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(54) **GLYCOL DILEVULINATES AS COUPLING AGENTS IN CLEANING FORMULATIONS**

GLYCOLDILEVULINATE ALS KOPPLUNGSMITTEL IN REINIGERFORMULIERUNGEN

DILÉVULINATES DE GLYCOL COMME AGENTS DE COUPLAGE DANS DES FORMULATIONS DE NETTOYAGE

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EP 2 872 611 B1

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DescriptionField of the Invention

5 **[0001]** The present invention relates to cleaning formulations comprising water, one or more organic solvents having low solubility in water such as aliphatic hydrocarbons, aromatic hydrocarbons, or other organic compounds, and an alkylene glycol dilevulinate. The alkylene glycol dilevulinates are excellent solvents for coupling the organic solvents with water.

10 Background of the Invention

[0002] Organic solvents are compounds that can be used to dissolve, soften, melt, or extract another compound, such as grease, soil, oil, paint, glue, stains, etc., and, therefore, are commonly used in cleaning formulations. Typical organic solvents include aliphatic hydrocarbons, isoparaffins, aromatic hydrocarbons, chlorinated hydrocarbons, terpenes and d-limonene, among others. Unfortunately, many organic solvents have limited solubility, or practically zero solubility, in water which severely limits the amounts that can be added to water-based cleaning formulations sometimes to the point where their beneficial effects cannot be realized.

15 **[0003]** Coupling agents are compounds that facilitate dissolution and dispersion of organic solvents, into water-based formulations, in greater amounts than otherwise possible, while the formulations retain their clarity, viscosity and homogeneity. Various coupling agents are known for use in cleaning formulations including propylene glycol, diethylene glycol, glycol ethers, and surfactants, among others. See U.S. Patent Nos. 4,511,488. However, lower glycol ethers are volatile organic compounds (VOCs) which are environmentally undesirable. Some higher glycol ethers have lesser solubility in water-based systems, which limits their utility as coupling agents.

20 **[0004]** WO 2010/138907 discloses a solution comprises a solute dissolved in an aqueous cosolvent mixture, where the aqueous cosolvent is a mixture that includes water and at least one alkyl ketal ester that is miscible in water at the relative proportions of it present in the cosolvent mixture. The preferred alkyl ketal esters are based upon levulinic acid. Esters of levulinic acid are well known and described in the art as plasticizers and solvents. For example, GB423919 describes the production of esters of levulinic acid with modified polyhydric alcohols which are useful as plasticizers for cellulose derivatives in coating applications.

25 **[0005]** For example, U.S. Patent No. 2,654,723 describes the preparation of diethylene glycol dilevulinate by heating a mixture of levulinic acid and diethylene glycol, in a solvent such as toluene and in the presence of an acid catalyst.

[0006] International Patent Application No. WO 2010/102203 describes the preparation of alkyl levulinates by an acid-catalyzed reaction of furfuryl alcohol with other alcohols including methanol, ethanol, propanol, isopropanol, butanol, and isobutanol.

30 **[0007]** In U.S. Patent No. 3,203,964, a process is described for manufacturing levulinic acid esters by heating furfuryl alcohol with another alcohol selected from the group consisting of unsubstituted primary and secondary carbon chain and oxygen-carbon chain aliphatic and carbon ring and oxygen-carbon ring cycloaliphatic alcohols containing from 1 to 10 carbon atoms, in the presence of an acid catalyst. U.S. Patent No. 3,203,964 states that the levulinic acid esters are useful as plasticizers or solvents.

35 **[0008]** International Patent Application Publication No. WO2007/094922 describes the use of ester derivatives of levulinic acid to replace traditional plasticizers and coalescent solvents in polymer compositions, plastics and water-based coatings, thereby to lowering their VOC content.

[0009] GB478854 describes the use of lower alkylene glycol dilevulinates (e.g., dilevulinates of propylene glycol, diethylene glycol, ethylene glycol, trimethylene glycol (1,3-propanediol), 1,3-butylene glycol and dimethyl-dimethylol) as suitable high boiling softening agents for cellulosic pellicles. U.S. Patent No. 2,581,008 discloses the preparation of dilevulinates of mono-, di- and tri-ethoxylated diols and their use as plasticizers for polyvinyl acetals and other polymers.

40 **[0010]** Furfuryl alcohol and levulinic acid are two of the reactants that can be used to manufacture esters of levulinic acid, e.g., alkylene glycol dilevulinates. They are both inexpensive renewable feedstocks available from biomass. Thus, the use of levulinates as solvents in water-based cleaning formulations would be economically and environmentally beneficial.

45 **[0011]** A solvent which would facilitate the use of organic solvents having low water solubility in water-based systems, such as aqueous cleaning formulations, would provide significant advantages relative to solvents traditionally used as coupling agents. The present invention provides for the use of alkylene glycol dilevulinates as new alternative coupling agent solvents in water-based formulations.

50 Summary of the Invention

[0012] The present invention provides a cleaning formulation comprising: (A) an aqueous solvent comprising water;

(B) an active component comprising an organic solvent; and (C) a coupling agent comprising an alkylene glycol dilevulinate. The alkylene glycol dilevulinate has the general formula, $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}-\text{R}-\text{O}(\text{O})\text{CCH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3$, wherein R is a C_2 - C_8 straight chain or branched alkylene moiety, and the two levulinate groups ($\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}$ -) may be attached to adjacent, or non-adjacent, carbon atoms of the alkylene moiety. In some embodiments, for example, R may be a C_2 - C_3 alkylene moiety, and the alkylene glycol dilevulinate may be selected from the group consisting of: ethylene glycol dilevulinate, 1,2-propylene glycol dilevulinate and 1,3-propylene glycol dilevulinate. The organic solvent may have a solubility of no more than 10%, or no more than 5%, by weight, in water at 25°C and atmospheric pressure, based on the total weight of the organic solvent and water in solution. Furthermore, the organic solvent may be at least one compound selected from the group consisting of: an aliphatic hydrocarbon, an aromatic hydrocarbon, a chlorinated hydrocarbon, a terpene, lemon oil, pine oil, methyl soyate and d-limonene.

[0013] In one embodiment of the cleaning formulation of the present invention, the aqueous solvent comprising water (A) may be present in an amount of from 90% to 98% by weight, the active component comprising an organic solvent (B) may be present in an amount of from 0.1% to 5.0% by weight, and the coupling agent comprising an alkylene glycol dilevulinate (C) may be present in an amount of from 0.1% to 6.0%, all weight percentages based on the total weight of the cleaning formulation.

Brief Description of the Drawings

[0014] A more complete understanding of the present invention will be gained from the embodiments discussed hereinafter and with reference to the accompanying figures in which:

Figure 1 is a schematic grid diagram of the general layout of sample formulations, each containing various types of glycol ethers as coupling agents, various amounts of d-limonene fragrance, and 1% sodium lauryl sulfate (SLS) surfactant, which were tested for coupling effectiveness as shown in Figures 2-4;

Figures 2, 3 and 4 are diagrams in accordance with the general layout of Figure 1, showing coupling effectiveness of the glycol ethers at 25°C, 40°C and 50°C, respectively;

Figure 5 is a schematic grid diagram of the general layout of sample formulations, each containing various types of glycol ethers as coupling agents, various amounts of d-limonene fragrance, and 0% SLS surfactant, which were tested for coupling effectiveness as shown in Figures 6-8;

Figures 6, 7 and 8 are diagrams in accordance with the general layout of Figure 5, showing coupling effectiveness of the glycol ethers at 25°C, 40°C and 50°C, respectively;

Figure 9 is a schematic grid diagram of the general layout of sample formulations, each containing various types of alkylene glycol dilevulinate as coupling agents, various amounts of d-limonene fragrance, and 1% SLS surfactant, and tested for stability as shown in Figures 10-12;

Figures 10, 11 and 12 are diagrams in accordance with the general layout of Figure 9, showing the stability of formulations containing the alkylene glycol dilevulinate at 25°C, 40°C and 50°C, respectively;

Figure 13 is a schematic grid diagram of the general layout of sample formulations, each containing various types of alkylene glycol dilevulinate as coupling agents, various amounts of d-limonene fragrance, and 0% SLS surfactant, and tested for stability as shown in Figures 14-16; and

Figures 14, 15 and 16 are diagrams in accordance with the general layout of Figure 13, showing stability of formulations containing the alkylene glycol dilevulinate at 25°C, 40°C and 50°C, respectively.

Detailed Description of the Invention

[0015] The present invention relates to the use of alkylene glycol dilevulinate or mixtures of alkylene glycol dilevulinate in water-based cleaning formulations to couple active components comprising organic compounds such as solvents or fragrances, having low or zero water solubility, with water. Alkylene glycol dilevulinate can be economically produced from levulinic acid and a glycol. Levulinic acid is available from biomass and is, therefore, a renewable environmentally-friendly resource. Additionally, glycols such as 1,2-propylene glycol and 1,3-propylene glycol are biorenewable and, therefore, also environmentally-friendly materials.

[0016] Alkylene glycol dilevulinate are high boiling, clear liquids with minimal odor and are not volatile organic compounds (VOCs). These particular characteristics provide benefits and advantages to their use as alternative coupling agents in water-based cleaning formulations. For example, traditional coupling agents such as propylene glycol, diethylene glycol and lower glycol ethers are volatile organic compounds (VOCs) which are environmentally undesirable. Also, with the exception of dipropylene glycol methyl ether, glycol ethers are not as effective couplers as the alkylene glycol dilevulinate. The alkylene glycol dilevulinate are partially to completely water soluble and are not VOCs. Since it is widely understood by persons of ordinary skill in the relevant art that diesters are typically not water soluble, the fact that alkylene glycol dilevulinate are water soluble and, therefore, useful as coupling agents in water-based systems is

a surprising and unexpected benefit. Furthermore, applicants have discovered that alkylene glycol dilevulinates provide better coupling performance which allows the use of greater amounts of organic solvents having low or zero water solubility with water, than when traditional coupling agents are used. Inclusion of greater amounts of the organic solvents increases cleaning efficiency while maintaining preferred formulation characteristics such as homogeneity, clarity, stability and viscosity.

[0017] It is also believed that alkylene glycol dilevulinates could be particularly useful in aerosol products such as hair care products, sanitizers, and insecticides, and spray applied consumer products. These dilevulinate solvents allow the formulation of more efficient, safer and more environmentally friendly formulations and may facilitate the development of many novel formulations suitable for cleaning, coatings, pigment dispersants, pesticides, and agricultural applications.

[0018] As used hereinafter, the terms "an alkylene glycol dilevulinate" and "alkylene glycol dilevulinates" are both meant to include the presence of one or more compounds having the general formula, $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}-\text{R}-\text{O}(\text{O})\text{CCH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3$, wherein R is a C_2-C_8 straight chain or branched alkylene moiety, and the two levulinate groups ($\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}-$) may be attached to adjacent, or non-adjacent, carbon atoms of the alkylene moiety. Thus, an "alkylene glycol dilevulinate" may be one compound which satisfies the foregoing general formula, or a mixture of such compounds. Where a mixture of alkylene glycol dilevulinates is synthesized or otherwise available, it is not necessary that the various species from one another before using the mixture in a cleaning formulation in accordance with the present invention.

[0019] As also used hereinafter, the term "organic active components" is meant to include organic materials that perform a particular function in the cleaning formulations, such as organic solvents, fragrances, etc. "Organic solvents," as the term is used herein, means compounds that dissolve, soften, melt, or extract another compound, such as grease, soil, oil, paint, glue, stains, etc., and which are, therefore, commonly used in cleaning formulations. Typical organic solvents include, without limitation, aliphatic hydrocarbons, isoparaffins, aromatic hydrocarbons, chlorinated hydrocarbons, and terpenes, among others. "Fragrances," as the term is used herein, means organic compounds that impart a particular odor to the cleaning formulation, and may or may not also provide the same function as organic solvents. Typical fragrances include, for example, d-limonene, lemon oil and pine oil.

[0020] The term "coupling agents" as used herein means compounds that facilitate dissolution and dispersion of organic solvents, into water-based formulations, in greater amounts than otherwise possible, while the formulations retain their preferred characteristics of clarity, viscosity and homogeneity. Traditional coupling agents used in cleaning formulations include, without limitation, propylene glycol, diethylene glycol, glycol ethers, and some surfactants, among others.

[0021] It is noted that in the following description, endpoints of ranges are considered to be definite and are recognized to incorporate within their tolerance other values within the knowledge of persons of ordinary skill in the art, including, but not limited to, those which are insignificantly different from the respective endpoint as related to this invention (in other words, endpoints are to be construed to incorporate values "about" or "close" or "near" to each respective endpoint). The range and ratio limits, recited herein, are combinable. For example, if ranges of 1-20 and 5-15 are recited for a particular parameter, it is understood that ranges of 1-5, 1-15, 5-20, or 15-20 are also contemplated and encompassed thereby.

[0022] All percentages stated herein are weight percentages, unless otherwise stated.

[0023] The cleaning formulations of the present invention comprise an aqueous solvent comprising water, an active component comprising at least one organic solvent, and at least one alkylene glycol dilevulinate.

[0024] The aqueous solvent may comprise up to 100% water. Furthermore, cleaning formulation may comprise the aqueous solvent comprising water in an amount between 70 and 98% by weight, based on the total weight of the formulation. For example, the aqueous solvent comprising water may be present in an amount between 94 and 98% by weight.

[0025] The organic active component may be an organic solvent or fragrance and may have a solubility in water of not more than 10% by weight at 25°C and atmospheric pressure, or for example, not more than 5%, or even 1%, by weight at 25°C and atmospheric pressure, based on the total weight of the organic solvent or fragrance and water in solution. Typical examples include, without limitation, d-limonene, lemon oil, pine oil, methyl soyate, and terpenes.

[0026] In accordance with the present invention, the cleaning formulations may comprise an organic active component in an amount between 0.1 to 20.0% by weight, based on the total weight of the formulation. For example, without limitation, the organic active component may be present in an amount between 0.5 to 3.0% by weight.

[0027] The alkylene glycol dilevulinates suitable for use in the present invention are lower alkylene glycol dilevulinates of general formula $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}-\text{R}-\text{O}(\text{O})\text{CCH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3$, derived from alkylene glycols having the general formula $\text{HO}-\text{R}-\text{OH}$, wherein R is a C_2-C_8 straight chain or branched alkylene moiety, and the two hydroxyl groups may be on adjacent carbons, for example ethylene glycol and 1,2-propylene glycol, or on non-adjacent carbons, for example 1,3-propanediol or 1,6-hexanediol. Particularly suitable are alkylene glycol dilevulinates of the foregoing general formula, wherein R is a C_2-C_3 alkylene, such as ethylene, 1,2-propylene, or 1,3-propylene.

[0028] In particular, applicants have found that diesters of ethylene glycol, 1,2-propylene glycol, and 1,3-propylene

glycol with levulinic acid are surprisingly good solvents for coupling aromatic and aliphatic hydrocarbons and other organic materials with water. Ethylene glycol dilevulinate (EGDL) is 100% water soluble while 1,2-propylene glycol dilevulinate (1,2-PGDL) is 10% soluble by weight in water, and 1,3-propylene glycol dilevulinate (1,3-PGDL) is 25% soluble. All three compounds also dissolve aromatic hydrocarbon compounds such as toluene and xylene, while having limited solubility for simple aliphatic hydrocarbons such as hexane and cyclohexane. Thus, C₂-C₃ alkylene glycol dilevulinates appear to provide the greatest benefits when used as coupling agents in water-based cleaning formulations.

[0029] The cleaning formulations may suitably comprise the alkylene glycol dilevulinate in an amount between 0.1 and 6.0% by weight, based on the total weight of the formulation. For example, without limitation, the alkylene glycol dilevulinate may be present in the cleaning formulations in an amount between 0.5 and 3.0% by weight. Processes for preparing esters of levulinates are well known and commercially practiced. For example, International Patent Application No. WO 2010/102203 describes reacting furfuryl alcohol with other alcohols (e.g., methanol, ethanol, propanol, isopropanol, butanol, and isobutanol), in equimolar amounts, in the presence of an acid catalyst, to produce corresponding alkyl levulinates.

[0030] Alkylene glycol dilevulinates suitable for use in accordance with the cleaning formulation of the present invention may be prepared by any process known now or in the future and is not particularly limited. For example, U.S. Patent No. 2,654,723 describes the preparation of diethylene glycol dilevulinate to involve mixing appropriate amounts of levulinic acid, diethylene glycol and toluene (as the reaction solvent), heating the mixture to react the levulinic acid and diethylene glycol and to remove water produced by that reaction, followed by removing the toluene by stripping to yield an amount of diethylene glycol dilevulinate, which has a boiling point above 200°C. From this source, it is seen that production of a dilevulinate from levulinic acid and an alkylene glycol requires providing these reactants at a molar ratio of (levulinic acid):(alkylene glycol) of at least 2:1.

[0031] Laboratory quantities of the glycol dilevulinates may be conveniently prepared, for instance, by the method described in the examples provided hereinbelow.

[0032] Thus, alkylene glycol dilevulinates suitable for use in the present invention include, without limitation, those prepared from any linear or branched C₂-C₈ mono-, di-, or tri-alkylene glycol, and levulinic acid.

[0033] As with other, known cleaning formulations, cleaning formulations in accordance with the present invention may contain ingredients in addition to water, an organic active component and a coupling agent. For example, the cleaning formulations may also comprise one or more surfactants, buffers, chelating agents, biocides, fragrances, viscosity modifiers, colorants, and polymers, among other things.

[0034] Suitable surfactants, for example include, without limitation, sodium linear alkylbenzene sulfonates, alkyl sulfates, alpha olefin sulfonates, acyl sarcosinates, sodium salt of coconut fatty acids, sulfonated alkyl esters, alkyl polyglucosides, primary alcohol ethoxylates, alkyl polyentasides, secondary alcohol ethoxylates, EO-PO and EO-BO block polymers, and sodium 3-dodecylamino-propionate. Suitable buffers include, for example, without limitation, sodium hydroxide (NaOH), alkanolamines, amines, ammonia, alkali metal carboxylates, citric acid, sodium citrate, and lactic acid.

[0035] Suitable chelating agents, for example include, without limitation, ethylene diamine-N,N'-tetraacetic acid, the mono-, di-, tri-, and tetra sodium salts of (EDTA), nitriloacetic acid, trisodium salt (NTA), hydroxyl ethyl iminodiacetic acid, disodium salt (HEIDA), methyl glycinediacetic acid, trisodium salt (MGDA), glutamic acid, N,N-diacetic acid tetrasodium salt (GLDA), iminodiacetic acid, tetrasodium salt, (IDS), tri(hydroxymethyl)amino methane (TRIS), 2-amino-2-ethyl 1,3-propanediol, 2-amino-2-methyl propanol, 2-amino-2-methyl-1,3-propanediol, and polyamines.

[0036] Suitable colorants, for example include, without limitation, dyes.

[0037] Polymers suitable for use in the cleaning formulations of the present invention, for example include, without limitation, polyacrylate homopolymers and copolymers, METHOCELS, ETHOCELS, hydroxyethyl cellulose, POLYOXs, polyethylene glycols, polypropylene glycols, polyvinylpyrrolidones, and polyvinyl alcohols.

[0038] The use, application and benefits of the present invention will be clarified by the following discussion and description of exemplary embodiments and applications of the cleaning formulations of the present invention.

EXAMPLES

Preparation of Ethylene Glycol Dilevulinate

[0039] In the laboratory, we prepared the glycol dilevulinates using an acid catalyst (Dowex DR-2030 resin beads, a strong cation exchange resin) and the procedure described below:

Ethylene glycol (99.17 g, 1.598 moles), levulinic acid (378.4 g, 3.259 moles), and 8.08 g of Dowex DR-2030 resin beads were placed in a 1 L round-bottom flask. The flask was attached to a Büchi Rotavapor and heated in a 95°C bath while water aspirator vacuum was applied. Water produced by the reaction was collected in the Rotavapor catch flask. After 14 hours, the Dowex DR-2030 beads were filtered from the orange solution which was placed in a 500 mL round-bottom flask. A 1 foot jacketed Vigreux column surmounted by a standard vacuum distillation head

EP 2 872 611 B1

with a thermometer and water-cooled condensing finger was attached to the flask, and distillation at about 0.5 mm Hg at elevated temperature was begun. Six fractions were then collected at increasing distillation temperatures. Fractions 3 to 5 ranged from 95 to 98 area % purity based on gas chromatographic analysis, and represented an overall 67% yield based on ethylene glycol used. Identity of the product as ethylene glycol dilevulinate was confirmed by ¹H and ¹³C NMR spectroscopy.

[0040] 1,3-propanediol dilevulinate and 1,2-propanediol dilevulinate were prepared in a similar manner with overall yields of 70% and 59% respectively.

Examples 1-24 - Relative Coupling Effectiveness With Fragrances

[0041] The following study was performed to evaluate the stability and coupling capabilities of alkylene glycol dilevulinates in different formulations containing one of three fragrances, outdoor, orange, lemon.

[0042] To speed up the preparation of cleaning formulations for testing, we created stock solutions that contained the main components which didn't change throughout Examples 1-24, along with stock solutions with surfactant combinations. These stock solutions were used along with the other components to formulate the samples by weight percent. 20-gram samples of each formulation were prepared.

[0043] Each formulation contained the following ingredients in the following amounts shown in the following TABLE OF STANDARD INGREDIENTS Examples 1-24:

TABLE OF STANDARD INGREDIENTS - Examples 1-24

Name	Amount (wt %)	Description/Comment
VERSENE HEIDA	1.00	Chelating agent, commercially available from the Dow Chemical Company of Midland, Michigan, U.S.A. An aqueous solution of disodium ethanoldiglycine which is readily biodegradable. It is particularly useful for chelation of iron in mildly alkaline solutions
Diisopropanolamine (DiPA)	0.50	A buffer, replaces traditional monoethanolamine (MEA) buffer
Sodium Hydroxide (NaOH)	0.20	Buffer, pH adjuster
Water	variable	Aqueous solvent
Fragrance	0.50	one of the following as listed in TABLE 1 "outdoor" "orange" "lemon"

Coupling Agents / Solvents Tested

[0044] Each formulation contained 2.00 wt% of one of the following solvent/couplers, as indicated in TABLE 1:

- PG-Dilevulinate = 1,2-propylene glycol dilevulinate
- 1,3-PG-Dilevulinate = 1,3-propylene glycol dilevulinate
- EG-Dilevulinate = ethylene glycol dilevulinate
- DOWANOL DPnP = di-propylene glycol propyl ether (a P-series glycol ether)

[0045] After the desired formulations with the fragrances were prepared, we checked their stability at 5°C, 20°C, and 50°C and noted if the sample was clear, hazy or cloudy. To evaluate slight haze, we took a piece of paper with black text written on it, and held it behind the vial containing the formulation. If we could see the black text clearly, we noted the formulation as clear. If we could not see the text at all, we noted the formulation as cloudy. Finally, if we could see the text, but it was not a vibrant black, the formulation was described as hazy. The less haze or cloudiness, the better the coupling achieved between the water and the fragrance (organic solvent)

[0046] The following TABLE 1 presents the results of testing various formulations containing difficult-to-couple fragrances (organic active ingredients), i.e., "outdoor", "orange" and "lemon," using the aforesaid testing procedure.

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TABLE 1

	Fragrance (0.5%)	Solvent/Coupler (2.00 wt %)	"Green" Surfactants **			% Water	Stability		
			TERGITOL 15-S-15	ECOSURF EH-6	ECOSURF EH-9		5°C	20°C	50°C
1	Outdoor	PG-Dilevulinate	0.50	0.25	0.25	95.30	Cloudy	Haze	Cloudy
2	Outdoor	PG-Dilevulinate	1.00	0.50	0.50	94.30	Clear	Clear	Cloudy
3	Orange	PG-Dilevulinate	0.50	0.25	0.25	95.30	Haze	Clear	Cloudy
4	Orange	PG-Dilevulinate	1.00	0.50	0.50	94.30	Clear	Clear	Cloudy
5	Lemon	PG-Dilevulinate	0.50	0.25	0.25	95.30	Clear	Clear	Cloudy
6	Lemon	PG-Dilevulinate	1.00	0.50	0.50	94.30	Clear	Clear	Clear
7	Outdoor	1,3-PG-Dilevulinate	0.50	0.25	0.25	95.30	Cloudy	Haze	Cloudy
8	Outdoor	1,3-PG-Dilevulinate	1.00	0.50	0.50	94.30	Clear	Clear	Clear
9	Orange	1,3-PG-Dilevulinate	0.50	0.25	0.25	95.30	Clear	Clear	Cloudy
10	Orange	1,3-PG-Dilevulinate	1.00	0.50	0.50	94.30	Clear	Clear	Clear
11	Lemon	1,3-PG-Dilevulinate	0.50	0.25	0.25	95.30	Clear	Clear	Cloudy
12	Lemon	1,3-PG-Dilevulinate	1.00	0.50	0.50	94.30	Clear	Clear	Clear
13	Outdoor	EG-Dilevulinate	0.50	0.25	0.25	95.30	Clear	Clear	Cloudy
14	Outdoor	EG-Dilevulinate	1.00	0.50	0.50	94.30	Clear	Clear	Clear
15	Orange	EG-Dilevulinate	0.50	0.25	0.25	95.30	Clear	Clear	Cloudy
16	Orange	EG-Dilevulinate	1.00	0.50	0.50	94.30	Clear	Clear	Clear
17	Lemon	EG-Dilevulinate	0.50	0.25	0.25	95.30	Clear	Clear	Cloudy
18	Lemon	EG-Dilevulinate	1.00	0.50	0.50	94.30	Clear	Clear	Clear
19	Outdoor	DOWANOL DPnP	0.50	0.25	0.25	95.30	Haze	Cloudy	Clear
20	Outdoor	DOWANOL DPnP	1.00	0.50	0.50	94.30	Clear	Clear	Clear
21	Orange	DOWANOL DPnP	0.50	0.25	0.25	95.30	Clear	Haze	Cloudy
22	Orange	DOWANOL DPnP	1.00	0.50	0.50	94.30	Clear	Clear	Clear
23	Lemon	DOWANOL DPnP	0.50	0.25	0.25	95.30	Clear	Haze	Clear
24	Lemon	DOWANOL DPnP	1.00	0.50	0.50	94.30	Clear	Clear	Clear

** Green Surfactants: each formulation also contained one of two possible combinations of three eco-friendly surfactants, each of which is commercially available from Dow Chemical Company of Midland, Michigan, U.S.A.:

TERGITOL 15-S-15 = a high hydrophilic-lipophilic balance emulsifier and dispersant

ECOSURF EH-6 = a water soluble nonionic surfactant

ECOSURF EH-9 = a water soluble nonionic surfactant

Example Set I (Comparative) & Set II (Working) - Figures 1-16

[0047] Two sets of experiments (I & II) were performed to determine the relative coupling effectiveness of fragrance (d-limonene)-containing aqueous formulations having various traditional coupling agents (glycol ethers) and those having various alkylene glycol dilevulinate as the coupling agents, at various temperatures (5°C, room temperature (25°C) and 40°C). The details are provided below and the results are shown in diagrams provided in Figures 1-16 and explained hereinbelow.

[0048] Stock solutions were prepared that contained the main components which didn't change throughout these experiments. Each formulation contained the following standard ingredients:

TABLE OF STANDARD INGREDIENTS - Sets I & II

Name	Amount (wt %)	Description/Comment
sodium lauryl sulfate (SLS)	none or 1%	Surfactant
Water	variable	Aqueous solvent
D-Limonene (fragrance)	various	Amounts of fragrance were varied among 0.5%, 0.75%, 1.5% and 3% by weight

[0049] More particularly, the cleaning formulations were in either:

Set I - Comparative Examples (see Figures 1-8), which included a known coupling agent selected from one of the following glycol ethers, in an amount of 1, 5, 10 or 20 weight percent as indicated in the figures:

- BuCb = diethylene glycol n-butyl ether
- BTG = triethylene glycol n-butyl ether
- HxCb = diethylene glycol n-hexyl ether
- ETG = triethylene glycol ethyl ether
- MTG = triethylene glycol methyl ether
- TPM = tripropylene glycol methyl ether

or the Set II - Working Examples (see Figures 9-16) that included an alkylene glycol dilevulinate according to the present invention, or DOWANOL DPM, dipropylene glycol monomethyl ether, in an amount of 1, 5, 10 or 20 weight percent, and selected from the following compounds:

- 1,2 EGDL = ethylene glycol dilevulinate,
- 1,2-PGDL = 1,2-propylene glycol dilevulinate,
- 1,3-PGDL = 1,3-propylene glycol dilevulinate,
- 1,2 EGDL + 1,2-PGDL = 50/50 mix of 1,2-ethylene glycol dilevulinate and 1,2-propylene glycol dilevulinate,
- DPM = dipropylene glycol methyl ether.

[0050] With reference now to the figures, Figures 1-8 relate to the Set of Comparative Examples. Each circle represents

one sample formulation. More particularly, each of Figures 1 & 5 provide a schematic grid diagram of the general layout of sample formulations having various types of glycol ethers as coupling agents and various amounts of d-limonene fragrance, in the presence of 1% SLS surfactant and absence (0% SLS) of surfactant.

[0051] For instance, rows A & B of the grid in Figure 1 were formulations that each had 0.25% by weight d-limonene. Thus, rows A & B of each of Figures 2-4 & 6-8 depict formulations that had 0.25% by weight d-limonene.

[0052] Columns 1 & 2 of the grid in Figure 1 were formulations that contained various amounts of BuCb, a glycol ether, as the coupling agent. More specifically, Column 1 of the grid in Figure 1 shows that for each vertical pair of formulations, the top formulation had 1% by weight BuCb and the bottom one had 10% by weight BuCb. Similarly, Column 2 of the grid in Figure 1 shows that for each vertical pair of formulations, the top formulation had 5% by weight BuCb and the bottom one had 20% by weight BuCb. This information can be similarly translated to Columns 1 & 2 of Figures 2-4.

[0053] Thus, to provide a random example, the sample formulation at Row D, Column 6 contained the standard ingredients listed in the TABLE above for Sets I & II, as well as 0.75% by weight d-limonene and 20% by weight HxCb as the coupling agent, based on the total weight of the formulation.

[0054] Figures 2-4 & 6-8 show the results (clear/white or cloudy/black) for the sample formulations identified in the grids of Figures 1 and 5 at 5°C, room temperature (25°C), and 40°C, respectively. Clear indicates successful coupling of the d-limonene and cloudy indicates poor or no coupling.

[0055] Generally speaking, a review of Figures 6-8 appears to indicate that the glycol ethers were somewhat successful at coupling d-limonene in aqueous formulations, but only when the amount of d-limonene is relatively low, i.e., 0.25% by weight.

[0056] More specifically, sample formulation at Row D, Column 6 which contained 0.75% by weight d-limonene and 20% by weight HxCb, was cloudy at 5°C (Figure 2), clear at room temperature (Figure 3), and cloudy at 40°C.

[0057] Figures 9-16 relate to the Set II of Working Examples. As with Figures 1-8, each circle represents one sample formulation. More particularly, Figure 9 provides a schematic grid diagram of the general layout of sample formulations having various types of alkylene glycol dilevulinate as coupling agents and various amounts of d-limonene fragrance. For instance, rows A & B of the grid in Figure 9 were formulations that each had 0.25% by weight d-limonene. Thus, rows A & B of each of Figures 10-12 & 14-16 depict formulations that had 0.25% by weight d-limonene.

[0058] Furthermore, Columns 1 & 2 of the grid in Figure 9 were formulations that contained various amounts of 1,2-ethylene glycol dilevulinate (1,2-EGDL) as the coupling agent, in accordance with the present invention. More specifically, Column 1 of the grid in Figure 9 shows that for each vertical pair of formulations, the top formulation had 1% by weight 1,2-EGDL and the bottom one had 10% by weight 1,2-EGDL. Similarly, Column 2 of the grid in Figure 9 shows that for each vertical pair of formulations, the top formulation had 5% by weight 1,2-EGDL and the bottom one had 20% by weight 1,2-EGDL. This information can be similarly translated to Columns 1 & 2 of Figures 10-12 & 14-16.

[0059] Thus, to provide a random example, the sample formulation at Row F, Column 6 contained the standard ingredients listed in the TABLE above for Sets I & II, as well as 1.5% by weight d-limonene and 20% by weight 1,2-EGDL as the coupling agent, based on the total weight of the formulation.

[0060] Figures 10-12 & 14-16 show the results (clear/white or cloudy/black) for the sample formulations identified in the grids of Figures 9 & 13 at 5°C, room temperature (25°C), and 40°C, respectively. Clear indicates successful coupling of the d-limonene and cloudy indicates poor or no coupling.

[0061] Generally speaking, a review of Figures 10-12 & 14-16 appears to indicate that the alkylene glycol dilevulinate are more successful at coupling d-limonene in aqueous formulations over a broader range of temperatures and concentrations of d-limonene than the commonly used glycol ethers.

[0062] More specifically, sample formulation at Row F, Column 6 which contained 1.5% by weight d-limonene and 20% by weight 1,2-EGDL, was clear at 5°C (Figure 2), clear at room temperature (Figure 3), and cloudy at 40°C.

[0063] Figures 1-16 showed the phase stability data of glycol ethers and alkylene glycol dilevulinate with varying levels of d-limonene in the presence of 1% SLS surfactant and absence (0% SLS) of surfactant.

[0064] In the absence of added SLS surfactant, most of the glycol ether solvents tested were unable to couple more than 0.25% d-limonene into an aqueous mixture. The only exception was DOWANOL DPM. In contrast, the experimental glycol dilevulinate solvents were fairly effective at coupling d-limonene in the absence of surfactant. Ethylene glycol dilevulinate and 1,3-propylene glycol dilevulinate were better than 1,2-propylene glycol dilevulinate. This is in agreement with their observed water solubility.

[0065] In the presence of 1% SLS, all of the solvents tested showed improvement in probability to be clear. Hexyl CARBITOL, DOWANOL DPM, and the glycol dilevulinate solvents at a 20% level were able to successfully couple even the highest d-limonene level tested, 3%.

Examples A - FF - Relative Cleaning Performance of Formulations

[0066] These experiments were intended to measure how well cleaning formulations containing various solvent/cou-

EP 2 872 611 B1

pling agents, as well as different combinations of surfactants, performed in terms of leaving films or streaks, and how efficiently they cleaned.

[0067] Again, we created stock solutions that contained the main components which didn't change throughout each set of formulations, along with stock solutions with surfactant combinations, being either 0.5% or 1.0% total surfactant as shown in TABLE 2 below. These stock solutions were used along with the other components to formulate the samples by weight percent. None of these sample formulations contained any fragrance since the goal was to see how well the cleaning formulations containing different coupling agent and surfactant combinations cleaned. 20-gram samples of each formulation were prepared.

[0068] Each formulation contained the following ingredients in the following amounts shown in the following TABLE OF STANDARD INGREDIENTS Examples A-FF:

TABLE OF STANDARD INGREDIENTS - Examples A-FF

Name	Amount (wt %)	Description/Comment
VERSENE HEIDA	0.5	Chelating agent, commercially available from the Dow Chemical Company of Midland, Michigan, U.S.A. An aqueous solution of disodium ethanoldiglycine which is readily biodegradable. It is particularly useful for chelation of iron in mildly alkaline solutions
Diisopropanolamine (DiPA)	0.50	A buffer, replaces traditional monoethanolamine (MEA) buffer
Sodium Hydroxide (NaOH)	0.20	Buffer, pH adjuster
Water	variable	Aqueous solvent

Coupling Agents / Solvents Tested

[0069] Each formulation contained 1.00 wt% of one of the following solvent/couplers, as indicated in TABLE 2:

PGDL = PG-Dilevulinate = 1,2-propylene glycol dilevulinate

1,3PGDL = 1,3-PG-Dilevulinate = 1,3-propylene glycol dilevulinate

EGDL = EG-Dilevulinate = ethylene glycol dilevulinate

DPnP = DOWANOL DPnP = di-propylene glycol propyl ether (a P-series glycol ether)

Surfactants and Combinations Thereof Tested

[0070] Each formulation contained a total of either 0.5% or 1.0% surfactants, as follows and indicated in TABLE 2 below:

Different combinations of the following three eco-friendly ("green") surfactants, but always totaling either 0.5 or 1.0 wt%, were tested among the cleaning formulations. Each of the following surfactants is commercially available from Dow Chemical Company of Midland, Michigan, U.S.A.:

TERGITOL 15-S-15 = a high hydrophilic-lipophilic balance emulsifier and dispersant

ECOSURF EH-6 = a water soluble nonionic surfactant

ECOSURF EH-9 = a water soluble nonionic surfactant

[0071] For some formulations, one of the following other, less environmentally-friendly materials (both commercially available from Shell Chemical LP of Houston, Texas, U.S.A.) was substituted for the surfactant in amounts of either 0.5 or 1.0 wt %. NEODOL 25-7 = a C₁₂-C₁₅ alcohol mixture containing an average of 7 moles of ethylene oxide per mole of alcohol.

NEODOL 45-7 = a C₁₄-C₁₅ alcohol mixture containing an average of 7 moles of ethylene oxide per mole of alcohol.

[0072] After the desired formulations with the various coupling agents and surfactant combinations were prepared, their performance was tested with respect to cleaning efficiency (filming and streaking) and stability (appearance at 5°C, 20°C and 60°C), as follows.

Filming and Streaking

5 [0073] To test the residue left by the cleaning formulation, filming and streaking tests were done on glass tiles. Ten drops in a circular pattern were applied to a glass tile and wiped with a folded piece of clean cheese cloth with five passes. No downward pressure was applied on the tile, only pressure to create a back and forth motion. The tiles were left to dry for 30 minutes. The tiles were rated on a scale of 1-10 for both filming and streaking compared to standards where WINDEX®: Filming=1 Streaking=1 and FANTASTIK®: Filming = 10 Streaking = 10. All tiles were rated by the same operator to minimize discrepancies in rating and to eliminate operator to operator differences.

10 Hard Surface Cleaning: Spring Compression Device (SCiD)

15 [0074] Hard surface cleaning power of the formulations was tested by the removal of soil from a vinyl tile. Vinyl tiles were cut to match the sample size of 11.5 cm x 7.5 cm and 500 µL of 3% Carbon Black Brazil soil was applied to the grooved side of the tile using a foam applicator. The tiles were set to dry for approximately 24 hours, and then the tile was placed in the SCiD plate and set on the orbital shaker. 400 µL of the cleaning solutions were dispensed into each well along with one carpeted scrubbie, and the samples were run on the shaker for five minutes. For each sample, 3 wells were tested, and the samples were run side by side with a good and bad cleaning standard. The samples were scanned into the computer and analyzed by the ImageJ software. The cleaning power was measured by the average gray value of the well, and the cleaning power of the sample was measured by the average of the gray value of the three wells. A higher gray value corresponds to a lighter circle and a higher cleaning power, while a lower gray value corresponds to a darker circle and a lower cleaning power.

20 [0075] The following TABLE 2 presents the results of testing various formulations containing different coupling agents and surfactant combinations, using the aforesaid testing procedure. It is noted that values for filming and streaking each run from 1 to 10, with the lowest numbers representing the least filming or streaking and, therefore, being the preferred values. For the "average grey" performance characteristic, the higher values are considered more preferable.

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TABLE 2

	----Solvent/Coupler (%)--				----"Green" Surfactants-----				Other Surfactants---			--Cleaning Perf.----			-----Stability*-----	
	DPnP	PGDL	EGDL	1,3-PDGL	ECOSURF EH-6	ECOSURF EH-9	TERGITOL 15-S-15	NEODOL 25-7	NEODOL 45-7	Water (%)	Filming (1-10)	Streaking (1-10)	60°C	5°C	AVG Grey Values	
A		1.00			0.13	0.13	0.25			97.3	3	2	Clear	Clear	69.66	
B		1.00			0.25	0.25	0.50			96.8	4	4	Clear	Clear	93.52	
C		1.00			0.17	0.17	0.17			97.3	4	4	Clear	Clear	82.96	
D		1.00			0.33	0.33				96.8	5	5	Clear	Clear	94.82	
E		1.00					0.50			97.3	5	6	Cloudy	Cloudy	83.67	
F		1.00					1.00			96.8	3	2	Cloudy	Cloudy	91.09	
G		1.00						0.50		97.3	4	3	Cloudy	Cloudy	73.13	
H		1.00						1.00		96.8	5	5	Cloudy	Cloudy	85.96	
I			1.00		0.13	0.13	0.25			97.3	4	5	Clear	Clear	99.50	
J			1.00		0.25	0.25	0.50			96.8	6	6	Clear	Clear	126.84	
K			1.00		0.17	0.17	0.17			97.3	5	5	Clear	Clear	114.50	
L			1.00		0.33	0.33	0.33			96.8	6	6	Clear	Clear	164.02	
M			1.00				0.50			97.3	5	6	Cloudy	Cloudy	86.77	
N			1.00				1.00			96.8	5	5	Cloudy	Cloudy	115.17	
O			1.00					0.50		97.3	5	6	Cloudy	Cloudy	61.33	
P			1.00					1.00		96.8	6	6	Cloudy	Cloudy	63.716	
Q				1.00	0.13	0.13	0.25			97.3	5	5	Clear	Clear	79.37	
R				1.00	0.25	0.25	0.50			96.8	7	7	Clear	Clear	97.50	
S				1.00	0.17	0.17	0.17			97.3	5	5	Clear	Clear	84.14	
T				1.00	0.33	0.33	0.33			96.8	6	6	Clear	Clear	119.47	
U				1.00				0.50		97.3	6	6	Cloudy	Cloudy	84.88	
V				1.00				1.00		96.8	7	7	Cloudy	Cloudy	129.51	
W				1.00					0.50	97.3	7	7	Cloudy	Cloudy	60.44	

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(continued)

	----Solvent/Coupler (%)--			----"Green" Surfactants-----				Other Surfactants---			--Cleaning Perf.----			-----Stability*-----	
	DPnP	PGDL	EGDL	1,3-PDGL	ECOSURF EH-6	ECOSURF EH-9	TERGITOL 15-S-15	NEODOL 25-7	NEODOL 45-7	Water (%)	Filming (1-10)	Streaking (1-10)	60°C	5°C	AVG Grey Values
X				1.00					1.00	96.8	8	8	Cloudy	Cloudy	92.77
Y	1.00				0.13	0.13	0.25			97.3	3	4	Clear	Clear	104.54
Z	1.00				0.25	0.25	0.50			96.8	6	5	Clear	Clear	121.08
AA	1.00				0.17	0.17	0.17			97.3	4	5	Clear	Clear	129.60
BB	1.00				0.33	0.33	0.33			96.8	5	5	Clear	Clear	138.14
CC	1.00							0.50		97.3	5	5	Cloudy	Clear	121.33
DD	1.00							1.00		96.8	6	5	Cloudy	Clear	143.99
EE	1.00								0.50	97.3	4	5	Cloudy	Cloudy	97.69
FF	1.00							1.00	1.00	96.8	5	5	Cloudy	Cloudy	114.68

* NOTE: All formulations remained clear at 20°C

Claims

1. A cleaning formulation comprising:

5 (A) an aqueous solvent comprising water;
 (B) an active component comprising an organic solvent; and
 (C) a coupling agent comprising an alkylene glycol dilevulinate having the general formula,
 $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}-\text{R}-\text{O}(\text{O})\text{CCH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3$, wherein R is a C_2 - C_8 straight chain or branched alkylene
 10 moiety, and the two levulinate groups ($\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}-$) may be attached to adjacent, or non-adjacent,
 carbon atoms of the alkylene moiety.

2. The cleaning formulation according to Claim 1, wherein said organic solvent has a solubility of no more than 10%,
 by weight, in water at 25°C and atmospheric pressure, based on the total weight of the organic solvent and water
 15 in solution.

3. The cleaning formulation according to Claim 1, wherein said organic solvent is at least one compound selected from
 the group consisting of: an aliphatic hydrocarbon, an aromatic hydrocarbon, a chlorinated hydrocarbon, a terpene,
 lemon oil, pine oil, methyl soyate and d-limonene.

20 4. The cleaning formulation according to Claim 1, wherein R is a C_2 - C_3 alkylene moiety.

5. The cleaning formulation according to Claim 4, wherein said alkylene glycol dilevulinate is one or more compounds
 selected from the group consisting of: ethylene glycol dilevulinate, 1,2-propylene glycol dilevulinate and 1,3-propylene
 25 glycol dilevulinate.

6. The cleaning formulation according to Claim 1, wherein the aqueous solvent comprising water (A) is present in an
 amount of from 90% to 98% by weight, the active component comprising an organic solvent (B) is present in an
 amount of from 0.1% to 5.0% by weight, and the coupling agent comprising an alkylene glycol dilevulinate (C)
 30 is present in an amount of from 0.1% to 6.0%, all weight percentages based on the total weight of the cleaning
 formulation.

7. The cleaning formulation according to Claim 6, wherein the aqueous solvent comprising water (A) is present in an
 amount of from 94% to 98% by weight,

35 8. The cleaning formulation according to Claim 6, wherein the active component comprising an organic solvent (B) is
 present in an amount of from 0.5% to 3.0% by weight,

9. The cleaning formulation according to Claim 6, wherein the coupling agent comprising an alkylene glycol dilevulinate
 (C) is present in an amount of from 0.5% to 3.0% by weight.

40 10. The cleaning formulation according to Claim 1, further comprising one or more of the following additional components:

(D) surfactants;
 (E) chelating agents;
 45 (F) buffers / pH adjusters;
 (G) biocides;
 (H) fragrances;
 (I) viscosity modifiers;
 (J) colorants; and
 50 (K) polymers.

Patentansprüche

55 1. Eine Reinigungsformulierung, die Folgendes beinhaltet:

(A) ein wässriges Lösungsmittel, das Wasser beinhaltet;
 (B) eine aktive Komponente, die ein organisches Lösungsmittel beinhaltet; und

EP 2 872 611 B1

(C) ein Kopplungsmittel, das ein Alkylenglycoldilevulinat mit der allgemeinen Formel $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}-\text{R}-\text{O}(\text{O})\text{CCH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3$ beinhaltet, wobei R ein geradkettiger oder verzweigter C_2 - C_8 -Alkylenanteil ist und die zwei Levulinatgruppen ($\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}-$) an angrenzende oder nicht angrenzende Kohlenstoffatome des Alkylenanteils gebunden sein können.

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2. Reinigungsformulierung gemäß Anspruch 1, wobei das organische Lösungsmittel in Wasser bei 25 °C und einem atmosphärischen Druck, bezogen auf das Gesamtgewicht des organischen Lösungsmittels und Wassers in der Lösung, eine Löslichkeit von nicht mehr als 10 Gew.-% aufweist.
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3. Reinigungsformulierung gemäß Anspruch 1, wobei das organische Lösungsmittel mindestens eine Verbindung ist, die aus der Gruppe ausgewählt ist, die aus Folgendem besteht: einem aliphatischen Kohlenwasserstoff, einem aromatischen Kohlenwasserstoff, einem chlorierten Kohlenwasserstoff, einem Terpen, Zitronenöl, Kiefernöl, Methylsoyat und d-Limonen.
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4. Reinigungsformulierung gemäß Anspruch 1, wobei R ein C_2 - C_3 -Alkylenanteil ist.
5. Reinigungsformulierung gemäß Anspruch 4, wobei das Alkylenglycoldilevulinat eine oder mehrere Verbindungen ist, die aus der Gruppe ausgewählt ist/sind, die aus Folgendem besteht: Ethylenglycoldilevulinat, 1,2-Propylenglycoldilevulinat und 1,3-Propylenglycoldilevulinat.
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6. Reinigungsformulierung gemäß Anspruch 1, wobei das wässrige Lösungsmittel, das Wasser beinhaltet, (A), in einer Menge von 90 Gew.-% bis 98 Gew.-% vorhanden ist, wobei die aktive Komponente, die ein organisches Lösungsmittel beinhaltet, (B), in einer Menge von 0,1 Gew.-% bis 5,0 Gew.-% vorhanden ist, und wobei das Kopplungsmittel, das ein Alkylenglycoldilevulinat beinhaltet, (C), in einer Menge von 0,1 Gew.-% bis 6,0 Gew.-% vorhanden ist, wobei sich alle Gewichtsprozentage auf das Gesamtgewicht der Reinigungsformulierung beziehen.
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7. Reinigungsformulierung gemäß Anspruch 6, wobei das wässrige Lösungsmittel, das Wasser beinhaltet, (A), in einer Menge von 94 Gew.-% bis 98 Gew.-% vorhanden ist.
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8. Reinigungsformulierung gemäß Anspruch 6, wobei die aktive Komponente, die ein organisches Lösungsmittel beinhaltet, (B), in einer Menge von 0,5 Gew.-% bis 3,0 Gew.-% vorhanden ist.
9. Reinigungsformulierung gemäß Anspruch 6, wobei das Kopplungsmittel, das ein Alkylenglycoldilevulinat beinhaltet, (C), in einer Menge von 0,5 Gew.-% bis 3,0 Gew.-% vorhanden ist.
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10. Reinigungsformulierung gemäß Anspruch 1, die weiter eine oder mehrere der nachfolgenden zusätzlichen Komponenten beinhaltet:
- (D) Tenside;
- 40 (E) Chelatbildner;
- (F) Puffer/Mittel zur Regulierung des pH-Werts;
- (G) Biozide;
- (H) Duftstoffe;
- (I) Viskositätsmodifizierungsmittel;
- 45 (J) Farbstoffe; und
- (K) Polymere.

Revendications

- 50
1. Une formulation de nettoyage comprenant :
- (A) un solvant aqueux comprenant de l'eau ;
- (B) un constituant actif comprenant un solvant organique ; et
- 55 (C) un agent de couplage comprenant un dilévulinate d'alkylène glycol ayant la formule générale, $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}-\text{R}-\text{O}(\text{O})\text{CCH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3$, dans laquelle R est un groupement alkylène à chaîne droite ou ramifié en C_2 - C_8 , et les deux groupes lévulinate ($\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}-$) peuvent être fixés à des atomes de carbone adjacents, ou non adjacents, du groupement alkylène.

EP 2 872 611 B1

2. La formulation de nettoyage selon la revendication 1, dans laquelle ledit solvant organique a une solubilité de pas plus de 10 %, en poids, dans de l'eau à 25 °C et à la pression atmosphérique, rapporté au poids total du solvant organique et de l'eau en solution.
- 5 3. La formulation de nettoyage selon la revendication 1, dans laquelle ledit solvant organique est au moins un composé sélectionné dans le groupe constitué : d'un hydrocarbure aliphatique, d'un hydrocarbure aromatique, d'un hydrocarbure chloré, d'un terpène, d'essence de citron, d'essence de pin, de méthyl soyate et de d-limonène.
- 10 4. La formulation de nettoyage selon la revendication 1, dans laquelle R est un groupement alkylène en C₂-C₃.
5. La formulation de nettoyage selon la revendication 4, dans laquelle ledit dilévulinate d'alkylène glycol est un ou plusieurs composés sélectionnés dans le groupe constitué : de dilévulinate d'éthylène glycol, de dilévulinate de 1,2-propylène glycol et de dilévulinate de 1,3-propylène glycol.
- 15 6. La formulation de nettoyage selon la revendication 1, dans laquelle le solvant aqueux comprenant de l'eau (A) est présent dans une quantité allant de 90 % à 98 % en poids, le constituant actif comprenant un solvant organique (B) est présent dans une quantité allant de 0,1 % à 5,0 % en poids, et l'agent de couplage comprenant un dilévulinate d'alkylène glycol (C) est présent dans une quantité allant de 0,1 % à 6,0 %, les pourcentages en poids étant tous rapportés au poids total de la formulation de nettoyage.
- 20 7. La formulation de nettoyage selon la revendication 6, dans laquelle le solvant aqueux comprenant de l'eau (A) est présent dans une quantité allant de 94 % à 98 % en poids.
- 25 8. La formulation de nettoyage selon la revendication 6, dans laquelle le constituant actif comprenant un solvant organique (B) est présent dans une quantité allant de 0,5 % à 3,0 % en poids.
9. La formulation de nettoyage selon la revendication 6, dans laquelle l'agent de couplage comprenant un dilévulinate d'alkylène glycol (C) est présent dans une quantité allant de 0,5 % à 3,0 % en poids.
- 30 10. La formulation de nettoyage selon la revendication 1, comprenant en sus un ou plusieurs des constituants additionnels suivants :
- (D) des tensioactifs ;
 - (E) des agents chélatants ;
 - 35 (F) des tampons/ajusteurs de pH ;
 - (G) des biocides ;
 - (H) des parfums ;
 - (I) des modificateurs de viscosité ;
 - (J) des colorants ; et
 - 40 (K) des polymères.
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Figure 1

Various Glycol Ethers General Layout

SLS: 1%

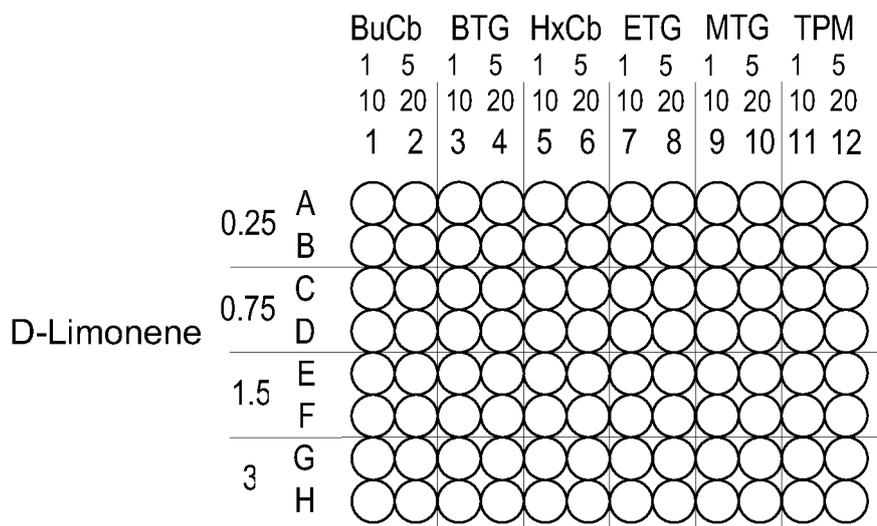


Figure 2

Various Glycol Ethers Stability at 25°C

SLS: 1%

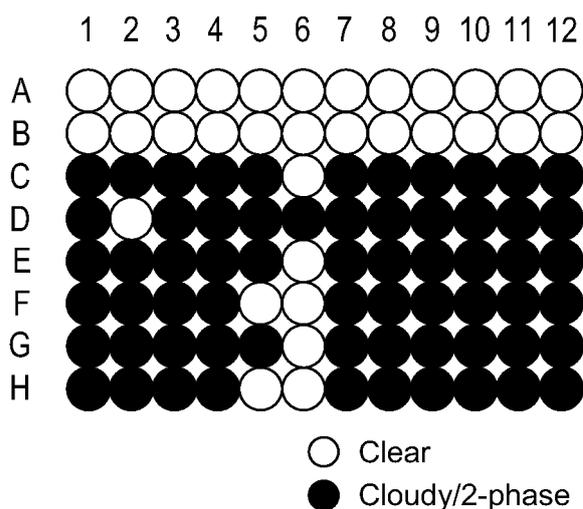


Figure 3

Various Glycol Ethers Stability at 40°C

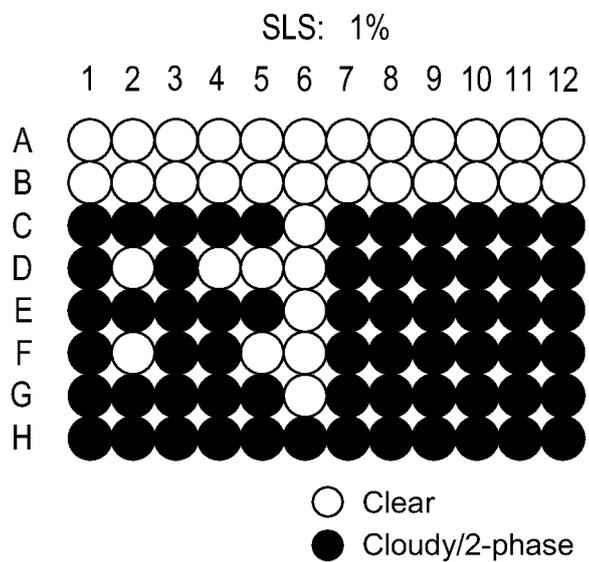


Figure 4

Various Glycol Ethers Stability at 5°C

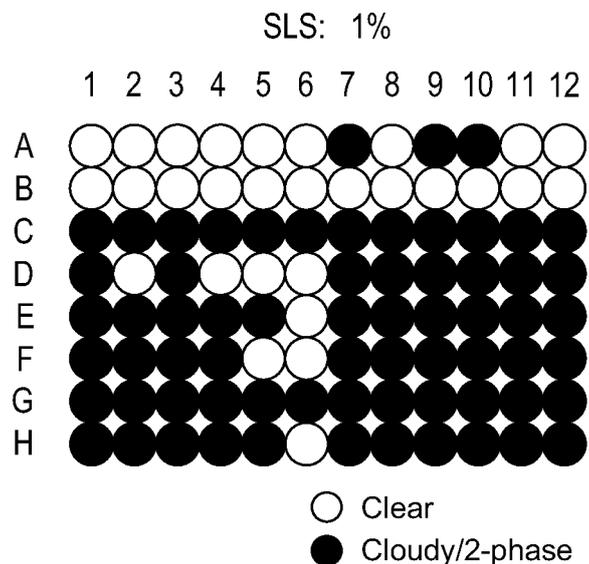


Figure 5

Various Glycol Ethers General Layout

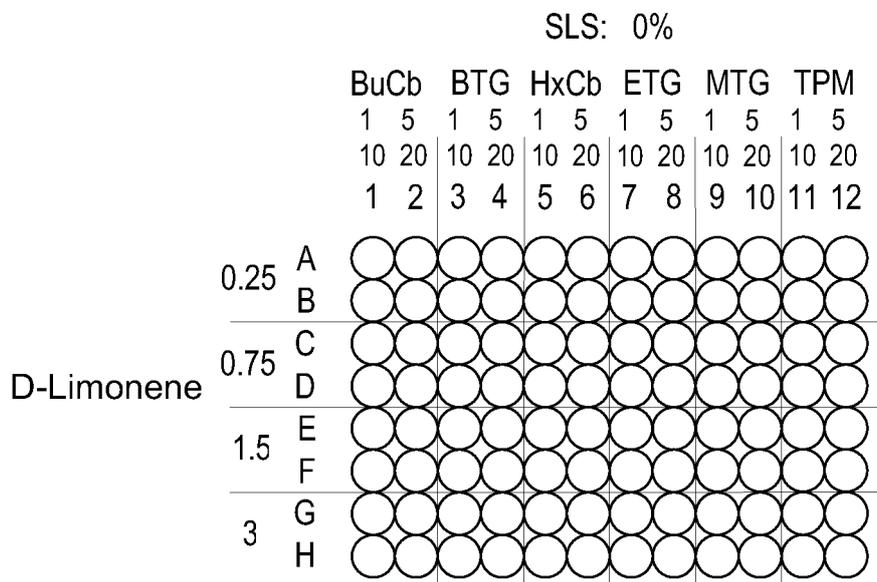


Figure 6

Various Glycol Ethers Stability at 25°C

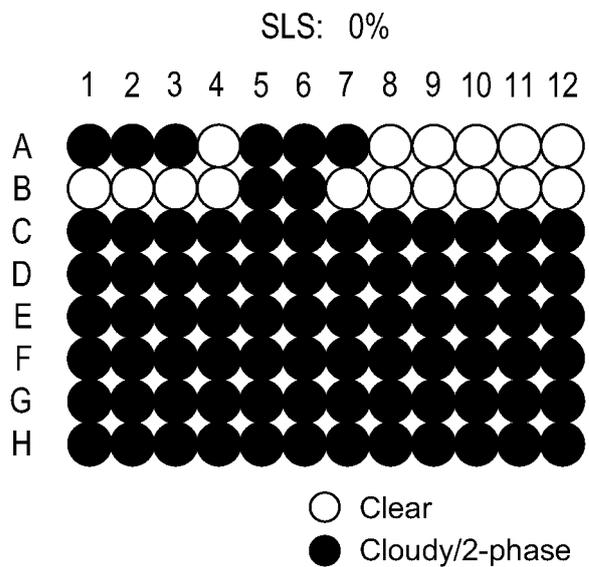


Figure 7

Various Glycol Ethers Stability at 40°C

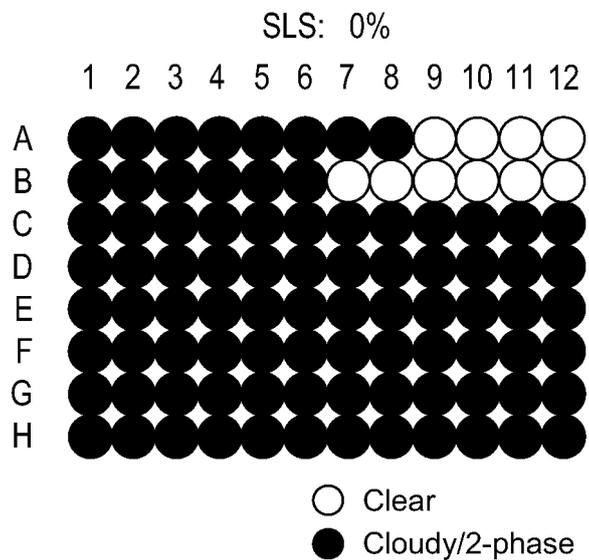


Figure 8

Various Glycol Ethers Stability at 5°C

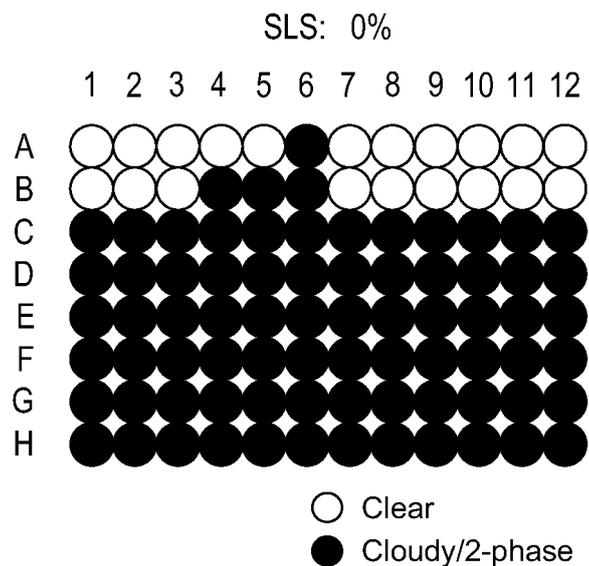


Figure 9

Various Dilvulicates and DMP General Layout

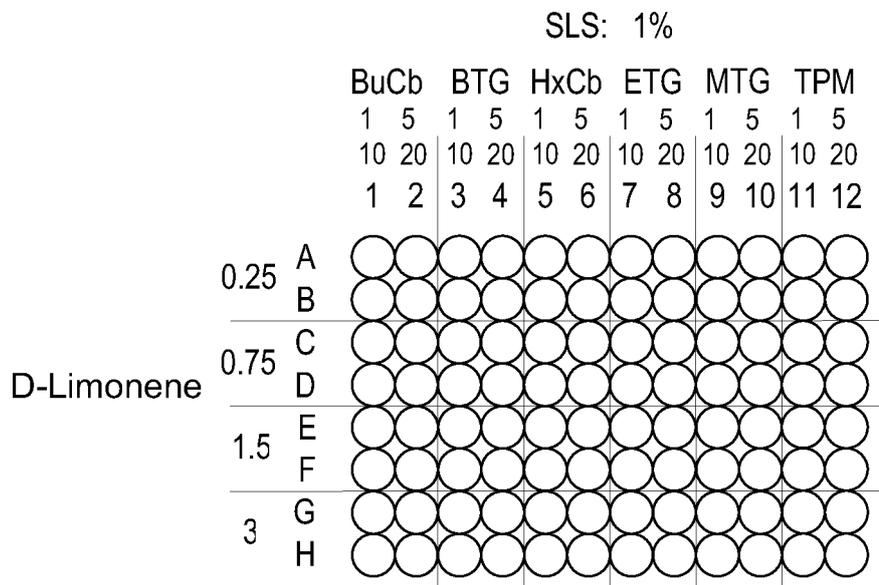


Figure 10

Various Dilevulicates and DPM Stability at 25°C

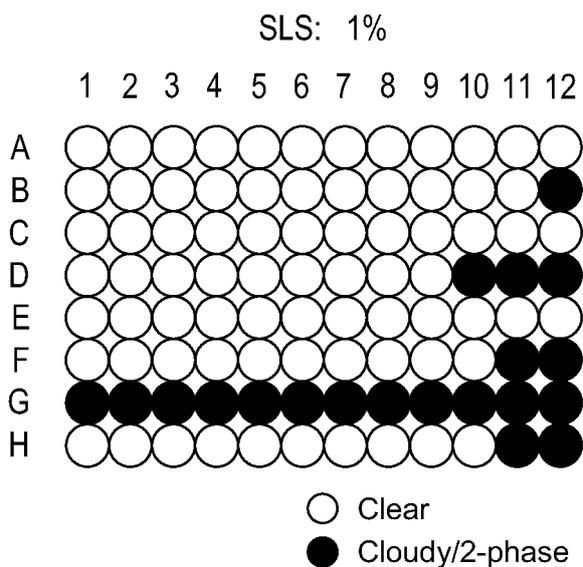


Figure 11

Various Dievulnates and DPM Stability at 40°C

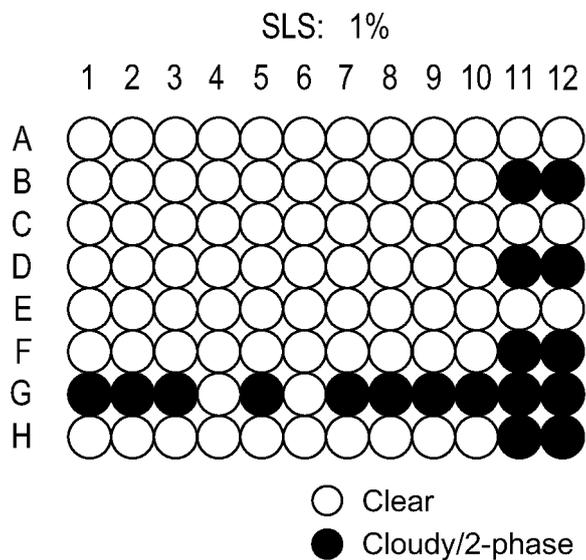


Figure 12

Various Dilevulnates and DPM Stability at 5°C

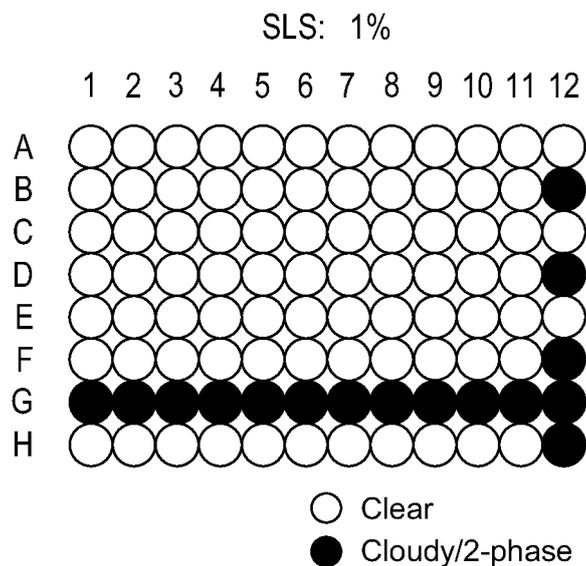


Figure 13

Various Dilvulicates and DMP General Layout

SLS: 0%

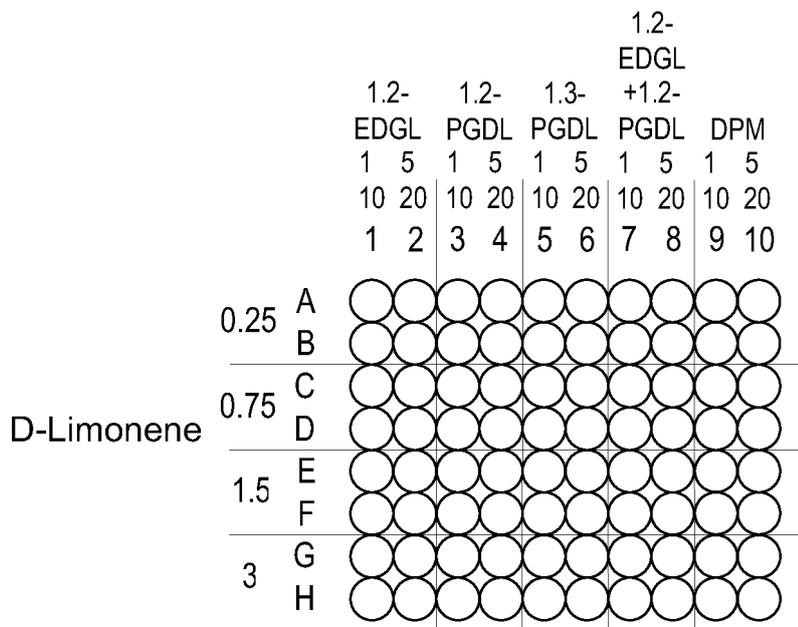


Figure 14

Various Dilevulicates and DPM Stability at 25°C

SLS: 0%

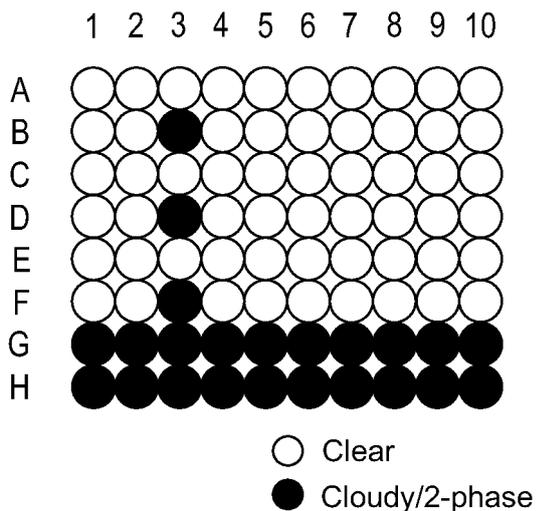


Figure 15

Various Dilevulicates and DPM Stability at 40°C

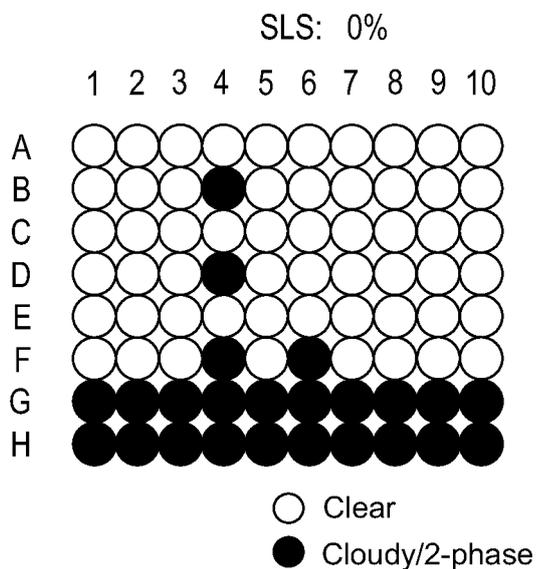
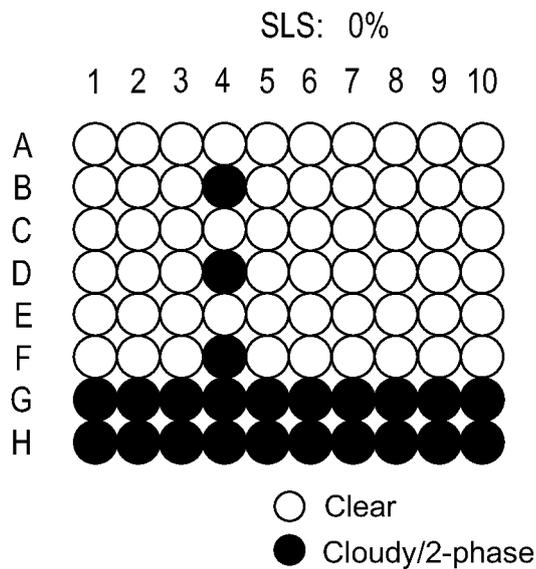


Figure 16

Various Dilevulicates and DPM Stability at 5°C



REFERENCES CITED IN THE DESCRIPTION

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