

METHOD AND COMPOSITION PROVIDING DESIRABLE CHARACTERISTICS BETWEEN A  
MOLD AND A POLYMERIZABLE COMPOSITION

BACKGROUND OF THE INVENTION

[0001] The field of invention relates generally to nano-  
5 fabrication of structures. More particularly, the present invention  
is directed to a method of providing desirable wetting and release  
characteristics between a mold and a polymerizable composition  
suitable for use in imprint lithographic processes.

[0002] Nano-scale fabrication involves the fabrication of very  
10 small structures, e.g., having features on the order of one nano-  
meter or more. A promising process for use in nano-scale fabrication  
is known as imprint lithography. Exemplary imprint lithography  
processes are described in detail in numerous publications, such as  
United States published patent application 2004-0065976 filed as  
15 United States patent application 10/264,960, entitled "Method and a  
Mold to Arrange Features on a Substrate to Replicate Features having  
Minimal Dimensional Variability"; United States published patent  
application 2004-0065252 filed as United States patent application  
10/264,926, entitled "Method of Forming a Layer on a Substrate to  
20 Facilitate Fabrication of Metrology Standards"; and United States  
published patent application 2004-0046271 filed as United States  
patent application 10/235,314, entitled "Method and a Mold to Arrange  
Features on a Substrate to Replicate Features having Minimal  
Dimensions Variability"; all of which are assigned to the assignee of  
25 the present invention.

[0003] Referring to Fig. 1, the basic concept behind imprint  
lithography is forming a relief pattern on a substrate that may  
function as, *inter alia*, an etching mask so that a pattern may be  
formed into the substrate that corresponds to the relief pattern. A  
30 system 10 employed to form the relief pattern includes a stage 11  
upon which a substrate 12 is supported. A template 14 has a mold 16  
with a patterning surface 18 thereon. Patterning surface 18 may be  
substantially smooth and/or planar, or may be patterned so that one  
or more recesses are formed therein. Template 14 is coupled to an  
35 imprint head 20 to facilitate movement of template 14. A fluid  
dispense system 22 is coupled to be selectively placed in fluid  
communication with substrate 12 so as to deposit polymerizable  
material 24 thereon. A source 26 of energy 28 is coupled to direct  
energy 28 along a path 30. Imprint head 20 and stage 11 are  
40 configured to arrange mold 16 and substrate 12, respectively, to be

in superimposition, and is disposed in path 30. Either imprint head 20, stage 11, or both vary a distance between mold 16 and substrate 12 to define a desired volume therebetween that is filled by polymerizable material 24.

5    [0004]       Typically, polymerizable material 24 is disposed upon substrate 12 before the desired volume is defined between mold 16 and substrate 12. However, polymerizable material 24 may fill the volume after the desired volume has been obtained. After the desired volume is filled with polymerizable material 24, source 26 produces energy  
10   28, which causes polymerizable material 24 to solidify and/or cross-link, forming polymeric material conforming to the shape of the substrate surface 24 and mold surface 18. Control of this process is regulated by processor 32 that is in data communication with stage 11, imprint head 20, fluid dispense system 22, and source 26,  
15   operating on a computer readable program stored in memory 34.

      [0005]       An important characteristic with accurately forming the pattern in the polymerizable material is to reduce, if not prevent, adhesion to the mold of the polymeric material, while ensuring suitable adhesion to the substrate. This is referred to as  
20   preferential release and adhesion properties. In this manner, the pattern recorded in the polymeric material is not distorted during separation of the mold therefrom. Prior art attempts to improve the release characteristics employ a release layer on the surface of the mold. The release layer is typically hydrophobic and/or has low  
25   surface energy. The release layer adheres to the mold. Providing the release layer improves release characteristics by minimizing distortions in the pattern recorded into the polymeric material that are attributable to mold separation. This type of release layer is referred to, for purposes of the present discussion, as an *a priori*  
30   release layer, i.e., a release layer that is solidified to the mold.

      [0006]       Another prior art attempt to improve release properties is described by Bender et al. in Multiple Imprinting in UV-based Nanoimprint Lithography: Related Material Issues, *Microelectronic Engineering* 61-62 (2002), pp. 407-413. Specifically, Bender et al.  
35   employ a mold having an *a priori* release layer in conjunction with a fluorine-treated UV curable material. To that end, a UV curable layer is applied to a substrate by spin-coating a 200 cPs UV curable fluid to form a UV curable layer. The UV curable layer is enriched with fluorine groups to improve the release properties.

[0007] A drawback with the release layers of the prior art is that the same usually increases the time required to wet a surface, thereby reducing the overall throughput of the process. This, it is believed, results from the hydrophobicity of the release layers.

5 Specifically, the hydrophobicity is inversely related to the work required to achieve release and directly related to the time required to wet a surface. Thus, there is a conflict between the wetting characteristics and the release characteristics desired for imprint lithographic processes.

10 [0008] There is a need, therefore, to improve the preferential release and adhesion properties of a mold employed in imprint lithography processes.

#### SUMMARY OF THE INVENTION

[0009] The present invention provides a method that features  
15 compositions that feature improved wetting characteristics while allowing preferential adhesion and release characteristics with respect to a substrate and a mold having imprinting material disposed therebetween. The method includes coating a surface of the mold with a volume of surfactant containing solution. The surfactant in the  
20 solution includes a hydrophobic component consisting essentially of a plurality of fluorine-containing molecules. The distribution of the plurality of fluorine-containing molecules throughout the volume provides a desired contact angle with respect to a polymerizable composition disposed on the substrate. The contact angle is in a  
25 range of 50° or less.

[0010] The compositions feature improved preferential adhesion and release characteristics with respect to a substrate and a mold having imprinting material disposed therebetween. The compositions facilitate bifurcation of the imprinting material into a surfactant-  
30 component-rich sub-portion and a surfactant-component-depleted sub-portion located between said surfactant-component-rich sub-portion and said substrate. This surfactant-component-rich sub-portion attenuates the adhesion forces between the mold and the imprinting material, once solidified. A method is also disclosed that takes  
35 advantage of the characteristics of the composition. These and other embodiments are described herein.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Fig. 1 is a perspective view of a lithographic system in accordance with the prior art;

[0012] Fig. 2 is a simplified elevation view of a template and imprint material disposed on a substrate in accordance with the present invention;

5 [0013] Fig. 3 is a simplified elevation view of the template and substrate shown in Fig. 2, with the imprinting material being shown as patterned and solidified;

[0014] Fig. 4 is a detailed view of the droplets of imprint material, shown in Fig. 2, showing the bifurcation of the droplets into surfactant-rich regions and surfactant-depleted regions;

10 [0015] Fig. 5 is a detailed view of a layer of imprinting material, deposited employing spin-on techniques, showing the bifurcation of the layer into surfactant-rich regions and surfactant-depleted regions;

[0016] Fig. 6 is a cross-sectional view of the template contacting imprinting material, deposited as shown in either Figs. 4 or 5, demonstrating the formation of the weak boundary lamella between solidified imprinting material and a template; and

[0017] Fig. 7 is a cross-sectional view of the template shown in Fig. 6 having a layer of surfactant containing solution disposed thereon, in accordance with the present invention.

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#### DETAILED DESCRIPTION OF THE INVENTION

[0018] Referring to Figs. 1 and 2, a mold 36, in accordance with the present invention, may be employed in system 10, and may define a surface having a substantially smooth or planar profile (not shown).  
25 Alternatively, mold 36 may include features defined by a plurality of spaced-apart recessions 38 and protrusions 40. The plurality of features defines an original pattern that is to be transferred into a substrate 42. Substrate 42 may be comprised of a bare wafer or a wafer with one or more layers disposed thereon. To that end, reduced is a distance "d" between mold 36 and substrate 42. In this manner, the features on mold 36 may be imprinted into a conformable region of substrate 42, such as an imprinting material disposed on a portion of surface 44 that presents a substantially planar profile. It should  
35 be understood that the imprinting material may be deposited using any known technique, e.g., spin-coating, dip coating and the like. In the present example, however, the imprinting material is deposited as a plurality of spaced-apart discrete droplets 46 on substrate 42. Imprinting layer 34 is formed from a composition that may be

selectively polymerized and cross-linked to record the original pattern therein, defining a recorded pattern.

[0019] Specifically, the pattern recorded in the imprinting material is produced, in part, by interaction with mold 36, e.g.,  
5 electrical interaction, magnetic interaction, thermal interaction, mechanical interaction and the like. In the present example, mold 36 comes into mechanical contact with the imprinting material, spreading droplets 36, so as to generate a contiguous formation 50 of the imprinting material over surface 44. In one embodiment, distance "d"  
10 is reduced to allow sub-portions 52 of imprinting layer 34 to ingress into and fill recessions 38.

[0020] To facilitate filling of recessions 38, the imprinting material is provided with the requisite properties to completely fill recessions 38 while covering surface 44 with a contiguous formation  
15 of the imprinting material. In the present embodiment, sub-portions 54 of imprinting layer 34 in superimposition with protrusions 40 remain after the desired, usually minimum distance "d" has been reached. This action provides formation 50 with sub-portions 52 having a thickness  $t_1$ , and sub-portions 54, having a thickness  $t_2$ .  
20 Thicknesses " $t_1$ " and " $t_2$ " may be any thickness desired, dependent upon the application. Thereafter, formation 50 is solidified by exposing the same to the appropriate curing agent, e.g., actinic radiation. This causes the imprinting material to polymerize and cross-link. The entire process may occur at ambient temperatures and  
25 pressures, or in an environmentally controlled chamber with desired temperatures and pressures. In this manner, formation 50 is solidified to provide side 56 thereof with a shape conforming to a shape of a surface 58 of mold 36.

[0021] Referring to Figs. 1, 2 and 3, the characteristics of the  
30 imprinting material are important to efficiently pattern substrate 42 in light of the unique patterning process employed. For example, it is desired that the imprinting material have certain characteristics to facilitate rapid and even filling of the features of mold 36 so that all thicknesses  $t_1$  are substantially uniform and all thicknesses  
35  $t_2$  are substantially uniform. To that end, it is desirable that the viscosity of the imprinting material be established, based upon the deposition process employed, to achieve the aforementioned characteristics. As mentioned above, the imprinting material may be deposited on substrate 42 employing various techniques. Were the  
40 imprinting material deposited as a plurality of discrete and spaced-

apart droplets 46, it would be desirable that the composition from which the imprinting material is formed have relatively low viscosity, e.g., in a range of 0.5 to 20 centipoises (cPs). Considering that the imprinting material is spread and patterned concurrently, with the pattern being subsequently solidified into formation 50 by exposure to radiation, it would be desired to have the composition wet surface of substrate 42 and/or mold 36 and to avoid subsequent pit or hole formation after polymerization. Were the imprinting material deposited employing spin coating techniques, it would be desired to use higher viscosity materials, e.g. having a viscosity greater than 10 cPs and typically, several hundred to several thousand cPs.

[0022] In addition to the aforementioned characteristics, referred to as liquid phase characteristics, it is desirable for the composition to provide the imprinting material with certain solidified phase characteristics. For example, after solidification of formation 50, it is desirable that preferential adhesion and release characteristics be demonstrated by the imprinting material. Specifically, it is beneficial for the composition from which the imprinting material is fabricated to provide formation 50 with preferential adhesion to substrate 42 and preferential release of mold 36. In this fashion, reduced is the probability of distortion in the recorded pattern resulting from the separation of mold 36 therefrom due to, *inter alia*, tearing, stretching or other structural degradation of formation 50.

[0023] The constituent components that form the imprinting material to provide the aforementioned characteristics may differ. This results from substrate 42 being formed from a number of different materials. As a result, the chemical composition of surface 44 varies dependent upon the material from which substrate 42 is formed. For example, substrate 42 may be formed from silicon, plastics, gallium arsenide, mercury telluride, and composites thereof. Additionally, substrate 42 may include one or more layers, e.g., dielectric layer, metal layer, semiconductor layer, planarization layer and the like, upon which formation 50 is generated. Additionally, mold 36 may be formed from several materials, e.g., fused-silica, quartz, indium tin oxide diamond-like carbon, MoSi, sol-gels and the like.

[0024] It has been found that the imprinting material from which formation 50 is generated may be fabricated from several different

families of bulk materials. For example, the imprinting material may be fabricated from vinyl ethers, methacrylates, epoxies, thiol-enes and acrylates, just to name a few.

[0025] Exemplary bulk materials for the imprinting material are as follows:

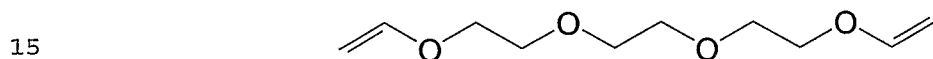
VINYL ETHER/BULK MATERIAL-A1

triethyleneglycol divinyl ether

tris(4-vinyloxybutyl)trimellitate

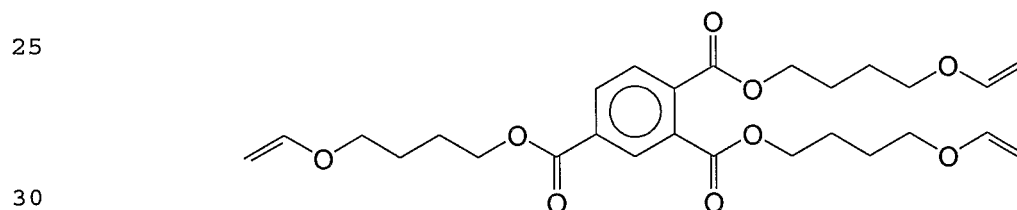
photoinitiator

A first vinyl ether component, triethyleneglycol divinyl ether, has the following structure:



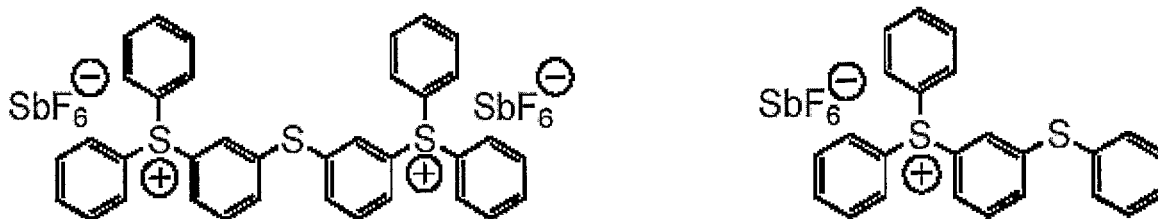
and comprises approximately 67.9% of the bulk material by weight. As a result, the mechanical properties of formation 50 are primarily attributable to triethyleneglycol divinyl ether. An exemplary source for triethyleneglycol divinyl ether is the BASF Corporation of Mount Olive, New Jersey available under the product name DVE-3.

[0026] A second vinyl ether component tris(4-vinyloxybutyl)trimellitate has the following structure:



and comprises approximately 29.1 % of the bulk material. The component tris(4-vinyloxybutyl)trimellitate is available from Morflex Inc. of Greensboro, North Carolina under the tradename Vectomer 5015.

[0027] The photoinitiator component is a cationic photoinitiator that is a mixture of triarylsulfonium hexafluoroantimonate salts in propylene carbonate having the following structure:

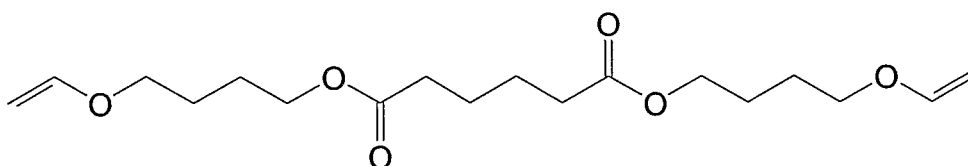


The photoinitiator component comprises approximately 3% of the bulk material and is available from the Dow Chemical Company of Midland, Michigan under the product name UVI 6976.

VINYL ETHER 2/BULK MATERIAL-A2

5                   bis(4-vinyloxybutyl)adipate  
vinyl ether terminated polyester polymer  
photoinitiator

[0028]           A first vinyl ether component, bis(4-  
10 vinyloxybutyl)adipate, has the following structure:



and comprises approximately 19.4% of the bulk material by weight. An  
15 exemplary source for bis(4-vinyloxybutyl)adipate is Morflex, Inc. of Greensboro, North Carolina under the product name Vectomer 4060.

[0029]           The second vinyl ether component is a vinyl ether  
terminated polyester polymer that comprises approximately 77.6% of  
the bulk material by weight. As a result, the mechanical properties  
20 of formation 50 are primarily attributable to the vinyl ether  
terminated polyester polymer. An exemplary source for the vinyl  
ether polyester polymer is Morflex, Inc. of Greensboro, North  
Carolina under the product name Vectomer 1312. The photoinitiator  
comprises approximately 3% of the bulk material, by weight, and is  
25 that same as described above with respect to VINYL ETHER BULK  
MATERIAL 1: UVI 6976.

METHACRYLATE/BULK MATERIAL-A3

organic modified silicate  
30

[0030]           An exemplary organic modified silicate ORMOSIL that may  
comprise 100% of the bulk material is Ormomer® b66 available from  
Micro Resist Technology GmbH, Berlin, Germany. The material is  
fabricated through a sol-gel process. Methacryl and epoxy  
35 functionality is attached to the material, with a photoinitiator  
component being incorporated for UV curing through the methacryl  
functionality.

EPOXY/BULK MATERIAL-A4

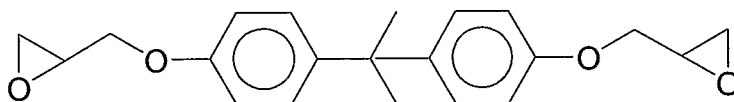
diglycidyl ether of bisphenol A

cationic photoinitiator

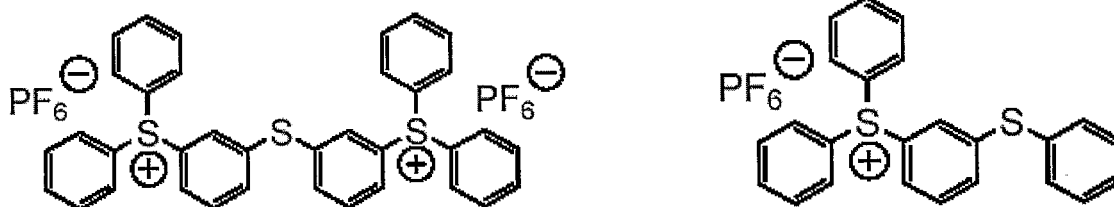
5

[0031] The diglycidyl ether of bisphenol A component has the following structure:

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and comprises approximately 97% of the bulk material by weight. As a result, the mechanical properties of formation 50 are primarily attributable to the diglycidyl ether of bisphenol A component. An exemplary source of diglycidyl ether of bisphenol A is Dow Chemical Company of Midland, Michigan under the product name DER 332. The cationic photoinitiator component of the bulk material includes a mixture of triarylsulfonium hexafluorophosphate salts in propylene carbonate, providing the following structure:



and comprises approximately 3% of the bulk material, by weight. An exemplary source of the cationic photoinitiator is Dow Chemical Company of Midland, Michigan under the product name UVI 6992.

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THIOL-ENE/BULK MATERIAL-A5

triethyleneglycol divinyl ether

1,2-Bis(2-mercaptoethoxy)ethane

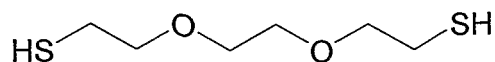
triallyl isocyanurate

30

ethyl 2, 4, 6-trimethylbenzoylphenylphosphinate

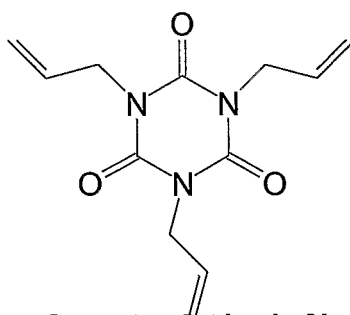
[0032] The vinyl ether component comprises approximately 36.7% of the bulk material by weight and has the structure discussed above with respect to the product sold under the product name DVE-3. The 1,2-Bis(2-mercaptoethoxy)ethane component has the following structure:

35



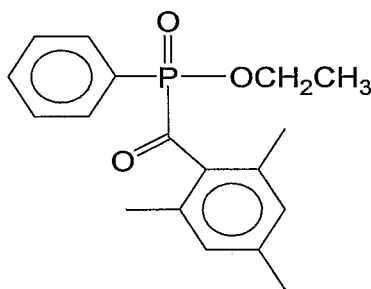
and comprises approximately 47.3% of the bulk material by weight. An exemplary source of the 1,2-Bis(2-mercaptoethoxy)ethane component is the Aldrich Chemical Company of Milwaukee, Wisconsin under the product name DMDO. As a result, the mechanical properties of formation 50 are primarily attributable to the triethyleneglycol divinyl ether and 1,2-Bis(2-mercaptoethoxy)ethane components.

[0033] The triallyl isocyanurate component has the following structure:



and comprises approximately 13% of the bulk material by weight. An exemplary source of the triallyl isocyanurate component is the Aldrich Chemical Company of Milwaukee, Wisconsin under the product name TAIC.

[0034] The ethyl 2, 4, 6-trimethylbenzoylphenyl-phosphinate component comprises approximate 3% of the bulk material by weight and has the following structure:

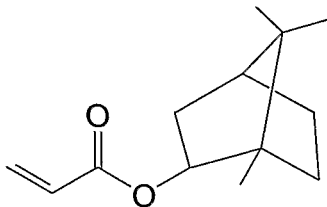


An exemplary source of the ethyl 2, 4, 6-trimethylbenzoylphenylphosphinate component is the BASF Corporation of Mount Olive, New Jersey under the product name TPO-L.

ACRYLATE/BULK MATERIAL-A6

isobornyl acrylate  
n-hexyl acrylate  
ethylene glycol diacrylate  
2-hydroxy-2-methyl-1-phenyl-propan-1-one

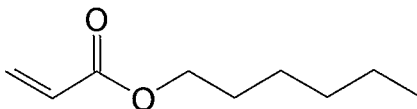
[0035] The acrylate component, isobornyl acrylate (IBOA), has the following structure:



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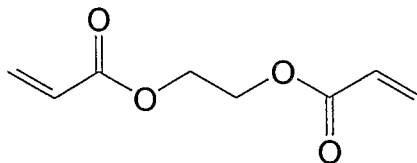
and comprises approximately 55% of bulk material by weight, but may be present in a range of 20% to 80%, inclusive. As a result, the mechanical properties of formation 50 are primarily attributable to IBOA. An exemplary source for IBOA is Sartomer Company, Inc. of  
10 Exton, Pennsylvania available under the product name SR 506.

[0036] The component n-hexyl acrylate (n-HA) has the following structure:



15 and comprises approximately 27% of bulk material by weight, but may be present in a range of 0% to 50%, inclusive. Also providing flexibility to formation 50, n-HA is employed to reduce the viscosity of the prior art bulk material so that bulk material, in the liquid phase, has a viscosity in a range 2-9 Centipoises, inclusive. An  
20 exemplary source for the n-HA component is the Aldrich Chemical Company of Milwaukee, Wisconsin.

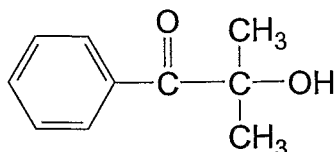
[0037] A cross-linking component, ethylene glycol diacrylate, has the following structure:



25

and comprises approximately 15% of bulk material by weight, and may be present in a range of 10% to 50%, inclusive. EGDA also contributes to the modulus and stiffness buildup, as well as  
30 facilitates cross-linking of n-HA and IBOA during polymerization of the bulk material.

[0038] An initiator component, 2-hydroxy-2-methyl-1-phenyl-propan-1-one is available from Ciba Specialty Chemicals of Tarrytown, New York under the trade name DAROCUR® 1173, and has the following structure:



and comprises approximately 3% of the bulk material by weight, and may be present in a range of 1% to 5%, inclusive. The initiator is responsive to a broad band of ultra-violet radiation generated by a medium-pressure mercury lamp. In this manner, the initiator facilitates cross-linking and polymerization of the components of the bulk material.

ACRYLATE/BULK MATERIAL-A7

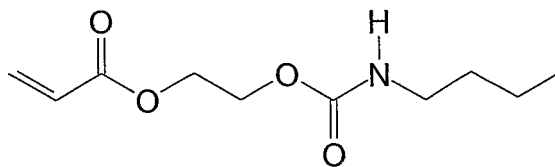
isobornyl acrylate  
n-hexyl acrylate  
ethylene glycol diacrylate  
2-hydroxy-2-methyl-1-phenyl-propan-1-one

[0039] As can be seen, BULK MATERIAL-A7 is identical to BULK MATERIAL-A6 in terms of the identity of the constituent components. The two materials differ in terms of the percentage of each of the constituent components present. In BULK MATERIAL-A7, IBOA comprises approximate 47% of the material by weight and n-HA and EGDA each comprises 25% of the bulk material by weight. DAROCUR® 1173, 2-hydroxy-2-methyl-1-phenyl-propan-1-one component comprises approximately 3% of the material by weight.

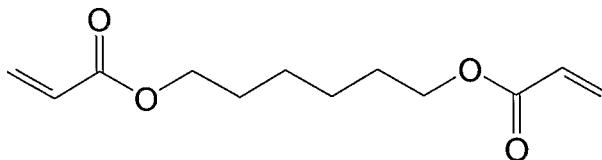
ACRYLATE/BULK MATERIAL-A8

genomer 1122  
isobornyl acrylate  
1,6-Hexanediol Diacrylate  
2-hydroxy-2-methyl-1-phenyl-propan-1-one

[0040] The first acrylate component, genomer 1122 is an aliphatic urethane acrylate available from Rahn USA Corporation of Aurora, Illinois and has the following structure:



and comprises approximately 21% of the bulk material by weight, but may be present in a range of 0 to 50%. The acrylate component isobornyl acrylate (IBOA) is as described above and comprises approximately 56% by weight of the composition, but may be present in a range of 20 to 80%. The acrylate component 1,6-hexanediol diacrylate is available from UCB Chemicals, Smyrna, Georgia and has the following structure:



and comprises approximately 20% of bulk material by weight, but may be present in a range of 10% to 50%, inclusive. The initiator component, 2-hydroxy-2-methyl-1-phenyl-propan-1-one is as described above and comprises approximately 3% of the composition by weight. To provide improved wetting characteristics of BULK MATERIAL A8, additional fluorinated acrylates, such as 1H,1H-perfluoro-n-decyl acrylate may be included to lower the contact angle of the same. This fluorinated acrylate is available from Exfluor Research Corporation, Round Rock, Texas under the tradename C10ACRY. One advantage with bulk material A-8 is that it has a viscosity of approximately 11 cPs which makes the same suitable for both drop-dispense and spin-coating techniques.

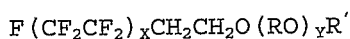
[0041] It was discovered, however, that desirable preferential adhesion and release properties, as discussed above, may be achieved by producing a weak boundary layer, lamella 60, between mold 36, surface 58 and formation 50. Lamella 60 remains after solidification of the imprinting material. As a result, the adhesion forced between mold 36 and formation 50 are minimal. To that end, found beneficial was employing a composition for the imprinting material that includes one of the bulk materials discussed above along with a component that contains low surface energy groups, referred to herein as a surfactant component. After deposition of the imprinting material, the surfactant component rises, after a period of time, to the air

liquid interface, providing droplets 146 of imprinting material with a bifurcated concentration of materials.

[0042] In a first portion, droplets 146 include a higher concentration of the surfactant component, referred to as a surfactant-component-rich (SCR) sub-portion 136, than the second portion, referred to as a surfactant-component-depleted (SCD) sub-portion 137. SCD sub-portion 137 is positioned between surface 44 and SCR sub-portion 136. SCR sub-portion 136 attenuates the adhesion forces between mold and the imprinting material, once solidified. Specifically, the surfactant component has opposed ends. When the imprinting material is in the liquid phase, i.e., polymerizable, one of the opposed ends has an affinity for the bulk material included in the imprinting material. The remaining end has a fluorine component. As a result of the affinity for the bulk material, the surfactant component is orientated so that the fluorine component extends from an air-liquid interface defined by the imprinting material and the surrounding ambient. Upon solidification of the imprinting material, a first portion of the imprinting material generates a lamella 60 and a second portion of the imprinting material is solidified, i.e., polymeric material shown as formation 50. Lamella 60 is positioned between formation 50 and mold 36. Lamella 60 results from the presence and location of the fluorine components in the SCR sub-portion 136. Lamella 60 prevents strong adhesion forces from being developed between mold 36 and formation 50. Specifically, formation 50 has first and second opposed sides 62 and 64. Side 62 adheres to substrate 42 with a first adhesion force. Side 64 adheres to mold 36 with a second adhesion force. Lamella 60 results in the second adhesion force being less than the first adhesion force. As a result, mold 36 may be easily removed from formation 50 while minimizing distortions and/or the force required to separate mold 36 therefrom. Although formation 50 is shown with side 62 being patterned, it should be understood that side 62 may be smooth, if not planar. Furthermore, if desired, it is possible to generate lamella 60 so as to be disposed between formation 50 and substrate 42. This may be achieved, for example, by applying imprinting material to mold 36 and subsequently contacting substrate with the imprinting material. In this manner, it can be said that formation 50, i.e., polymeric material, will be disposed between lamella 60 and the body, mold 36 or substrate 42, upon which the polymerizable material is deposited.

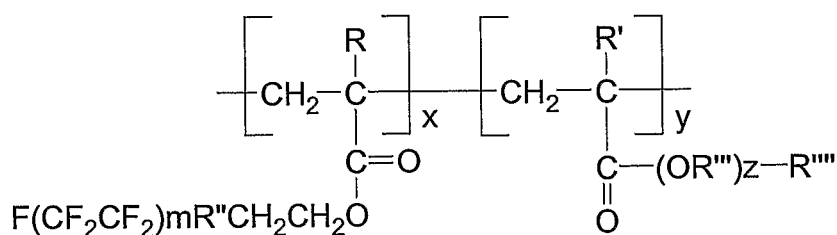
[0043] It should be understood that were the imprinting material deposited employing spin-coating techniques, similar bifurcated concentration of materials occurs, as shown in Fig. 5 with respect to SCR sub-portion 236 and second and SCD sub-portion 237. The time required for the bifurcation is dependent upon several factors, including the size of molecules in the imprinting material and the viscosity of the imprinting material. Only a few seconds is needed to achieve the aforementioned bifurcation of imprinting material with viscosity below twenty cPs. Imprinting material with viscosity in the hundreds of cPs, however, may require a few seconds to several minutes.

[0044] Various surfactant components, or combinations of surfactant components, can be included in the bulk materials to form lamella 60. These include nonionic fluorinated surfactant components having the following general formula:



where  $(RO)_y$  is a poly(oxyalkylene) group, that includes groups having two to four carbon atoms such as  $-CH_2CH_2-$ ,  $-CH_2CH_2CH_2-$ ,  $-CH(CH_3)CH_2-$ , or  $-CH(CH_3)CH(CH_3)-$ , and  $R'$  is a terminal group of H or  $C_1$  to  $C_4$  alkyl, preferably H or methyl and X and Y are integers.

[0045] Another example of nonionic fluorinated surfactant components has the following general formula:

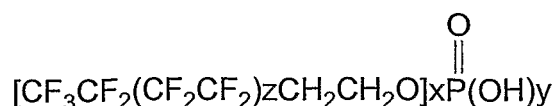


where R and  $R'$  can be either H or methyl; R and  $R'$  can be identical or differ.  $R''$  is a linking group that may be omitted or a sulfonyl group such as  $-SO_2N(R''''')-$ , with  $R'''''$  being  $C_1$  to  $C_6$  alkyl and typically  $C_1$  to  $C_4$  alkyl. The component  $(OR''')_z$  is a poly(oxyalkylene) group, typically including groups having 2 to 4 carbon atoms such as  $-CH_2CH_2-$ ,  $-CH_2CH_2CH_2-$ ,  $-CH(CH_3)CH_2-$ , or  $-CH(CH_3)CH(CH_3)-$ .  $R'''''$  is a terminal group of methyl, H or  $C_1$  to  $C_4$  alkyl and typically H or methyl. The ratio of x to y is in a range of 1:2 to 3:1 and more preferably in a range of 1:1 to 2:1.

[0046] It should be understood that the oxyalkylene groups in the poly(oxyalkylene) group may be the same, as in poly(oxyethylene), or two or more of differing oxyalkylene units may be irregularly distributed in the poly(oxyalkylene) group. More specifically, the poly(oxyalkylene) group may be made up of straight or branched chain oxypropylene units alone or oxyethylene units alone, or straight or branched oxypropylene units and oxyethylene units may be present in alternate blocks. In the case of alternate blocks of oxyethylene and oxypropylene, the ratio the oxyethylene to oxypropylene is in a range of 2.0-0.5 to 1. Also, unattached blocks of poly(oxyalkylene) may be present in the polymer matrix. Chain transfer agents such as octyl mercaptan may be also present.

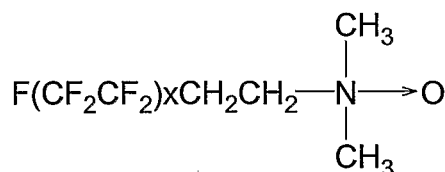
[0047] Exemplary nonionic fluorinated surfactant components that may be employed are fluoro-aliphatic polymeric esters, fluorosurfactants of the polyoxyethylene or polyalkyl ether type, or fluoroalkyl polyethers as set forth in U.S. Pat. Nos. 3,403,122, 3,787,351, 4,803,145, 4,835,084, 4,845,008, 5,380,644, 5,747,234, and 6,664,354 which are incorporated herein by reference. Suitable commercially available examples of the surfactant components included are sold by Dupont under product names ZONYL<sup>®</sup> FSO, ZONYL<sup>®</sup> FSO-100, ZONYL<sup>®</sup> FSN-100, ZONYL<sup>®</sup> FS-300; sold by 3M Company under the product names FC-4432, FC-4430, FC430; sold by Mason Chemical Company of Arlington Heights, Illinois under the product names MASURF<sup>®</sup> FS425, MASURF<sup>®</sup> FS1700, MASURF<sup>®</sup> FS-2000, MASURF<sup>®</sup> FS-1230; sold by Ciba-Geigy Corp under the product names Lodyne S-107B, Lodyne S-220N, Lodyne S-222N; sold by Daikin of Japan under the product names Unidyne NS1602, Unidyne NS1603, Unidyne NS1606; and sold by Dainippon Ink & Chemical under the product name MegaFace R-08. In addition to, or in lieu of the nonionic fluorinated surfactant components, ionic fluorinated surfactant components may be employed in the composition from which the imprinting material is formed, along with the bulk materials discussed above.

[0048] In lieu of, or in addition to, the non-ionic fluorinated surfactant components, the ionic type of fluorinated surfactant components can work as well. An exemplary ionic surfactant is an anionic phosphate fluorosurfactant sold by DuPont of Wilmington, Delaware under the tradename ZONYL<sup>®</sup> UR, which has the following formula:

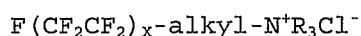


wherein,  $x=1$  or  $2$ ,  $y=2$  or  $1$ ,  $x+y=3$ ,  $z=0$  to about  $6$ . In addition to  
 5 ZONYL<sup>®</sup> UR, other anionic surfactant components based upon fluorinated  
 phosphoric, polyphosphoric acid ester, sulfonic acid ester, alkyl  
 surface and carboxylic acid ester types may be employed.

[0049] In lieu of, or in addition to, the non-ionic and anionic  
 surfactant components, a zwitterionic surfactant may be employed with  
 10 the bulk materials discussed above for the composition from which the  
 imprinting material is fabricated. An exemplary zwitterionic  
 surfactant has the following general formula:



15 [0050] A commercially available zwitterionic surfactant is a  
 fluoroaliphatic amine oxide available from the Mason Chemical Company  
 under the tradename MASURF<sup>®</sup> FS230. Cationic surfactant components  
 may be employed, as well, such as fluorinated surfactant components  
 like quaternary ammonium salts available from DuPont under the trade  
 20 name ZONYL<sup>®</sup> FSD which has the following formula:



where  $x$  is an integer in a range of  $1$  to  $7$ , inclusive. Additionally  
 25 a surfactant containing both fluorine and silicon atoms can work, as  
 well. An exemplary surfactant containing silicon is MEGAFACE<sup>®</sup> R-08  
 mentioned above.

[0051] Although the foregoing has been discussed with respect to  
 having fluorine-containing surfactant components, it is possible to  
 30 employ non-fluorine-containing surfactant components. This is  
 particularly useful when a mixture of surfactant components is  
 employed, wherein one of the surfactant components is fluorine-  
 containing with the remaining surfactant components of the mixture of  
 surfactant components being a non-fluorine-containing surfactant  
 35 and/or a fluorine-containing surfactant. An exemplary mixture of

surfactant components may include one or more of the fluorine-containing surfactant components described above. The remaining surfactant components may be one or more of a siloxane-based-surfactant and/or a hydrocarbon-based-surfactant. Examples of siloxane-based surfactant components are available from Dow Corning of Midland, Michigan under the trade names Q2-5211 and SYLGARD® 309, both of which are trisiloxane-type surfactant components. Siloxane polyether types may be employed, as well.

[0052] Hydrocarbon surfactant components suitable for use in the present invention include any that facilitate providing a composition with low "dynamic" surface tension and/or increasing the solubility of the fluorinated surfactant into the bulk materials. Exemplary hydrocarbon surfactant components are available from BASF of Ontario, Canada under the tradename TETRONIC®, e.g., TETRONIC® 701, which are believed to be tetrafunctional block copolymers of propylene oxide, ethylene oxide, and ethylene diamine. Other hydrocarbon surfactant components are available from Dow Chemical Company of Midland, Michigan under the trade names TERGITOL® and TRITON®, e.g., TERGITOL® NP-10, TRITON® X-100 and TRITON® X-45. The TERGITOL® surfactant components are alkyl polyethylene oxides, and the TRITON® surfactant components are alkyl phenyl polyethylene oxides. Uniqema Americas of New Castle, Delaware also provides suitable hydrocarbon surfactant components containing polyethoxylated alcohols and esters under the tradename BRIJ®, e.g., BRIJ® 30. Acetylenic polyethylene oxide-containing hydrocarbon surfactant components are available from Air Products and Chemicals, Inc. of Allentown, Pennsylvania under the trade names SULFYNOL® and DYNOL®, e.g., SULFYNOL® 104, SULFYNOL® 440, SULFYNOL® 2502, and DYNOL® 604.

[0053] Typically, the composition formed employing the bulk materials mentioned above includes a quantity of surfactant components, or mixture of surfactant components, that is in a range of 0.05% to 5% of the composition by weight, and more particularly 0.25% to 2% by weight. The remaining portion of the composition comprises one or more of the bulk materials, described above. Typically the composition from which the imprinting material is fabricated is applied employing either drop-dispense techniques at room temperatures and in the presence of a helium-purged environment, e.g., a helium-saturated atmosphere. The drop-dispense technique is employed for compositions having viscosities in a range of 1 - 20 cPs at room temperature. For higher viscosity compositions, e.g., in a

range of 10-500,000 cPs, but more particularly, compositions from 10-20,000 cPs, at room temperature, spin-coating techniques may be employed.

5 [0054] To demonstrate the improved preferential adhesion and preferential release provided by the presence of the surfactant components described above in imprinting material, several compositions including the bulk materials and surfactant components described above were tested. Specifically, the following surfactant components were employed:

10

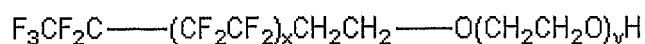
S1  
FC-4430

15 [0055] As mentioned above, the surfactant FC-4430 is available from the 3M Company of St. Paul, Minnesota as the NOVEC<sup>®</sup> Fluorosurfactant FC-4430. The NOVEC<sup>®</sup> FC-4430 fluorosurfactant is a non-ionic acrylic copolymer based fluorochemical surfactant containing perfluorobutane sulfonate (PFBS) segments.

20

S2  
FS-1230

25 [0056] The surfactant FS-1230 is believed to originate from Asahi Glass, in Japan and distributed in the United States of America US by Mason Chemical of Arlington Heights, Illinois under the product name MASURF<sup>®</sup> FS-1230 and has the following general formula:

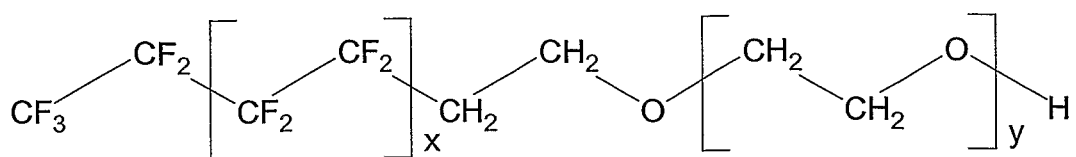


where X and Y are integers. MASURF<sup>®</sup> FS-1230 is a 30% active fluoroaliphatic polyoxyethylene fluorosurfactant in a  
30 water/isopropanol solution. In the experiments that resulted in the data recited below, the water and isopropanol were removed before the surfactant was incorporated into the composition for the imprinting material.

35

S3  
FSO-100

[0057] The surfactant FSO-100 is an ethoxylated nonionic fluorosurfactant that has the following structure:



where x is an integer in a range of 0 to 6, inclusive; and y is an integer in a range of 0 to 15, inclusive.

5

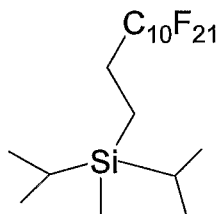
S4  
FC-4432

[0058] As mentioned above, the surfactant FC-4432 is available from the 3M Company of St. Paul, Minnesota as the NOVEC<sup>®</sup> Fluorosurfactant FC-4432. It is a non-ionic polymeric fluorochemical surfactant. The NOVEC<sup>®</sup> FC-4432 fluorosurfactant is based on perfluorobutane sulfonate (PFBS) chemistry.

15

S5  
F021004

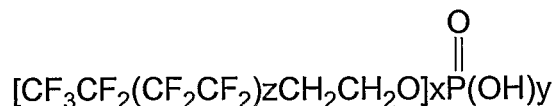
[0059] The component F021004 is a surfactant-like component that is available from Fluorous Technologies, Inc. of Pittsburgh, Pennsylvania. The chemical name is Diisopropyl(1H,1H,2H,2H-perfluorododecyl)silane. The surfactant-like component F021004 has the following structure:



25

S6  
ZONYL<sup>®</sup> UR

[0060] The surfactant ZONYL<sup>®</sup> UR is an anionic phosphate fluorosurfactant available from Dupont of Wilmington, Delaware that has the following structure:



30 where x is an integer having a value of 1 or 2; y is an integer having a value of 2 or 1; Z is an integer having a value in a range of 0 to 6, inclusive, where x+y=3.

S7

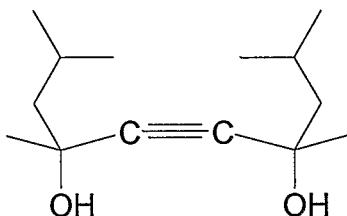
## COMBINATION OF FSO-100 AND R-08

[0061] The surfactant R-08 is a nonionic fluorinated acrylic copolymer based surfactant. As mentioned above, the surfactant R-08 is available from Dainippon Ink & Chemical of Japan under the product name is MEGAFACE® R-08. The combination surfactant S7 is 50% FSO-100 and 50% R-08.

S8

## COMBINATION OF FSO-100 SURFYNOL® 104

[0062] The surfactant SURFYNOL® 104 is an acetylenic hydrocarbon-based surfactant having the chemical name 2,4,7,9-tetramethyl-5-decyne-4,7-diol. The surfactant SURFYNOL® is available from Air Products and Chemicals, Inc. of Allentown, Pennsylvania and has the following structure:



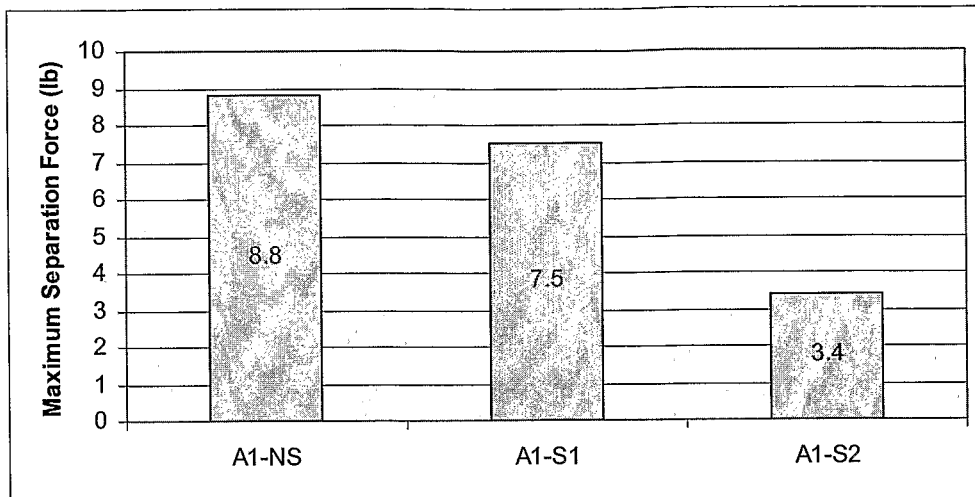
15

The combination surfactant S8 is 50% FSO-100 and 50% SURFYNOL® 104.

[0063] The surfactant components and bulk materials described above were employed to formulate additional compositions to generate comparative data of the preferential adhesion and preferential release properties with respect to the twelve compositions and the eight bulk materials, discussed above. The compositions and/or bulk materials were deposited and then solidified between two glass slides. Each glass slide was approximately 1 mm thick, 75x25 mm in the lateral dimension. Droplets of fluidic imprinting material were disposed on a glass slide; the second slide was laid in a cross direction pattern. The imprinting material was subsequently cured. A four-point bending compression force was applied to separate the slides. To that end, a four-point bending fixture (not shown) was adopted for the adhesion test and technique, similar to that described in "Measurement of Adhesive Force Between Mold and Photocurable Resin in Imprint Technology" Japanese Journal of Applied Physics, Vol.41 (2002) pp. 4194-4197. The maximum force/load was taken as the adhesion value. The beam distance of the top and bottom

two points is 60 mm. The load was applied at the speed of 0.5 mm per minute. The compositions and test results are as follows:

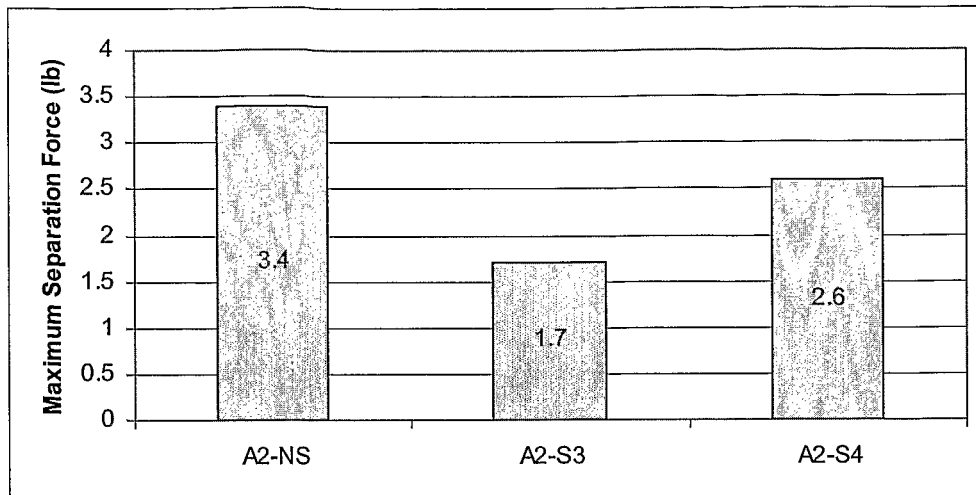
IMPRINTING MATERIALS INCLUDING BULK MATERIAL-A1



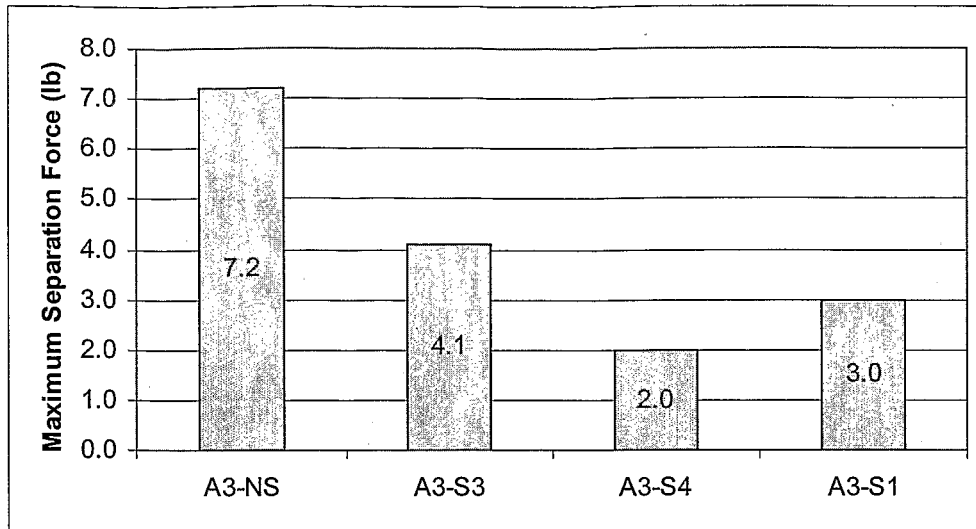
5

[0064] As seen in A1, only 3.4 pounds of separation force is required to separate superimposed glass-slides (not shown) having a cured imprinting material disposed therebetween formed from a composition bulk material A1 and surfactant S2, shown as A1-S2. This is much less than the 7.5 pounds of separation force required to separate cured imprinting material formed from a composition of about 99.5% bulk material A1 and about 0.5% surfactant S1, shown as A1-S1. More telling is the 61% reduction in the separation force realized when compared to the separation force required to separate superimposed glass slides (not shown) having a cured bulk material A1, disposed therebetween, not having a surfactant included therein, shown as A1-NS. The A1-NS, A1-S1 and A1-S2 compositions each have a room temperature viscosity of approximately 8cPs and deposited at room temperature employing drop-dispense techniques. The A1-S2 composition consisted of approximately 99.5% of bulk material A1 and 0.5% of surfactant S2. The A1-S1 composition consisted of approximately 99.5% of bulk material A1 and 0.5% of surfactant S1.

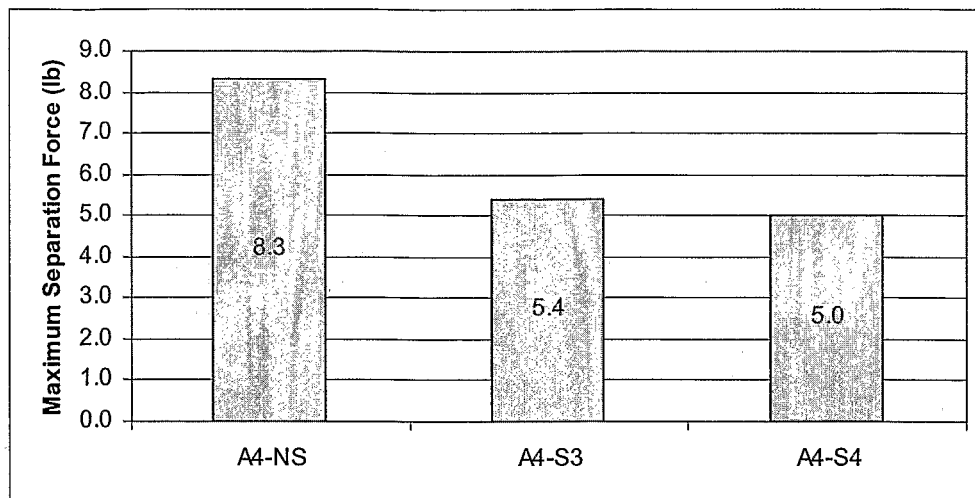
20

IMPRINTING MATERIALS INCLUDING BULK MATERIAL-A2

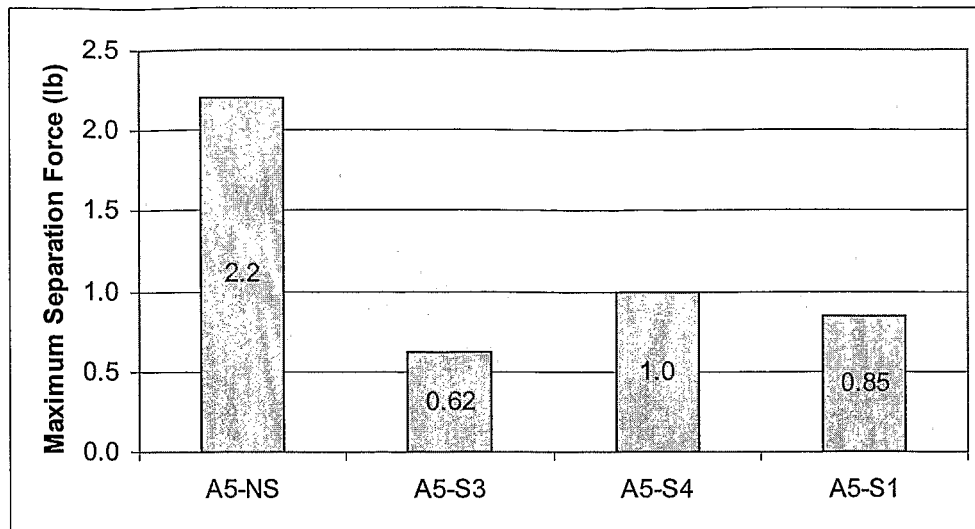
[0065] As seen from the separation data concerning bulk material  
5 A2, 1.7 pounds of separation force was required to separate  
superimposed glass-slides (not shown) having cured imprinting  
material. A composition containing bulk material A2 and surfactant  
S3, shown as A2-S3 was employed to form the cured imprinting  
material. This separation force required is much less than the 2.6  
10 pounds of separation force required in the presence of cured  
imprinting material formed from a composition of bulk material A2 and  
surfactant S4, shown as A2-S4. More telling is the 50% reduction in  
the separation force realized when compared to the separation force  
required to separate superimposed glass slides (not shown) having a  
15 cured bulk material A2, disposed therebetween, in the absences of a  
surfactant, shown as A2-NS. The A2-NS, A2-S3 and A2-S4 compositions  
each has a room temperature viscosity of approximately 300cPs and  
deposited at room temperature employing spin-on techniques. The A2-  
S3 composition consisted of approximately 99.5% of bulk material A2  
20 and 0.5% of surfactant S3. The A2-S4 composition consisted of  
approximately 99.5% of bulk material A2 and 0.5% of surfactant S4.

IMPRINTING MATERIALS INCLUDING BULK MATERIAL-A3

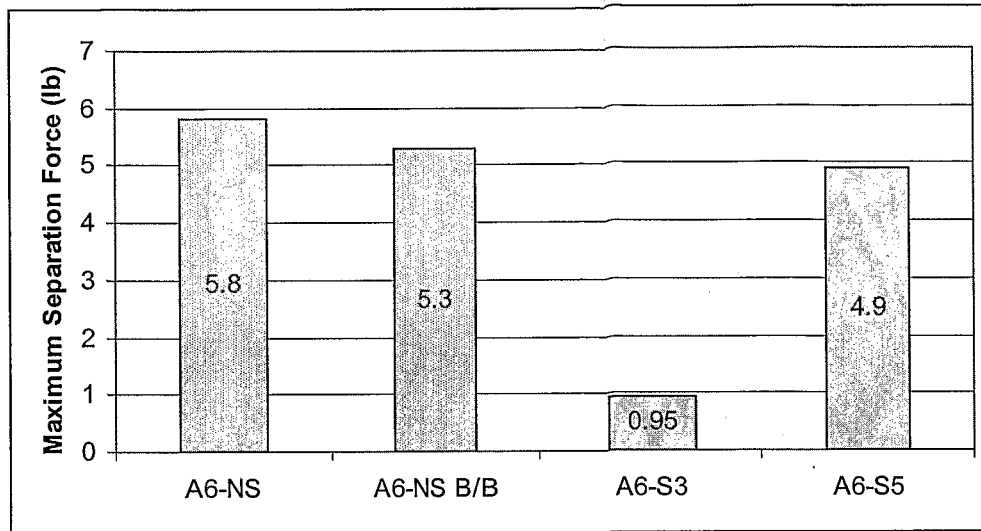
[0066] As seen from the separation data concerning bulk material A3, only 2.0 pounds of separation force was required to separate superimposed glass-slides (not shown) having a cured imprinting material disposed therebetween. The cured imprinting material was formed from a composition containing bulk material A3 and surfactant S4, shown as A3-S4. This is much less than the 3.0 pounds of separation force required in the presence of cured imprinting material formed from composition of bulk material A3 and surfactant S1, shown as A3-S1. The separation force associated with A3-S4 is also less than the separation force required in the presence of cured imprinting material formed from a composition of bulk material A3 and surfactant S3, shown as A3-S3. More telling is the 72% reduction in the separation force realized when compared to the separation force required to separate superimposed glass slides (not shown) having a cured bulk material A3, disposed therebetween, in the absence of a surfactant, shown as A3-NS. The A3-NS, A3-S1, A3-S3 and A3-S4 compositions each has a room temperature viscosity in a range of approximately 10,000 to 12,000 cPs, inclusive, and deposited at room temperature employing spin-on techniques. The A3-S1 composition consisted of approximately 99.5% of bulk material A3 and 0.5% of surfactant S1. The A3-S3 composition consisted of approximately 99.5% of bulk material A3 and 0.5% of surfactant S3. The A3-S4 composition consisted of approximately 99.5% of bulk material A3 and 0.5% of surfactant S4.

IMPRINTING MATERIALS INCLUDING BULK MATERIAL-A4

[0067] As seen from the separation data concerning bulk material A4, the reduction of forces required for separating the superimposed glass-slides (not shown) having a cured composition disposed therebetween containing bulk material A4 and surfactant S4, shown as A4-S4, required only 5.0 pounds. This is less than the 5.4 pounds of separation force required for a composition of bulk material A4 and surfactant S3, shown as A4-S3. More telling is the 40% reduction in the separation force realized when compared to the separation force required to separate superimposed glass slides (not shown) having a cured bulk material A4, disposed therebetween, in the absence of a surfactant, shown as A4-NS. The A4-NS, A4-S3 and A4-S4 compositions each has a room temperature viscosity approximately 5,000cPs and deposited at room temperature employing spin-on techniques. The A4-S1 composition consisted of approximately 99.5% of bulk material A4 and 0.5% of surfactant S1. The A4-S3 composition consisted of approximately 99.5% of bulk material A4 and 0.5% of surfactant S3. The A4-S4 composition consisted of approximately 99.5% of bulk material A4 and 0.5% of surfactant S4.

IMPRINTING MATERIALS INCLUDING BULK MATERIAL-A5

[0068] As seen from the separation data concerning bulk material A5, only 0.62 pounds of separation force is required for separating the superimposed glass-slides (not shown) having a cured imprinting material disposed therebetween. The cured imprinting material was formed from a composition of bulk material A5 and surfactant S3, shown as A5-S3. This is less than the separation force required for cured imprinting material formed from a composition of either bulk material A5 and surfactant S1, shown as A5-S1 or bulk material A5 and surfactant S4, shown as A5-S4. More telling is the 72% reduction in the separation force realized when compared to the separation force required to separate superimposed glass slides (not shown) having a cured bulk material A5, disposed therebetween, in the absence of a surfactant, shown as A5-NS. The A5-NS, A5-S1, A5-S3 and A5-S4 compositions each has a room temperature viscosity in a range of approximately 20 to 30 cPs, inclusive, and deposited at room temperature employing spin-on techniques. The A5-S1 composition consisted of approximately 99.5% of bulk material A5 and 0.5% of surfactant S1. The A5-S3 composition consisted of approximately 99.5% of bulk material A5 and 0.5% of surfactant S3. The A5-S4 composition consisted of approximately 99.5% of bulk material A5 and 0.5% of surfactant S4.

IMPRINTING MATERIALS INCLUDING BULK MATERIAL-A6

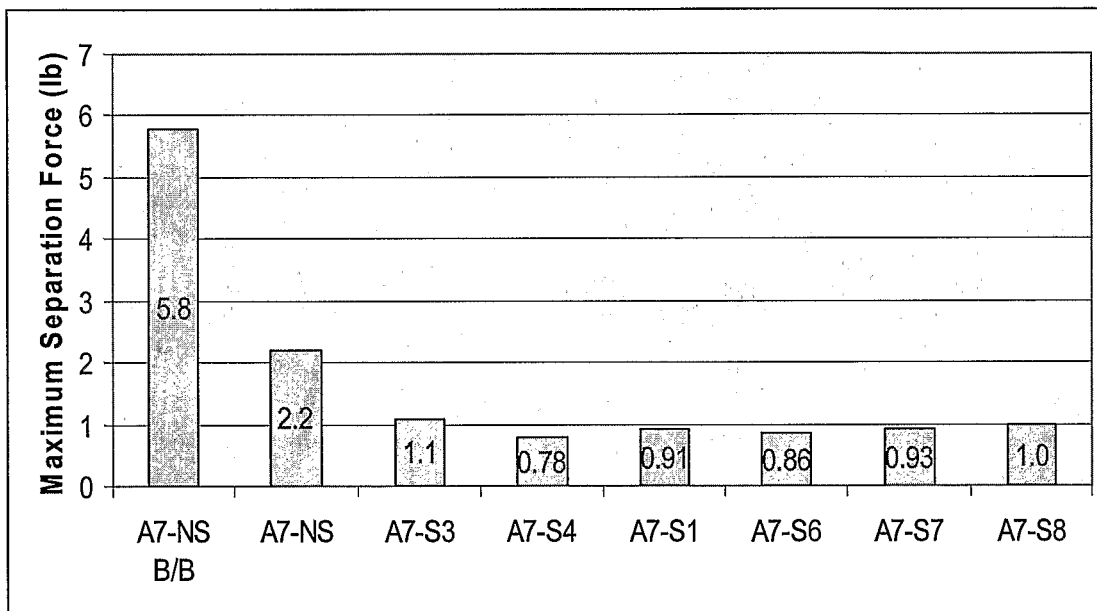
[0069] The separation force data concerning bulk material A6 in the absence of a surfactant being cured between two superimposed transfer layers is shown as A6-NS B/B. Specifically, each of two superimposed glass slides (not shown) has a layer of DUV30J formed thereon. DUV30J is available from Brewer Science, Inc. of Rolla, Missouri. It is desired that the cured bulk material A6 adheres well to the transfer layer (not shown) and easily releases from the surface of an imprint template (not shown). Also shown is the separation force data concerning bulk material A6 in the absence of a surfactant with respect to being cured between two superimposed glass slides (not shown) having no previous layer thereon, shown as A6-NS.

[0070] As seen for the separation data concerning bulk material A6, the separation force required for separating the superimposed glass-slides (not shown), without the aforementioned transfer layer being present and having a cured composition disposed therebetween containing bulk material A6 and surfactant S3, shown as A6-S3, required only 0.95 pounds. This is less than the pounds of separation force required for a composition of bulk material A6 and surfactant S5, shown as A6-S5 or the separation forces required for A6-NS B/B. More telling is the 84% reduction in the separation force realized when compared to the separation force required to separate superimposed glass slides (not shown) having a cured bulk material A6-NS.

[0071] The data suggests that selective adhesion has been achieved. Although S3 and S5 have perfluoro-hydrophobic groups, S3 appears to be much more efficient in reducing the adhesion than S5.

It is believed, therefore, that structure variations of the fluorinated additives will have significant impacts on the release performance. For example, S3 has a surfactant molecule that contains both a hydrophobic tail and a hydrophilic head, which as shown provides desirable release characteristics. The A6-NS, A6-S3 and A6-S5 compositions have a room temperature viscosity of approximately 4cPs and deposited at room temperature employing drop-dispense techniques. The A6-S3 composition consisted of approximately 99.5% of bulk material A6 and 0.5% of surfactant S3. The A6-S5 composition consisted of approximately 99.5% of bulk material A6 and 0.5% of surfactant S5.

IMPRINTING MATERIALS INCLUDING BULK MATERIAL-A7



[0072] The separation force data concerning bulk material A7 in the absence of a surfactant being cured between two superimposed transfer layers is shown as A7-NS B/B. Specifically, each of two superimposed glass slides (not shown) has a layer of DUV30J formed thereon, as discussed above. Also shown is the separation force data concerning bulk material A7 in the absence of a surfactant with respect to being cured between two superimposed glass slides (not shown) having no previous layer thereon, shown as A7-NS. As is expected from a review of the previous data, the presence of surfactant components provides greatly improved release properties for compositions imprinting material including bulk material A7. Also demonstrated is the success of combination surfactant components, such as S7 and S8, in reducing the separation force

required. The A7-NS, A7-S1, A7-S3, A7-S4, A7-S5, A7-S6, A7-S7 and A7-S8 compositions each has a room temperature viscosity of approximately 4 cPs and deposited at room temperature employing drop-dispense techniques. The A7-S1 composition consisted of  
5 approximately 99.5% of bulk material A7 and 0.5% of surfactant S1. The A7-S3 composition consisted of approximately 99.5% of bulk material A7 and 0.5% of surfactant S3. The A7-S4 composition consisted of approximately 99.5% of bulk material A7 and 0.5% of surfactant S4. The A7-S5 composition consisted of approximately  
10 99.5% of bulk material A7 and 0.5% of surfactant S5. The A7-S6 composition consisted of approximately 99.5% of bulk material A7 and 0.5% of surfactant S6. The A7-S7 composition consisted of approximately 99.5% of bulk material A7 and 0.5% of surfactant S7. The A7-S8 composition consisted of approximately 99.5% of bulk  
15 material A7 and 0.5% of surfactant S8.

[0073] Referring to Fig. 2, one consideration with providing surfactants is that introduction of the same into imprinting material may increase the time required to fill the features of mold 36. As mentioned above, layer 70 is formed on surface 58 that results from  
20 contact with the imprinting material. The release properties provided by the surfactants result from the hydrophobicity of the same, which conflict with the wetting characteristics that are desired to rapidly cover the features of mold 36. Specifically, it is believed that, in the case of surfactants that include fluorine-  
25 atoms within a molecule, too great a quantity of the fluorine atoms within a molecule and coupling with too great a quantity of the fluorine-containing molecules results in the generation of clusters of fluorine-containing molecules. These clusters, especially with CF<sub>3</sub> end groups extending from the air-liquid interface, is believed  
30 to provide layer 70 with an undesirable hydrophobicity profile that may substantially affect the wetting characteristics of the imprinting material with respect to surface 58.

[0074] It is believed that by appropriately distributing the fluorine atoms within a surfactant molecule, as well as the  
35 distribution of the fluorine-containing molecules throughout the volume of layer 70, and therefore, referred to collectively as the distribution of the fluorine atoms throughout the volume, an acceptable hydrophobicity profile may be achieved. Upon achieving the desired distribution of fluorine atoms within a surfactant  
40 molecule and fluorine-containing molecules in layer 70, lamella layer

60 is provided with an optimum fluorine density to provide the desired preferential release and adhesion, without unduly limiting the wettability of surface 58 by the imprinting material. As a result satisfactory fill and release properties are provided to the imprint process. This typically occurs upon lamella layer 60 having a thickness of approximately 1nm.

[0075] One manner, in which to determine that the desired distribution of fluorine atoms within a surfactant molecule and fluorine-containing molecules are present involves measuring the contact angle of the imprinting material in contact with surface 58. To that end, a goniometer is used for contact angle measurement. Molds 56 formed from fused silica were cleaned in a piranha solution and stored in a nitrogen purged environment. The piranha solution consisted of a mixture of 2 parts concentrated  $H_2SO_4$  and 1 part  $H_2O_2$  mixed at room temperature. Mold 36 is then rinsed with a surfactant component Isopropyl Alcohol (IPA) mixture, e.g., the IPA mixture contained 0.01% of the surfactant component with the remainder consisting essential of IPA. After the rinse, mold 36 was subjected to a stream of nitrogen fluid, e.g., nitrogen gas, to blow-dry the same. Once again, mold 36 was exposed to the same IPA mixture and then dried by exposure to the nitrogen fluid stream. Droplets of imprinting material were then deposited upon mold 36 in volumes of in a range of 2  $\mu l$  to 5  $\mu l$ , approximately. Measured is the contact angle of several different droplets located at various locations over surface 58. In the present example contact angle measurements are made corresponding to 7 different locations on mold 36, using the goniometer. An average value of the seven contact angle measurements are made to obtain the final contact angle values. Considering that layer 70 is replenished each time the same contacts imprinting material on substrate, the foregoing experiment is believed to be an accurate determination of the relative wetting properties of differing imprinting material compositions.

[0076] The contact angle, surfactant treatment solution, and filling performance are shown below

Wettability Characteristics for Bulk Material A7-1

| Surfactant    | FSO-100 | FC-4430 &<br>FC-4432 | FC-4430&<br>R-08 | R-08  | R-08 &<br>FS-1230 |
|---------------|---------|----------------------|------------------|-------|-------------------|
| Contact Angle | 43.2°   | 20.2°                | 13.8°            | 17.3° | 22.7°             |

Bulk material A7-1 is identical to BULK MATERIAL-A7 in terms of the identity of the constituent components, excepting the addition of a surfactant component. The two materials differ in terms of the percentage of each of the constituent components present. In Bulk Material A7-1, approximately 46.875% of the composition by weight is IBOA, 24.875% of the composition by weight is nHA, 24.875% of the composition by weight is EGDA, 2.875% of the composition by weight is Darocur 1173; and approximately 0.5% of the composition being a surfactant component. Specifically, with 0.5% of the Bulk Material A7-1 consisting of the surfactant FSO-100, the least desirable wettability characteristics are provided. The contact angle is the greatest at 43.2°. Compare the contact angle of 13.8° provided upon Bulk Material A7-1 consisting of 0.5% of the combination surfactant R-08 and FC-4430, wherein R-08 and FC-4430 each comprises 0.25% of Bulk Material A7-1. As a result, the time required to fill the features of mold 36 is less for layer 70 including combination surfactant R-08 and FC-4430 than for layer 70 including FSO-100. For the remaining measurements, a contact angle of approximately 20.2° when the combination surfactant FC-4430 and FC-4432 included in the Bulk Material A7-1 wherein FC-4430 comprises approximately 0.333% of the composition by weight and FC-4432 comprises approximately 0.167% of the composition by weight. Another surfactant combination consisting of R-08 and FS-1230 presented a contact angle of approximately 22.7°, in which R-08 comprised of approximately 0.4% by weight of Bulk Material A7-1, by weight, and FS-1230 comprised of approximately 0.1% of Bulk Material A7-1, by weight.

Wettability Characteristics for Bulk Material A8-1

| Surfactant    | FSO-100 | FC-4432 | FC-4430 | FS-2000 | R-08  | S-222N |
|---------------|---------|---------|---------|---------|-------|--------|
| Contact Angle | 49.7°   | 26.5°   | 17.2°   | 21.4°   | 18.2° | 19.2°  |

Bulk material A8-1 is identical to BULK MATERIAL-A8 in terms of the identity of the constituent components, excepting the addition of a surfactant component. The two materials differ in terms of the percentage of each of the constituent components present. In Bulk Material A8-1, approximately 20.875% of the composition by weight is the acrylate component Genomer 1122 and 55.875% of the composition by weight is IBOA. The acrylate component HDODA is approximately 19.875% by weight, and Darocur 1173 is approximately 2.875% of the composition by weight. The remaining 0.5% of the composition is a

surfactant component. Specifically, with 0.5% of the Bulk Material A8-1 consisting of FSO-100, the least desirable wettability characteristics are provided. The contact angle is the greatest at 49.7°. Compare the contact angle of 17.2° provided upon Bulk

5 Material A8-1 consisting of 0.5% of the surfactant FC-4430. As a result, the time required to fill the features of mold 36 is less for layer 70 including surfactant FC-4430 than for layer 70 including FSO-100. For the remaining measurements, a contact angle of approximately 18.2° was presented when the R-08 surfactant is

10 included in Bulk Material A8-1. With surfactant S-222N included in Bulk Material A8-1 a contact angle of 19.2 ° is presented, and a contact angle of 21.4° is presented when the surfactant FS-2000 is included in Bulk Material A8-1. A contact angle of 26.5° is presented when surfactant FC-4432 is included in Bulk Material A8-1.

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[0077] It should be understood that similar benefits of preferential adhesion and release with desirable wettability characteristics may be achieved by varying the surfactant composition on mold 36 or in the bulk material or both. For example, increasing

20 the surfactant concentration in bulk material A8-1 to 0.7% of the composition by weight with 0.2% comprising Tergitol NP-10 and 0.5% being FS-2000 presented the second best wetting characteristics evidenced by a contact angle of approximately 17.4°. It should be noted that for this measurement, about .012% of the IPA mixture, mentioned above, consisted of the surfactant mixture FS-2000 and

25 Tergitol NP-10, instead of 0.01% of the solution. In this example, a surfactant mixture is employed in which fluorine-containing and non-fluorine-containing surfactants are employed. Tergitol NP-10 is a hydrocarbon surfactant that has a faster dynamic speed than

30 fluorinated surfactants, such as FS-2000.

[0078] Additionally, the surfactant composition may be modified by employing a differing surfactant in layer 70 than is included in the imprinting material that is contacted by the mold. For example,

35

## Bulk Material A7-2

| Surfactant    | FC-4430 | FC-4432 | FC-4430 | R-08  | FC-4430 & FC-4432 | R-08 & FC-4430 |
|---------------|---------|---------|---------|-------|-------------------|----------------|
| Contact Angle | 43.2°   | 26°     | 18.1°   | 20.0° | 22°               | 14.7°          |

[0079] Bulk material A7-2 includes all of the constituent components of material A7-1 and includes a surfactant FSO-100. In Bulk Material A7-2, approximately 46.875% of the composition by weight is IBOA, 24.875% of the composition by weight is nHA, 24.875% of the composition by weight is EGDA, 2.875% of the composition by weight is Darocur 1173; and approximately 0.5% of which is FSO-100. Specifically, surface 58 coated with the IPA mixture including FSO-100, the least desirable wettability characteristics are provided, with the contact angle being the greatest at 43.2°. With surface 58 coated with the combination surfactant R-08 and FC-4430, each of which is comprised of 0.5% of the IPA mixture, that contact angle presented is 14.7%. For the remaining measurements, a contact angle of approximately 18.1° is presented when surface 58 is coated with the FC-4430 surfactant, and a contact angle of approximately 20° is present when surface 58 is coated with the R-08 surfactant. When surface 58 is coated with a combination surfactant that includes FC-4430 and FC-4432 is deposited in layer 70, a contact angle of approximately 22° is presented. FC-4430 comprises 0.333% of the IPA mixture and FC-4432 and comprises 0.167% of the IPA mixture, by weight. When surface 58 is coated with FC-4432, absent any other surfactant, a contact angle of approximately 26.0° is presented. As can be seen, therefore, by properly selecting the surfactant component in each of the bulk materials, the desired wetting characteristics may be obtained, along with the desired preferential adhesion and release characteristics.

[0080] The embodiments of the present invention described above are exemplary. Many changes and modifications may be made to the disclosure recited above, while remaining within the scope of the invention. The scope of the invention should, therefore, be determined not with reference to the above description, but instead should be determined with reference to the appended claims along with their full scope of equivalents.

WHAT IS CLAIMED IS:

1. A method of providing desirable wetting and release characteristics between a mold, having a surface, and a polymerizable composition, said method comprising:
  - 5 coating said surface with a volume of surfactant containing solution, with said surfactant including a hydrophobic component consisting essentially of a plurality of atoms, with a distribution of said fluorine atoms throughout said volume providing a desired contact angle with respect to said polymerizable  
10 composition.
  2. The method as recited in claim 1 wherein coating further includes distributing said plurality of fluorine atoms throughout said volume to provide said contact angle with a magnitude  
15 that is less than 50°.
  3. The method as recited in claim 1 wherein coating further includes distributing said fluorine atoms throughout said volume to provide said contact angle with a magnitude that is less  
20 than 20°.
  4. The method as recited in claim 1 wherein coating further includes arranging said volume of said surfactant-containing-solution to have a surfactant-rich region and a surfactant-depleted  
25 region, disposed between said surfactant-rich-region and said surface.
  5. The method as recited in claim 1 wherein coating further includes depositing a quantity of said surfactant-containing-solution on said surface and contacting said polymerizable  
30 composition with said quantity to generate said volume.
  6. The method as recited in claim 1 wherein coating further includes depositing a quantity of said surfactant-containing-solution on said surface and contacting said polymerizable  
35 composition with said quantity to generate said volume to have a surfactant-rich region and a surfactant-depleted region, disposed between said surfactant-rich-region and said surface.

7. The method as recited in claim 1 wherein said surfactant-containing solution and said polymerizable composition are formed from the same constituent components.

5 8. The method as recited in claim 1 wherein said surfactant-containing solution and said polymerizable composition are formed from differing constituent components.

10 9. The method as recited in claim 1 wherein said plurality of fluorine atoms are included in fluorine-containing molecules having  $\text{CF}_3$  and  $\text{CF}_2$  groups.

10. A method of reducing adhesion forces between a substrate and a mold, said method comprising:  
15 locating imprinting material between said mold and said substrate, with said imprinting material being bifurcated into a surfactant-component-rich sub-portion and a surfactant-component-depleted sub-portion located between said surfactant-component-rich sub-portion and said substrate.

20 11. The method as recited in claim 10 wherein locating said imprinting material further includes depositing a composition that forms an air-liquid interface, said composition including a surfactant component, having opposed ends, and a bulk material, with  
25 one of said opposed ends having an affinity for said bulk material and the remaining end having a fluorine component and further including orientating a sub-portion of said composition so that said fluorine component extends from said air-liquid interface.

30 12. The method as recited in claim 10 wherein locating said imprinting material further includes depositing a plurality of droplets of a composition including a bulk material and a surfactant component.

35 13. The method as recited in claim 10 wherein locating said imprinting material further includes spin-coating, onto said substrate, a composition including a bulk material and a surfactant component.

14. The method as recited in claim 10 further including solidifying said imprinting material to form a solidified formation and a lamella disposed between said mold and said solidified formation.

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15. The method as recited in claim 10 further including fabricating said mold from a material selected from a set of materials consisting essentially of fused-silica, quartz, indium tin oxide diamond-like carbon, MoSi and sol-gels.

10

16. A composition defining an air-liquid interface, said composition comprising:

a polymerizable bulk material; and

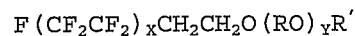
15 a surfactant component, having opposed ends, one of which has an affinity for said bulk material and the remaining end having a fluorine component.

17. The composition as recited in claim 16 wherein said fluorine component extends from said air-liquid interface.

20

18. The composition as recited in claim 16 wherein said surfactant component is selected from a set of surfactants consisting essentially of ionic, non-ionic, cationic and zwitterionic.

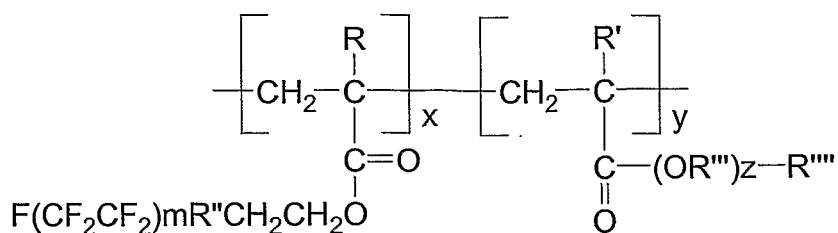
25 19. The composition as recited in claim 16 wherein said surfactant component has the following formula:



30 where  $(RO)_Y$  is a poly(oxyalkylene) group, that includes groups having two to four carbon atoms such as  $-CH_2CH_2-$ ,  $-CH_2CH_2CH_2-$ ,  $-CH(CH_3)CH_2-$ , or  $-CH(CH_3)CH(CH_3)-$ , and  $R'$  is a terminal group of H or  $C_1$  to  $C_4$  alkyl, preferably H or methyl and X and Y are integers.

35

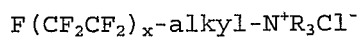
20. The composition as recited in claim 16 wherein said surfactant component has the following structure:



where the ratio of x to y is in a range of 1:2 to 3:1.

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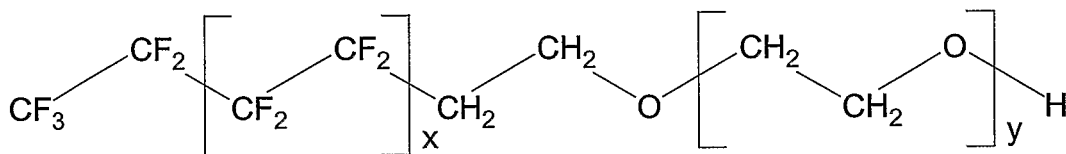
21. The composition as recited in claim 16 wherein said surfactant component has the following structure:



where X is an integer in a range of 1 to 7, inclusive.

10

22. The composition as recited in claim 16 wherein said surfactant component has the following structure:

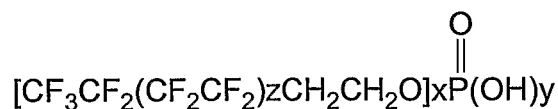


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where x is an integer in a range of 0 to 6, inclusive; and y is an integer in a range of 0 to 15, inclusive.

23. The composition as recited in claim 16 wherein said surfactant component has the following structure:

20



where x is an integer having a value of 1 to 2; y is an integer having a value of 2 to 1; Z is an integer having a value in a range of 0 to 6, inclusive.

25

24. The composition as recited in claim 16 wherein said surfactant includes fluorine and silicon atoms.

25. The composition as recited in claim 16 wherein said surfactant component consists of a mixture of a fluorine-containing surfactant and an additional surfactant, with said additional surfactant being selected from a set of surfactants consisting  
5 essentially of a siloxane-based-surfactant, a hydrocarbon-based-surfactant and a fluorinated surfactant.