CLAIMS

What is claimed is:

1. A photoacid generator (PAG)-free resist composition comprising:

(A) a phenolic resin component, wherein the phenolic resin component is a Novolak derivative comprising:

(i) Novolak repeat units with free phenolic hydroxy moieties and

(ii) Novolak repeat units having phenolic hydroxy moieties protected with an acid cleavable acetal moiety, wherein the acid cleavable acetal moiety is one or more of:

(a) a monofunctional alkyl acetal moiety,

(b) an acetal moiety functionalized with a photoactive non-sulfonic acid generating photoactive diazonaphthoquinonesulfonate (PAC) component comprising a 2,1,5 diazonaphthoquinonesulfonate moiety, or a derivative thereof,

(c) a di-functional linking acetal moiety protecting a hydroxy moiety on each of two different Novolak polymer chains;

(B) a photoactive non-sulfonic acid generating photoactive (PAC) component comprising 2,1,5 diazonaphthoquinonesulfonate moiety or a derivative thereof,

wherein the PAC component is one or more of:

(i) the acetal moiety functionalized with a PAC moiety, and

(ii) a free PAC component; and

(C) a solvent component,

wherein the composition is free of added photoacid generators (PAGs).

2. The composition of claim 1 consisting of:

(A) a phenolic resin component, wherein the phenolic resin component is a Novolak derivative comprising:

(i) Novolak repeat units with free phenolic hydroxy moieties and

(ii) Novolak repeat units having phenolic hydroxy moieties protected with an acid cleavable acetal moiety, wherein the acid cleavable acetal moiety is one or more of:

(a) a monofunctional alkyl acetal moiety,

(b) an acetal moiety functionalized with a PAC moiety,

(c) a di-functional linking acetal moiety protecting a hydroxy moiety on each of two different Novolak polymer chains;

(B) photoactive non-sulfonic acid generating photoactive (PAC) component comprising a 2,1,5 diazonaphthoquinonesulfonate moiety, or a derivative thereof,

wherein the PAC component is one or more of:

(i) said acetal moiety functionalized with a photoactive non-sulfonic acid generating photoactive 2,1,5-diazonaphthoquinonesulfonate (PAC), and

(ii) a free PAC component; and

(C) a solvent component,

wherein the composition is free of added photoacid generators (PAGs).

3. The composition of claims 1 to 2, wherein the phenolic resin component comprises at least two repeat units selected from structures (I), (II), (III), (IV), (V) and (VI), preferably a repeat unit of structure (I) and at least one repeat unit selected from structures (II), (III), (IV), (V) and (VI): wherein (i) Ra, Rc, Rg, Rk, Rn and Rp are each independently a C-1 to C-4 alkyl,

(ii) Rb, Rd, Rh, Rl, Ro, and Rq are each independently a -X-Phenol where X is -O- , $-C(CH_3)_2-$, -(C=O)- or $-SO_2-$,

(iii) na, nc, ng, nk, nn and np are each independently 0 to 3, the sum of na and nb, the sum of nc and nd, the sum of ng and nh, the sum of nk and nl, the sum nn of no, the sum of np and nq and each respectively does not exceed 3, (vi) Re, Rf, Ri, Rm, Rm2, and Rr are each independently selected from a C-1 to C-4 alkyl,

(vii) the repeat units having structures (III) is attached to either the repeat unit of structure (IV) or the repeat unit of structure (V) through the positions designated by "∿∿∿" thereby forming a di-functional acetal moiety providing a linking point in the phenolic resin component between two different polymer chains,

(viii) Xa is an alkylene, an -alkyleneoxyalkylene- moiety or an $-alkylene(-O-alkylene)_{x'}-$ moiety where x' is 2 to 6

(viv) Xb is -O-, $-C(CH_3)_2-$, -(C=O)- or $-SO_2$,

(vv) Xc is an alkylene, an -alkyleneoxyalkylene- moiety or an $-alkylene(-O-alkylene)_{x'}-$ moiety where x' is 2 to 6

(vvi) the PACb moiety is a PAC component in the repeat unit having structure (VI) attached through a linking group Xd, wherein Xd is selected from the group consisting of:

a) a direct valence bond,

b) an alkylene moiety,

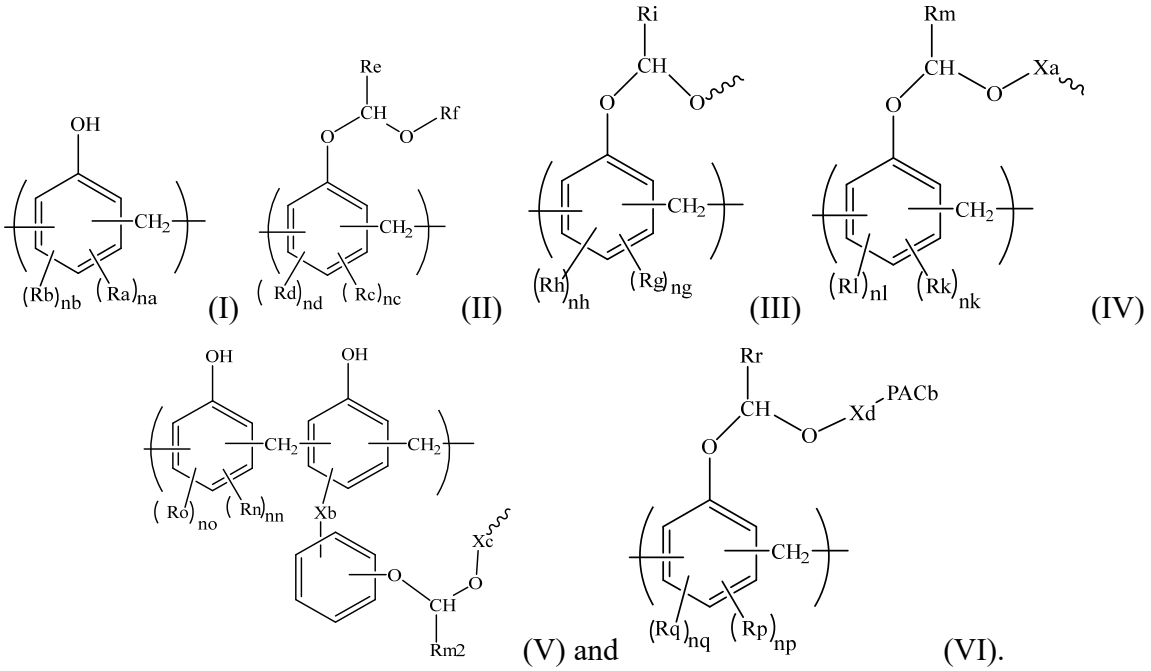
c) an alkyleneoxy moiety where an alkylene end is attached to an acetal oxygen moiety of the repeat unit of structure (VI) and an oxy end of the alkyleneoxy moiety is attached to the PACb moiety, and

d) a moiety comprising an acetal selected from the group consisting of

i) an alkyleneacetal moiety (-alkylene-O-CH(CH_3)-O-),

ii) an alkyleneoxyalkyleneacetal moiety (-alkylene-O-alkylene-O-CH(CH_3)-O-), and

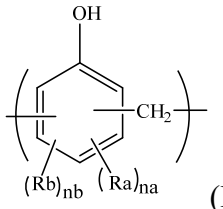
iii) an alkylene(oligooxyalkylene)acetal moiety (-alkylene (-O-alkylene)$_x$-O-CH(CH_3)-O-) where x is 2 to 6, and further wherein, the alkylene end of said moiety comprising an acetal is attached to the acetal oxygen moiety of the repeat unit of structure (VI), and the acetal portion of said moiety comprising an acetal is attached to the PACb moiety;



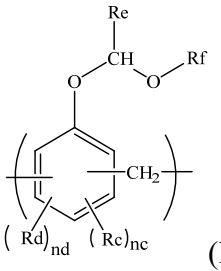
4. The composition of claim 3, wherein the phenolic resin component comprises repeat units having structures (I) and (II) and

wherein (i) Ra and Rc are each independently a C-1 to C-4 alkyl, (ii) Rb and Rd are each independently a -X-Phenol where X is -O-, -C(CH_3)$_2$-, -(C=O)- or -SO_2-, (iii) na and nc are each independently 0 to 3, (iv) nb and nd are each independently 0 or 1, (v) the sum of na and nb and the sum of nc and nd

each respectively does not exceed 3 and (vi) Re and Rf are each independently selected from a C-1 to C-4 alkyl;

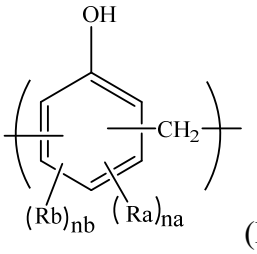


(I)

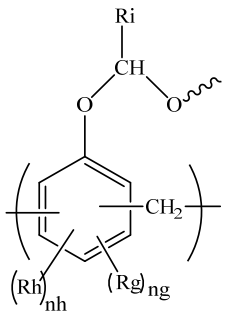


(II).

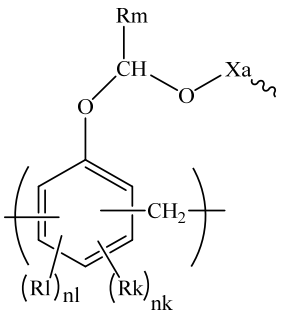
5. The composition of claim 3, wherein the phenolic resin component comprises repeat units having structures (I), (III) and (IV) where the repeat units having structures (III) and (IV) are attached together through the positions designated by "∿∿∿" thereby forming a di-functional acetal moiety providing a linking point in the phenolic resin component between two different polymer chains and wherein (i) Ra, Rg and Rk are each independently a C-1 to C-4 alkyl, (ii) Rb, Rh, and Rl are each independently a -X-Phenol where X is -O-, -$C(CH_3)_2$-, -(C=O)- or -SO_2-, (iii) na, ng and nk are each independently are 0 to 3, (iv) nb, nh and nl are each independently 0 or 1, (v) the sum of na and nb, the sum of ng and nh and the sum of nk and nl each respectively does not exceed 3, (vi) Ri and Rm are each independently selected from a C-1 to C-4 alkyl, (vii) Xa is an alkylene, an -alkyleneoxyalkylene- moiety or an -alkylene(-O-alkylene)$_{x'}$- moiety where x' is 2 to 6;



(I)



(III)

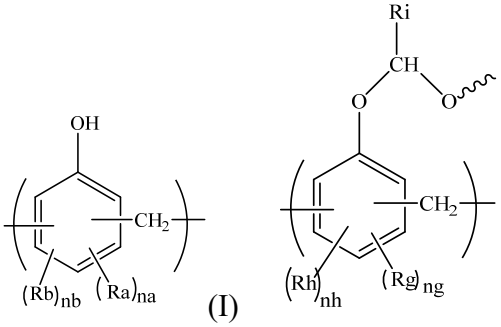


(IV).

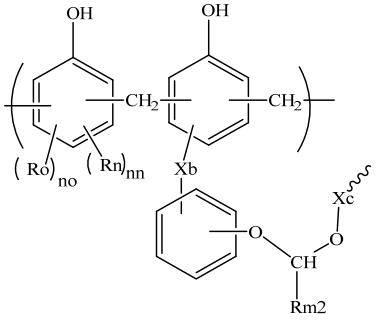
6. The composition of claim 3, wherein the phenolic resin component comprises repeat units having structures (I), (III) and (V), wherein

the repeat units having structures (III) and (V) are attached together through the positions designated by "∿∿∿" thereby forming a di-functional acetal moiety providing a linking point in the phenolic resin component between two different polymer chains, and

(i) Ra, Rg and Rn are each independently a C-1 to C-4 alkyl, (ii) Rb, Rh and Ro are each independently a -X-Phenol where X is -O-, -$C(CH_3)_2$-, -(C=O)- or -SO_2-, (iii) na, ng, and nn are each independently 0 to 3, (iv) nb, nh and no are each independently 0 or 1, (v) the sum of na and nb, the sum of ng and nh and the sum of nn and no each respectively does not exceed 3, (vi) Ri and Rm2 are each independently selected from a C-1 to C-4 alkyl, (vii) Xb is -O-, -$C(CH_3)_2$-, -(C=O)- or -SO_2, (viii) Xc is an alkylene, an -alkyleneoxyalkylene- moiety or an -alkylene(-O-alkylene)$_{x'}$- moiety where x' is 2 to 6;


(I)

(III)


(V).

7. The composition of claim 3, wherein the phenolic resin component comprises repeat units having structures (I), (II)and (VI), wherein

(i) Ra, Rc and Rp are each independently a C-1 to C-4 alkyl, (ii) Rb, Rd, and Rq are each independently a -X-Phenol where X is -O- , -$C(CH_3)_2$-, -(C=O)- or -SO_2-, (iii) na, nc and np are each independently 0 to 3, (iv) nb, nd and nq are each independently 0 or 1, (v) the sum of na and nb (*i.e.*, na + nb), the sum of nc and nd (*i.e.*, nc + nd) and the sum of np and nq (*i.e.*, np + nq) each respectively does not exceed 3, (vi) Re, Rf and Rr are each independently selected from a C-1 to C-4 alkyl, (vii) the PACb moiety is a PAC component in the repeat unit having structure (VI) attached through a linking group Xd, wherein Xd is selected from the group consisting of:

a) a direct valence bond,

b) an alkylene moiety,

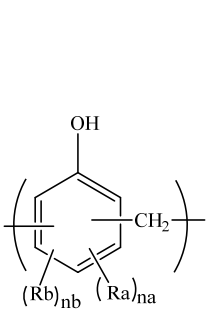
c) an alkyleneoxy moiety where an alkylene end is attached to an acetal oxygen moiety of the repeat unit of structure (VI) and an oxy end of the alkyleneoxy moiety is attached to the PACb moiety, and

d) a moiety comprising an acetal selected from the group consisting of

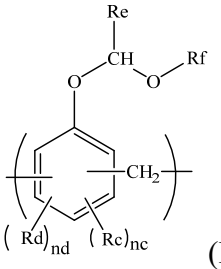
i) an alkyleneacetal moiety (-alkylene-O-$CH(CH_3)$-O-),

ii) an alkyleneoxyalkyleneacetal moiety (-alkylene-O-alkylene-O-$CH(CH_3)$-O-), and

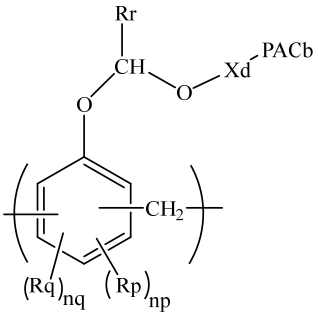
iii) an alkylene(oligooxyalkylene)acetal moiety (-alkylene (-O-alkylene)$_x$-O-CH(CH_3)-O-) where x is 2 to 6, and further wherein, the alkylene end of said moiety comprising an acetal is attached to the acetal oxygen moiety of the repeat unit of structure (VI), and the acetal portion of said moiety comprising an acetal is attached to the PACb moiety;



(I)



(II)



(VI).

8. The composition of claim3, wherein the phenolic resin component comprises repeat units having structures (I), (III), (IV) and (VI) wherein,

the repeat units having structures (III) and (IV) are attached together through the positions designated by "∿∿∿" thereby forming a di-functional acetal moiety providing a linking point in the phenolic resin component between two different polymer chains and wherein,

(i) Ra, Rg, Rk and Rp are each independently a C-1 to C-4 alkyl, (ii) Rb, Rh, Rl and Rq are each independently a -X-Phenol where X is -O-, -C(CH_3)$_2$-, -(C=O)- or -SO_2-, (iii) na, ng, nk and np are each independently 0 to 3, (iv) nb, nh, nl and nq are each independently 0 or 1, (v) the sum of na and nb, the sum of nh and ng, the sum of nl and nk and the sum of np and nq each respectively does not exceed 3, (vi) Ri Rm and Rr are each independently selected from a C-1 to C-4 alkyl and (vii) Xa is an alkylene, an -alkyleneoxyalkylene- moiety or an -alkylene(-O-alkylene)$_{x'}$- moiety where x' is 2 to 6 (viii) the PACb moiety is a PAC component in the repeat unit having structure (VI) attached through a linking group Xd, wherein Xd is selected from the group consisting of:

a) a direct valence bond,

b) an alkylene moiety,

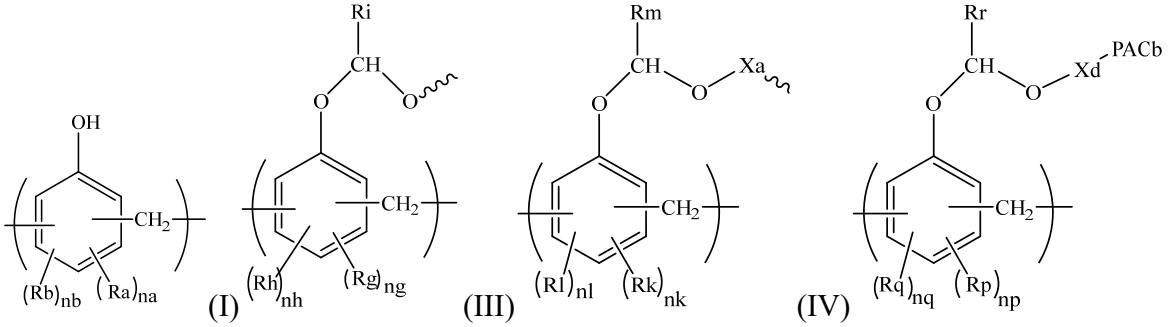
c) an alkyleneoxy moiety where an alkylene end is attached to an acetal oxygen moiety of the repeat unit of structure (VI) and an oxy end of the alkyleneoxy moiety is attached to the PACb moiety, and

d) a moiety comprising an acetal selected from the group consisting of

i) an alkyleneacetal moiety (-alkylene-O-CH(CH_3)-O-),

ii) an alkyleneoxyalkyleneacetal moiety (-alkylene-O-alkylene-O-CH(CH_3)-O-), and

iii) an alkylene(oligooxyalkylene)acetal moiety (-alkylene (-O-alkylene)$_x$-O-CH(CH_3)-O-) where x is 2 to 6, and further wherein, the alkylene end of said moiety comprising an acetal is attached to the acetal oxygen moiety of the repeat unit of structure (VI), and the acetal portion of said moiety comprising an acetal is attached to the PACb moiety;



9. The composition of claim 3, wherein the phenolic resin component comprises repeat units having structures (I), (III), (V) and (VI) wherein,

the repeat units having structures (III) and (V) are attached together through the positions designated by "∿∿∿"thereby forming a di-functional acetal providing a linking point in the phenolic resin component between two different polymer chains and

(i) Ra, Rg, Rn and Rp are each independently a C-1 to C-4 alkyl, (ii) Rb, Rh, Ro and Rq are each independently a -X-Phenol where X is -O-, -C(CH_3)$_2$-, -(C=O)-, or -SO_2-, (iii) na, ng, nn and np are each independently 0 to 3, (iv) nb, nh, no and nq are each independently 0 or 1, (v) and the sum of na and nb, the sum of nn and no, the sum of nl and nk and the sum of np and nq each respectively does not exceed 3, (vi) Ri and Rr are independently a C-1 to C-4 alkyl, (vii) Xb is -O-, -C(CH_3)$_2$-, -(C=O)- or -SO_2-, (viii) Xc is an -alkylene(-O-alkylene)$_{x'}$- moiety where x' is 2 to 6, and (viv) the PACb moiety is a PAC component in the repeat unit having structure (VI) attached through a linking group Xd, wherein Xd is selected from the group consisting of:

a) a direct valence bond,

b) an alkylene moiety,

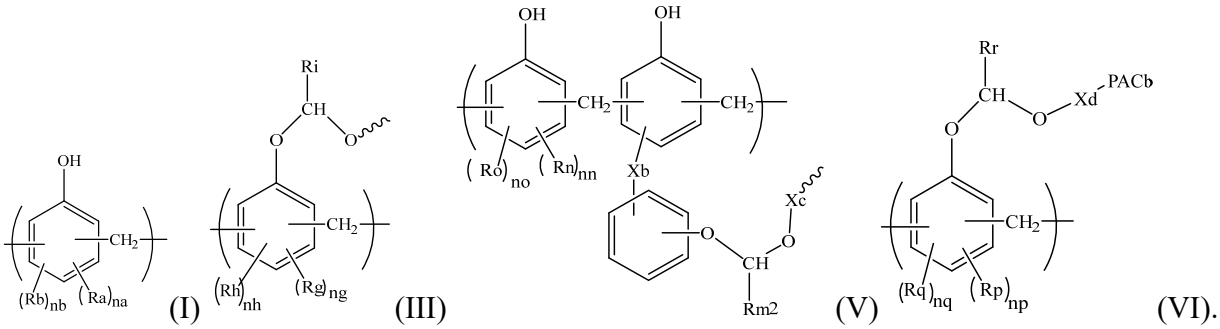
c) an alkyleneoxy moiety where an alkylene end is attached to an acetal oxygen moiety of the repeat unit of structure (VI) and an oxy end of the alkyleneoxy moiety is attached to the PACb moiety, and

d) a moiety comprising an acetal selected from the group consisting of

i) an alkyleneacetal moiety (-alkylene-O-CH(CH_3)-O-),

ii) an alkyleneoxyalkyleneacetal moiety (-alkylene-O-alkylene-O-CH(CH_3)-O-), and

iii) an alkylene(oligooxyalkylene)acetal moiety (-alkylene (-O-alkylene)$_x$-O-CH(CH_3)-O-) where x is 2 to 6, and further wherein, the alkylene end of said moiety comprising an acetal is attached to the acetal oxygen moiety of the repeat unit of structure (VI), and the acetal portion of said moiety comprising an acetal is attached to the PACb moiety;

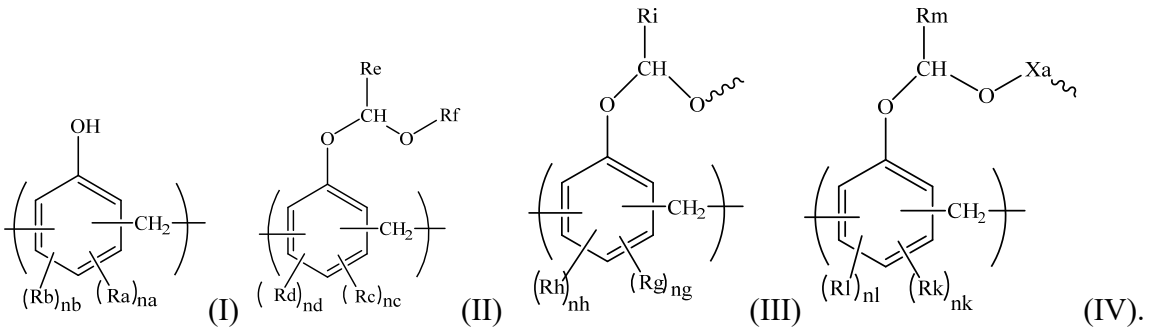


10. The composition of claim 3, wherein the phenolic resin component comprises repeat units having structures (I), (II), (III) and (IV) wherein,

the repeat units having structures (III) and (IV) can be attached together through the positions designated by "∿∿∿" thereby forming a di-functional acetal moiety linking point between two different polymer chains in the phenolic resin component and

wherein (i) Ra, Rc, Rg and Rk are each independently a C-1 to C-4 alkyl, (ii) Rb, Rd, Rh and Rl are each independently a -X-Phenol, where X is -O-, -C(CH_3)$_2$-, -(C=O)- or -SO_2-, (iii) na, nc, ng and nk are each independently 0 to 3, (iv) nb, nd, nh and nl are each independently 0 or 1, (v) the sum of na and nb, the sum of nd and nc, the sum of ng and nh and the sum of nk and nl each respectively does not exceed 3, (vi)Re, Rf, Ri and Rm are each independently selected from a C-1 to C-4 alkyl, (vii) Xa

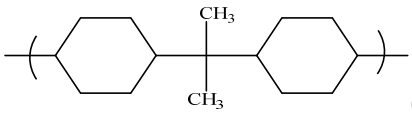
is an alkylene, an -alkyleneoxyalkylene- moiety, or an -alkylene(-O-alkylene)$_{x'}$- moiety where x' is 2 to 6;


(I) (II) (III) (IV).

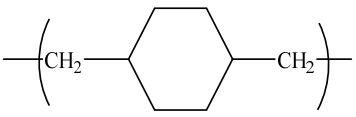
11. The composition of claim 3, wherein the phenolic resin component comprises repeat units having structure (II) where (i) Rc is C-1 to C-4 alkyl, (ii) Rd is a -X-Phenol where X is -O-, -C(CH$_3$)$_2$-, -(C=O)- or -SO$_2$-, (iii) nc is 0 to 3, (iv) nd is 0 or 1, (v) the sum of nc and nd does not exceed 3.

12. The composition of claim 3, wherein the phenolic resin component comprises repeat units having structure (IV) where Xa is an alkylene, an -alkyleneoxyalkylene- moiety or an -alkylene(-O-alkylene)$_{x'}$- moiety where x' is 2 to 6 and

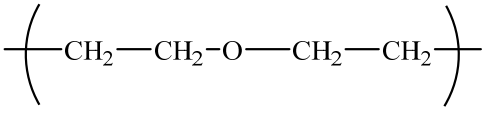
wherein Xa includes at least one alkylene that is an ethylene moiety, a propylene moiety, a butylene moiety, a moiety of structure (VII):


(VII),

a moiety of structure (VIIa):

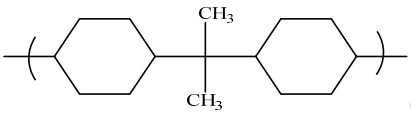

(VIIa), and

a moiety of structure (VIIb):


(VIIb).

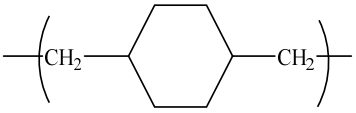
13. The composition of claim 3, wherein the phenolic resin component comprises repeat units having structure (V) where Xc is an alkylene, an -alkyleneoxyalkylene- moiety or an -alkylene(-O-alkylene)$_{x'}$- moiety where x' is 2 to 6 and

wherein Xc includes at least one alkylene that is an ethylene moiety, a propylene moiety, a butylene moiety, a moiety of structure (VII):



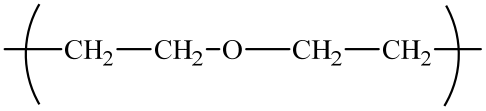
(VII),

a moiety of structure (VIIa):



(VIIa), and

a moiety of structure (VIIb):



(VIIb).

14. The composition of claim 3, wherein the phenolic resin component comprises repeat units having structure (V) where Xb is -O-, -$C(CH_3)_2$-, -(C=O)- or -SO_2-.

15. The composition of claim 3, wherein the phenolic resin component comprises repeat units having structure (VI) where Xd is selected from the group consisting of

a) a direct valence bond,

b) an alkylene moiety,

c) an alkyleneoxy moiety where an alkylene end is attached to an acetal oxygen moiety of the repeat unit of structure (VI) and an oxy end of the alkyleneoxy moiety is attached to the PACb moiety, and

d) a moiety comprising an acetal selected from the group consisting of

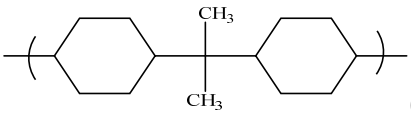
i) an alkyleneacetal moiety (-alkylene-O-$CH(CH_3)$-O-),

ii) an alkyleneoxyalkyleneacetal moiety (-alkylene-O-alkylene-O-$CH(CH_3)$-O-), and

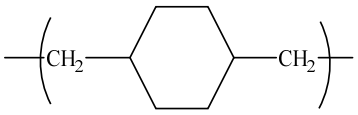
iii) an alkylene(oligooxyalkylene)acetal moiety (-alkylene (-O-alkylene)$_x$-O-$CH(CH_3)$-O-) where x is 2 to 6, and further wherein, the alkylene end of said moiety comprising an acetal is attached to the acetal oxygen moiety of the repeat

unit of structure (VI), and the acetal portion of said moiety comprising an acetal is attached to the PACb moiety.

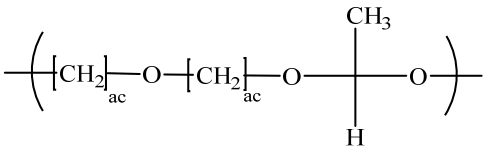
16. The composition of claim 3, wherein the phenolic resin component comprises repeat units having structure (VI) where Xd is an alkyleneacetal moiety (-alkylene-O-CH(CH_3)-O) or an an alkyleneoxyalkyleneacetal moiety (-alkylene-O-alkylene-O-CH(CH_3)-O-) and
wherein Xd includes at least one alkylene that is an ethylene moiety, a propylene moiety, a butylene moiety, a moiety of structure (VII):


(VII),

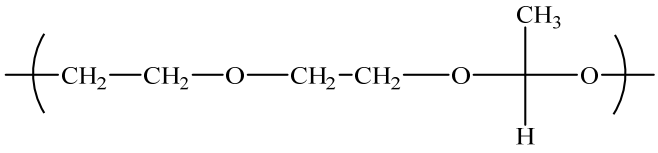
a moiety of structure (VIIa):


(VIIa),

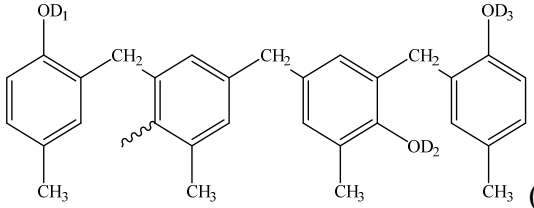
a moiety having structure (VIIc):


(VIIc)

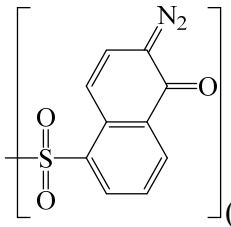
where ac is an integer from 2 to 4, and
a moiety having structure (VIId):


(VIId).

17. The composition of claim 3, wherein the photoactive 2,1,5-diazonaphthoquinonesulfonate (PAC) component comprises a PACb moiety comprising structure (VIII):

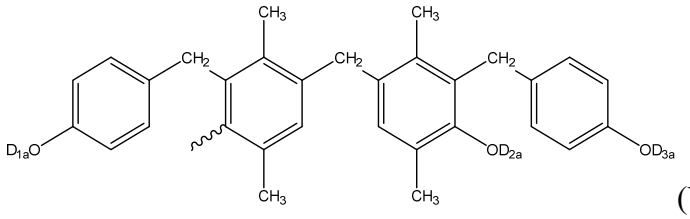

(VIII)

where (i) D_1, D_2 and D_3 are each independently selected from H or a moiety having structure (VIIIa):

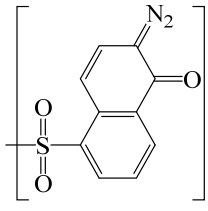

(VIIIa)

and (ii) where at least one of D_1, D_2 or D_3 is a moiety having structure (VIIIa).

18. The composition of claim 3, wherein the photoactive 2,1,5-diazonaphthoquinonesulfonate (PAC) component comprises a PACb moiety comprising structure (VIIIc):

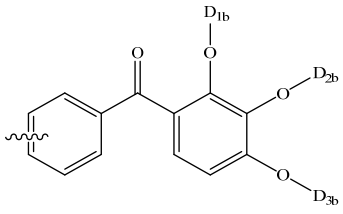

(VIIIc)

where (i) "∿∿∿" designates an attachment point to a repeat unit of the phenolic resin component, (ii) D_{1a}, D_{2a} and D_{3a} are each independently selected from H or a moiety having structure (VIIIa):

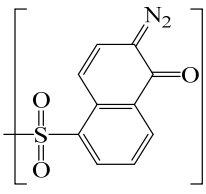

(VIIIa)

and (iii) where at least one of D_{1a}, D_{2a} or D_{3a} is a moiety having structure (VIIIa).

19. The composition of claim 3, wherein the photoactive 2,1,5-diazonaphthoquinonesulfonate (PAC) component comprises a PACb moiety comprising structure (VIIId):

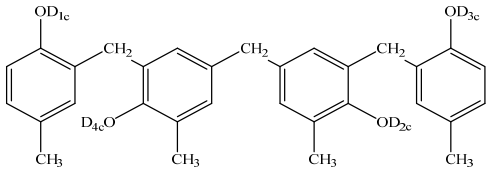

(VIIId)

where (i) "∿∿∿" designates an attachment point to a repeat unit of the phenolic resin component, (ii) D_{1b}, D_{2b} and D_{3b} are each independently selected from H or a moiety having structure (VIIIa):

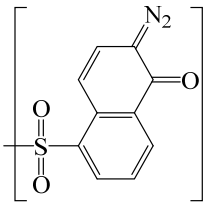

(VIIIa)

and (iii) where at least one of D_{1b}, D_{2b} or D_{3b} is a moiety having structure (VIIIa).

20. The composition of claim 3, wherein the photoactive 2,1,5-diazonaphthoquinonesulfonate (PAC) component comprises a compound having structure (X):

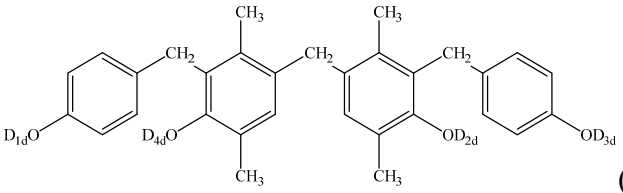

(X)

where (i) D_{1c}, D_{2c}, D_{3c} and D_{4c} are each independently selected from H or a moiety having structure (VIIIa):

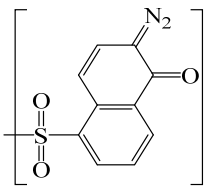

(VIIIa)

and (ii) at least one of D_{1c}, D_{2c}, D_{3c} or D_{4c} is a moiety including structure (VIIIa).

21. The composition of claim 3, wherein the photoactive 2,1,5-diazonaphthoquinonesulfonate (PAC) component comprises a compound having structure (Xa):

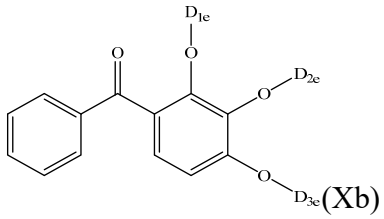

(Xa)

where (i) D_{1d}, D_{2d}, D_{3d} and D_{4d} are each independently selected from H or a moiety having structure (VIIIa):


(VIIIa)

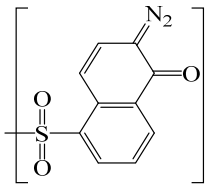
and (ii) at least one of D_{1d}, D_{2d}, D_{3d} or D_{4d} is a moiety including structure (VIIIa).

22. The composition of claim 3, wherein the photoactive 2,1,5-diazonaphthoquinonesulfonate (PAC) component comprises a compound having structure (Xb):



(Xb)

where (i) D_{1e}, D_{2e} and D_{3e} are each independently selected from H or a moiety having structure (VIIIa):



(VIIIa)

and (ii) at least one of D_{1e}, D_{2e} or D_{3e} is a moiety including structure (VIIIa).

23. The composition of claim 3, wherein a weight ratio of the phenolic resin component to the free PAC component is from about 95/5 to about 70/30.

24. The composition of claim 3, further comprising a thiol.

25. A process for imaging a resist comprising the steps;

i) coating the composition of any one of claims 1 to 24 on a substrate to form a resist film;

ii) selectively exposing the resist film to UV light using a mask to form a selectively exposed resist film;

iii) developing the selectively exposed film to form a positively imaged resist film over the substrate.

26. A process for imaging a resist comprising the steps;

ia) coating the composition of claim 1 on a substrate to form a resist film;

iia) selectively exposing the resist film to UV light using a mask to form a selectively exposed resist film;

iiia) baking the selectively exposed resist film to form a baked selectively exposed resist film;
iva) developing the selectively exposed and baked resist film to form a positively imaged resist film over the substrate.