that the nonreactive hydrophilic polymer helps to stabilize the colorant within the ink composition.

The nonreactive hydrophilic polymer may be a polyamide. As used herein, the term "polyamide" refers to polymers and copolymers comprising repeating units containing amide groups. The polyamide may comprise cyclic amide groups, acyclic amide groups and combinations thereof. Acyclic polyamides comprise pendant acyclic amide groups. Cyclic polyamides comprise cyclic amide groups.

Examples of suitable acyclic polyamides include polymers and copolymers comprising repeating units of Formulae G1 and G2:



Formula G1

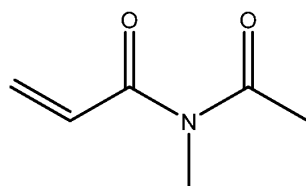


Formula G2

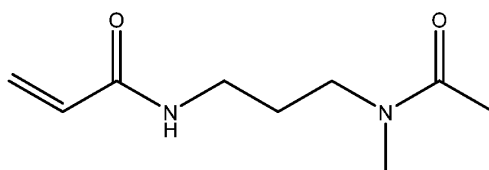
wherein X is a direct bond, $-(CO)-$, or $-(CONHR_{44})-$, wherein R_{44} is a C_1 to C_3 alkyl group; R_{40} is selected from H, straight or branched, substituted or unsubstituted C_1 to C_4 alkyl groups; R_{41} is selected from H, straight or branched, substituted or unsubstituted C_1 to C_4 alkyl groups, amino groups having up to two carbon atoms, amide groups having up to four carbon atoms, and alkoxy groups having up to two carbon groups; R_{42} is selected from H, straight or branched, substituted or unsubstituted C_1 to C_4 alkyl groups; or methyl, ethoxy, hydroxyethyl, and hydroxymethyl; R_{43} is selected from H, straight or branched, substituted or unsubstituted C_1 to C_4 alkyl groups; or methyl, ethoxy, hydroxyethyl, and hydroxymethyl; wherein the number of carbon atoms in R_{40} and R_{41} taken together is 8 or less, including 7, 6, 5, 4, 3, or less; and wherein the number of carbon atoms in R_{42} and R_{43} taken together is 8 or less, including 7, 6, 5, 4, 3, or less. The number of carbon atoms in R_{40} and R_{41} taken together may be 6 or less or 4 or less. The number of carbon atoms in R_{42} and R_{43} taken together may be 6 or less. As used herein substituted alkyl groups include alkyl groups substituted with an amine, amide, ether, hydroxyl, carbonyl or carboxy groups or combinations thereof.

R_{40} and R_{41} may be independently selected from H, substituted or unsubstituted C_1 to C_2 alkyl groups. X may be a direct bond, and R_{40} and R_{41} may be independently selected from H, substituted or unsubstituted C_1 to C_2 alkyl groups. R_{42} and R_{43} can be independently selected from H, substituted or unsubstituted C_1 to C_2 alkyl groups, methyl, ethoxy, hydroxyethyl, and hydroxymethyl.

Acyclic polyamides may comprise a majority of the repeating units of Formula G1 or Formula G2, or the acyclic polyamides can comprise at least 50 mole percent of the repeating unit of Formula G1 or Formula G2, including at least 70 mole percent, and at least 80 mole percent. Specific examples of repeating units of Formula G1 and Formula G2 include repeating units derived from N-vinyl-N-methylacetamide, N-vinylacetamide, N-vinyl-N-methylpropionamide, N-vinyl-N-methyl-2-methylpropionamide, N-vinyl-2-methylpropionamide, N-vinyl-N,N'-dimethylurea, N, N-dimethylacrylamide, methacrylamide, and acyclic amides of Formulae G3 and G4:

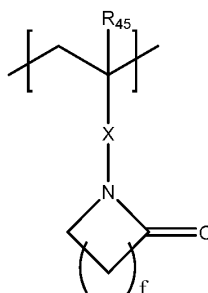


Formula G4



Formula G4

Examples of suitable cyclic amides that can be used to form cyclic polyamides include α -lactam, β -lactam, γ -lactam, δ -lactam, and ϵ -lactam. Examples of suitable cyclic polyamides include polymers and copolymers comprising repeating units of Formula G5:



Formula G5

wherein R_{45} is a hydrogen atom or methyl group; wherein f is a number from 1 to 10; wherein X is a direct bond, $-(CO)-$, or $-(CONHR_{46})-$, wherein R_{46} is a C_1 to C_3 alkyl group. In Formula G5, f may be 8 or less, including 7, 6, 5, 4, 3, 2, or 1. In Formula G5, f may be 6 or less, including 5, 4, 3, 2, or 1. In Formula G5, f may be from 2 to 8, including 2, 3, 4, 5, 6, 7, or 8. In Formula G5, f may be 2 or 3. When X is a direct bond, f may be 2. In such instances, the cyclic polyamide may be polyvinylpyrrolidone (PVP).

Cyclic polyamides may comprise 50 mole percent or more of the repeating unit of Formula G5, or the cyclic polyamides can comprise at least 50 mole percent of the repeating unit of Formula G5, including at least 70 mole percent, and at least 80 mole percent.

The polyamides may also be copolymers comprising repeating units of both cyclic and acyclic amides. The polyamides may be selected from the group polyvinylpyrrolidone (PVP), polyvinylmethacrylamide (PVMA), polydimethylacrylamide (PDMA), polyvinylacetamide (PNVA), poly(hydroxyethyl(meth)acrylamide), polyacrylamide, and copolymers and mixtures thereof. The polyamide may be a mixture of PVP (e.g., PVP K90) and PVMA (e.g., having a M_w of about 570 KDa).

A preferred nonreactive hydrophilic polymer is PVP. PVP polymers suitable for use in the invention are commercially available or can be readily prepared by those skilled in the art. A preferred commercially available PVP is PVP K30, which has a weight average molecular weight of about 55,000 daltons. Another preferred commercially available PVP is PVP K60, which has a weight average molecular weight of about 400,000 daltons. Further preferred are mixtures of PVP K30 and PVP K60. The PVP K30 and PVP K90 may be used at various weight ratios, for instance at a weight ratio of PVP K30:PVP K90 ranging from 5:1 to 1:5, or 4:1 to 1:1, or 3:1 to 1:1, or 2:1 to 1:1. For instance, the PVP K30:PVP K90 weight ratio may be 3:1, or 2:1, or 1.7:1, or 1:1.

Further exemplary nonreactive hydrophilic polymers that may be used in the ink compositions of the invention include, but are not limited to, dextran, poly(ethylene oxide), polyvinyl alcohol (PVA), poly (N-isopropylacrylamide), poly(oligoethylene oxide), polyethylene glycol (PEG), poly (N,N-dimethylaminoethyl acrylate), poly(imine), poly(acrylic acid), or mixtures of two or more thereof.

Preferably the nonreactive hydrophilic polymer has a weight average molecular weight from about 30,000 to about 500,000, or from about 40,000 to about 80,000, or from about 50,000 to about 60,000. Suitable molecular weight ranges may include, for instance, from 40,000 to 500,000, or from 40,000 to 80,000, or from 200,000 to 500,000.

The ink composition may contain a total amount of all nonreactive hydrophilic polymer of at least 1 percent, or at least 2 percent or at least 3 percent, by weight based on the total weight of the ink composition (including solvent). The ink composition may contain a total amount of all nonreactive hydrophilic polymer of 50 percent or less, or 40 percent or less, or 35 percent or less, or 25 percent or less, or 20 percent or less, or 15 percent or less, or 10 percent or less, based on the total weight of the ink composition (including solvent). For instance, the total amount of

all nonreactive hydrophilic polymer may range from 1 percent to 40 percent, or from 3 percent to 35 percent.

The ink composition of the invention may contain a binder polymer. The binder polymer may comprise a copolymer formed from at least one hydrophilic monomer comprising functionality selected from the group consisting of hydroxyalkyl, aminoalkyl, and mixtures thereof, at least one silicone-containing macromer; and optionally a silicone-containing monomer.

The binder polymer may be formed from at least one hydrophilic monomer comprising a C₂-C₈ linear or branched hydroxyalkyl (meth)acrylate, a C₂-C₈ linear or branched dihydroxyalkyl (meth)acrylate, a C₂-C₈ linear or branched trihydroxyalkyl (meth)acrylate, a N- C₂-C₆ linear or branched hydroxyalkyl (meth)acrylamide, a N,N-bis C₂-C₆ linear or branched hydroxyalkyl (meth)acrylamide, a N-C₂-C₈ linear or branched dihydroxyalkyl (meth)acrylamide, a N,N-bis C₂-C₈ linear or branched dihydroxyalkyl (meth)acrylamide, a N- C₂-C₈ linear or branched trihydroxyalkyl (meth)acrylamide, a N,N-bis C₂-C₈ linear or branched trihydroxyalkyl (meth)acrylamide, or mixtures thereof.

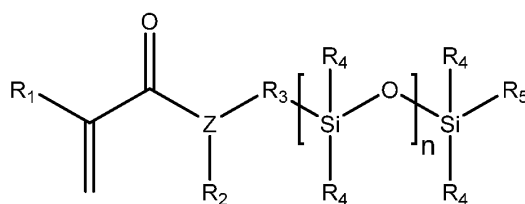
The binder polymer may be formed from at least one hydrophilic monomer comprising 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2,3-dihydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, N-(2-hydroxyethyl) (meth)acrylamide, N,N-bis(2-hydroxyethyl) (meth)acrylamide, N-(2-hydroxypropyl) (meth)acrylamide, N,N-bis(2-hydroxypropyl) (meth)acrylamide, N-(3-hydroxypropyl) (meth)acrylamide, N-(2-hydroxybutyl) (meth)acrylamide, N-(3-hydroxybutyl) (meth)acrylamide, N-(4-hydroxybutyl) (meth)acrylamide, or mixtures thereof.

The binder polymer may be formed from a reactive monomer mixture comprising at least one hydrophilic monomer selected from the group consisting of acrylamide, N,N-dimethylacrylamide (DMA), N-vinylpyrrolidone (NVP), N-vinyl acetamide (NVA), N-vinyl N-methyl acetamide (VMA), N-isopropyl acrylamide, polyethylene glycol monoacrylate, polyethylene glycol monomethacrylate, acrylic acid (AA), methacrylic acid (MAA), N-[(ethenoxy)carbonyl]-β-alanine, 3-acrylamidopropanoic acid (ACA1), 5-acrylamidopropanoic acid (ACA2), 2-(methacryloyloxy)ethyl trimethylammonium chloride (METAC or Q salt), 2-acrylamido-2-methylpropane sulfonic acid (AMPS), 1-propanaminium, N-(2-carboxyethyl)-N,N-

dimethyl-3-[(1-oxo-2-propen-1-yl)amino]-, inner salt (CBT); 1-propanaminium, N,N-dimethyl-N-[3-[(1-oxo-2-propen-1-yl)amino]propyl]-3-sulfo-, inner salt (SBT); 3,5-dioxa-8-aza-4-phosphaundec-10-en-1-aminium, 4-hydroxy-N,N,N-trimethyl-9-oxo-, inner salt, 4-oxide (9CI) (PBT), and mixtures thereof.

The binder polymer may be formed from a silicone-containing macromer, preferably in addition to a hydrophilic monomer, such as one or more of the hydrophilic monomers described above. The silicone-containing macromer may comprise one polymerizable functional group selected from the group consisting of (meth)acrylate, (meth)acrylamide, styryl, vinyl, N-vinyl lactam, N-vinylamides, O-vinylethers, O-vinylcarbonates, and O-vinylcarbamates, and may have between about 1 and about 200 divalent disubstituted siloxane repeating units and be terminated with a C₁ to C₈ linear, branched or cyclic alkyl group.

The silicone-containing macromer may comprise a chemical structure shown in Formula I:

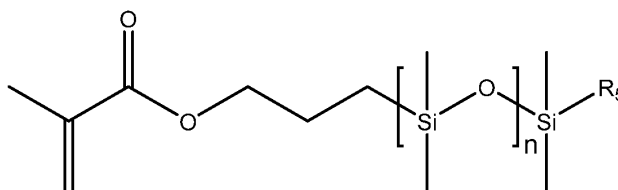


Formula I

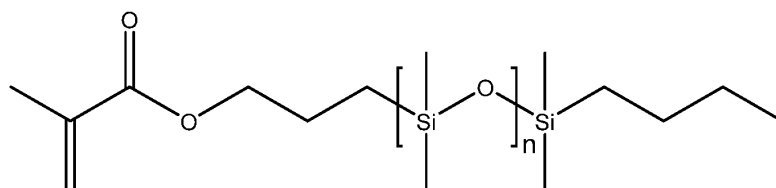
wherein Z is selected from O, N, S or NCH₂CH₂O; when Z = O or S, R₂ is not required; wherein R₁ is a hydrogen atom or methyl; wherein n is a whole number between 1 and 200, or between 1 and 100, or between 1 and 50, or between 1 and 20; wherein R₃ is an alkylene segment (CH₂)_y in which y is a whole number from 1 to 6, 1 to 4, or 2 to 4, and each methylene group may be optionally further and independently substituted with a group selected from the group consisting of ethers, amines, esters, ketones, carbonyls, carboxylates, and carbamates, or when y is 2 or more a non-terminal methylene group is optionally replaced with a carbamate group; or wherein R₃ is an oxyalkylene segment O(CH₂)_z in which z is a whole number from 1 to 3, or wherein R₃ is a mixture of alkylene and oxyalkylene segments and the sum of y and z is between 1 and 9; wherein R₂ and R₄ are independently a hydrogen atom, a linear, branched, or cyclic alkyl group containing between one and six carbon atoms, a linear, branched, or cyclic alkoxy group containing between one and six carbon atoms, a linear or branched

polyethylenoxyalkyl group, an alkyl-siloxanyl-alkyl group, a phenyl group, a benzyl group, a substituted or un-substituted aryl group, a fluoroalkyl group, a partially fluorinated alkyl group, a perfluoroalkyl group, a fluorine atom, a mono-, di, or tri-hydroxyalkyl group containing between one and six carbon atoms, or combinations thereof; and wherein R_5 is a substituted or un-substituted linear, branched, or cyclic alkyl group having 1 to 8 carbon atoms or an aryl group, any of which may be further substituted with one or more fluorine atoms or trimethylsiloxy groups.

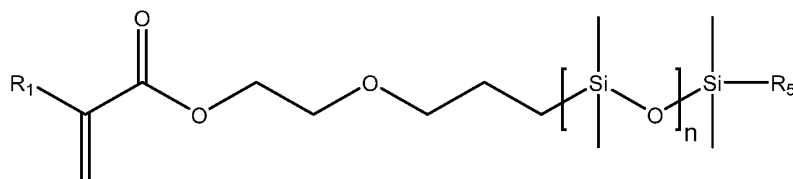
Non-limiting examples of these silicone-containing macromers include mono-n-alkyl terminated mono-methacryloxypropyl terminated polydimethylsiloxanes as shown in Formula II wherein n is between 3 and 50; between 3 and 25; and between 3 and 15 and R_5 is a linear, branched, or cyclic alkyl group containing between 1 and 8 carbon atoms; mono-n-butyl terminated mono-methacryloxypropyl terminated polydimethylsiloxanes (mPDMS) as shown in Formula III wherein n is between 3 and 50; between 3 and 25; or between 3 and 15; and macromers having the chemical structures as shown in Formulae IV through XI, wherein R_1 is a hydrogen atom or methyl group; R_2 and R_4 are independently a hydrogen atom, a linear, branched, or cyclic alkyl group containing between one and six carbon atoms, a linear, branched, or cyclic alkoxy group containing between one and six carbon atoms, a linear or branched polyethylenoxyalkyl group, a phenyl group, a benzyl group, a substituted or un-substituted aryl group, a fluoroalkyl group, a partially fluorinated alkyl group, a perfluoroalkyl group, a fluorine atom, or combinations thereof; and R_5 is a linear, branched, or cyclic alkyl group containing between 1 and 8 carbon atoms; and wherein n is between 3 and 50; between 3 and 25; or between 3 and 15.



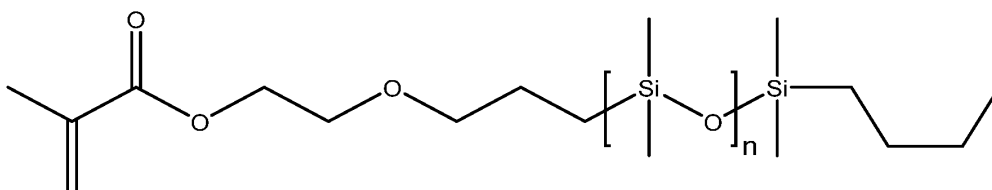
Formula II



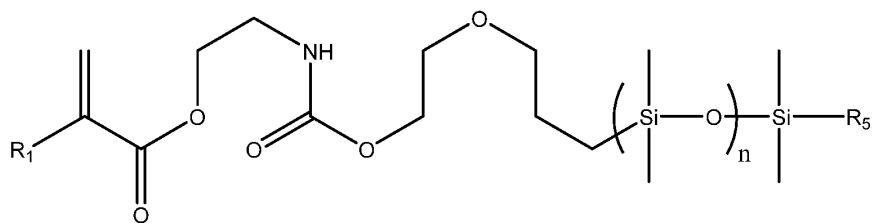
Formula III (mPDMS)



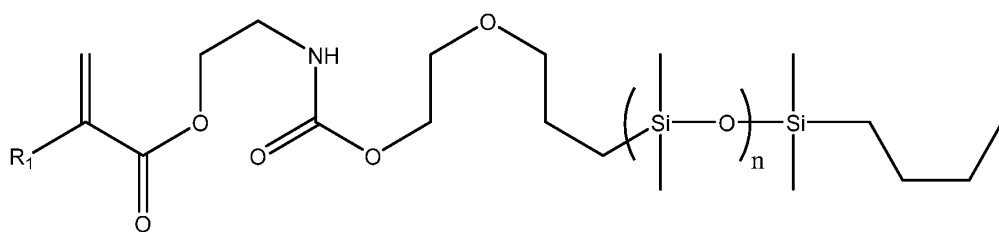
Formula IV



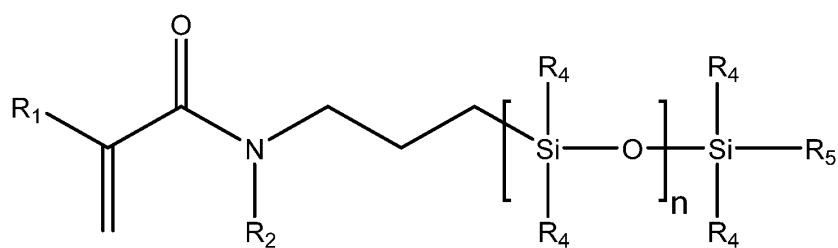
Formula V



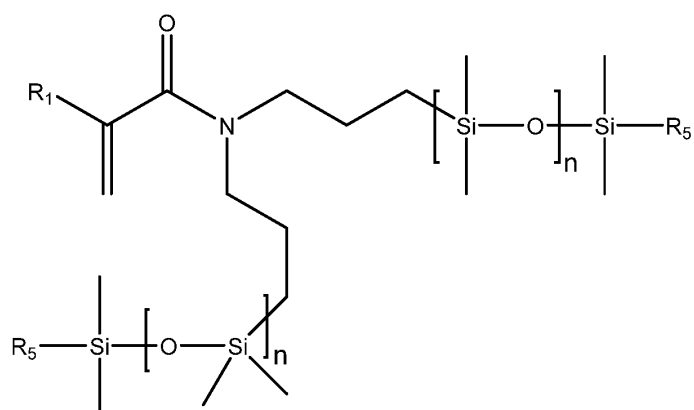
Formula VI



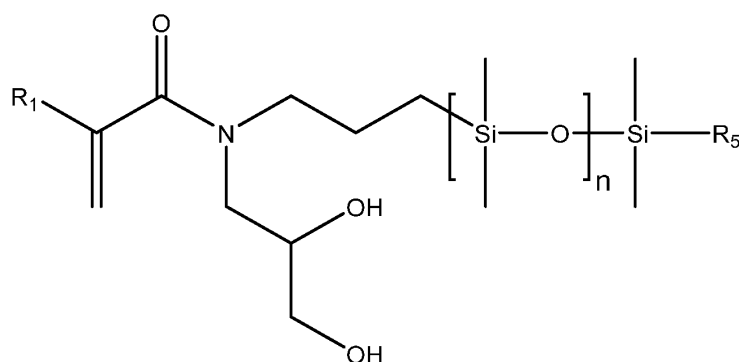
Formula VII



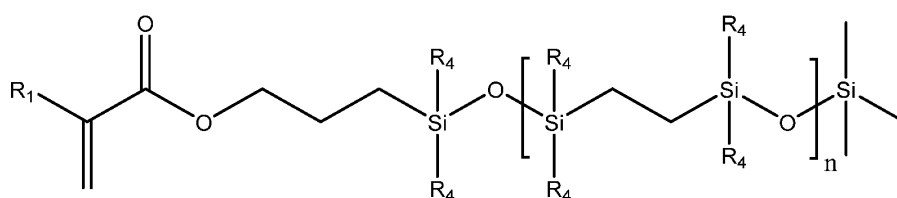
Formula VIII



Formula IX



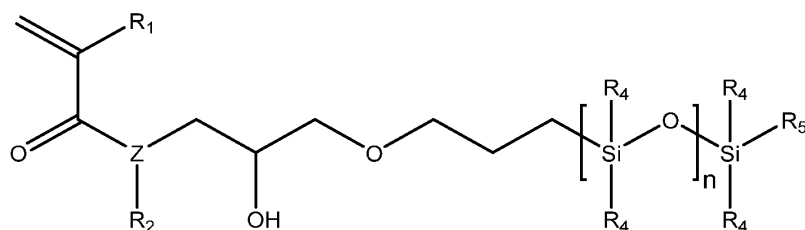
Formula X



Formula XI

Examples of suitable mono-alkyl terminated mono(meth)acryloxyalkyl terminated polydialkylsiloxanes include mono-n-butyl terminated mono(meth)acryloxypropyl terminated polydimethylsiloxane, mono-n-methyl terminated mono(meth)acryloxypropyl terminated polydimethylsiloxane, mono-n-butyl terminated mono(meth)acryloxypropyl terminated polydiethylsiloxane, mono-n-methyl terminated mono(meth)acryloxypropyl terminated polydiethylsiloxane, mono-alkyl terminated mono(meth)acrylamidoalkyl terminated polydialkylsiloxanes, mono-alkyl terminated mono(meth)acryloxyalkyl terminated polydiarylsiloxanes, and mixtures thereof.

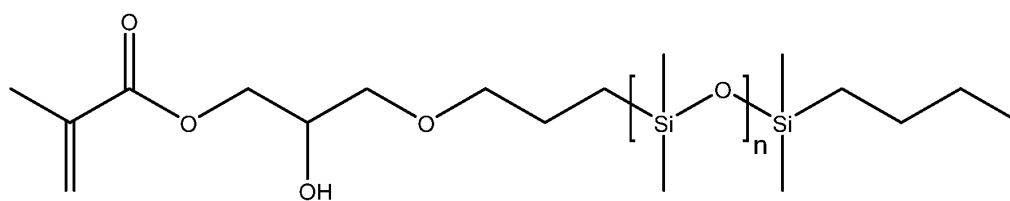
The silicone-containing macromer may comprise a mono-functional hydroxyl-substituted poly(dialkylsiloxane) with a chemical structure shown in Formula XII



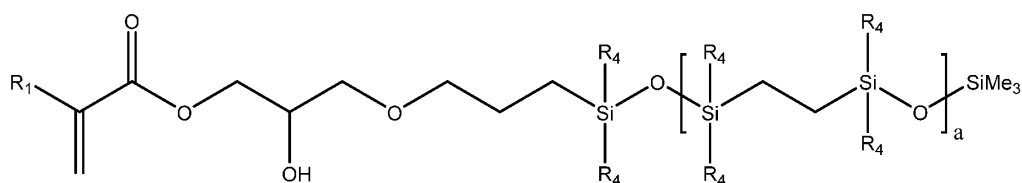
Formula XII

wherein Z is selected from O, N, S or NCH₂CH₂O; when Z = O or S, R₂ is not required; wherein R₁ is a hydrogen atom or methyl; wherein n is a whole number between 1 and 200; wherein R₂ and R₄ are independently a hydrogen atom, a linear, branched, or cyclic alkyl group containing between one and six carbon atoms, a linear, branched, or cyclic alkoxy group containing between one and six carbon atoms, a linear or branched polyethylenoxyalkyl group, a phenyl group, a benzyl group, a substituted or un-substituted aryl group, a fluoroalkyl group, a partially fluorinated alkyl group, a perfluoroalkyl group, a fluorine atom, or combinations thereof; and wherein R₅ is a substituted or un-substituted linear, branched, or cyclic alkyl group having 1 to 8 carbon atoms or an aryl group, any of which may be further substituted with one or more fluorine atoms or trimethylsiloxy groups.

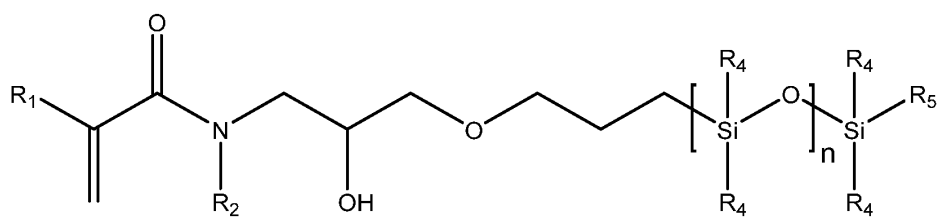
Examples of hydroxyl containing macromers include mono-(2-hydroxy-3-methacryloxypropyl)propyl ether terminated mono-n-butyl terminated polydimethylsiloxanes (OH-mPDMS) as shown in Formula XIII wherein n is between 4 and 30; between 4 and 8; or between 10 and 20; and macromers having the chemical structures as shown in Formulae XIV and XV wherein R₁ is a hydrogen atom or methyl group; wherein n between 4 and 30; between 4 and 8; or between 10 and 20; wherein R₄ is independently a hydrogen atom, a linear, branched, or cyclic alkyl group containing between one and six carbon atoms, a linear, branched, or cyclic alkoxy group containing between one and six carbon atoms, a linear or branched polyethylenoxyalkyl group, a phenyl group, a benzyl group, a substituted or un-substituted aryl group, a fluoroalkyl group, a partially fluorinated alkyl group, a perfluoroalkyl group, a fluorine atom, or combinations thereof; and wherein R₅ is a substituted or un-substituted linear, branched, or cyclic alkyl group having 1 to 8 carbon atoms or an aryl group, any of which may be further substituted with one or more fluorine atoms or trimethylsiloxy groups.



Formula XIII (OH-mPDMS)

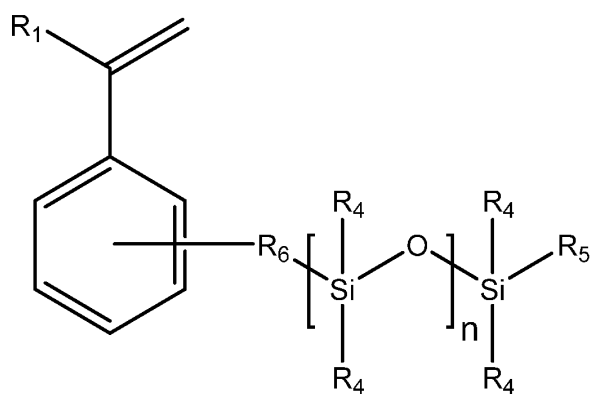


Formula XIV



Formula XV

The silicone-containing macromer may comprise the chemical structure shown in Formula XVI.



Formula XVI

wherein R₁ is a hydrogen atom or methyl; wherein n is a whole number between 1 and 200; wherein R₄ is independently a hydrogen atom, a linear, branched, or cyclic alkyl group containing between one and six carbon atoms, a linear, branched, or cyclic alkoxy group containing between one and six carbon atoms, a linear or branched polyethylenoxyalkyl group, a phenyl group, a benzyl group, a substituted or un-substituted aryl group, a fluoroalkyl group, a partially fluorinated alkyl group, a perfluoroalkyl group, a fluorine atom, or combinations thereof; wherein R₅ is a substituted or un-substituted linear, branched, or cyclic alkyl group having 1 to 8 carbon atoms or an aryl group, any of which may be further substituted with one or more fluorine atoms or trimethylsiloxy groups; and wherein R₆ is an alkylene segment (CH₂)_y in which y is a whole number from 0 to 6, 0 to 4, and 0 to 2, and each methylene group may be optionally further and independently substituted with a group selected from the group consisting of ethers, amines, alcohols, esters, carbonyls, carboxylates, and carbamates.

The silicone-containing macromer may be a mixture of macromers having the chemical structures shown in Formulae I to XVI.

Preferably, the silicone-containing macromer is selected from the group consisting of monoalkyl terminated, mono(meth)acrylate terminated poly(dialkylsiloxanes), monoalkyl terminated, monoalkyl terminated, mono(meth)acrylate terminated poly(diarylsiloxanes), monoalkyl terminated, mono(meth)acrylate terminated poly(alkylarylsiloxanes), and mixtures thereof.

Most preferably, the silicone-containing macromer is selected from the group consisting of mono-n-butyl terminated monomethacryloxypropyl terminated polydimethylsiloxane (Formula III), mono-n-butyl terminated mono-(2-hydroxy-3-methacryloxypropyl)-propyl ether terminated polydimethylsiloxane (Formula XIII), and mixtures thereof.

The silicone containing macromer may have a number average molecular weight between about 500 Daltons and about 10,000 Daltons, or between about 500 Daltons and about 5,000 Daltons, or between about 500 Daltons and about 2,000 Daltons.

Preferably, the binder polymer is a copolymer of a silicone-containing macromer and a hydrophilic monomer and is comprised of repeating units of the silicone-containing macromer between about 30 and about 80 weight percent; or between about 30 and about 70 weight percent; or between about 40 and about 60 weight percent; or between about 45 and about 55 weight percent; or about 50 weight percent of the copolymer.

The binder polymer may comprise repeating units derived from mono-n-butyl terminated monomethacryloxypropyl terminated polydimethylsiloxane (mPDMS), mono-n-butyl terminated mono-(2-hydroxy-3-methacryloxypropyl)-propyl ether terminated polydimethylsiloxane (OH-mPDMS), and combinations thereof.

Most preferably, the binder polymer comprises repeating units derived from mono-n-butyl terminated monomethacryloxypropyl terminated polydimethylsiloxane (mPDMS) and 2-hydroxyethyl methacrylate (HEMA). Preferably the mPDMS comprises between about 30 and about 80 weight percent; or between about 30 and about 70 weight percent; or between about 40 and about 60 weight percent; or between about 45 and about 55 weight percent; or about 50 weight percent of the copolymer.

The binder polymer may have a weight average molecular weight in the range of about 10 to about 100 kDa; or in the range of about 20 to about 80 kDa; or in the range of about 20 to about 60 kDa; or in the range of about 20 to about 50 kDa.

Preferably, the binder polymer is not a block co- or tri-polymer. Preferably, the binder polymer is a random polymer, such as a random copolymer.

Binder polymers as described herein may be made by methods known to those skilled in the art. For instance, a binder polymer may be formed via any free radical polymerization reaction involving at least two monomers or macromers, regardless of the statistics of the copolymerization, producing a random or statistical or statistically random or graft copolymer. Graft copolymers are formed from macromers when the composition of the macromer's side chains is different than the copolymer's backbone. The copolymer may be blocky based on the statistics of the copolymerization; however, a copolymer that may be legitimately categorized as a diblock or triblock copolymer (e.g., based on known methods of making such diblock and triblock copolymers) are excluded from the definition of copolymer as used in this application.

The ink composition preferably further includes a solvent to facilitate mixing of the components and formation of a cosmetic lens. Suitable solvents include, but are not limited to, ethanol, 1-propanol, 2-propanol, 1-ethoxy-2-propanol (1E2P), t-butyl alcohol, t-amyl alcohol, and 3,7-dimethyl-1,7-octanediol (D3O), tripropylene glycol methyl ether (TPME), isopropyl lactate (IPL), 1-(2-hydroxy ethyl)-2-pyrrolidone (HEP), glycerol, or mixtures of two or more thereof. Preferred solvents are 1E2P, IPL, D3O, HEP, 1-propanol, or mixtures thereof.

Preferred ink compositions according to the invention comprise: from 0.1 to about 25 weight percent, preferably from about 5 to about 15 weight percent of a colorant; from about 1 to about 50 weight percent, preferably from about 10 to about 40 weight percent, of a nonreactive hydrophilic polymer; from about 1 to 60 weight percent, preferably from about 5 to about 40 weight percent, of the tri-block copolymer; and from about 50 to about 95 weight percent, preferably from about 55 to about 80 weight percent, of solvent, each based on the total weight of the ink composition.

The ink composition may be applied to, or printed on, one or more surfaces of a lens or may be printed onto one or more surfaces of a mold into which a lens forming material will be deposited and cured. In a preferred method for forming cosmetic lenses incorporating the ink composition of the invention, a thermoplastic optical mold, made from any suitable material including, without limitation, cyclic polyolefins and polyolefins such as polypropylene or polystyrene resin is used. The ink composition is deposited onto the desired portion of the molding surface of the mold. By "molding surface" is meant the surface of a mold or mold half used to form a surface of a lens. Preferably, the deposition is carried out by pad printing as follows.

A metal plate, preferably made from steel and more preferably from stainless steel, is covered with a photo resist material that is capable of becoming water insoluble once cured. The elements are selected or designed and then reduced to the desired size using any of a number of techniques such as photographic techniques, placed over the metal plate, and the photo resist material is cured. The plate is subsequently washed with an aqueous solution and the resulting image is etched into the plate to a suitable depth, for example about 20 microns. An ink composition is then deposited onto the elements to fill the depressions.

The metal plate can also be laser etched using appropriate software and lasers to extract the metal in the area that contains the preferred image, thus creating cavities replicating the image in 15um to 30um depth. Additionally, laser etching of the preferred pattern can occur on other substrates such as ceramic.

A silicon pad of a geometry suitable for use in printing on the surface and varying hardness is pressed against the image on the plate to remove the ink composition. The pad is then pressed against the molding surface of an optical mold. The mold is degassed for up to 12 hours to remove excess solvents and oxygen after which the mold is filled with lens material. A

complementary mold half is then used to complete the mold assembly and the mold assembly is exposed to conditions suitable to cure the lens material used. Such conditions are well known in the art and will depend upon the lens material selected. Once curing is completed and the lens is released from the mold, it is equilibrated in a buffered saline solution.

In a preferred embodiment, a clear coat is first applied to the molding surface and dried prior to the addition of the ink composition. Preferably such clear coat forms the entirety of the lens' outermost surface. The clear coat, may for example, be the same as the ink composition described herein but without the colorant. Other materials may, however, be used for the clear coat. In addition, multiple layers of clear coat and/or ink composition may be applied to the mold before addition of the lens material, in order to form a desired cosmetic pattern.

The ink composition of the invention may be used to provide colored hard or soft contact lenses made of any known lens-forming material, or material suitable for manufacturing such lenses. Preferably, the lenses of the invention are soft contact lenses, the material selected for forming the lenses being any material suitable for producing soft contact lenses. Suitable preferred materials for forming soft contact lenses using the method of the invention include, without limitation, silicone elastomers, silicone-containing macromers including, without limitation, those disclosed in U.S. Pat. Nos. 5,371,147, 5,314,960, and 5,057,578 incorporated in their entireties herein by reference, hydrogels, silicone-containing hydrogels, and the like and combinations thereof. More preferably, the lens is made from a material containing a siloxane functionality, including, without limitation, polydimethyl siloxane macromers, methacryloxypropyl polyalkyl siloxanes, and mixtures thereof, a silicone hydrogel or a hydrogel made of monomers containing hydroxy groups, carboxyl groups, or both and combinations thereof.

Materials for making soft contact lenses are well known and commercially available. For example, a silicone hydrogel may be made from at least one hydrophilic component and at least one silicone-containing component that, when polymerized, form the base material of the lens. Examples of suitable families of hydrophilic components that may be present in the reactive mixture from the which the lens is formed include (meth)acrylates, styrenes, vinyl ethers, (meth)acrylamides, N-vinyl lactams, N-vinyl amides, N-vinyl imides, N-vinyl ureas, O-vinyl carbamates, O-vinyl carbonates, other hydrophilic vinyl compounds, and mixtures thereof. Silicone-containing components are well known and have been extensively described in the

patent literature. For instance, the silicone-containing component may comprise at least one polymerizable group (e.g., a (meth)acrylate, a styryl, a vinyl ether, a (meth)acrylamide, an N-vinyl lactam, an N-vinylamide, an O-vinylcarbamate, an O-vinylcarbonate, a vinyl group, or mixtures of the foregoing), at least one siloxane group, and one or more linking groups connecting the polymerizable group(s) to the siloxane group(s). The silicone-containing components may, for instance, contain from 1 to 220 siloxane repeat units. The silicone-containing component may also contain at least one fluorine atom.

By way of further example, the lens material may be any of aquafilcon, asmoafilcon, balafilcon, comofilcon, delefilcon, enfilcon, fanfilcon, formofilcon, galyfilcon, lotrafilcon, narafilcon, riofilcon, samfilcon, senofilcon, somofilcon, and stenfilcon, including all of their variants, as well as silicone hydrogels as prepared in US Patent Nos. 4,659,782, 4,659,783, 5,244,981, 5,314,960, 5,331,067, 5,371,147, 5,998,498, 6,087,415, 5,760,100, 5,776,999, 5,789,461, 5,849,811, 5,965,631, 6,367,929, 6,822,016, 6,867,245, 6,943,203, 7,247,692, 7,249,848, 7,553,880, 7,666,921, 7,786,185, 7,956,131, 8,022,158, 8,273,802, 8,399,538, 8,470,906, 8,450,387, 8,487,058, 8,507,577, 8,637,621, 8,703,891, 8,937,110, 8,937,111, 8,940,812, 9,056,878, 9,057,821, 9,125,808, 9,140,825, 9,156,934, 9,170,349, 9,244,196, 9,244,197, 9,260,544, 9,297,928, 9,297,929 as well as WO 03/22321, WO 2008/061992, US 2010/0048847, and U.S. application serial number 15/691,829. In another embodiment, the lens may be made from a conventional hydrogel material, for example, etafilcon, genfilcon, hilafilcon, lenefilcon, nelfilcon, nesofilcon, ocuafilcon, omafilcon, polymacon, and vifilcon, including all of their variants.

A preferred composition for the lens material comprises: a hydrophilic component selected from N, N-dimethylacrylamide ("DMA"), 2-hydroxyethyl methacrylate ("HEMA"), and mixtures thereof; a silicone-containing component selected from 2-hydroxy-3-[3-methyl-3,3-di(trimethylsiloxy)silylpropoxy]-propyl methacrylate (SiMAA), mono-methacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane (mPDMS), mono-(2-hydroxy-3-methacryloxypropyl)-propyl ether terminated mono-n-butyl terminated polydimethylsiloxane (OH-mPDMS), and mixtures thereof; an internal wetting agent (preferably a polyamide such as poly(N-vinylpyrrolidone) (PVP), poly(N,N-dimethylacrylamide) (PDMA), or polyvinylmethacrylamide (PVMA)); and a free radical initiator. For the hydrophilic component, mixtures of DMA and HEMA are preferred. For the silicone containing component, OH-

mPDMS or mixtures of SiMAA and mPDMS are preferred. The composition may contain other ingredients known in the art for making soft contact lenses including, but not limited to, diluents, crosslinkers, light absorbing compounds (e.g., UV or high energy visible light blockers), and the like.

The following non-limiting examples further illustrate the invention.

EXAMPLES

Imaging was used to qualitatively assess the overall quality of a printed pattern in comparison to the desired design (“smear” in the tables); the level of smear was categorized based on severity (“minor, moderate, severe, or none” in the tables). Imaging was also used to assess the degree of roundness and level of distortion of the lenses (“round or out of round (OOR)” in the tables). Unacceptable levels of haze or translucency were also noted by imaging (hazy or none). Images of the silicone hydrogel printed contact lenses were captured using a Nikon SMZ18 stereo microscope with a P2-DBF Fiber diascope illumination base (1X objective with 0.75 – 1X magnification). The printed silicone hydrogel contact lenses were placed concave side up into a crystal cell completely filled with borate buffered packing solution. Samples were placed in the viewing window, and the microscope adjusted to focus the image.

The durability of the printed pattern was assessed by rubbing the printed surface with a cotton swab. The test consists of 50 swipes of the lens. Each swipe started at the lens center on the printed surface and then proceeded in a single direction. Each lens was systematically evaluated, swiping in four orthogonal directions. If the pattern stayed intact for 50 such swipes, then it is deemed permanent (“no rub off” in the tables). Otherwise, if any portion of the printed pattern is dislodged, disturbed, or removed during the 50 swipes, then the pattern was deemed to rub off (“rubs off” in the tables).

Wettability of lenses was determined using a sessile drop technique using KRUSS DSA-100 TM instrument at room temperature and using deionized water as probe solution (“Sessile Drop” in the tables). The lenses to be tested were rinsed in deionized water to remove carry over from packing solution. Each test lens was placed on blotting lint free wipes which were dampened with packing solution. Both sides of the lens were contacted with the wipe to remove surface water without drying the lens. To ensure proper flattening, lenses were placed “bowl side down” on the convex surface of contact lens plastic molds. The plastic mold and the lens were placed in the sessile drop instrument holder, ensuring proper central syringe alignment. A 3 to 4

microliter drop of deionized water was formed on the syringe tip using DSA 100-Drop Shape Analysis software ensuring the liquid drop was hanging away from the lens. The drop was released smoothly on the lens surface by moving the needle down. The needle was withdrawn away immediately after dispensing the drop. The liquid drop was allowed to equilibrate on the lens for 5 to 10 seconds, and the contact angle was measured between the drop image and the lens surface. Typically, three to five lenses were evaluated, and the average contact angle reported. The standard deviations were determined and reported in the tables in parentheses ().

The following abbreviations will be used throughout the Examples and have the following meanings:

L: liter(s)

mL: milliliter(s)

equiv. or eq.: equivalent(s)

kg: kilogram(s)

g: gram(s)

mg: milligram(s)

mol: mole

mmol: millimole

min: minute(s)

cm: centimeter(s)

nm: nanometer(s)

rpm: revolutions per minute

Da: dalton or grams/mole

kDa: kilodalton or an atomic mass unit equal to 1,000 daltons

wt. %: weight percent

TL03 lights: Phillips TLK 40W/03 bulbs

BC: base curve plastic mold

FC: front curve plastic mold

PP: polypropylene which is the homopolymer of propylene and is used as a plastic mold resin or component

TT: Tuftec which is a hydrogenated styrene butadiene block copolymer (Asahi Kasei Chemicals) and is used as a plastic mold resin or component

Z: Zeonor which is a polycycloolefin thermoplastic polymer (Nippon Zeon Co Ltd) and is used as a plastic mold resin or component

RMM: reactive monomer mixture(s)

DMA: N, N-dimethylacrylamide (Jarchem)

NVP: N-vinylpyrrolidone

HEMA: 2-hydroxyethyl methacrylate (Bimax)

PVP, PVP K30, PVP K60, PVP K90: poly(N-vinylpyrrolidone) (ISP Ashland)

TEGDMA: tetraethylene glycol dimethacrylate (Esstech)

Omnirad 1870: blend of bis(2,6-dimethoxybenzoyl)-2,4,4-trimethyl-pentylphosphineoxide and

mPDMS: mono-n-butyl terminated monomethacryloxypropyl terminated polydimethylsiloxane ($M_n = 800-1500$ daltons) (Gelest)

SiMAA: 2-propenoic acid, 2-methyl-2-hydroxy-3-[3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propoxy]propyl ester (Toray) or 3-(3-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)propoxy)-2-hydroxypropyl methacrylate

Norbloc: 2-(2'-hydroxy-5-methacryloxyethylphenyl)-2H-benzotriazole (Janssen)

Blue HEMA: 1-amino-4-[3-(4-(2-methacryloyloxy-ethoxy)-6-chlorotriazin-2-ylamino)-4-sulfophenylamino]anthraquinone-2-sulfonic acid, as described in US Patent No. 5,944,853

Borate Buffered Packing Solution: 18.52 grams (300 mmol) of boric acid, 3.7 grams (9.7 mmol) of sodium borate decahydrate, and 28 grams (197 mmol) of sodium sulfate were dissolved in enough deionized water to fill a 2-liter volumetric flask.

AIBN: azobisisobutyronitrile

FTIR: Fourier Transform Infrared Spectroscopy

DCA: Dynamic Contact Angle wettability

DIW: deionized water

IPA: isopropyl alcohol

THF: tetrahydrofuran

D3O: 3,7-dimethyl-3-octanol (Vigon)

1E2P: 1-ethoxy-2-propanol

3E3P: 3-ethyl 3-pentanol

HEP: 1-(2-hydroxyethyl)-2-pyrrolidone

IPL: isopropyl lactate

Borate Buffered Packing Solution: 18.52 grams (300 mmol) of boric acid, 3.7 grams (9.7 mmol) of sodium borate decahydrate, and 28 grams (197 mmol) of sodium sulfate were dissolved in enough deionized water to fill a 2-liter volumetric flask.

Preparation 1

An AIBN solution was prepared by dissolving 4 grams of AIBN in 300 grams of 1-propanol. The AIBN solution was deaerated with nitrogen gas for 15-20 minutes prior to its use. A monomer solution was prepared by dissolving 98 grams of HEMA and 98 grams of mPDMS in 91 grams of 1-propanol. The monomer solution was deaerated with nitrogen gas for 15-20 minutes prior to its use.

A two-liter jacketed reactor containing 279 grams of 1-propanol was heated to 70°C under a nitrogen gas atmosphere using a water bath. Using a Watson-Marlow pump, the AIBN and monomer solutions were added to the reactor over four hours. The reaction mixture was stirred overnight after which the temperature was reduced to 50°C, and monomer conversion was monitored by FTIR until the carbon-carbon double bond band disappeared. Complete conversion required about 24 hours.

The reaction mixture was transferred into a clear glass jar. The copolymer was isolated by precipitation into water, suction filtration, and vacuum drying to obtain about 182 grams of product (Copolymer #1).

Example 1

Ink compositions 1A - 1D were prepared by adding 9 weight percent black iron oxide pigment (Sicovit® black 85 E 172, Rockwood Italia SpA-Divisione Silo) to the clear coat solutions listed in Table 1. The inks were mixed using a bench-scale ball mill (Ultra-Turrax® Tube Drive (UTTD) System, IKA). In addition, inks may be further manually mixed using a jar roller or use of an overhead mixer at 700 – 1800 rpm for 30 minutes.

Table 1

Component	Clear Coat 1A (weight %)	Clear Coat 1B (weight %)	Clear Coat 1C (weight %)	Clear Coat 1D (weight %)
Copolymer #1	8.4	7.3	3	3
PVP K60	0	0	5.7	6.75
PVP K30	19.6	14.7	23.3	20.25
HEP	0	0	6.8	0

IPL	36	0	0	0
D3O	0	7.7	0	23.1
1E2P	36	70.3	61.2	46.9
Total	100	100	100	100

Example 2

Front curve molds were printed using a laboratory scale pad printer first with a clear coating (Clear Coats 1A-1D) and then with a Vivid® cliché pattern using Inks 1A-1D. These printed front curve molds were degassed for at least 12 hours under nitrogen. Printed contact lenses were fabricated in a glove box wherein the oxygen gas level was maintained between 0.5 and 5%. About 100 microliters of RMM#1 listed in Table 2 were dosed into the printed front curve molds at ambient temperature. The time between dosing RMM#1 and placing the BC is termed "Dwell 1." The nominal Dwell 1 time was not more than 5 seconds unless noted otherwise. The base curve molds were then placed over the RMM#1. Next, a clear quartz plate was placed on top of the mold assemblies. The pallets containing the mold assemblies were then moved into the curing chamber at 60-70°C. The time between placing the weight and starting cure is termed "Dwell 2." The nominal Dwell 2 was not less than 5 minutes unless noted otherwise. Cure is started via irradiation of the pallets containing the mold assemblies with TL 20W/03 T fluorescent bulbs (Philips) and positioned to achieve an intensity of 4.0 mW/cm² for 8 minutes.

Table 2

Component	Weight Percent
mPDMS	28
SIMAA	31
DMA	22.6
HEMA	6
PVP K90	9
TEGDMA	1.25
Norbloc	1.8
Blue HEMA	0.02
OmniRad 1870	0.33

Σ Reactive Components	100
The final reactive monomer mixture RMM#1 was prepared by combining the component mixture listed above with D3O diluent to make a solution comprised of 77 weight percent reactive components and 23 weight percent D3O diluent.	

The printed lenses were manually de-molded with most lenses adhering to the FC and released by submerging the lenses in 70 percent IPA for about one or two hours, followed by washing two times with 70 percent IPA, optionally two times with 25 percent IPA, two times with DI, and finally two times with borate buffered packaging solution. Each washing step lasted about 30 minutes. A person of ordinary skill recognizes that the exact lens release process can be varied depending on the lens formulation and mold materials, regarding the concentrations of the aqueous isopropanol solutions, the number of washings with each solvent, and the duration of each step. The purpose of the lens release process is to release all lenses without defects and transition from diluent swollen networks to the packaging solution swollen hydrogels. The lenses were transferred into vials and subsequently sterilized by autoclaving at 122°C for 30 minutes. The sterile printed lenses (2A-2D, made from ink compositions 1A-1D respectively) were evaluated for haze, smear, durability, and shape, and the results listed in Table 3 [Dwell 1 = 5 seconds; Dwell 2 = 300 seconds].

Table 3

Test	Printed Lens 2A (weight %)	Printed Lens 2B (weight %)	Printed Lens 2C (weight %)	Printed Lens 2D (weight %)
Haze	None	None	None	None
Smear	None	None	Moderate	Minor
Durability	Rubs Off	No Rub Off	No Rub Off	No Rub Off
Shape	Round	Round	Round	Round
Sessile Drop	--	--	78 (11.0)	78 (3.0)

As shown in Table 3, printed lenses 2B and 2D were transparent and round and exhibited no print rub off with only minor or no smear. Printed lens 2D was also wettable.

Example 3

Ink compositions 3A – 3C were prepared by adding 9 weight percent black iron oxide pigment (Sicovit® black 85 E 172, Rockwood Italia SpA-Divisione Silo) to the clear coat solutions listed in Table 4. The inks were mixed using a bench-scale ball mill (Ultra-Turrax® Tube Drive (UTTD) System, IKA). In addition, inks may be further manually mixed using a jar roller or use of an overhead mixer at 700 – 1800 rpm for 30 minutes.

Table 4

Component	Clear Coat 3A (weight %)	Clear Coat 3B (weight %)	Clear Coat 3C (weight %)
Copolymer #1	3	3	6.0
PVP K60	5.7	6.75	7.75
PVP K30	23.3	20.25	13.25
HEP	6.8	0	14.0
IPL	0	0	38
D3O	0	23.1	0
1E2P	61.2	46.9	16.0
1-Propanol	0	0	5
Total	100	100	100

Example 4

Front curve molds were printed using a laboratory scale pad printer first with a clear coating (Clear Coats 3A-3C) and then with a Vivid® cliché pattern using Inks 3A-3C. These printed front curve molds were degassed for at least 12 hours under nitrogen. Printed contact lenses were fabricated in a glove box wherein the oxygen gas level was maintained between 0.5 and 5%. About 100 microliters of RMM#1 listed in Table 2 were dosed into the printed front curve molds at ambient temperature. The time between dosing RMM#1 and placing the BC is termed "Dwell 1." The nominal Dwell 1 time was not more than 5 seconds unless noted otherwise. The base curve molds were then placed over the RMM#1. Next, a clear quartz plate was placed on top of the mold assemblies. The pallets containing the mold assemblies were then moved into the curing chamber at 60-70°C. The time between placing the weight and starting cure is termed "Dwell 2." The nominal Dwell 2 was not less than 5 minutes unless noted otherwise. Cure is started via irradiation of the pallets containing the mold assemblies with TL 20W/03 T fluorescent bulbs (Philips) and positioned to achieve an intensity of 4.0 mW/cm² for 8 minutes.

The printed lenses were manually de-molded with most lenses adhering to the FC and released by submerging the lenses in 70 percent IPA for about one or two hours, followed by washing two times with 70 percent IPA, optionally two times with 25 percent IPA, two times with DI, and finally two times with borate buffered packaging solution. Each washing step lasted about 30 minutes. A person of ordinary skill recognizes that the exact lens release process can be varied depending on the lens formulation and mold materials, regarding the concentrations of the aqueous isopropanol solutions, the number of washings with each solvent, and the duration of each step. The purpose of the lens release process is to release all lenses without defects and transition from diluent swollen networks to the packaging solution swollen hydrogels. The lenses were transferred into vials and subsequently sterilized by autoclaving at 122°C for 30 minutes. The sterile printed lenses (4A-4C, made from ink compositions 3A-3C respectively) were evaluated for haze, smear, durability, and shape, and the results listed in Table 5 [Dwell 1 = 5 seconds; Dwell 2 = 300 seconds].

Table 5

Test	Printed Lens 4A (weight %)	Printed Lens 4B (weight %)	Printed Lens 4C (weight %)
Haze	None	None	None
Smear	Moderate	Minor	None
Durability	No Rub Off	No Rub Off	No Rub Off
Shape	Round	Round	Round
Sessile Drop	78 (11.1)	77.7 (2.9)	93 (10)

As shown in Table 5, printed lenses 4B and 4C were transparent and round and exhibited no print rub off with only minor or no smear. Printed lens 4B was also wettable.

Example 5

Ink compositions 5A - 5D were prepared by adding 9 weight percent black iron oxide pigment (Sicovit® black 85 E 172, Rockwood Italia SpA-Divisione Silo) to the clear coat solutions listed in Table 6. The inks were mixed using a bench-scale ball mill (Ultra-Turrax® Tube Drive (UTTD) System, IKA). In addition, inks may be further manually mixed using a jar roller or use of an overhead mixer at 700 – 1800 rpm for 30 minutes.

Table 6

Component	Clear Coat 5A (weight %)	Clear Coat 5B (weight %)	Clear Coat 5C (weight %)	Clear Coat 5D (weight %)
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PVP K60	10	8	8	8.75
PVP K30	19	24	24	26.25
HEP	0	0	0	6.5
IPL	0	51	17	0
D3O	7	0	0	0
1E2P	64	17	51	58.5
Total	100	100	100	100

Example 6

Front curve molds were printed using a laboratory scale pad printer first with a clear coating (Clear Coats 5A-5D) and then with a Vivid® cliché pattern using Inks 5A-5D. These printed front curve molds were degassed for at least 12 hours under nitrogen. Printed contact lenses were fabricated in a glove box wherein the oxygen gas level was maintained between 0.5 and 5%. About 100 microliters of RMM#1 listed in Table 2 were dosed into the printed front curve molds at ambient temperature. The time between dosing RMM#1 and placing the BC is termed "Dwell 1." The nominal Dwell 1 time was not more than 5 seconds unless noted otherwise. The base curve molds were then placed over the RMM#1. Next, a clear quartz plate was placed on top of the mold assemblies. The pallets containing the mold assemblies were then moved into the curing chamber at 60-70°C. The time between placing the weight and starting cure is termed "Dwell 2." The nominal Dwell 2 was not less than 5 minutes unless noted otherwise. Cure is started via irradiation of the pallets containing the mold assemblies with TL 20W/03 T fluorescent bulbs (Philips) and positioned to achieve an intensity of 4.0 mW/cm² for 8 minutes.

The printed lenses were manually de-molded with most lenses adhering to the FC and released by submerging the lenses in 70 percent IPA for about one or two hours, followed by washing two times with 70 percent IPA, optionally two times with 25 percent IPA, two times with DI, and finally two times with borate buffered packaging solution. Each washing step lasted about 30 minutes. A person of ordinary skill recognizes that the exact lens release process can be varied depending on the lens formulation and mold materials, regarding the concentrations of the aqueous isopropanol solutions, the number of washings with each solvent, and the duration of each step. The purpose of the lens release process is to release all lenses without defects and transition from diluent swollen networks to the packaging solution swollen hydrogels. The lenses were transferred into vials and subsequently sterilized by autoclaving at 122°C for 30 minutes.

The sterile printed lenses (6A-6D, made from ink compositions 5A-5D respectively) were evaluated for haze, smear, durability, and shape, and the results listed in Table 7 [Dwell 1 = 5 seconds; Dwell 2 = 300 seconds].

Table 7

Test	Printed Lens 6A (weight %)	Printed Lens 6B (weight %)	Printed Lens 6C (weight %)	Printed Lens 6D (weight %)
Haze	None	None	None	None
Smear	Severe	Moderate	Minor	Minor
Durability	No Rub Off	No Rub Off	No Rub Off	No Rub Off
Shape	Round	Round	Round	Round
Sessile Drop	89 (7.1)	69 (15.2)	70 (38.8)	61.5 (3.2)

As shown in Table 7, printed lenses 6C and 6D were transparent and round and exhibited no print rub off with only minor smear. Printed lenses 6C and 6D were also wettable.

Example 7

Ink composition 7A was prepared by adding 9 weight percent black iron oxide pigment (Sicovit® black 85 E 172, Rockwood Italia SpA-Divisione Silo) to the clear coat solutions listed in Table 8. Ink set compositions 7B were prepared by adding a combination of black, blue, and white pigments at various concentrations between 3.8-9.0 weight percent, to the clear coat solutions listed in Table 8 to create a set of 3 colored inks. The Set of 3 inks were used to create one cosmetic ink design for printed lens 7B. The inks were mixed using a bench-scale ball mill (Ultra-Turrax® Tube Drive (UTTD) System, IKA). In addition, inks may be further manually mixed using a jar roller or use of an overhead mixer at 700 – 1800 rpm for 30 minutes.

Table 8

Component	Clear Coat 7A (weight %)	Clear Coat 7B (weight %)
PVP K60	8.0	15.0
PVP K30	14.0	0
Binding Polymer	6.0	5.0
Glycerol	0	1.0
HEP	10.0	6.0
IPL	25.0	13.0
1E2P	37.0	60.0

Total	100	100
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Front curve molds were printed using a pad printer first with a clear coating (Clear Coats 7A and 7B) and then with cliché patterns using Inks 7A or 7B. Printed contact lenses were fabricated in a pilot facility production line wherein the oxygen gas level was maintained between 0.5 and 5%. About 100 microliters of RMM#2 listed in Table 9 were dosed into the printed front curve molds at ambient temperature. The time between dosing RMM#2 and placing the BC is termed "Dwell 1." The nominal Dwell 1 time was not more than 5 seconds unless noted otherwise. The base curve molds were then placed over the RMM#2. Next, precure weights were placed on top of the mold assemblies. The pallets containing the mold assemblies were then moved into the heated precure tunnel at 30°C. The time between placing the weight and starting cure is termed "Dwell 2." The nominal Dwell 2 was not less than 5 minutes unless noted otherwise. Cure is started via irradiation of the pallets containing the mold assemblies with TL 20W/03 T fluorescent bulbs (Philips) and positioned to achieve an intensity of 4.0 mW/cm² for 8 minutes.

Table 9: RMM#2

Component	Weight Percent
mPDMS	31.0
SIMAA	28.0
DMA	24.0
HEMA	5.85
PVP K90	7
TEGDMA	1.66
Norbloc	2.0
Blue HEMA	0.02
OmniRad 184	0.14
OmniRad 1870	0.34
Σ Reactive Components	100

The final reactive monomer mixture RMM#2 was prepared by combining the component mixture listed above with D3O diluent to make a solution comprised of 77 weight percent reactive components and 23 weight percent D3O diluent.

The printed lenses were de-molded with most lenses adhering to the FC and released by submerging the lenses in 70 percent IPA for about one or two hours, followed by washing two times with 70 percent IPA, optionally two times with 25 percent IPA, two times with DI, and finally once with borate buffered packaging solution. Each washing step lasted about 30 minutes. A person of ordinary skill recognizes that the exact lens release process can be varied depending on the lens formulation and mold materials, regarding the concentrations of the aqueous isopropanol solutions, the number of washings with each solvent, and the duration of each step. The purpose of the lens release process is to release all lenses without defects and transition from diluent swollen networks to the packaging solution swollen hydrogels. The lenses were inspected and packaged in heat sealed blisters and subsequently sterilized by autoclaving at 121°C for 18 minutes. The sterile printed lenses (7A-7B, made from ink compositions 7A-7B respectively) were evaluated for haze, smear, durability, shape, and wettability and the results listed in Table 3 (Dwell 1 = 5 seconds; Dwell 2 = 300 seconds).

Table 10

Test	Printed Lens 7A	Printed Lens 7B
Colored layers	1	3
Haze	None	None
Smear	None	None
Durability	No Rub Off	No Rub Off
Shape	Round	Round
DCA	60(10)	64(17)
Sessile Drop	77.1(7)	97.9(8)

As shown in Table 10, printed lenses 7A and 7B were transparent, round, exhibited no print rub off or smear, and were wettable.

Example 8

Ink set compositions 8A were prepared by adding a combination of black, blue, and white pigments at various concentrations between 3.8-9.0 weight percent, to the Ink Base solutions listed in Table 8 to create a set of 3 colored inks. The Set of 3 inks were used to create one cosmetic ink design for printed lens 8A. The inks were mixed using a bench-scale ball mill (Ultra-Turrax® Tube Drive (UTTD) System, IKA). In addition, inks may be further manually mixed using a jar roller or use of an overhead mixer at 700 – 1800 rpm for 30 minutes.

Table 11

Component	Ink Base 8A
PVP K60	0
PVP K30	22.5
Binding Polymer	7.5
Glycerol	1
HEP	0
IPL	24.0
1E2P	45.0
Total	100

Front curve molds were printed using a pad printer first with a clear coating (Clear Coat 7B from example 7) and then with cliché patterns using Ink set 8A. Printed contact lenses were fabricated on a pilot facility production line wherein the oxygen gas level was maintained between 0.5 and 5%. About 100 microliters of RMM#2 listed in Table 9 were dosed into the printed front curve molds at ambient temperature. The time between dosing RMM#2 and placing the BC is termed "Dwell 1." The nominal Dwell 1 time was not more than 5 seconds unless noted otherwise. The base curve molds were then placed over the RMM#2. Next, precure weights were placed on top of the mold assemblies. The pallets containing the mold assemblies were then moved into the heated precure tunnel at 30°C. The time between placing the weight and starting cure is termed "Dwell 2." The nominal Dwell 2 was not less than 5 minutes unless noted otherwise. Cure is started via irradiation of the pallets containing the mold assemblies with TL 20W/03 T fluorescent bulbs (Philips) and positioned to achieve an intensity of 4.0 mW/cm² for 8 minutes.

The printed lenses were de-molded with most lenses adhering to the FC and released by submerging the lenses in 70 percent IPA for about one or two hours, followed by washing two

times with 70 percent IPA, optionally two times with 25 percent IPA, two times with DI, and finally once with borate buffered packaging solution. Each washing step lasted about 30 minutes. A person of ordinary skill recognizes that the exact lens release process can be varied depending on the lens formulation and mold materials, regarding the concentrations of the aqueous isopropanol solutions, the number of washings with each solvent, and the duration of each step. The purpose of the lens release process is to release all lenses without defects and transition from diluent swollen networks to the packaging solution swollen hydrogels. The lenses were inspected and packaged in heat sealed blisters and subsequently sterilized by autoclaving at 121°C for 18 minutes. The sterile printed lenses (78A, made from clear coat 7B and ink composition set 8A respectively) were evaluated for haze, smear, durability, shape, and wettability and the results listed in Table 3 (Dwell 1 = 5 seconds; Dwell 2 = 300 seconds).

Table 12

Test	Printed Lens 8A
Colored layers	3
Haze	None
Smear	None
Durability	No Rub Off
Shape	Round
DCA	50(6)
Sessile Drop	100(11)

As shown in Table 12, printed lenses 8A using dissimilar ink layer compositions, were transparent, round, exhibited no print rub off or smear, and were wettable.

Claims

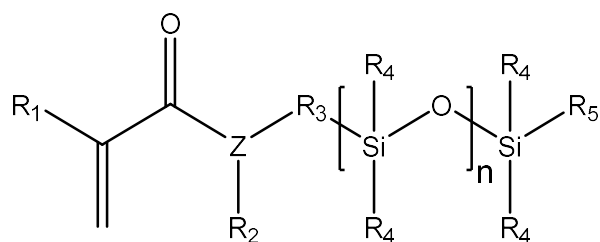
1. A method for making a cosmetic silicone hydrogel contact lens, the method comprising: (i) applying a clear coat to a lens forming surface of a first lens forming mold; (ii) applying to the clear coat an ink composition; (iii) optionally repeating step (i), step (ii), or both step (i) and step (ii); (iv) dispensing a lens material to the first lens forming mold; (v) applying a second lens forming mold; and (vi) curing the lens material to form the cosmetic silicone hydrogel contact lens;

wherein the clear coat does not comprise a colorant; and comprises a nonreactive hydrophilic polymer; and a binder polymer;

wherein the ink composition comprises a colorant; a nonreactive hydrophilic polymer; and a binder polymer;

wherein the binder polymer of the clear coat and ink composition comprises a copolymer formed from a hydrophilic monomer comprising functionality selected from the group consisting of hydroxyalkyl, aminoalkyl, and mixtures thereof; a silicone-containing macromer; and optionally a silicone-containing monomer;

wherein the silicone-containing macromer comprises a chemical structure shown in Formula I:



Formula I

wherein Z is selected from O, N, S or NCH₂CH₂O; when Z = O or S, R₂ is not required; wherein R₁ is a hydrogen atom or methyl; wherein n is a whole number between 1 and 200; wherein R₃ is an alkylene segment (CH₂)_y in which y is a whole number from 1 to 6, and each methylene group may be optionally further and independently substituted with a group selected from the group consisting of ethers, amines, esters, ketones, carbonyls, carboxylates, and carbamates, or when y

is 2 or more a non-terminal methylene group is optionally replaced with a carbamate group; or wherein R_3 is an oxyalkylene segment $O(CH_2)_z$ in which z is a whole number from 1 to 3, or wherein R_3 is a mixture of alkylene and oxyalkylene segments and the sum of y and z is between 1 and 9; wherein R_2 and R_4 are independently a hydrogen atom, a linear, branched, or cyclic alkyl group containing between one and six carbon atoms, a linear, branched, or cyclic alkoxy group containing between one and six carbon atoms, a linear or branched polyethylenoxyalkyl group, an alkyl-siloxanyl-alkyl group, a phenyl group, a benzyl group, a substituted or unsubstituted aryl group, a fluoroalkyl group, a partially fluorinated alkyl group, a perfluoroalkyl group, a fluorine atom, a mono-, di, or tri-hydroxyalkyl group containing between one and six carbon atoms, or combinations thereof; and wherein R_5 is a substituted or unsubstituted linear, branched, or cyclic alkyl group having 1 to 8 carbon atoms or an aryl group, any of which may be further substituted with one or more fluorine atoms or trimethylsiloxy groups.

2. The method of claim 1 wherein:

(a) the nonreactive hydrophilic polymer of the clear coat and/or ink composition comprises a polyamide; or

(b) wherein the nonreactive hydrophilic polymer of the clear coat and/or ink composition comprises: dextran, poly(ethylene oxide), polyvinyl alcohol (PVA), poly (N-isopropylacrylamide), poly(oligoethylene oxide), polyethylene glycol (PEG), poly (N,N-dimethylaminoethyl acrylate), poly(imine), poly(acrylic acid), or mixtures of two or more thereof; or

(c) wherein the nonreactive hydrophilic polymer of the clear coat and/or ink composition comprises a cyclic polyamide.

3. The method of any of claims 1 or 2, wherein the clear coat and/or ink composition further comprises a solvent; optionally wherein the solvent comprises: ethanol, 1-propanol, 2-propanol, 1-ethoxy-2-propanol (1E2P), t-butyl alcohol, t-amyl alcohol, and 3,7-dimethyl-1,7-octanediol (D3O), tripropylene glycol methyl ether (TPME), isopropyl lactate (IPL), 1-(2-hydroxy ethyl)-2-pyrrolidone (HEP), glycerol or mixtures of two or more thereof.

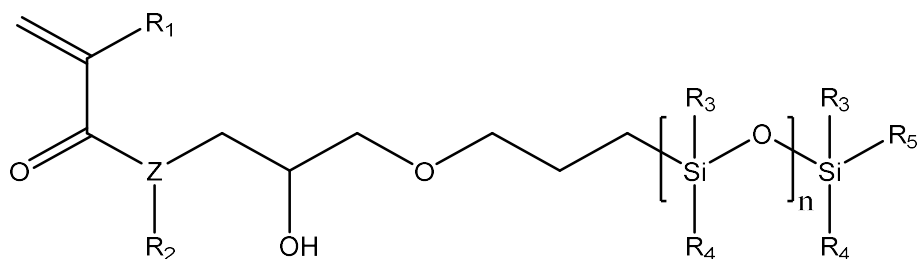
4. The method of any one of claims 1 to 3 wherein the colorant comprises: phthalocyanine blue, phthalocyanine green, carbazole violet, vat orange #1, iron oxide black, iron oxide brown, iron oxide yellow, iron oxide red, titanium dioxide, dichlorotriazine, vinyl sulfone-based dyes, and mixtures of two or more thereof.
5. The method of any one of claims 1 to 4, wherein the ink composition comprises: from 0.1 to about 25 weight percent of the colorant; from about 1 to about 50 weight percent of the nonreactive hydrophilic polymer; from about 1 to 60 weight percent of the binder polymer; and from about 50 to about 95 weight percent of a solvent, each based on the total weight of the ink composition.
6. The method of any of any one of claims 1 to 5 wherein the binder polymer of the clear coat and/or ink composition
- (a) has a weight average molecular weight in the range of about 10 to about 100 kDa; and/or
 - (b) is not a block co- or tri-polymer; and/or
 - (c) is a random copolymer.
7. The method of any of claims 1 to 6 wherein the nonreactive hydrophilic polymer of the clear coat and/or ink composition
- (a) is poly(vinylpyrrolidone); and/or
 - (b) has a weight average molecular weight from about 30,000 to about 500,000.
8. The method of any one of claims 1-7, wherein the hydrophilic monomer comprises 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2,3-dihydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, N-(2-hydroxyethyl) (meth)acrylamide, N,N-bis(2-hydroxyethyl) (meth)acrylamide, N-(2-hydroxypropyl) (meth)acrylamide, N,N-bis(2-hydroxypropyl) (meth)acrylamide, N-(3-hydroxypropyl) (meth)acrylamide, N-(2-hydroxybutyl) (meth)acrylamide, N-(3-hydroxybutyl) (meth)acrylamide, N-(4-hydroxybutyl) (meth)acrylamide, or mixtures thereof;

optionally wherein the hydrophilic monomer is 2-hydroxyethyl (meth)acrylate.

9. The method of any one of claims 1 to 8, wherein the silicone-containing macromer

(a) is selected from the group consisting of monoalkyl terminated, mono(meth)acrylate terminated poly(dialkylsiloxanes), monoalkyl terminated, monoalkyl terminated, mono(meth)acrylate terminated poly(diarylsiloxanes), monoalkyl terminated, mono(meth)acrylate terminated poly(alkylarylsiloxanes), and mixtures thereof; optionally wherein the silicone-containing macromer is mono-n-butyl terminated monomethacryloxypropyl terminated polydimethylsiloxane; and/or

(b) comprises a chemical structure shown in Formula VIII:



Formula VIII

wherein Z is selected from O, N, S or NCH₂CH₂O; wherein R₁ is independently hydrogen atom or methyl group; wherein R₂, R₃, and R₄ are independently a hydrogen atom or a linear, branched, or cyclic alkyl group containing one to eight carbon atoms, any of which may be further substituted with at least one hydroxy group, and which may be optionally substituted with amido, ether, amino, carboxyl, carbonyl groups and combinations thereof; for Z = O and S, R₂ is not required; wherein n is the number of siloxane repeating units and is from 4 to 200; and wherein R₅ is selected from straight or branched C₁ to C₈ alkyl groups; and/or

(c) is mono-n-butyl terminated mono-(2-hydroxy-3-methacryloxypropyl)-propyl ether terminated polydimethylsiloxane; and/or

(d) is selected from the group consisting of mono-n-butyl terminated monomethacryloxypropyl terminated polydimethylsiloxane, mono-n-butyl terminated mono-(2-hydroxy-3-methacryloxypropyl)-propyl ether terminated polydimethylsiloxane, and mixtures thereof.

10. The method of any one of claims 1 to 9, wherein the silicone-containing macromer has a number average molecular weight greater than 500 Daltons or between about 500 Daltons and about 20,000 Daltons.

11. The method of any of claims 1 to 10, wherein the repeating units of the silicone-containing macromer are present in the range of about 30 and about 80 weight percent of the total weight of the binder polymer.

12. The method of any of claims 1 to 11, wherein the silicone-containing monomer is selected from the group consisting of: 3-methacryloxypropyl tris(trimethylsiloxy)silane, 3-acryloxypropyl tris(trimethylsiloxy)silane, 3-methacrylamidopropyl tris(trimethylsiloxy)silane, 3-acrylamidopropyl tris(trimethylsiloxy)silane, tris(trimethylsiloxy)silyl styrene, 2-methyl-2-hydroxy-3-[3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propoxy]propyl ester, N-(2,3-dihydroxypropyl) N-(3-tetra(dimethylsiloxy)dimethylbutylsilane)propyl) acrylamide and mixtures thereof.

13. A cosmetic silicone hydrogel contact lens obtained by the method of any one of claims 1 to 12.

14. The cosmetic contact lens of claim 13 further comprising an internal wetting agent.

15. The cosmetic contact lens of claims 13 or 14

(a) wherein the lens comprises multiple layers of ink composition wherein the multiple layers of ink composition may be the same or different; and/or

(b) further comprising an ink layer that is free of nonreactive hydrophilic polymer.