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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 06-050426-00004-0000

Fecha: 2008-05-13 15:44:30 Dep. 2020 NUECREACIONE
Tra. 11 PATENTE/II Eve: 379 FASENACIONALII
Act. 538 PETICION Folios: 4

Clarke, Modet & C^o

COLOMBIA

SEÑORES
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES
E.S.D.

REF: EXPEDIENTE No. 06050426
SOLICITANTE: SVENSKA LANTMÄNNEN EK FÖR
FECHA DE LA SOLICITUD: MAYO 25, 2006

ASUNTO: SOLICITUD EXAMEN DE PATENTABILIDAD

DILIA RODRÍGUEZ D'ALEMAN identificada como aparece al pie de mi firma, domiciliada en Bogotá, en la Carrera 11 No. 86-53, piso 6, obrando como apoderada de la sociedad solicitante, pido a usted que se proceda a examinar si la invención, cuya patente se tramita en el expediente de la referencia, es patentable.

Adjunto al presente memorial el recibo No. 08-35,562 de 6 de mayo de 2008, 08-35,528 de mayo 6 de 2008 y 08-35,527 de mayo 6 de 2008 por la suma de \$211.000.00, con lo cual queda cubierta la tasa oficial correspondiente a dicho estudio.

Señor Superintendente,

DILIA RODRÍGUEZ D'ALEMAN
C.C. 41.654.882 Bogotá

p-781

ESTA CERTIFICACION DE EXCEDENTE DE PAGO SOLO PODRA SER UTILIZADA
COMO PARTE DE LA CANCELACION DE UNA TARIFA VIGENTE Y NO PODRA SER
SUSTITUIDA POR NINGUN RECIBO.

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

CERTIFICACION DE EXCEDENTE : 08 - 35,562
FECHA : MAYO 6 DE 2008

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 06-050426- -00004-0000

Fecha: 2008-05-13 15:44:30 Dep: 2020 NUECREACIONE
Tra: 11 PATENTE Y II Eje: 379 FASE NACIONAL II
Act: 638 PETICION Folios: 4

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CLARKE MODET Y CO. COLOMB	CONSIGNACION	BANCO DE BOGOTA	062754387	693055	06/05/2008	14,897,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-09	OTROS SERVICIOS DE PROPIEDAD I	99 OTROS SERVICIOS ADMINISTRATIVOS
			TOTAL : \$ 5,000.00

SON: CINCO MIL PESOS

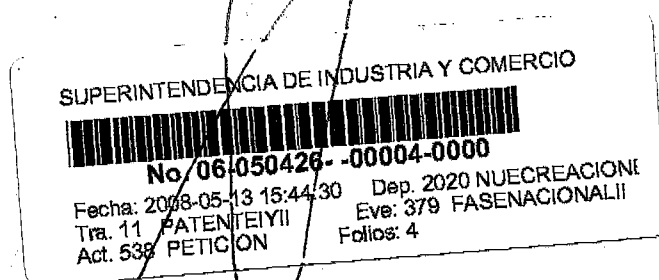
RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 08 - 35,528
FECHA : MAYO 6 DE 2008



***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CLARKE MODET Y CO. COLOMB	CONSIGNACION	BANCO DE BOGOTA	062754387	693055	06/05/2008	14,897,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-03	CAMBIO DE MODALIDAD Y MODIFICA	12 MARCAS Y LEMAS COMERCIALES
		TOTAL :	\$ 103,000.00

SON: CIENTO TRES MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

104
203

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 08 - 35,527
FECHA : MAYO 6 DE 2008

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 06-050426-00004-0000

Fecha: 2008-05-13 15:44:30 Dep. 2020 NUECREACIONE
Tia. 11 PATENTEIYI Eve: 379 FASENACIONALI
Act. 533 PETICION Folios: 4

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CLARKE MODET Y CO. COLOMB	CONSIGNACION	BANCO DE BOGOTA	062754387	693055	06/05/2008	14,897,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-03	CAMBIO DE MODALIDAD Y MODIFICA	12 MARCAS Y LENAS COMERCIALES
			103,000.00
		TOTAL :	\$ 103,000.00

SON: CIENTO TRES MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

DIVISIÓN DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 06-50426

EL EXTRACTO DE LA PRESENTE SOLICITUD DE PATENTE DE INVENCION

FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No 583 DE

FECHA 18 DE DICIEMBRE DE 2007 EL TÉRMINO HÁBIL SEÑALADO POR LA

LEY EXPIRA EL 14 DE MARZO DE 2008

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI _____

NO X

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES**

2020

Bogotá, D. C., 14 de agosto de 2009

Doctora

Dilia María Rodríguez D'Aleman

Representante **Svenska Lantmännen Ek För**

ASUNTO

Radicación **06-50426**

Trámite **002**

Evento **001**

Actuación **430**

Oficio **9684**

Folios **026**

Patente de Invención

☒

Patente de Modelo de Utilidad

☐

Vía Nacional

☐

Vía PCT (fase nacional)

☒

Cap. I

☐

Cap. II

☒

No. Sol. Internacional

PCT/SE2004/001734

Fecha de Presentación Internal.

25 de noviembre de 2004

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

1. Documentos estudiados

1.1. Descripción: Folios: 22 a 50 tal como se radicó inicialmente

1.2. Reivindicaciones: Folios 51 a 54 tal como se radicó inicialmente

1.3. Prioridad:

1.3.1. Fecha 26 de noviembre de 2003

País Estados Unidos

Número 60/524860

1.3.2. Fecha 26 de noviembre de 2003

País Suecia

Número 0303176-2

2. Objeto de la invención

- Título de la solicitud (folio 1) **Método para la producción de recubrimientos térmicamente curados**
- Las reivindicaciones 1 a 106 de la solicitud en estudio se refieren a:

- 107
206
- 1.- Un método para la producción de un recubrimiento sobre un sustrato sólido que comprende las etapas de aplicar una composición de recubrimiento líquido que comprende: Una resina polifuncional, un ácido graso o un derivado de éste y opcionalmente un agente de curación y/o uno o más aditivos, En donde la resina comprende grupos funcionales capaces de reaccionar con grupos carboxilo, o acilo del ácido graso derivado de éste, sobre el sustrato, y curar el recubrimiento mediante activación con calor
 - 7.- Un sustrato sólido que tiene un recubrimiento producido de acuerdo al método de una cualquiera de las reivindicaciones 1-6.
 - 8.- Una composición de recubrimiento líquido...
 - Los anteriores productos y procedimiento buscan mejorar los recubrimientos térmicamente curados.
 - La Clasificación Internacional de Patentes (IPC) para esta solicitud es C09D7/12.

3. De la solicitud de Patente

Descripción (Artículo 28 D. 486)

La descripción de la solicitud en estudio presenta los siguientes defectos:

- El título de la solicitud debe contener todo lo que el solicitante quiere que le sea protegido. Por consiguiente el actual título debe ser complementado.

Por lo anterior, la descripción no cumple con el requisito de claridad y/o divulgación completa que permita su comprensión y ejecución de acuerdo al art. 28 de la Decisión 486 y/o art. 22 del Tratado PCT

4. Determinación del Estado de la Técnica

- La fecha que se ha tenido en cuenta para determinar el estado de la técnica es 26 de noviembre de 2003
- Teniendo en cuenta la fecha indicada se realizó la búsqueda en el estado de la técnica de documentos relacionados con la solicitud encontrándose los siguientes documentos más relevantes:

Nº	Documento	Título	Fecha de publicación
D1	WO 9731073	Coating Composition comprising a bicyclo- or spiro orthoester functional compound	28.08.1997
D2	US 4 426 227	Printing compositions	17.01.1984
D3	US 2002/0151629	Protective coating	17.10.2002

5. Análisis de patentabilidad (Artículo 14 D. 486)

El solicitante pretende que se le proteja un método para la producción de un recubrimiento sobre un sustrato sólido que comprende las etapas de aplicar una composición de recubrimiento líquido que comprende: Una resina polifuncional, un ácido graso o un derivado de éste y opcionalmente un agente de curación y/o uno o más aditivos, En donde la resina comprende grupos funcionales capaces de reaccionar con grupos carboxilo, o acilo del ácido graso derivado de éste, sobre el sustrato, y curar el recubrimiento mediante activación con calor

El documento D1 enseña composiciones de recubrimiento como resinas las cuales pueden ser polifuncionales (como poliésteres de poliol), diversidad de ácidos grasos o sus derivados y otros aditivos. Nótese que se emplea como recubrimiento y que es en esencia lo mismo que el solicitante desea proteger para Colombia.

D2 enseña una composición que puede ser aplicada sobre metales que comprende una resina como la acrílica, compuestos derivados de ácidos grasos y otros aditivos. La forma de recubrir es igual a lo planteado en la presente solicitud.

D3 muestra un recubrimiento de una superficie metálica con una composición que incorpora ácidos grasos saturados o ésteres grasos de 4 - 24 carbonos, resinas alquídicas o acrílicas y otros componentes. En esencia lo mismo que el solicitante pretende proteger.

6. Conclusión:

Los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

N°	Documento N°	Reivindicaciones afectadas	Requisito que afecta
D1	WO 9731073	1 - 12	Novedad
			Nivel Inventivo
D2	US 4 426 227	1 - 12	Novedad
			Nivel Inventivo
D3	US 2002/0151629	1 - 12	Novedad
			Nivel Inventivo

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de SESENTA días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única N° 10 de 2001.

Alix Carmenza Céspedes De Vergel

Jefe de División de Nuevas Creaciones

Concepto Técnico No. 2797

Examinador Técnico 202003

El anterior requerimiento fue notificado por fijación en lista, de fecha _____

21 AGO. 2009

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

(51) International Patent Classification 6:

C09D 17S/04, C07D 493/08, 493/10,
C08F 8/14, C08G 18/30, 63/91, C09D
201/06, C08G 85/00

(51) International Patent Classification 6 :
C09D 175/04, C07D 493/10, A1

International Publication Number: _____

International Publication Date: _____

WO 97/31073

WO 97/31073
15 August 1997 (28.08.97)

(21) International Application Number: PCT/EP97/00892

21 February 1997 (21.02.97)

(30) Priority Data:
1802427
23 February 1996 (23.02.96) NL

(71) Applicant: AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 RM Arnhem (NL).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V.,
Patent Dept. (Dept. APTA), P.O. Box 9300, NL-6800 SB
Arnhem (NL).

(54) Title: COATING COMPOSITION COMPRISING A BICYCLO- OR SPERO-ORTHOESTER-FUNCTIONAL COMPOUND

Abstract

The invention pertains to a coating composition comprising a first compound comprising at least one bicyclo- or spiro-orthoester group and a second compound comprising at least two hydroxyl-reactive groups. The invention also comprises a process for curing the present coating composition. More particularly, the latent hydroxyl groups of the bicyclo- or spiro-orthoester groups leave to be deblocked and reacted with the hydroxyl-reactive groups of the second compound if the present coating composition is to be cured. Further, a process is disclosed for making bicyclo-orthoester compounds from the corresponding acetone compound is described, as are polymers comprising at least one bicyclo- or spiro-orthoester group.

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GA	Gabon	MR	Mauritania		VM	Viet Nam

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COATING COMPOSITION COMPRISING A BICYCLO- OR SPIRO-ORTHOESTER-FUNCTIONAL COMPOUND

- 5 The invention pertains to a coating composition comprising a first compound comprising at least one bicyclo- or spiro-orthoester group.

The use of compounds comprising bicyclo-orthoester groups in coating compositions is known from US patent publication No. 4,338,240. In this patent publication the use and the preparation of bicyclo-orthoester-functional compounds (hereinafter bicyclo-orthoester will be abbreviated to BOE) is described. Described are, e.g., BOE-functional compounds, which are the adduct of two compounds comprising one hydroxyl group and one BOE group and one compound comprising two isocyanate groups. The compounds are cross-linked by means of cationic ring opening homopolymerisation of the BOE groups. In that case, however, the presence of moisture has to be excluded. Furthermore, energy in the form of ultraviolet, infrared or microwave irradiation or heat has to be supplied during the polymerisation process.

- 20 The invention now provides a coating composition of the aforementioned type which is free of said drawbacks. For that reason the coating composition mentioned in the opening paragraph is characterised in that it comprises a second compound comprising at least two hydroxyl-reactive groups.

A coating composition comprising a compound comprising at least one bicyclo- or spiro-orthoester group (hereinafter spiro-orthoester will be abbreviated to SOE) is a composition having latent hydroxyl groups. In the presence of water or moisture from the air the BOE or SOE groups will be hydrolysed, forming hydroxyl groups. This reaction is also known as deblocking. During deblocking few if any volatile components are released.

- When the BOE- or SOE-group is deblocked in this manner, it is not possible to obtain a homopolymer of BOE- or SOE groups by cationic polymerization. However, it has now been found that when a second compound comprising at least two hydroxyl-reactive groups is present in the composition, the deblocked hydroxyl groups can react with the hydroxyl-reactive groups to give a cross-linked polymer.

BOE- and SOE-functional compounds may be used as main binders or as reactive diluents in the coating compositions of the present invention.

- 10 The use of compounds comprising BOE or SOE groups in coating compositions has several advantages over the use of compounds having free hydroxyl groups, such as hydroxyl-functional reactive diluents, hydroxyl-functional main binders, e.g. polyester polyols and acrylate polyols, and even compounds where the BOE or SOE groups have already been hydrolysed.

- Firstly, the viscosity of compounds comprising BOE or SOE groups is lower than that of the corresponding hydrolysed compounds. In consequence, less viscosity-reducing solvent which evaporates in air is needed in the coating composition.

- Secondly, because of the stability of the BOE- and SOE-functional compounds the pot life:drying time ratio of compositions according to the invention is particularly favourable, for hydrolysis only takes place in the presence of water or moisture.

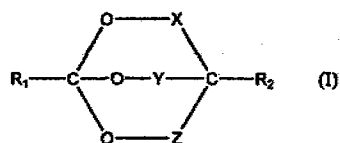
- Thirdly, in coating compositions of the present invention BOE- and SOE-functional compounds have the advantage that hydrolysis of the BOE or

SOE group produces a substantial increase in the composition's viscosity. A high viscosity will give reduced sagging of the coating composition on the substrate.

- 5 Finally, it has been found that the coating compositions of the present invention provide a high build behavior.

By BOE groups are meant in this connection groups having a structure according to formula I

10



wherein

- X and Z are independently from each other selected from linear or
 15 branched alk(en)ylene groups with 1-4 carbon atoms optionally containing an oxygen or a nitrogen atom;
 Y is nothing or is selected independently of X and Z from linear or branched alk(en)ylene groups with 1-4 carbon atoms optionally containing an oxygen or a nitrogen atom;
 20 R₁ and R₂ may be the same or different and are selected from the group of monovalent radicals comprising hydrogen, hydroxyl, alk(en)yl groups comprising 1-30 carbon atoms which may be linear or branched and may optionally contain one or more heteroatoms and groups selected from the group of oxygen, nitrogen,
 25 sulphur, phosphorus, sulphone, sulphony, and ester, optionally substituted with epoxy, cyano, amino, thiol, hydroxyl, halogen, nitro, phosphorus,

sulphony, amido, ether, ester, urea, urethane, thioester, thioamide, amide, carboxyl, carbonyl, aryl, and acyl groups, and

divalent radicals comprising

alk(en)ylene groups having 1-10 carbon atoms which groups may be linear

- 5 or branched and may optionally contain one or more heteroatoms and groups selected from the group of oxygen, nitrogen, sulphur, phosphorus, sulphone, sulphony, and ester, optionally substituted with epoxy, cyano, amino, thiol, hydroxyl, halogen, nitro, phosphorus, sulphony, amido, ether, ester, urea, urethane, thioester, thioamide, amide, carboxyl, carbonyl, aryl,
 10 and acyl groups, ester groups; ether groups; amide groups; thioester groups; thioamide groups; urethane groups; urea groups; and a single bond.

Preferably, X, Y, and Z are methylene. R₁ and R₂ in that case are linked to
 15 a divalent 2,6,7-trioxabicyclo[2.2.2]octane radical.

- In the case of R₁ and R₂ being both monovalent radicals, the BOE group as defined by formula I is the same as the BOE-functional compound. Monovalent radicals R₁ and R₂ are preferably independently from each
 20 other selected from the group of hydrogen, hydroxyl, and linear or branched alk(en)yl groups having 1-20 carbon atoms, optionally substituted with one or more hydroxyl groups and optionally comprising an ester group. Examples of such groups are: methyl, methylol, ethyl, ethylol, propyl, propylol, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, a -CH₂-
 25 CH₂ - O - CO - C₁₋₂₀ alk(en)yl group, and mixtures thereof.

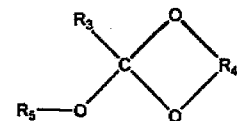
Preferably, R₁ is linear or branched alk(en)yl having 1-20 carbon atoms, optionally substituted with hydroxyl, while R₂ is methyl or ethyl. Alternatively, R₁ can be methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl,

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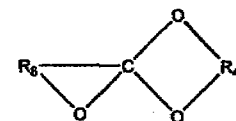
octyl, nonyl, decyl, undecyl, and mixtures thereof, while R_2 can be methylol, ethyl, ethylol or a $-\text{CH}_2 - \text{CH}_2 - \text{O} - \text{CO} - \text{C}_{1-20} \text{ alk(en)yl}$ group.

- When a divalent radical is selected for either or both R_1 or R_2 groups, high-molecular weight BOE-functional compounds can be formed. These may be adducts or polymers comprising several BOE groups. Thus two BOE groups can form an adduct by selecting a monovalent radical for one of the two R_1 and R_2 groups, and a divalent radical for the other. The BOE groups will then be linked together via the divalent radical. BOE groups may also be linked via the divalent radicals to monomer or oligomer compounds. Such BOE-functional compounds are, e.g. described in above-mentioned US 4,338,240. For example, two BOE groups may be linked to a dimer fatty acid, e.g. Pripol 1009, ex. Unichema. Alternatively, in the aforementioned configuration the BOE groups can function as side groups or terminal groups in a polymer chain. The polymers can be, e.g., polyesters, polyethers, polyacrylates, polyamides or polyurethanes. When the divalent radical is a single bond, the BOE group is bonded directly to the polymer. When the R_1 and R_2 groups are both divalent, the BOE groups can be incorporated into the main chain of a polymer or they can serve to link two polymer chains together. Preferably, one or both R_1 and R_2 groups are selected from the group of ester, ether, urethane, a single bond, and alk(en)ylene groups having 1-10 carbon atoms which may be linear or branched and may contain one or more ester, ether, or urethane groups.
- The term SOE groups in this case refers to groups having a structure according to formula II or III

6



(II)



(III)

wherein

- R_3 and R_5 are independently from each other selected from the group of linear or branched alk(en)yl, aryl or acyl optionally containing one or more oxygen, nitrogen, sulphur or phosphorus atoms, optionally substituted with a halogen atom; and
- R_4 and R_6 are independently from each other selected from an alkylene group having 1-3 carbon atoms optionally substituted with one or more groups selected from monovalent radicals such as linear or branched alk(en)yl, aryl or acyl groups optionally containing one or more oxygen, nitrogen, sulphur, and phosphorus atoms; and
- divalent radicals
- such as a single bond and an alkylene group having 1-10 carbon atoms with or without one or more atoms and groups selected from oxygen, nitrogen, sulphur, and phosphorus atoms, and ether, ester, and urethane groups.
- Preferably, R_3 and R_5 are selected independently from linear or branched alk(en)yl groups having 1-4 carbon atoms, e.g., a methyl or ethyl group.
- in the case that neither of R_4 and R_6 is substituted with a divalent radical, the SOE group as defined by formulae II and III is the same as the SOE-functional compound.

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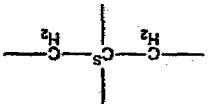
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When a divalent radical is selected as substituent for either or both R_4 and R_6 groups, high-molecular weight SOE-functional compounds can be prepared in the same manner as described above for high-molecular BOE compounds. When R_4 or R_6 has one divalent radical substituent, adducts or polymers can be made which have SOE groups as terminal or side groups. In formula III, R_4 and R_6 can both have divalent radicals as substituents, in which case the SOE group can be incorporated into the main chain. The polymers may be, e.g., polyacrylate, polyester, polyether, polyamide or polyurethane.

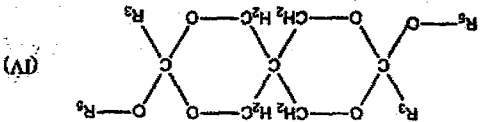
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Alternatively, R_4 can be



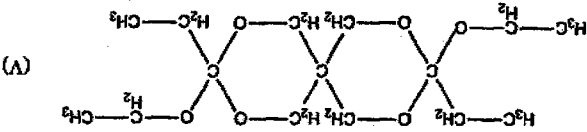
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with the compound formed being point symmetrical to C^* , giving a SOE compound according to formula IV:



20

Preferably, formula IV is:



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The deblocking of the latent hydroxyl groups of the BOE and SOE compounds takes place under the influence of water in the form of, e.g., moisture from the air or added water. This deblocking is preferably catalysed by a first catalyst selected from the group of Lewis acids, such as $AlCl_3$, $SbCl_5$, BF_3 , BCl_3 , $BeCl_2$, $FeCl_3$, $FeBr_3$, $SnCl_4$, $TiCl_4$, $ZnCl_2$ and $ZrCl_4$ and organic complexes thereof, e.g., $BF_3 \cdot Et_2O$, $BF_3 \cdot 2CH_3COOH$, $BF_3 \cdot 2H_2O$, $BF_3 \cdot H_2PO_4$, $BF_3 \cdot (CH_3)_2O$, $BF_3 \cdot THF$, $BF_3 \cdot 2CH_3OH$, $BF_3 \cdot 2C_2H_5OH$, and $BF_3 \cdot C_6H_5CH_3$ and Brønsted acids. Preferably, use is made of Brønsted acids having a $pK_a < 3$, such as a mono- or dialkyl phosphate, a carboxylic acid having at least one chlorine and/or fluorine atom, an alkyl or aryl sulphonate or an (alkyl)phosphonic acid, more particularly methanesulphonic acid, paratoluene sulphonate, optionally substituted naphthalene sulphonate, dodecyl benzene sulphonate, dibutyl phosphate, trichloroacetic acid, phosphoric acid, and mixtures thereof.

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Said first catalysts may be blocked, if so desired, resulting in the release of the Lewis or Brønsted acid under the influence of, e.g., electromagnetic irradiation (light or UV), heat or moisture. Acid generating photoinitiators are described, int. al., in G. Li Bassi et al., "Photoinitiators for the

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Simultaneous Generation of Free Radicals and Acid Hardening Catalysts," Radcure 86 Processings, e.g. 2-methyl-1-[4-(methylthio)phenyl]-2-[4-methylphenyl]sulphonyl propan-1-one (MDTA), ex. Fratelli Lambert Spa, Varese, Italy. Alternatively, use may be made of Lewis acid generating compounds such as ligacure® 261 ex Ciba Geigy and trimethyl silyl benzene sulphonate ester.

The first catalyst can be used alone or as a mixture of catalysts in effective amounts. The term effective amount in this case is dependent on the use of the BOE- or SOE-functional compound. When the BOE- or SOE-functional compound is used as a main binder, sufficient catalyst will have to be present to hydrolyse practically all BOE- or SOE-functional compounds. However, if the BOE- or SOE-functional compound is used primarily as a reactive diluent while other compounds are present as main binders, the hydrolysis of at least a portion of the BOE- or SOE-functional compound will suffice.

Amounts of 0 to 10 wt.% relative to the BOE- and SOE-functional compounds of the first catalyst may be sufficient. Preferably, 0.3 to 8 wt.%, more specifically, 0.5 to 6 wt.%, will be present.

The reaction of the deblocked hydroxyl groups of the BOE or SOE compound, the hydroxyl-reactive groups of the second compound, and, optionally, third compounds present in the composition comprising hydroxyl groups or hydroxyl-reactive groups, takes preferably place under the influence of a second catalyst. Such catalysts are known to the skilled person. The second catalyst is used in an amount of 0 to 10 wt.%, preferably 0.001 to 5 wt.%, more preferably in an amount of 0.01 to 1 wt.%, calculated on solid matter (i.e., the amount of BOE or SOE, the hydroxyl-

reactive compound, and, optionally, the above-mentioned third compounds).

As an example for the various hydroxyl-reactive groups the following catalysts may be mentioned. Polyisocyanates: dimethyl tin dilaurate, dibutyl tin dilaurate, dibutyl tin dioctate, tin octoate, zinc octoate, aluminum chelate, and dimethyl tin dichloride; polyepoxy compounds: tertiary amines and Lewis acids such as BF_3 or organic complexes thereof; polyacetals compounds: paratoluene sulphonate and dodecyl benzene sulphonate acid; polycarboxylic compounds: dodecyl benzene sulphonate acid, polyanhydride compounds: organotin compounds; alkoxysilane compounds: organotin compounds, phosphonic acid, paratoluene sulphonate acid, dodecyl benzene sulphonate acid, and tertiary amines; and amino resins: dodecyl benzene sulphonate acid.

As can be noted from the above, the first and the second catalyst may be the same in some coating compositions. In that case, the amount of catalyst may be higher than indicated for the first or second catalyst alone.

The coating composition according to the invention may be part of a components system, for instance a 2-component system. For example, one component may comprise both the BOE- or SOE-functional compound and the hydroxyl-reactive compound. The second component may comprise the catalyst for the hydrolysis of the BOE- or SOE-functional compound

Alternatively, a 3-component system may be employed. For example, one component may comprise the BOE- or SOE-functional compound. A second component may comprise the hydroxyl-reactive compound. A third

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component may comprise the catalyst for the hydrolysis of the BOE- or SOE-functional compound.

5 In addition, a coating composition such as described may contain the usual additives such as solvents, pigments, fillers, levelling agents, emulsifiers, anti-foaming agents and rheology control agents, reducing agents, antioxidants, HALS-stabilisers, UV-stabilisers, water traps such as molecular sieves, and anti-settling agents.

10 Application onto a substrate can be via any method known to the skilled person, e.g., via rolling, spraying, brushing, flow coating, dipping, and roller coating. Preferably, a coating composition such as described is applied by spraying.

15 The coating composition of the present invention may be applied to any substrate. The substrate may be, for example, metal, e.g., iron, steel, and aluminium, plastic, wood, glass, synthetic material, paper, leather, or another coating layer. The other coating layer may be comprised of the coating composition of the current invention or it may be a different coating composition. The coating compositions of the current invention show particular utility as clearcoats (over base coats, water-borne and solvent-borne), base coats, pigmented topcoats, primers, and fillers. The compositions are particularly suitable for refinishing motor vehicles and transportation vehicles and in finishing large transportation vehicles such as trains, trucks, buses, and aeroplanes.

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The applied coating composition can be cured very effectively at a temperature of, e.g., 0-50°C. If so desired, the coating composition may be baked, e.g., at a temperature in the range of 50-120°C.

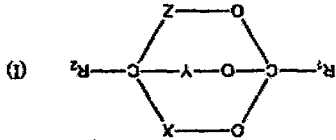
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Claims

1. A coating composition comprising a first compound comprising at least one bicyclo-orthoester group or spiro-orthoester group, characterised in that the coating composition comprises a second compound comprising at least two hydroxyl-reactive groups.

2. A coating composition according to claim 1, characterised in that the bicyclo-orthoester group has a structure according to formula I



wherein

X and Z are independently from each other selected from linear or branched alk(en)ylene groups with 1-4 carbon atoms optionally containing an oxygen or a nitrogen atom;

Y is nothing or is selected independently of X and Z from linear or branched alk(en)ylene groups with 1-4 carbon atoms optionally containing an oxygen or a nitrogen atom;

R₁ and R₂ may be the same or different and are selected from the group of monovalent radicals comprising

hydrogen, hydroxyl, alk(en)yl groups comprising 1-30 carbon atoms which may be linear or branched and may optionally contain one or more heteroatoms and groups selected from the group of oxygen, nitrogen, sulphur, phosphorus, sulphone, sulphonyl, and ester, optionally substituted with epoxy, cyano, amino, thiol, hydroxyl, halogen, nitro, phosphorus, sulphonyl, amido, ether, ester, urea,

urethane, thioester, thioamide, amide, carboxyl, carbonyl, aryl, and acyl groups, and

divalent radicals comprising

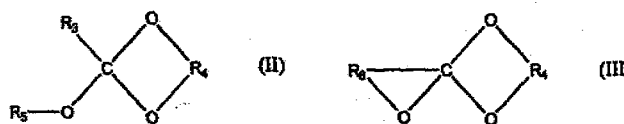
alk(en)ylene groups having 1-10 carbon atoms which groups may be linear or branched and may optionally contain one or more heteroatoms and groups selected from the group of oxygen, nitrogen, sulphur, phosphorus, sulphone, sulphonyl, and ester, optionally substituted with epoxy, cyano, amino, thiol, hydroxyl, halogen, nitro, phosphorus, sulphonyl, amido, ether, ester, urea, urethane, thioester, thioamide, amide, carboxyl, carbonyl, aryl, and acyl groups, ester groups, ether groups, amide groups, thioester acyl groups, thioamide groups, urethane groups, urea groups, and a single bond.

A coating composition according to claim 2, characterised in that X, Y, and Z are methylene.

4. A coating composition according to one or more of claims 2 and 3, characterised in that in the case of monovalent radicals R₁ and R₂ are independently from each other selected from the group of 1-20 carbon atoms, optionally substituted with one or more hydroxyl groups and optionally containing an ester group.

5. A coating composition according to claim 4, characterised in that R₁ and R₂ are independently from each other selected from the group of methyl, ethyl, ethylol, propyl, propylol, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, and a -CH₂-CH₂-O-CO-CO-C_n-alk(en)yl group.

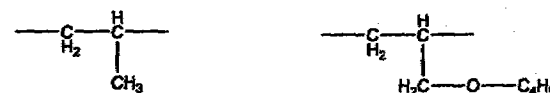
6. A coating composition according to claim 2, characterised in that one or both R_1 and R_2 groups is a divalent radical, with the first compound being a polymer comprising at least one bicyclo-orthoester group.
7. A coating composition according to claim 6, characterised in that one or both R_1 and R_2 groups are selected from the group of ester, ether, urethane, a single bond, and linear or branched alk(en)ylene groups having 1-10 carbon atoms optionally containing one or more ester, ether or urethane groups.
8. A coating composition according to claim 1, characterised in that the spiro-orthoester group has a structure according to formula II or III



wherein

R_3 and R_5 are independently from each other selected from the group of linear or branched alk(en)yl, aryl or acyl optionally containing one or more oxygen, nitrogen, sulphur or phosphorus atoms, optionally substituted with a halogen atom; and

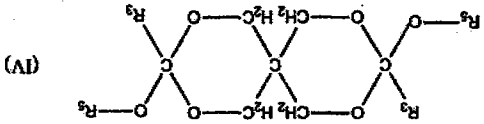
- R_4 and R_6 are independently from each other selected from an alkylene group having 1-3 carbon atoms optionally substituted with one or more groups selected from monovalent radicals such as linear or branched alk(en)yl, aryl or acyl groups optionally containing one or more oxygen, nitrogen, sulphur, and phosphorus atoms; and divalent radicals such as a single bond and an alkylene group having 1-10 carbon atoms with or without one or more atoms and groups selected from oxygen, nitrogen, sulphur, and phosphorus atoms, and ether, ester, and urethane groups.
9. A coating composition according to claim 8, characterised in that R_3 and R_5 are independently from each other selected from linear or branched alk(en)yl groups having 1-4 carbon atoms.
10. A coating composition according to one or more of claims 8 and 9, characterised in that R_4 is ethylene optionally substituted with a linear or branched alkyl group having 1-5 carbon atoms, optionally containing one or more oxygen and nitrogen atoms.
11. A coating composition according to claim 10, characterised in that R_4 is



12. A coating composition according to one or more of claims 8, 9, 10 or 11, characterised in that R_6 is propylene.

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13. A coating composition according to one or more of claims 8 and 9, characterised in that the first compound is a spiro-orthoester-functional compound according to formula IV



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14. A coating composition according to one or more of claims 8 and 9, characterised in that one or both R₄ and R₅ groups is substituted with a divalent radical, with the first compound being a polymer comprising at least one spiro-orthoester group.

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15. A coating composition according to one or more of the preceding claims, characterised in that the second compound comprises at least two hydroxy-reactive groups selected from the group of isocyanate groups, epoxy groups, acetal groups, carboxyl groups, anhydride groups, and alkoxyisilane groups, or the second compound is an amino resin.

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16. A coating composition according to claim 15, characterised in that the hydroxy-reactive compound is an aliphatic, alicyclic or aromatic compound comprising at least two isocyanate groups or adducts thereof.

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17. A coating composition according to claim 16, characterised in that the second compound is selected from the group of biurets, isocyanurates, allophanates, uretidiones, and mixtures thereof.

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18. A coating composition according to one or more of the preceding claims, characterised in that the coating composition contains additionally at least one compound selected from the group of hydroxy-reactive functional binders, hydroxy-reactive oligomers and monomers, ketone resins, aspartyl acid esters, and latent or non-latent amino-functional compounds.

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19. A coating composition according to claim 18, characterised in that the hydroxy-reactive binders are selected from polyester polyols, polyether polyols, polyacrylate polyols, polyurethane polyols, cellulose acetobutyrate, hydroxy-functional epoxy resins, alkyls, and dendrimeric polyols.

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20. A process for curing a coating composition according to one or more of the preceding claims, characterised in that the latent hydroxyl groups of the bicyclo-orthoester groups or spiro-orthoester groups are deblocked in the presence of water, optionally in the presence of a first catalyst, and reacted with the hydroxy-reactive groups of the second compound, optionally in the presence of a second catalyst.

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21. A process according to claim 20, characterised in that the first catalyst is selected from the group of Lewis acids and Brønsted acids.

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22. A process according to claim 21, characterised in that the Lewis acid is BF₃·Et₂O.

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23. A process according to claim 22, characterised in that the Brønsted acid has a $pK_a < 3$.

24. A process according to claim 23, characterised in that the Brønsted acid is selected from the group of a mono- or dialkyl phosphate, a carboxylic acid having at least one chlorine and/or fluorine atom, an alkyl or aryl sulphononic acid or an (alkyl)phosphonic acid.

25. 10 A process according to claim 24, characterised in that the Brønsted acid is selected from the group of methane sulphononic acid, paratoluene sulphononic acid, optionally substituted naphthalene sulphononic acids, dodecyl benzene sulphononic acid, dibutyl phosphate, trichloroacetic acid, phosphonic acid, and mixtures thereof

26. 15 A process according to one or more of claims 20-25, characterised in that use is made of 0 to 10 wt.% of the first catalyst, calculated on BOE-functional and SOE-functional compounds.

27. 20 A process according to claim 26, characterised in that use is made of 0.3 to 8 wt.% of first catalyst.

28. A process according to one or more of claims 20-27, characterised in that the second catalyst is selected from the group of dimethyl tin dilaurate, dibutyl tin dilaurate, dibutyl tin diacetate, tin octoate, zinc octoate, aluminium chelate, dimethyl tin dichloride, tertiary amines, Lewis acids such as BF_3 or organic complexes thereof, paratoluene sulphononic acid, dodecyl benzene sulphononic acid, phosphonic acid, and mixtures thereof.

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29. A process according to claim 28, characterised in that the second catalyst is present in an amount of 0.001 to 5 wt.%, calculated on solid matter.

30. 5 A two-component system, characterised in that one component comprises at least one bicyclo- or spiro-orthoester compound and at least one hydroxy/-reactive compound and the second component comprises a first catalyst for the hydrolysis of the bicyclo- or spiro-orthoester compound.

31. 10 A three-component system, characterised in that one component comprises at least one bicyclo- or spiro-orthoester compound, a second component comprises at least one hydroxy/-reactive compound, and a third component comprises a first catalyst for the hydrolysis of the bicyclo- or spiro-orthoester compound.

32. A process for the preparation of a compound comprising at least one bicyclo-orthoester group in which a compound having at least one corresponding oxetane group is converted in the presence of a catalytic amount of a strong Brønsted or Lewis acid or organic complexes thereof.

33. A process according to claim 32, characterised in that the Lewis acid is $BF_3 \cdot Et_2O$, $BF_3 \cdot 2CH_3COOH$, and $SnCl_4$.

34. A process according to one or more of claims 32 and 33, characterised in that the catalyst is employed in amounts of 0.001-0.1 mole of catalyst per mole of oxetane group.

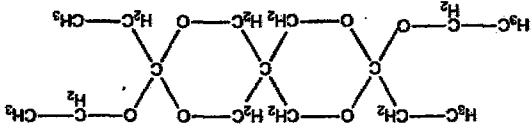
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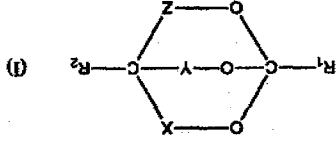
35. A process according to one or more of claims 32-34, characterised in that the reaction takes place in the presence of a small amount of solvent, preferably without solvent.

5 36. A process for the preparation of



10 characterised in that pentaerythritol is reacted with triethyl orthopropionate in the presence of paratoluene sulphonic acid, with trimethyl benzene being used as solvent.

37. A polymer comprising at least one bicyclo-orthoester group according to formula I



wherein

20 X and Z are independently from each other selected from linear or branched alk(en)ylene groups with 1-4 carbon atoms optionally containing an oxygen or a nitrogen atom;

Y is nothing or is selected independently of X and Z from linear or

branched alk(en)ylene groups with 1-4 carbon atoms optionally containing an oxygen or a nitrogen atom;

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comprising one of R₁ and R₂ is a monovalent radical and the other is a divalent radical or both groups are independently from each other selected from the group of divalent radicals, the monovalent radicals

hydrogen, hydroxyl, alk(en)yl groups comprising 1-30 carbon atoms which may be linear or branched and may optionally contain one or more heteroatoms and groups selected from the group of oxygen,

nitrogen, sulphur, phosphorus, sulphone, sulphonyl, and ester, optionally substituted with epoxy, cyano, amino, thiol, hydroxyl, halogen, nitro, phosphorus, sulphonyl, amido, ether, ester, urea, urethane, thioester, thioamide, amide, carboxyl, carbonyl, aryl, and acyl groups, and

divalent radicals comprising

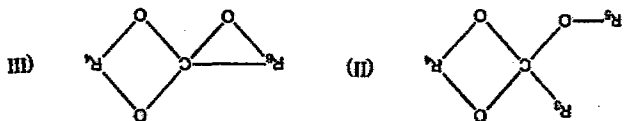
15 alk(en)ylene groups having 1-10 carbon atoms which groups may be linear or branched and may optionally contain one or more heteroatoms and groups selected from the group of oxygen, nitrogen, sulphur, phosphorus, sulphone, sulphonyl, and ester, optionally substituted with epoxy, cyano, amino, thiol, hydroxyl, halogen, nitro, phosphorus, sulphonyl, amido, ether, ester, urea, urethane, thioester, thioamide, amide, carboxyl, carbonyl, aryl, and acyl groups, ester groups, ether groups, amide groups, thioester groups, thioamide groups, urethane groups, urea groups, and a single bond.

38. A polymer comprising at least one spiro-orthoester group according to formula II or III

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wherein

5 R_3 and R_4 are independently from each other selected from the

group of linear or branched alk(en)yl, aryl or acyl optionally containing one or more oxygen, nitrogen, sulphur or phosphorus atoms, optionally substituted with a halogen atom; and

10 R_4 and R_5 are independently from each other selected from an alkylene group having 1-3 carbon atoms optionally substituted with one or more groups selected from monovalent radicals

such as linear or branched alk(en)yl, aryl or acyl groups optionally containing one or more oxygen, nitrogen, sulphur, and phosphorus atoms; and at least once substituted with a divalent radical selected from the group of a single bond and an alkylene group having 1-10 carbon atoms with or without one or more atoms and groups selected from oxygen, nitrogen, sulphur, and phosphorus atoms, and ether, ester, and urethane groups.

20 39. A polymer according to either of claims 38 and 37, characterised in that the polymer is a polyacrylate or a polyester.

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[54] PRINTING COMPOSITIONS

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[73] Assignee: Harrison Meyer Limited, Stoke-on-Trent, England

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[31] Int. Cl.³ C09D 11/02

[32] U.S. Cl. 106/27; 106/30;

260/DIG. 38; 523/160

[36] Field of Search 106/19, 27, 30, 291;

523/160; 260/DIG. 38

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PRINTING COMPOSITIONS

This invention relates to printing compositions and is especially, but not exclusively, applicable to compositions for use in printing or decorating heat resistant substrates such as glass, ceramics, including tiles and tubelures, or enamelled metals.

Off-set printing techniques are known in which a printed image is transferred by a flexible pad or other carrier member from a printing station to a decorating station where the image is applied to an article to be decorated. Hitherto pads formed from gelatine were widely employed, but more recently silicone pads have been employed, and the decorating compositions or inks used for such purposes must be compatible with the silicone pad and likewise have been designed to dry on the decorated article by solvent evaporation or by a combination of solvent evaporation and oxidation.

Various problems are encountered in utilizing decorating inks of this kind. While such inks are generally suitable for relatively low printing speeds and for single colour printing, they are not entirely satisfactory when used for high speed multi-colour printing. Moreover, such inks do not always give 100% transfer from the pad to the article being decorated and hence, when used for multi-colour printing there is a tendency for the ink retained on the transfer pad at one decorating stage to be transferred to the article during subsequent stages thereby resulting in reject items. Moreover, inks of this type are subject to changes in rheological and rheological properties throughout the printing run due to the volatilisation of solvents. This necessitates frequent adjustment of ink and machine settings to ensure colour consistency which is time consuming and inconvenient. Many such inks also have a limited shelf life.

It is an object of the present invention to obviate or mitigate at least some of these disadvantages. According to one aspect of the invention there is provided a printing medium comprising a thermoplastic resin and a rheology-controlling diluent, the medium having a melting point of between 40° and 80° C. and being non-tacky at room temperature.

Preferably the rheology-controlling diluent comprises a liquid resin, a high molecular weight ester, a fatty alcohol or a saturated fatty acid. The term "high molecular weight ester" is used herein to refer to esters having molecular weights greater than 200. Preferably the medium comprises from 30% to 98% of thermoplastic resin and from 2% to 70% of diluent. Advantageously the thermoplastic resin component may comprise two or more resins to extend the thermoplasticity of the medium, one of the resins being a film forming resin such as an acrylic resin.

The medium may be used to form a printing ink composition by the addition of suitable quantities of a pigment, flux or other required constituent. According to a further aspect of the invention there is provided a printing composition which is fluid at temperatures between 40° and 80° C., will form a coherent film on a silicone transfer member and will release completely therefrom and solidify immediately on contact with the surface of an article to be decorated, to form a non-tacky coating thereon.

The invention also provides a method of decorating an article comprising forming an image of the decoration in a flowable ink composition on a heated support, picking up the image from the support on a silicone

transfer member at a lower temperature to form a flexible film on the transfer member in a semi-fluid condition, and applying the film to an article to be decorated within a period of time during which the composition remains semi-fluid whereby the surface of the article solidifies immediately on contact with the surface of the article to form a non-tacky coating thereon.

The term "complete release" is used herein to refer to a degree of release or transfer of the film leaving no visible or readily ascertainable trace thereof remaining on the transfer member.

The term "immediate" is used herein to refer to solidification which takes place instantaneously or within a few seconds.

The term "silicone" as used herein in relation to transfer members or pads is to be construed as referring to transfer members or pads at least the working surface of which consists of or incorporates a major proportion of silicone.

Any thermoplastic resin having the required thermoplasticity and thermal decomposition properties may be employed. Preferably, however, the resin is selected from cellulose ethers, styrenes, terpenes, methacrylates, rosin, modified rosin and rosin esters.

Suitable liquid resin diluents include triethylene glycol ester of rosin, hydrogenated methyl ester of rosin, low molecular weight (300-400) styrene resin and polyterpene derived from alpha-pinene.

Preferably the high molecular weight ester diluent is selected from materials within the melting point range 25°-50° C. and comprising the palmates, stearates and laurates. Methyl palmate (Melting Point 24° C.), methyl stearate (MP 36° C.), propylene glycol monoacetate (MP 38° C.), stearyl laurate (MP 41° C.) and diethylene glycol monoacetate (MP 44° C.) have been found particularly suitable. Other suitable esters include the phthalates such as diethoxyethyl phthalate (MP 34° C.) and dibenzoyl phthalate (MP 42° C.), and the benzoates such as neopentyl glycol dibenzoate (MP 49° C.) and tetraethylene glycol dibenzoate (MP 47° C.).

Preferably the fatty alcohol diluents are selected from fatty alcohols having from 12 to 18 carbon atoms in the chain, including myristyl alcohol (MP 39° C.), cetyl alcohol (MP 49° C.) and stearyl alcohol (MP 58° C.). The fatty acid diluents are preferably selected from those having 10 to 18 carbon atoms in the chain, including capric acid (MP 31.5° C.), lauric acid (MP 44° C.) and myristic acid (MP 58° C.).

The diluent must be compatible with the resin at elevated temperature since in the molten state (that is at operating temperature) it acts to reduce the melt viscosity of the resin in the required level for good printing performance.

Generally, two or more thermoplastic resins will be employed in combination to extend the thermoplasticity of the ink composition. Preferably one resin has a softening point within the range 105°-170° C. and the other a softening point within the range 5°-99° C. It is particularly advantageous that one of the resins used should be a true film former in order to impart high internal cohesion to the ink film and to assist in maintaining its integrity during the transfer operation from the silicone surface to the article being printed.

The viscosity of the composition may be altered to suit desired requirements. Relatively low viscosity compositions are desirable when dialing with patterns or decorations having fine detail, whereas higher viscosity can be used in other cases. The viscosity can be con-

trolled by means of the proportion of resin to diluent without substantially affecting the physical performance of the composition. Suitable viscosities are those within the range 1-60 poises at a shear rate of 615 sec⁻¹ within the operational temperature range of 40°-80° C.

The following are examples, given by way of illustration only, of decorating mediums according to the invention, all proportions being by weight.

EXAMPLE 1
Underglaze Medium for printing on to porous earthenware at a temperature of 65° C.-70° C.

Methacrylate Resin (softening point 120°-140° C.)	20%
Sterylene Resin (softening point 30° C.)	20%
Diethylene Glycol Monostearate (melting point 40° C.)	60%

EXAMPLE 2
Underglaze medium for printing on to vitrified earthenware at a temperature of 55°-60° C.

Methacrylate Resin (softening point 120°-140° C.)	30%
Terpene Resin (softening point 25° C.)	20%
Stearyl Laurate (melting point 40° C.)	50%

EXAMPLE 3
Onglaze pottery medium for printing at a temperature of 55° C.-60° C.

Methacrylate Resin (softening point 120°-140° C.)	20%
Sterylene Resin (softening point 30° C.)	5%
Propylene Glycol Monostearate (melting point 38° C.)	60%

EXAMPLE 4
Inglaze pottery medium for printing at a temperature of 50° C.-55° C.

Methacrylate Resin (softening point 120°-140° C.)	40%
Sterylene Resin (softening point 30° C.)	2%
Methyl Sebacate (melting point 30° C.)	58%

EXAMPLE 5
Borossilicate or soda glass medium for printing at a temperature of 60° C.-65° C.

Ethyl Cellulose (softening point 120°-140° C.)	12%
Terpene Resin (softening point 10° C.)	2%
Methyl Sebacate (melting point 25° C.)	10%

EXAMPLE 6
Medium for printing on to enamelled iron or enamelled aluminium at a temperature of 45° C.-50° C.

Methacrylate Resin (softening point 120°-140° C.)	10%
Terpene Resin (softening point 25° C.)	30%
Methyl Sebacate (melting point 30° C.)	60%

EXAMPLE 7
Underglaze medium for printing on to porous earthenware at 50° C.-55° C.

Glycerol Resin Ester (softening point 75°-78° C.)	20%
Isobutyl Methacrylate (softening point 105°-115° C.)	20%
Methyl Alcohol (melting point 30° C.)	60%

EXAMPLE 8
Borossilicate or sodalime medium for printing at a temperature of 70° C.-75° C.

Isobutyl Methacrylate (softening point 120°-140° C.)	11.5%
Sterylene Resin (softening point 30° C.)	74.5%
Cetyl Alcohol (melting point 30° C.)	34.5%

EXAMPLE 9
Underglaze medium for printing on to vitrified earthenware at a temperature of 60° C.-65° C.

Resin mastic pentamethylol ester (softening point 110°-120° C.)	15%
Isobutyl Methacrylate (softening point 105°-115° C.)	4%
Stearyl Alcohol (melting point 38° C.)	40%

EXAMPLE 10
Inglaze pottery medium for printing at a temperature of 75° C.-80° C.

Isobutyl Methacrylate (softening point 105°-115° C.)	12%
Terpene Resin (liquid)	88%

EXAMPLE 11
Medium for printing on to enamelled iron at a temperature of 55° C.-60° C.

Isobutyl Methacrylate (softening point 120°-140° C.)	25%
Sterylene Resin (softening point 30° C.)	34.5%
Lauric Acid (melting point 40° C.)	37.5%

Decorating compositions can be prepared from the carrier mediums set out in Examples 1-11 by dispersing in the medium a proportion of an appropriate colouring material or pigment to suit the article to be printed. In the case of underglaze decoration of pottery, underglaze colours would be utilised and likewise onglaze colours would be adopted in respect of mediums intended for use in the onglaze decoration of pottery. Generally the ink composition will consist of 40-80% colouring material and 60-20% carrier medium.

Decorating compositions according to the invention may be applied using a variety of different printing techniques. In one arrangement the composition may be applied to a heated flat plate on which the pattern to be printed is engraved or etched, the transfer pad serving to pick up the inked image from the plate and transfer it to the article. In an alternative arrangement the decorating ink may be applied through a heated screen on to a heated flat plate, the image being subsequently picked up from the flat plate by means of

the silicone transfer member. In a further arrangement, the pattern may be screened on to a heated silicone or silicone coated diaphragm, the diaphragm then being used as a carrier to transfer the screened pattern to a position above the ware where it is pressed into contact with the ware by the silicone pad or a similar conforming pressure member. Other forms of apparatus may also be used in association with decoration compositions according to the invention.

The operating conditions require to be such that the ink is fluid when the initial image is formed and will adhere satisfactorily to the transfer member or pad when picked up from the plate or the like on which the image is supported. A coherent film in a semi-fluid state is formed on the pad during transfer to the article but care is necessary to ensure that the film does not dry or solidify on the pad. This may be controlled by varying the proportion of diluent to resin.

The operating temperatures may be varied dependent on the composition of the medium, the article to be decorated and the apparatus utilized. In general however the plate or the like on which the image is supported will be at a temperature of 40°-80° C., and the pad will operate at a temperature of 25°-50° C., due to the heat imparted to the pad by contact with the ware. The time the composition remains on the pad may also vary considerably to suit individual circumstances but will generally be of the order of 0.01-30 seconds.

Decorating compositions of the kind described above have the advantage that once machine operating conditions are set there is little or no need for further adjustment throughout the production run. Furthermore, the physical properties of the composition do not change during the printing operation irrespective of the length of time for which printing is carried out. A multiplicity of colours may be printed one following the other without the problem of decorating ink remaining on the silicone transfer member and subsequently causing spoilage of the final decoration.

Ink compositions according to the invention also have a superior capability for resolving fine image detail compared with conventional decorating means. This is due to the fact that when the silicone transfer surface contacts the ink in its fluid state, the lower surface temperature of the silicone results in an instantaneous change in state of the ink rheology from fluid to semi-solid. Consequently, the ink does not flow or spread and the most minute image detail is maintained virtually in its original form.

Various modifications may be made without departing from the invention. For example, other compositions having the desired physical properties may be utilised and though principally evolved for the decoration of heat resistant substrates by means of silicone transfer members, ink compositions according to the invention may be used for the decoration of articles made of other materials such as plastics materials and using different forms of equipment.

We claim:
1. A solvent-free ink for use in offset printing by means of a silicone pad on an article of ceramic and like material, said ink consisting of:

40-80% by weight of colouring material, and
60-20% by weight of a printing medium which becomes fluid at a temperature of 40°-80° C., has a viscosity of 1-60 poises at a shear rate of 615 sec⁻¹

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in the temperature range of 40°-80° C., the printing medium consisting of:

a mixture of 30-98% by weight of a thermoplastic component consisting of a film-forming thermoplastic resin having a softening point within the range 105°-170° C. selected from the group consisting of methacrylate resin, ethyl cellulose, isobutyl methacrylate and rosin mastic pentamethylol ester and another thermoplastic resin of lower softening point within the range of 5°-50° C. selected from the group consisting of styrene resin, glycerol rosin ester and methyl ester of hydrogenated rosin, and 70-2% by weight of a diluent selected from the group consisting of (a) an ester selected from palmitates, stearates and laurates, (b) a fatty alcohol selected from myristyl alcohol, cetyl alcohol and stearyl alcohol and (c) a saturated fatty acid selected from capric acid, lauric acid and myristic acid.

said ink forming in use a coherent but semi-fluid film on the silicone pad and transferring in its entirety from the pad to the article to form immediately a solid coating on the article.

2. An ink according to claim 1, wherein the printing medium consists of methacrylate resin, styrene resin and diethylene glycol monostearate.

3. An ink according to claim 1, wherein the printing medium consists of methacrylate resin, styrene resin and propylene glycol monostearate.

4. An ink according to claim 1, wherein the printing medium consists of methacrylate resin, styrene resin and methyl sebacate.

5. An ink according to claim 1, wherein the printing medium consists of isobutyl methacrylate, glycerol rosin ester and myristyl alcohol.

6. An ink according to claim 1, wherein the printing medium consists of isobutyl methacrylate, styrene resin and cetyl alcohol.

7. An ink according to claim 1, wherein the printing medium consists of rosin mastic pentamethylol ester, methyl ester of hydrogenated rosin and stearyl alcohol.

8. An ink according to claim 1, wherein the printing medium consists of isobutyl methacrylate, styrene resin and lauric acid.

9. A solvent-free ink for use in offset printing by means of a silicone pad on an article of ceramic and like materials, said ink consisting of:
40-80% by weight of colouring material, and
60-20% by weight of a printing medium which becomes fluid at a temperature of 40°-80° C., has a viscosity of 1-60 poises at a shear rate of 615 sec⁻¹ in the temperature range of 40°-80° C., the printing medium consisting of:

a mixture consisting of a film-forming thermoplastic resin having a softening point within the range 105°-170° C. selected from the group consisting of methacrylate resin, ethyl cellulose, isobutyl methacrylate and rosin mastic pentamethylol ester, and a liquid resin diluent selected from the group consisting of triethylene glycol ester of rosin, hydrogenated methyl ester of rosin and styrene resin having a molecular weight of 300-400.

said ink forming in use a coherent but semi-fluid film on the silicone pad and transferring in its entirety from the pad to the article to form immediately a solid coating on the article.

10. An ink according to claim 1, wherein the ester is selected from methyl palmitate, methyl stearate, propylene glycol monostearate, stearyl laurate and diethylene glycol monostearate. * * * *



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(54) PROTECTIVE COATING

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(57) **ABSTRACT**
Compositions and methods for coatings that are curable to a protective film. In one aspect, the compositions may include a reactive diluent that is a carboxylic acid compound. In another aspect, the compositions may include allyl and acrylic resins. Concentrated dispersions, allyl, and coalescence compositions are also provided along with methods for making and using these compositions to produce a coating composition.

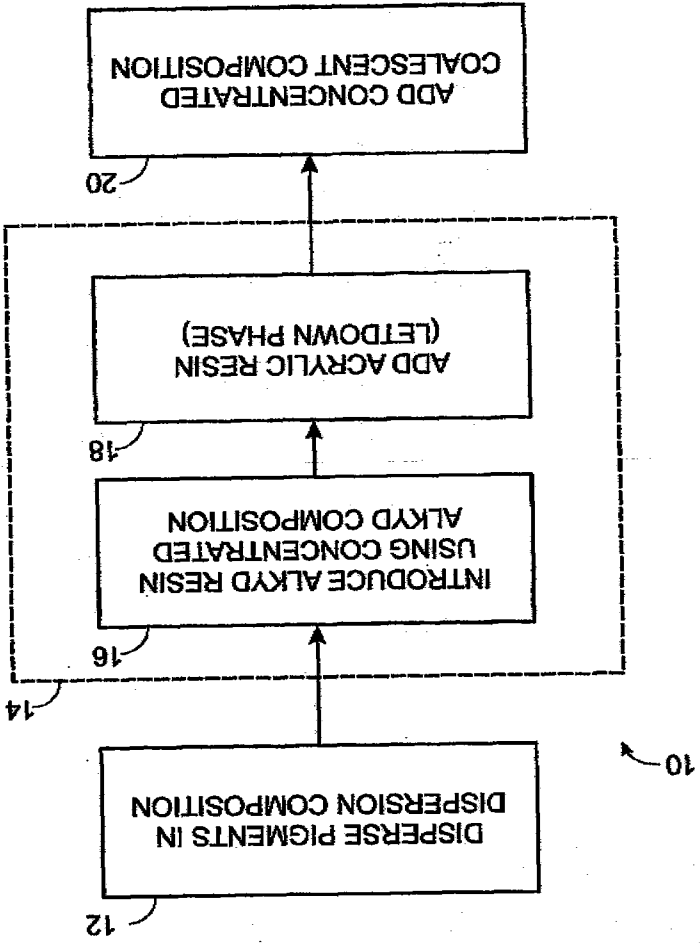
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Fig. 1



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Fig. 1

PROTECTIVE COATING

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is based upon and claims benefit under 35 U.S.C. §119 from the following U.S. Provisional Patent Application, which is incorporated herein by reference: Serial No. 60/267,563, naming Herbert C. Buffum and Albert R. Menebeg, filed Feb. 8, 2001.

FIELD OF THE INVENTION

[0002] The present invention relates generally to coating compositions, and more particularly to coating compositions that are curable to a protective film.

BACKGROUND

[0003] Polymeric coatings have a vast array of uses including paints, inks, sealants, and adhesives. One function of these coatings is to protect and insulate a more vulnerable material from exposure to the elements. For example, the exterior hulls of marine vessels are exposed to constant immersion in corrosive, high salinity water and to the constant forces exerted by water movement. In some cases, violent pounding forces. Many marine vessels are constructed of corrosion-sensitive metal alloys, thus it is essential to provide a curable coating that can withstand the harsh conditions imposed by ocean travel, while protecting the underlying material from corrosion or other degradation.

[0004] Many curable coatings that may be suitable for application to marine vessels include organic solvents to maintain hydrophobic components in solution and to allow these components to react efficiently. Examples of such solvents include toluene and xylene. However, since these organic solvents are generally volatile, their release into the atmosphere during curing has created considerable concern about the harmful effect of the solvents on the environment. For example, the United States Environmental Protection Agency (EPA) has set stringent standards that must be met in order for a coating composition to be designated as VOC-free. Currently, EPA test 24 requires coating compositions to contain less than 30 g/liter volatile organic compounds to be deemed VOC-free. In response to the EPA standards and other government regulations, coating manufacturers have increasingly attempted to decrease the fraction of volatile organic compounds (VOCs) in coating compositions.

[0005] Efforts to decrease VOCs in coating compositions have generally focused on replacing VOCs with non-volatile solvents and water, while still providing hydrophobic components in the composition as emulsions or dispersions. Surfactants and coalescents have been used to facilitate joining of the hydrophobic components in such emulsions and dispersions into a film during curing. For example, water-based acrylic latex coating compositions include a dispersion of resin particles and a coalescent to join the resin particles. However, these water-based acrylic coating compositions cure to produce a film with a latex-like pattern. Non-uniformity of latex films is at least partially a result of phase discontinuity in acrylic coating compositions immediately after application and during subsequent curing. Therefore, water-based acrylic compositions do not usually cure to provide the uniform protective barrier necessary for

into the coating composition. Finally, the coalescence composition adds coalescing agents that aid in curing the coating composition to a protective film.

[0011] The coating compositions of the present invention are typically free of volatile organic compounds and may be air-cured at ambient temperature to produce a protective film. In some embodiments curing may be mediated, or accelerated by any suitable means, such as by heat or ultraviolet radiation. Furthermore, the coating compositions are typically applied to a metal or metal alloy, but any suitable substrate may be used, including a wood product, paper, plastic, or concrete.

[0012] A method of making a coating composition in accordance with the present invention is shown in FIG. 1. Method 10 uses one or more concentrated compositions, as fully described in the following sections, to introduce components for pigment dispersion, resin addition and/or emulsification, and coalescence. As shown at step 12, pigments are dispersed and generally wetted and dis-agglomerated by mixing the pigments with a dispersion composition to produce a pigment mixture. This dispersion composition of method 10 may also be referred to as a grind phase. The present invention provides a concentrated dispersion composition that may be diluted with water, and optionally detergent and other additives, to create a dispersion composition suitable for pigment dispersion.

[0013] As shown at step 14, at least one resin is added to provide a binder for the coating composition. In this example, alkyl is introduced at step 15 as a concentrated composition that is diluted significantly during preparation of the coating composition. The concentrated alkyl composition may include a reactive diluent. At least one resin, in this case an acrylic resin, may be added at step 18, at a below phase, as part of a ledown composition. The ledown composition may include water, water and resin, or water, resin, and additives as defined below. In general, a ledown composition is any composition that increases water content of a dispersed pigment mixture by 50% or more. As shown at step 20, one or more coalescents may be added to the mixture as a concentrated coalescent composition that is diluted significantly during coating composition production. [0014] The remainder of the Detailed Description describes the present invention according to the following topic headings: A) Reactive Diluent; B) Coating Composition; C) Alkyl and/or Acrylic Coating Composition; D) Dispersion Composition; E) Concentrated Alkyl Composition; F) Concentrated Coalescence Composition; and Examples.

A. Reactive Diluent

[0015] In one aspect, the invention includes a reactive diluent. A reactive diluent is any compound or mixture of compounds that has a relatively low viscosity, is capable of diluting components (usually resins) of a coating composition, and reacts with one or more components of a coating composition to become incorporated into the film that is produced by curing the coating composition. A reactive diluent may be useful with high viscosity or solidifying resins to facilitate mixing these resins into the coating composition.

[0017] The reactive diluent of the present invention may be an organic acid, which in combination with a binder, may

be used to produce a VOC-free coating composition that is curable in air. In one embodiment, the reactive diluent of the invention is a carboxylic acid with the formula $R-(C=O)-OH$, where the R moiety has 8 to 35 carbons, and may be saturated or include one or more unsaturated carbon-carbon bonds. Furthermore, the R1 moiety may be unsubstituted or substituted one or more times, including substitution by hydroxy groups. The R1 moiety may incorporate at least one ester linkage of the form $(C=O)-O-$ or $-O-(C=O)-$, and may have 13 to 27 carbons, or 18 to 23 carbons. When an ester linkage is present in the reactive diluent, the reactive diluent is described as an ester acid or an ester carboxylic acid.

[0018] R¹ of the reactive diluent may have the following formula: $R^2-(C=O)-O-R^3-$. R² is a moiety having 13 to 23 carbons, 8 to 21 carbons, 13 to 19 carbons, 15 to 17 carbons, or 17 carbons. R² may be saturated or include one or more unsaturated carbon-carbon bonds, and may be unsubstituted or substituted one or more times, including substitution by hydroxy groups. R³ (and the attached, esterified carbon) may be provided by a synthetic mixture of at least two fatty acids derived from linseed oil, or R³ and the attached carbon may be provided by a natural mixture of the fatty acids present in linseed oil.

[0019] The R³ moiety is a linker having 1 to 16 carbons, 1 to 8 carbons, 1 to 6 carbons, 2 to 4 carbons, or 2 carbons. R³ is optionally saturated or unsaturated, and may be substituted or unsubstituted.

[0020] One form of the reactive diluent may be produced as the ester condensation product of 1) a fatty acid or mixture of fatty acids and 2) a hydroxy carboxylic acid, although any suitable synthetic route may be used to make the reactive diluent. A fatty acid is any carboxylic acid compound, whether synthetic, naturally-occurring, or created by a combination of these routes, where the carboxyl group is linked to a saturated or unsaturated, straight or branched hydrocarbon chain, optionally substituted with moieties such as hydroxy groups, or unsubstituted. Fatty acids include compounds with 4 to 24 carbons. The fatty acid or mixture of fatty acids may come from a natural source. Suitable natural sources for ester condensation to produce the reactive diluent may include fatty acids derived from corn, coconut, babassu, olive, peanut, perilla, linseed, tung, and castor oils; fatty acids obtained from drying oils; or a mixture of fatty acids from linseed oil. Linseed oil may be a commercially desirable source of chemically suitable fatty acids because of its low cost.

[0021] A hydroxy carboxylic acid is any carboxylic acid compound with a hydroxy group bonded to a carbon atom, where the carbon atom is distinct from the carboxyl group. The hydroxy carboxylic acid may have two to seven carbons. The hydroxy group may be on the 2-position of a hydroxy carboxylic acid, or on a 2-hydroxy propanoic acid, which is also known as lactic acid. In one form, the reactive diluent may correspond to the ester condensation product of linseed oil fatty acids and a substantially equimolar amount of lactic acid. A substantially equimolar ratio of fatty acid-silicic acid is about 0.8:1 to about 1.5:1.

B. Coating Composition

[0023] The reactive diluent of the present invention may be used in the coating composition presented in Table 1.

Each ingredient or component of this table, and all other tables in this description, includes three different concentration ranges that may be used. These concentration ranges are given as a weight range for each component, and the third concentration range listed for each component are intended to be considered independently for each ingredient or component.

[0024] The coating composition of Table 1 includes a binder and a reactive diluent, and typically includes pigments, and/or other additives. These components are dispersed, emulsified, or dissolved in an aqueous medium to create a coating composition that may be VOC-free. The water content may be about 20% to about 70%, about 25% to about 55%, or about 30% to about 50%.

TABLE 1

Coating Composition (% by weight)

Ingredients	Range
binder	5-35
reactive diluent	5-30
solvent	10-40
water	20-70

[0025] A suitable binder includes any components that inter-link or substantially solidify during curing to create a cured film. The binder may be present at about 3% to about 35%, about 5% to about 50%, or about 8% to about 40% by weight. The binder may be a single binder or a mixture of binders.

[0026] The binder is typically a polymer or resin. Examples of polymer or resin solutions, dispersions, or emulsions that may be used in the invention may be selected from, for example, polymers of alkyl esters of acrylic or methacrylic acid such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, lauryl methacrylate, 2-ethylhexyl methacrylate, nonyl methacrylate, benzyl methacrylate, the hydroxyalkyl esters of the same acids such as 2-hydroxyethyl methacrylate, 2-hydroxybutyl methacrylate, and 2-hydroxypropyl methacrylate, the amide and amides of the same acids such as acrylonitrile, methacrylonitrile, and methacrylamide, vinyl acetate, vinyl propionate, vinylidene chloride, vinyl chloride, and vinyl aromatic compounds such as styrene, t-butyl styrene and vinyl toluene, dialkyl malates, butadiene, chlorinated polyethylene and copolymers thereof. Suitable polymers containing carboxylic acid groups may include polymers derived from acrylic monomers such as acrylic acid, methacrylic acid, ethoxycrylic acid, itaconic acid, maleic acid, fumaric acid, monomethyl itaconate, itaconic anhydride, maleic anhydride, fumaric anhydride, and monomethyl itaconate, monomethyl maleate, monomethyl maleate, monomethyl itaconate, and monomethyl itaconate. Other polymers may include ethyl cellulose, nitrocellulose, linseed oil-modified alkyds, rosin-modified alkyds, pheno-modified alkyds, phenolic resins, polyesters, poly(vinyl toluene), polyisocyanate resins, polyurethanes, polyamides, chroman resins, dimer gum, ketone resins, polyamide acid resins, poly(benzothioetherylene-hexafluoropropylene), low-molecular weight polyethylene, pheno-modified pentaerythritol esters,

TABLE 2
Coating Composition (% by weight)

Ingredients	Range	EXAM- PLE 1
alkyd	0-15	1-5
reactive diluent	0-10	2-8
solvent	0-40	5-3
coupling agent	0-2	0.001-0.20
endocuring agent	0-5	0.01-0.5
pigment	0-80	10-60
defoaming agent	0-5	0.01-0.5
UV stabilizer	0-5	0.01-0.5
free-radical inhibitor	0-5	0.01-0.5
defoaming agent	0-5	0.01-0.5
biocidal agent	0-5	0.01-0.5
bodying agent	0-5	0.01-0.5
water	20-60	30-50

[0034] i. Alkyds and Reactive Diluent

[0035] Coating compositions that are made according to the present invention may include a non-zero amount of an alkyd at up to about 15%, about 0.5% to about 10%, or about 1% to about 5%. As used herein, an alkyd is any resin produced from the reaction of a polybasic carboxylic acid, a polyol, and a fatty acid. Examples of suitable polybasic acids include phthalic anhydride, isophthalic acid, terephthalic acid, succinic acid, adipic acid, sebacic acid, tetrahydrophthalic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, and citraconic anhydride.

[0036] A polyol is any polyhydric alcohol including two or more hydroxy groups per molecule. Suitable polyols may include glycerol, ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, trimethylene glycol, tetraethylene glycol, pentaerythritol, neopentyl glycol, diglycerol, triglycerol, pentaerythritol, dipentaerythritol, inositol, and sorbitol. Typically, the polyol used in alkyd preparation is glycerol, or an oil derivative thereof.

[0037] A fatty acid is any carboxylic acid compound, whether synthetic, naturally-occurring, or a combination thereof, where a carbonyl group is linked to a substituted or unsubstituted, straight or branched hydrocarbon chain. Fatty acids are compounds that have 4 to 24 carbons. In addition, fatty acids have hydrocarbon chains that may be modified with other moieties such as hydroxy groups. In the present invention, the polyol and fatty acids may be provided in an esterified form, esterified as oils, or as dehydrated or partially saponified oil derivatives. Suitable oils for use in the present invention include sun-drying and semi-drying oils such as coconut oil, palm oil, olive oil, castor oil, rice oil, cotton oil. Drying oils such as soybean oil, tung oil, or linseed oil are used more commonly.

[0038] Alkyds may be described as about oil, medium oil, or long oil. Oil length is a measurement of the percentage oil content by weight in the alkyd. A medium oil length is defined as 45%-55% oil content, with long oil alkyds 55% and short oil alkyds 45%. Primer coating compositions produced according to the present invention may include a short oil alkyd, and a topcoat composition may include a medium oil alkyd.

[0033] Coating compositions of the present invention may include the reactive diluent described above for the coating composition of Table 1. Reactive diluent may be included in the coating composition described in Table 2 at a non-zero amount of up to about 15% by weight, about 0.5% to about 10%, or about 1% to about 5%.

[0040] ii. Acrylic Resins

[0041] Coating compositions of the present invention may include an acrylic resin. Acrylic resin may be included in a coating composition at a non-zero amount of up to about 40%, about 2% to about 20%, or about 5% to about 15%. A suitable acrylic resin typically has a glass transition temperature high enough to maintain the desired hardness at the range of temperatures at which the resulting protective film will be used, selected from the range of about 10° C. to about 300° C. Suitable acrylic resins may include pure acrylic resins, an epoxy acrylic hybrid system, a copolymer of acrylic acid and acrylic acid ester, or combinations with vinyl resins or copolymers with vinyl monomers, such as vinyl acetate, styrene or butadiene. Acrylic resins are typically included in coating compositions of the present invention as particulate dispersions with suitable particle sizes selected from the range commonly used in acrylic latex paints. An acrylic resin that has been used successfully in an embodiment of the invention is UCAR LATEX 626, which is offered by Union Carbide Corp., Danbury, Conn.

[0042] A surface hardener may be included in some embodiments of the present invention, for example, as part of a concentrated coalescent composition that is added during production of the coating composition (see below). A surface hardener may include any material that forms part of the surface film and increases the overall hardness of the film. A suitable type of surface hardener is a very hard acrylic resin. During curing a very hard acrylic resin may become part of the forming film, but may provide a dull surface finish to the cured film. Therefore, surface hardeners are optional components of a coating and are generally used in low binder or flat coatings. Although any suitable hard acrylic resin may be used as a surface hardener, a powdered thermoplastic resin, B-66 ACRYLOID has been used successfully. B-66 ACRYLOID is a copolymer of methyl and butyl methacrylates from Rohm-America, Inc., of Piscataway, N.J.

[0043] iii. Coupling Agents

[0044] One or more coupling agents may be included in coating compositions of the present invention at a non-zero concentration of up to about 2%, about 0.002% to about 0.5%, or about 0.005% to about 0.20%. Coupling agents may be used to promote several properties of the coating composition. For example, coupling agents may facilitate the wetting of inorganic or organic pigments and other additives during the grind or dispersion phase of coating composition production. In this role coupling agents may function to provide a shorter grind/dispersion time. Second, they may aid in the emulsion of alkyds, reactive diluent, acrylic resin, or other hydrophobic components in an aqueous mixture. Third, coupling agents may play a coupling role by uniting reactive moieties. Fourth, coupling agents may act as catalysts in electron transfer reactions. Fifth, coupling agents may improve adhesion between pigment and binder, producing a stronger film.

[0045] Coupling agents, also called hyperelements, are typically organometallic derivatives that include the metals

titanium, zirconium, or silicon. Alternatively, coupling agents may include titanium or zinc, or may be organo-titanate or organo-zirconate coupling agents, or a combination thereof, such as the coupling agents described in U.S. Pat. No. 4,087,402, filed Apr. 19, 1976; U.S. Pat. No. 4,080,353, filed Jan. 30, 1976; U.S. Pat. No. 4,122,062, filed Sep. 30, 1975; U.S. Pat. No. 4,227,415, filed Aug. 28, 1979; U.S. Pat. No. 4,623,738, filed Apr. 22, 1985; and U.S. Pat. No. 4,634,785, filed Jan. 6, 1987. These patents are hereby incorporated by reference in their entirety. Coupling agents that may be suitable for use in the coating compositions and concentrated sub-compositions of the present invention are available from Du Pont under the name TYZOR and from Kenrich Petrochemicals, Inc., Bayonne, N.J. Although structurally similar compounds may be used from any source, coupling agents that have been used successfully in embodiments of the present invention are available from Kenrich. These coupling agents include KEN-REACT KR 55, a coordinate titanate; KEN-REACT LICA 36, a neosilky titanate; KEN-REACT LICA 12, a neosilky titanate; KEN-REACT KZ 55, a coordinate zirconate; and KEN-REACT NZ 38, a neosilky zirconate.

[0046] iv. Coalescents

[0047] Coating compositions of the present invention may include a non-zero amount of a coalescing agent, also referred to as a coalescent, at a concentration of up to about 5%, about 0.03% to about 1%, or about 0.1% to about 0.5% by weight. A coalescent is any compound that directly promotes uniting resin molecules into a film, and usually becomes incorporated into the film.

[0048] In the coating compositions of the present invention, coalescing agents may include one or more low molecular weight (typically monomer) multi-functional acrylate cross-linkers. Monomer multi-functional acrylate cross-linkers may be included at about 0.001% to about 0.5%, about 0.003% to about 0.25%, or about 0.01% to about 0.1%, by weight. Low molecular weight tri-functional cross-linkers that have been used successfully in preparing compositions of the present invention include SR-444 and SR-9035 from Sartomer, Company, Inc., Exton, Pa. SR-444 is pentaerythritol triacrylate, and includes a pendant hydroxy group, whereas SR-9035 is ethoxylated (15) trimethyloxypropane triacrylate. SR-444 may be more suitable in applications where a harder film or reduced water sensitivity is required. In contrast, SR-9035 may be suitable in applications where trace amounts of formaldehyde release are unacceptable.

[0049] In addition to multi-functional acrylate monomers, a monofunctional acrylate monomer may be used to facilitate cold temperature coalescence at temperatures near freezing. Such a cold-temperature coalescent may be included at a non-zero amount of up to about 0.5%, about 0.01% to about 0.4%, or about 0.03% to about 0.3% by weight. A cold-temperature coalescent acrylate monomer that may be suitable for this purpose is SR-495. SR-495 is available from Sartomer Company and is a monofunctional monomer of caprolactone acrylate.

[0050] Coating compositions of the present invention may also include a polyether polyol or copolyether polyol as a coalescing agent. The term polyether polyol is also meant to include copolyether polyols hereafter. Polyether polyols may be included at about 0.02% to about 2%, about 0.05%

to about 1%, or about 0.1% to about 0.5%, by weight. Examples of polyether polyols and copolyether polyols, and their use in coatings, are described in U.S. Pat. No. 5,708,058, filed Sep. 25, 1996, and U.S. Pat. No. 5,883,180, filed Nov. 9, 1995, which are hereby incorporated by reference in their entirety. Polyether polyols are the reaction products of one or more alkylene oxides and one or more aliphatic polyol, where the polyol includes 2 to 8 carbons. The resulting ethers may include up to 20 or more added alkoxy groups. In the present invention a polyether polyol may be an ethoxylated polyol, an alkoxylated butanol, an ethoxylated butanol, or a butoxy polyglycol such as BUTOXY-POLYGLYCOL BASIC, which is available from Union Carbide Corporation, Danbury, Conn.

[0051] v. Pigments

[0052] Coating compositions of the present invention may include at least one pigment. Pigment may be included in the coating composition at a non-zero amount of up to about 80%, about 10% to about 60%, or about 30% to about 55%, by weight. Pigment includes all particulate ingredients that are added to the coating composition and are distinct from binder, and may include functional properties listed above for pigment of Table 1.

[0053] Any suitable inorganic pigments may be used, for example titanium dioxide, zinc oxide, basic lead sulfate, calcium plumbate, zinc phosphate, aluminum phosphate, zinc molybdate, calcium molybdate, yellow lead, synthetic yellow iron oxide, transparent red oxide, titanium yellow, zinc yellow, strontium chromate, red oxide, red lead, chrome vermillion, basic lead chromate, chromium oxide, Prussian blue, ultramarine blue, cobalt blue, calcium carbanate, barium sulfate, talc, clay, silica, mica, graphite, iron black, and carbon black.

[0054] Any suitable organic pigments may also be used, such as monoazo red, quinacridone Red, monoazo red Mn salt, monoazo Bordeaux Mn salt, monoazo maroon Mn salt, anthanthrone red, anthraquinonyl red, perylene maroon, quinacridone Magenta, perylene Red, diketopyrrolopyrrole, benzimidazolone orange, quinacridone Gold, monoazo yellow, cis-azo Yellow, isindolinone yellow, metal complex salt azo yellow, quinophthalone yellow, benzimidazolone yellow, copper phthalocyanine green, brominated phthalocyanine green, copper phthalocyanine blue, indanthrene Blue, dioxane violet, fast yellow group, permanent yellow RR, acetanilide type monoazo yellow, Lake Red 4R, Permanent Carmine FB, Brilliant Fast Scarlet, Pyrazolone Red B, Watchung Red metal salts, Lithol Red Ba salt, Brilliant Carmine 6G, Bordeaux 10B, and Rhodamine 6G Lake.

[0055] Anti-corrosives are any additives that prevent corrosion of an underlying substrate, and are categorized as pigments. The coating composition may include anti-corrosives that act as rust inhibitors by oxidation in place of a metal substrate on which the coating composition has been applied. Anti-corrosives may be included at a non-zero amount of up to about 60%, about 5% to about 50%, or about 15% to about 40%, by weight. Although any anti-corrosives may be suitable, anti-corrosives that have been used successfully in embodiments of the present invention include zinc oxide, SW MOLY WHITE 501, available from Sherwin-Williams, and HALOX Z-PLEX 111, a zinc phosphate complex available from Huls, of Hammond, Ind. Sodium nitrite may be added to inhibit flash rusting at about 0.01%

to about 1%, about 0.03% to about 0.5%, or about 0.05% to about 0.3% by weight. Anti-corrosives may not be required in coating compositions that are applied to non-rusting materials such as wood.

[0056] vi. Detergents and pH Modifiers

[0057] Coating compositions of the present invention may include one or more detergents at a non-zero concentration of up to about 5%, about 0.05% to about 2%, or about 0.1% to about 1%. Detergents may include any ionic, polyelectrolyte, or non-ionic molecule with hydrophobic and hydrophilic portions. Detergents may function to lower surface tension and facilitate wetting of some pigments. In addition they may facilitate the formation of emulsions or solubilization of hydrophobic components. Detergents for pigment dispersion are well known in the art. Detergents that have been used successfully in embodiments of the present invention include TRITON CF-10 (Union Carbide, of Danbury, Conn.) or TAMOL 850 (Rohm and Haas).

[0058] The pH of coating compositions of the present invention may be adjusted by including a non-zero amount of a pH modifying agent with basic properties, up to about 5%, about 0.1% to about 2%, or about 0.2% to about 1% by weight. The pH modifying agent may include ethylenic unsaturation, or may be a dialkylaminoalkyl acrylate or methacrylate. Illustrative of these acrylates are 2-dimethylaminoethyl- and 2-diethylaminoethyl-acrylate or -methacrylate, 2-dimethylaminoethyl- and 2-diethylaminoethyl-propyl-acrylate or -methacrylate, 2-tert-butylaminoethyl-acrylate or -methacrylate, and the 3-dialkylamino-2,2-dimethylpropyl-1 acrylates and -methacrylates. Coating compositions of the present invention may include a tertiary amine neutralizing agent, 3,3-dimethylaminoethyl methacrylamide, abbreviated as DMAPMA (Rhône-Poulenc, Inc.). DMAPMA and related tertiary amines have been suggested to promote wet adhesion as described in U.S. Pat. No. 4,582,730, filed Jan. 28, 1985, and U.S. Pat. No. 5,312,663, filed Mar. 20, 1992, both of which are hereby incorporated by reference.

[0059] Ammonium hydroxide may be included as a pH modifier at a non-zero amount up to about 1%, 0.02% to about 0.5%, or about 0.05% to about 0.25%. In addition, ammonium hydroxide may be included to adjust the final pH of a coating composition to about 8.0 to about 9.5, about 8.5 to about 9.2, or about 8.8 to about 8.95.

[0060] Potassium tripolyphosphate (KTPP) may be included with a pH modifier to help stabilize the pH. KTPP may be included at a non-zero concentration of up to about 2%, about 0.05% to about 1%, or about 0.2% to about 0.6%. KTPP has been used successfully in selected embodiments of the present invention was obtained from Brenntag Southwest, Inc., of Longview, Tex.

[0061] vii. Drying Agents and Wet-Edge Modifiers

[0062] Drying agents may be included in coating compositions of the present invention at a non-zero concentration of up to about 0.3%, about 0.02% to about 0.25%, or about 0.05% to about 0.15%, by weight. Drying agents are any compounds that facilitate oxidative curing of the coating composition during exposure to air. Generally, drying agents catalyze cross-linking of fatty acid chains in an alkyl, but may catalyze any other reaction that promotes oxidative curing. Drying agents suitable for use in the present inven-

tion may include water emulsifiable driers such as cobalt alkanoate and manganese naphthenate, available as NUOCURE COBALT 10% and NUOCURE MANGANESE 6% from CONDEA Serve LLC, Piscataway, N.J.

[0063] Wet-edge modifiers may be included in coating compositions of the present invention at a non-zero concentration of up to about 5%, about 0.001% to about 0.25%, or about 0.01% to about 0.10%, by weight. A wet-edge modifier is any substance that temporarily inhibits the curing process after application of the coating composition or that helps otherwise stabilize the coating composition. This type of modifier may assist in applying a uniform layer of the coating composition, by preventing premature curing during the application process. A suitable wet-edge modifier may be 4-hydroxy-3-methoxybenzaldehyde, commonly known as vanillin or vanillin, combined with a polyether polyol. Vanillin may be combined with a polyether polyol, including vanillin at about 0.10% to about 10%, 0.30% to about 3%, or about 0.5% to about 2%. This vanillin/polyether polyol (wet-edge modifier) mixture may be included in the coating composition at a non-zero concentration of up to about 5%, about 0.001% to about 0.50%, or about 0.01% to about 0.20%, by weight. Overall, vanillin may be included in coating compositions of the present invention at about 0.0001% to about 0.010%, about 0.0002% to about 0.005%, or about 0.0005% to about 0.003%, by weight. Polyether polyols are described above under Coalescents. A wet-edge modifier may contribute not only functional properties, but vanillin produces a characteristic aroma during the curing process that may provide pleasant associations.

[0064] viii. Freeze-Thaw Stabilizers, and Defoaming, Biocidal, and Boding Agents

[0065] Coating compositions of the present invention may include a freeze-thaw stabilizer, at a non-zero concentration of up to about 1%, about 0.003% to about 0.3%, or about 0.01% to about 0.1%. A freeze-thaw stabilizer may protect the coating composition from cold weather damage and thus may increase the shelf-life and stability of the composition. The freeze-thaw stabilizer may include a polyvinyl alcohol. A polyvinyl alcohol used successfully in embodiments of the invention is AIRVOL-103 from Air Products and Chemicals, Inc., Allentown, Pa.

[0066] One more more defoaming agents may be included in coating compositions of the present invention at a non-zero concentration of up to about 1%, about 0.05% to about 2%, or about 0.1% to about 1% by weight. Defoaming agents are any compounds or mixtures that prevent the initial formation of foam or act to destabilize it once formed. These agents may minimize trapped air that could affect the evenness of application or otherwise adversely alter the quality of the cured film produced after application. PAT-COTE 841, available from American Ingredients Co., Kansas City, Mo., and DEE FO XJH-123 from Ultra Additives Inc., Paterson, N.J. have been used as defoaming agents in coating composition embodiments.

[0067] Biocidal agents may be included in coating compositions of the present invention at a non-zero concentration of up to about 2%, about 0.01% to about 0.8%, or about 0.05% to about 0.4%, by weight. Biocidal agents are any substances that inhibit growth of micro-organisms in a coating composition, or in or on the cured film produced after application of the coating composition. An anti-bacte-

[illegible]

Impurities	Range	EXAMPLE 1
coupling agent	1-30	6.3
polymer support	3-66	21.7
oil modifier	2-60	12.7
vanillin	0-3	0.35
decyl-lauryl	0-25	4.6
diethylhexyl	20-70	44.8

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[0084] The coacervation composition may include a poly-
ether polyol at about 5% to about 90%, about 40% to about
80%, or about 60% to about 75%. An acrylate monomer may
be included at about 2% to about 50%, about 5% to about
40%, or about 10% to about 30%. The acrylate monomer
may include one or more methyl-functional acrylate mono-
mers. An acrylate resin may be included at a non-zero
concentration of up to about 70%, about 2% to about 15%,
or about 5% to about 10%. The acrylate resin may be a
surface hardener. Vanillin may be included at a non-zero
concentration of up to about 1%, about 0.5% to about 1%,
or about 0.1% to about 0.6%. The vanillin:polyether polyol
ratio may be about 1:1, about 1:1.5, or about 1:2.00.
The composition may include a hardener at about 1:33 to about
1:330, or about 1:58 to about 1:200.

24. The coating composition of claim 23, further comprising a coupling agent that includes titanium or zirconium.

25. A coating composition that is suitable to a peroxidative film after application to a surface, the composition comprising:

ing:

an acrylic resin at a concentration of up to about 40% by weight;

a coalescent comprising a multi-functional acrylate monomer and a polyether polyol; and

a coupling agent.

26. The coating composition of claim 25, where the coupling agent is present at a concentration of up to about 3% by weight and includes titanium or zirconium.

27. The coating composition of claim 25, further including an acrylicamide pH modifier.

28. The coating composition of claim 27, where the acrylicamide pH modifier is a tertiary amine.

29. The coating composition of claim 25, where the acrylate monomer is present at a concentration of about 0.001% to about 0.5% by weight, and the polyether polyol is less than 30 grams per pound. The above composition comprises a coupling agent that is substantially aqueous and consists of up to about 95% of the dispersion composition by weight.

41. The dispersion composition of claim 40, where the coupling agent is present in the first part at a concentration of about 1% to about 30% and includes titanium or zirconium.

42. The dispersion composition of claim 40, where the polyether polyol is present in the first part at a concentration of about 3% to about 60% by weight.

43. The dispersion composition of claim 40, where the coupling agent and the polyether polyol are present in the composition in a weight ratio of about 1:50 to about 1:1.

44. The dispersion composition of claim 40, where the composition further comprises an acrylicamide pH modifier.

45. The dispersion composition of claim 40, where the pH modifier is present in the last part at a concentration of about 2% to about 60% by weight.

46. A concentrated slurry composition for use in a production coating composition that is curable to a product, less than 30 grams per pound. The above composition comprises a coupling agent and a metal complexed compound containing a second part that is substantially aqueous and consists of up to about 95% of the dispersion composition by weight.

position that is capable to a protective film, where the reaction heat mixture is produced by cast condensation of lactic acid and a mixture of at least two fatty acids obtained from linseed oil.

14. A coating composition that is capable to a protective film, comprising an alkyl, an acrylic resin, and a coupling agent.

15. The coating composition of claim 14, where the volatile organic compound content is less than about 30 grams per liter.

16. The coating composition of claim 17, where the coupling agent is present at a concentration of up to about 20% by weight and inactivated titanium or zirconium.

17. The coating composition of claim 14, further comprising a reactive diluent, where the alkyd-reactive diluent weight ratio is about 1:1 to about 1:5.

18. The coating composition of claim 14, where the coupling agent is present at a concentration of about 2% to about 20% by weight.

19. The coating composition of claim 14, further comprising a polyether polyol.

20. The coating composition of claim 19, where the polyether polyol includes an alkoxyaromatic polyol.

21. The coating composition of claim 19, further comprising a multi-functional acrylic monomer.

them, comprising: an alkyl, where the alkyl is present at a concentration of up to about 15% by weight; an acrylic resin, where the acrylic resin is present at a concentration of up to about 40% by weight; and a crosslinker, where the crosslinker comprises a multifunctional acrylic monomer and a polyether polyol. The resulting composition of claim 22, where the acrylic monomer is present at a concentration of about 0.01% to about 0.3% by weight, and the polyether polyol is present at a concentration of about 0.02% to about 2% by weight.

including a freeze-thaw stabilizer.
38. The freeze-thaw stabilizer includes a polyvinyl alcohol at a concentration of up to about 20% by weight.
39. The dispersion composition of claim 31, further including a freeze-thaw stabilizer at a concentration of up to about 3% by weight.
40. A dispersion composition suitable for dilution with water, designed for other uses and purposes, is a composition consisting of the dispersion composition comprising:
a first part that comprises a coupling agent and a polyether
polymer.

55. The alkyl composition of claim 51, further comprising an acrylamide pH modifier that is present at a concentration of about 0.5% to about 10% by weight.

56. The alkyl composition of claim 51, further comprising a styryl agent.

57. A concentrated coalescent composition that is suitable for use in preparing a curable coating composition, the coalescent composition comprising:

an acrylate monomer at a concentration of about 2% to about 50% by weight; and

a polyether polyol at a concentration of about 10% to about 90% by weight.

58. The coalescent composition of claim 57, further including vanillin at a concentration of up to about 2% by weight.

59. The coalescent composition of claim 58, where the vanillin and the polyether polyol are present in a weight ratio of about 1:10 to about 1:1000.

60. A method of dispersing pigment during preparation of a curable coating composition, comprising:

combining at least one pigment with a dispersion composition to produce a mixture, where the combining step results in dis-agglomeration of the pigment;

provided that the mixture comprises a titanium or zirconium coupling agent at a concentration of about 0.004% to about 1.2% by weight and a polyether polyol at a concentration of about 0.012% to about 2.4% by weight.

61. The method of claim 60, where the mixture further comprises an acrylamide pH modifier at a concentration of about 0.1% to about 10% by weight.

62. The method of claim 60, where the mixture further comprises a freeze-thaw stabilizer at a concentration of up to about 0.6% by weight.

63. The method of claim 60, further comprising diluting a concentrated dispersion composition about 10-fold to about 2000-fold to produce the dispersion composition, where the concentrated dispersion composition provides the coupling agent and the polyether polyol for the dispersion composition.

64. A method of dispersing pigment during preparation of a curable coating composition, comprising:

combining at least one pigment with a dispersion composition to produce a pigment mixture, where the combining step results in dis-agglomeration of the pigment;

provided that the pigment mixture comprises a titanium or zirconium coupling agent at a concentration of about 0.004% to about 1.2% by weight, and an acrylamide pH modifier at a concentration of about 1% to about 10% by weight.

65. The method of claim 64, further comprising diluting a concentrated dispersion composition about 10-fold to

about 2000-fold to produce the dispersion composition, where the concentrated dispersion composition provides the coupling agent for the dispersion composition.

66. A method of producing a coating composition that is curable to a protective film, comprising:

mixing an alkyl composition and a water-based mixture, where the alkyl composition comprises an alkyl and a reactive diluent, the alkyl and reactive diluent are each present at a concentration of about 10% to about 80% by weight, and the alkyl is diluted about 2-fold to about 40-fold by mixing.

67. The method of claim 66, where the water-based mixture comprises at least one pigment at a concentration of at least about 30% by weight.

68. The method of claim 66, where the alkyl composition further comprises a coupling agent at a concentration of about 0.5% to about 15% by weight.

69. The method of claim 66, further comprising the step of adding an acrylic resin to a final concentration of up to about 40% by weight.

70. The method of claim 66, further comprising the step of adding a coalescent composition that includes at least two coalescents.

71. A method of producing a coating composition that is curable to a protective film, comprising:

combining a coalescent composition with a water-based mixture that includes a binder, where the coalescent composition is diluted at least about 50-fold when combined and comprises at least two coalescing agents.

72. The method of claim 71, where the binder comprises an alkyl and an acrylic resin.

73. The method of claim 71, where the at least two coalescing agents include a polyether polyol.

74. A method of producing a coating composition that is curable to a protective film, comprising the steps of:

diluting a concentrated dispersion composition about 10-fold to about 2000-fold with water and pigment to make a pigment dispersion adapted to dis-agglomerate the pigment upon mixing;

combining binder with the pigment dispersion to make a binder mix; and

combining a concentrated coalescent composition with the binder mix, where the coalescent composition is diluted at least about 50-fold when combined.

75. The method of claim 74, where the concentrated dispersion composition includes a titanium or zirconium coupling agent.

76. The method of claim 74, where combining binder includes addition of a concentrated alkyl composition, where the concentrated alkyl composition includes an alkyl at a concentration of about 10% to about 80% by weight.

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