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(54) **CLEANING COMPOSITION AND USE THEREOF**

REINIGUNGSZUSAMMENSETZUNG UND DEREN VERWENDUNG

COMPOSITION DE NETTOYAGE ET SON UTILISATION

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(73) Proprietor: **OTI Greentech Group AG**
6300 Zug (CH)

(72) Inventors:
• **KEASEY, Alan**
North Ferriby
Yorkshire HU14 3JX (GB)
• **WAKHLOO, Jawahar**
66133 Saarbrücken (DE)

• **JOHNSON, Guy**
Worksop
Nottinghamshire S80 2DE (GB)
• **KELLY, Caroline**
Romanby Northallerton
Yorkshire DL7 8BJ (GB)

(74) Representative: **Rentsch Partner AG**
Kirchenweg 8
Postfach
8034 Zürich (CH)

(56) References cited:
WO-A1-96/21712 WO-A1-97/11150
FR-A- 1 472 561 FR-A1- 2 253 825
FR-A1- 2 296 687 FR-A1- 2 326 467
FR-A1- 2 645 876 FR-A5- 2 121 201
GB-A- 1 562 801 GB-A- 2 259 518
US-A- 3 983 078 US-A- 5 707 948
US-A1- 2009 023 626 US-A1- 2012 277 140
US-B1- 6 187 739

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Description

[0001] The present invention relates to a method for cleaning profiled hard surfaces, especially those coated with zinc silicate, and to compositions suitable for cleaning such surfaces.

[0002] Zinc silicate primers are extensively used throughout industry to coat ferrous metal structures and combat corrosion thereof by acting as a sacrificial anode. Examples of such primers typically include compositions formulated with a builder or binder such as a polysiloxane or epoxy resin. When applied to the surface of, for example, steel to a typical thickness of 60 to 70 microns and allowed to cure they produce a ceramic coating which is hard, abrasion resistant and resistant to oxidation. This makes them especially useful for coating the internal surfaces of tanks especially those used in marine applications where the possibility of physical damage and exposure to corrosive salt spray exists.

[0003] One drawback of such primed surfaces is that they are less smooth than the corresponding bare metal. This profiling makes them somewhat difficult to clean which in turn can lead to problems in certain circumstances. For example, when a ship's hold, which has previously contained say a heavy hydrocarbon, is to be used subsequently to transport another cargo, e.g. an alcohol such as methanol, the cleaning cycle can be lengthy and require the entry of humans into a closed, hazardous environment to ensure that cleaning is complete.

[0004] US 6716804 discloses a three-component cleaning composition comprising an amphoteric surfactant and two different non-ionic surfactants which are ethoxylates of differing water solubilities.

[0005] US 2012/0277140 generally discloses a surfactant system for surface cleaning comprising one or more anionic surfactants and one or more non-ionic surfactants. A wide range of candidate surfactants is speculated upon including unspecified EO/PO block copolymers but exemplified are systems in which a combination of two ethoxylate non-ionic surfactants, one of which is water soluble and the other water-insoluble, is also employed. In one embodiment an inorganic salt is also included.

[0006] WO96/21712 teaches an industrial or marine cleaner comprising an organic solvent; a blend of two non-ionic ethoxylated surfactants; a phosphate ester hydrotrope; a primary amino acid and water. None of the examples teach the use of a non-ionic surfactant component containing both propoxy and ethoxy units.

[0007] GB2259518 discloses a microemulsion cleaning composition comprising an anionic surfactant; a non-ionic surfactant system consisting of two ethoxylates; an aromatic hydrocarbon and water.

[0008] US5707948 discloses a cleaning composition comprising two ethoxylated non-ionic surfactants with differing numbers of ethoxy units; an optional alkoxylated solvent with a short chain alkyl group; a suds suppressor comprising a fatty acid and a secondary alcohol; potas-

sium carbonate and water.

[0009] We have now developed cleaning compositions which, relative to those currently in use today or disclosed in the above-mentioned references, represent an improvement in both the extent to and the speed with which tank cleaning can occur. Furthermore, their improved performance can reduce substantially the need for steam-cleaning thereby leading to significant environmental and energy savings. Thus, according to one aspect of the present invention, there is provided a liquid industrial hard surface cleaning composition characterised in that it is water dilutable and comprises a mixture of three surfactant types consisting of (a) from 5 to 50% by weight of an anionic surfactant, (b) from 5 to 50% by weight of a first non-ionic surfactant comprised of both ethoxy and propoxy groups and having the general formula $R'-(AO)_n-OH$ wherein R' is C_9 to C_{20} alkyl, each AO unit is either $-OCH_2CH_2-$ or $-OCH_2CH(CH_3)-$; the molar ratio $[-OCH_2CH(CH_3)-]/[-OCH_2CH_2-]$ is in the range up to 8 and n is greater than 6 and (c) from 5 to 50% by weight of a second non-ionic surfactant having the general formula, $R'-(OCH_2CH_2)_n-OH$ wherein R' is C_9 to C_{20} alkyl, and n is less than 6 each of said weight percentages being with respect to the total weight of (a), (b) and (c).

[0010] In certain circumstances, the various surfactants described above may be sourced in water-diluted as opposed to pure form. For example, commercially available anionic surfactants typically comprise a 25-40% solution of the active component in water. Since the various weight ranges defined herein are with respect to 100% actives, any dilution effect will need to be taken into account when making up any cleaning composition derived therefrom.

[0011] It will also be readily appreciated that in the cleaning compositions taught herein the density of the individual components are approximately equal to 1 g/cc so that the formulations can alternatively be made up using the same ranges on a volume basis to give substantially the same result.

[0012] In one working embodiment, the cleaning composition comprises a concentrate suitable for spot cleaning duties. In another, it comprises a corresponding diluted form derived from the concentrate by addition of water in one or more steps. Typically such diluted forms will comprises less than less than 5%, more preferably less than 1%, most preferably less than 0.75% by volume of the concentrate itself. In yet another embodiment, the diluted form of the cleaning composition will be one which is prepared directly by mixing water with the three constituent surfactants whose relative proportions are in accordance with the various ranges defined above. In use, the pH of the cleaning composition is suitably in the range from 6 to 9 most preferably from 7 to 8.

[0013] In addition to the three components of the cleaning composition described above it is envisaged that other useful additives, for example dyes, anti-foams and hydrotropes can be present if so desired.

[0014] In certain embodiments of the inventions dis-

closed herein, the first non-ionic surfactant has a cloud point in the range 50-90, preferably 60-70°C as determined by ASTM D-2024 09 at a 1% by weight level of the surfactant in deionised water and/or the second non-ionic surfactant has a cloud point in the range 30-70, preferably 40-60°C as determined with 5g surfactant in 25g of a 25% butyl diglycol (BDG) aqueous solution.

[0015] In other embodiments of the invention; (1) the anionic surfactant (in the un-ionised, acid form) has a $\log_{10}P$ value in the range 5 to 7 and/or (2) the first non-ionic surfactant has a $\log_{10}P$ value in the range 0.1 to 3 and/or (3) the second non-ionic surfactant has a $\log_{10}P$ value in the range 0.1 to 3. As used herein, the term $\log_{10}P$ means the logarithm of the partition coefficient P for the given component measured with respect to a standard two-phase n-octanol/water system. Further information about this methodology may be found, for example, in *Ecotoxicology and Environmental Safety*, 11(3) 1986, pp.251-260.

[0016] Turning to the anionic surfactant, in one embodiment it is one or a mixture of compounds selected from C_{12} to C_{18} alkyl sulphonic or sulphuric acids or a corresponding salt thereof, preferably a Group IA or Group IIA metal or an amine or alkanolamine salt, or from linear alkyl benzene sulfonic acids or a salt thereof, preferably a Group IA or Group IIA metal salt or an amine or alkanolamine salt. In another embodiment, it is selected from C_{12} to C_{18} alkyl polyether sulphuric acids or a corresponding salt thereof, preferably a Group IA or Group IIA metal or an amine or alkanolamine salt. Examples of preferable anionic surfactants include sodium lauryl sulphate or sulphate, magnesium lauryl sulphate or sulphate, tetraethylammonium lauryl sulphate or sulphate, mixed C_{14} to C_{16} alkyl sulphate or sulphate salts of sodium, potassium or magnesium and mixed C_{12} to C_{14} alkyl sulphate or sulphate salts of sodium, potassium or magnesium. Preferable linear alkyl benzene sulphonic acids or salts thereof include C_6 to C_{12} alkyl benzene sulphonic acids or salts thereof. In the case of polyether sulphates, which are characterised by a polyether unit between the aliphatic or aromatic component and the sulphate group, this is suitably a polyether comprised of up to 20 $-OCH_2CH_2-$ units. The alkyl groups in any of the above may be branched or unbranched.

[0017] When the anionic surfactant is an amine or alkanolamine salt, the corresponding cation is suitably selected from the genus of species having the general formula R_3NH^+ wherein each R group is independently H or a C_1 to C_6 substituted or un-substituted hydrocarbyl group with the proviso that at least one is a substituted hydrocarbyl group. As used herein, the term 'substituted hydrocarbyl group' means a hydrocarbyl, preferably an alkyl group of general formula C_xH_{2x+1} , which has been substituted with one or more polar groups such as $-OH$, $-SH$, $-NH_2$, $-NHR$ or the like. In one preferred embodiment, such substituted alkyl groups are hydroxyalkyl groups comprising at least one hydroxyl group; in a sub-embodiment at least one of these hydroxyl groups is at-

tached to the end of the alkyl group remote from that connected to the nitrogen. In another embodiment, at least two of the R groups are hydroxyalkyl groups and in yet another all three R groups are hydroxyalkyl groups. In preferred sub-embodiments, independently applicable to each of the embodiments and sub-embodiments described above, each R group is suitably independently H or a C_2 to C_6 un-substituted or substituted alkyl group; more preferably H or a C_2 to C_4 un-substituted or substituted alkyl group.

[0018] One especially preferred sub-genus of the R_3NH^+ cations described above is comprised of species which can be regarded as protonated mono-, di- or tri-alkanolamines in which each alkanol group has from two to four carbon atoms. Examples of such species include protonated mono-ethanolamine, di-ethanolamine, tri-ethanolamine, mono-propanolamine, di-n-propanolamine, tri-n-propanolamine, di-iso-propanolamine or tri-iso-propanolamine. Preferably the cation is protonated tri-ethanolamine or protonated tri-n-propanolamine. The first non-ionic surfactant, which is employed in the cleaning composition and which is relatively hydrophilic, is suitably one or mixture of compounds having the general formula, $R'-(AO)_n-OH$ wherein R' is C_9 to C_{20} alkyl, preferably C_9 to C_{16} alkyl; each AO unit is either $-OCH_2CH_2-$ or $-OCH_2CH(CH_3)-$ and n is greater than 6. In one embodiment, the molar ratio $[-OCH_2CH(CH_3)-]/[-OCH_2CH_2-]$ is in the range up to 8, preferably from 0.1 to 4 and/or n is from 7 to 15. The different AO units may be arranged randomly or in blocks. In some embodiments, the end block of the AO chain is made of $-OCH_2CH(CH_3)-$ units; in others it is made of $-OCH_2CH_2-$ units. The first non-ionic surfactants are typically prepared by alkoxyating the corresponding fatty alcohol $R'OH$ which itself can be derived from naturally-occurring sources or from precursor lower molecular weight alcohols using for example the Guerbet synthesis. Such surfactants are sometimes referred to as 'linker surfactants' and are characterised by exhibiting a critical micelle concentration (CMC) which is relatively low. The alkyl groups mentioned above can be branched or unbranched.

[0019] The second non-ionic surfactant, which is employed in the cleaning composition and which is relatively hydrophobic, is suitably one or mixture of compounds having the general formula, $R'-(OCH_2CH_2)_n-OH$ wherein R' is C_9 to C_{20} alkyl, preferably C_9 to C_{16} alkyl, and n is less than 6, preferably from 2 to 5. Such surfactants are also typically prepared by ethoxylating the corresponding fatty alcohol $R'OH$ which itself can be derived from naturally-occurring sources or from precursor lower molecular weight alcohols using by the Guerbet synthesis. The alkyl groups mentioned above can be branched or unbranched.

[0020] The R' groups employed in the first and second non-ionic surfactants can be the same or different.

[0021] Preferably either or both of the first and second non-ionic surfactants comprise from 10 to 45% by weight of the cleaning composition.

[0022] The use of the cleaning composition of the present invention is generally applicable to the cleaning of all fouled hard surfaces which have become profiled (i.e. roughened) by virtue of use, corrosion or being coated with a corrosion-resistant layer (e.g. a primer). Its use is beneficial where the hard surface includes a profiled, sacrificial coating of zinc silicate or an equivalent and is especially so for cleaning the dirty surfaces of coated stainless or mild steel storage tanks. It can be used to particular advantage to clean the cargo tanks or holds of ships where the space is confined and discharge of the waste cleaning composition is environmentally problematic. Any method of using the cleaning composition can be employed to effect cleaning although typically it will be brought into contact with the dirty surface using an industrial sprayer assembly which is adapted to collect and recirculate the liquid. If so desired, the surfaces can at the same time be brushed or scrubbed. Thereafter, once a suitable period of cleaning time has elapsed, the cleaned surfaces can be rinsed with clean water and/or a sample of the next cargo to be used. Suitably the cleaning composition is sprayed onto the dirty surfaces at a temperature of less than 100°C, typically from 60 to 80°C.

[0023] The cleaning composition of the present invention, which is designed for industrial as opposed to personal care or household use, is especially suitable for removing contaminants comprising high molecular weight hydrocarbons such as diesel, gas-oil, kerosene and vegetable oils from hard surfaces of the type mentioned above. Typical vegetable oils which can be removed with the cleaning compositions of the present invention include palm oil, soya bean oil, rapeseed oil, sunflower oil, peanut oil, olive oil, cottonseed oil, palm kernel oil and coconut oil along with refined fractions thereof.

[0024] The use of the cleaning composition of the present invention will now be illustrated with reference to the following tests which demonstrate the superiority of the cleaning compositions of the present invention over the prior art.

General Test Methodology for Examples 1 to 11

[0025] Test panels made of stainless steel or mild steel coated with an industry standard zinc silicate coating were immersed in ultra-low sulphur diesel for a period of three days to simulate the contamination occurring in a cargo tank. After removal and being allowed to drain, the panels were tested in a rig designed to remove as much of the residual diesel adhering to the panel as possible under a standard set of cleaning conditions. In this rig, the cleaning composition was applied to the test panel by means of a sprayer adapted for continuous liquid recycle thereby enabling the contaminated panel surfaces to be continuously contacted with the cleaning composition for a period of 2 hours. During this time, the temperature of the cleaning composition was maintained at 70°C. At the end of the test period, spraying was stopped,

the panels washed with clean water and the residual diesel on the panels determined by immersing the panels in a standard volume of methanol at room temperature for 5 minutes and then measuring the amount of diesel extracted using UV/visible spectroscopy. By calibration with standard samples of known concentrations, the amount of diesel in the methanol was quantified as an average residual hydrocarbon reading (ARHR) indicative of the effectiveness of the cleaning composition. Here, the higher the ARHR the less effective is the cleaning composition.

Example 1 (Comparative)

[0026] In this example, a baseline was established using water at 70°C. The ARHR reading was 550.

Example 2 (Comparative)

[0027] In this example, the cleaning composition was a 0.5% by weight aqueous solution of Accell®Clean (ex-Advanced BioCatalytics Corporation) a material which has been rated for use in cleaning marine tanks and which comprises a mixture of a surfactant and proteins having a pH in the range 5.5 to 6.5. The ARHR reading obtained was 50.

Example 3

[0028] In this example, the cleaning composition (pH 7-8) was a 0.5% by weight aqueous solution of a cleaning composition concentrate according to the present invention comprising (by volume):

45.0% Hansanol AS240A® (a 30% aqueous solution of a sodium salt of a sulphonated mono C₁₂ to C₁₄ alkyl ester surfactant; ex Hansa Group);
27.5% Berol 185® (a non-ionic surfactant of formula C₁₀₋₁₆(OCH₂CH₂)_p(OCH₂CH(CH₃))_qOH; cloud point 64-70°C in water; ex AkzoNobel);
27.5% Ethylan 1005® (a non-ionic surfactant of formula C₉(OCH₂CH₂)₅OH; cloud point 47-53°C in BDG solution; ex AkzoNobel) and
0.5% anti-foam JH FDP® (silicone anti-foam; ex Julius Hoesch).

The ARHR reading obtained was 25.

Example 4

[0029] Example 3 was repeated except that the weight component of the three surfactants was respectively 35%, 30% and 35% and no anti-foam was employed. The ARHR reading obtained was 35.

Example 5

[0030] Example 4 was repeated except that 35% Ser-

det DSK-30® (sodium salt of a C12-C14 alcohol sulphate (30% solution); ex Elementis Specialities) was employed instead of the Hansanol AS240A. The ARHR reading was 28.

Example 6 (Comparative)

[0031] In this example, the cleaning composition (pH 7-8) was a 0.8% by weight aqueous solution of a cleaning composition concentrate comprising (by volume):

25.0% BioSoft D-40® (sodium, 2-dodecylbenzene sulphonate surfactant; ex Stepan Company);
45% Lutensol XP90® (a non-ionic surfactant of formula $C_{10}(OCH_2CH_2)_9OH$; wherein the C_{10} alkyl group is branched and derived from a C_{10} Guerbet alcohol; ex BASF);
30% Ethylan 1005® (non-ionic surfactant of formula $C_{9-11}(OCH_2CH_2)_5OH$; ex AkzoNobel) and
0.5% anti-foam JH FDP® (silicone anti-foam; ex Julius Hoesch).

The ARHR reading obtained was 25.

Example 7 (Comparative)

[0032] In this example, the cleaning composition concentrate comprised 25% Serdet DLK-9/30®, 45% Lutensol XP90® and 30% Ethylan 1005® and was used at a 1% dilution level in water. The ARHR reading was 40.

Example 8 (Comparative)

[0033] In this example, a binary cleaning composition concentrate comprising 30% Hostapur SAS30® (sodium secondary C_{14-17} alkyl sulphonate; ex Hostapur) and 70% Lutensol XP90® was employed at 1% dilution. The ARHR reading was 48.

Example 9

[0034] In this example the cleaning composition concentrate comprised 25% by weight Biosoft D-40, 45% by weight Berol 185 and 30% by weight Ethylan 1005 together with 0.1% by weight of NFA antifoam. The product so obtained was used at a 0.5% dilution level in water. The ARHR reading was 48 (average of two results).

Example 10 (Comparative)

[0035] Example 9 was repeated except that the Berol 185 was replaced with Lutensol XP90. The product so obtained was used at a 0.5% dilution level in water. The ARHR reading was 60 (average of two results).

Example 11

[0036] Example 9 was repeated except that the Ethylan 1005 was replaced with a 50:50 by weight mixture of Ethylan 1005 and Dowanol EPH® (aromatic ethylene glycol ether $C_6H_5OCH_2CH_2OH$; ex Dow Chemicals). Thereafter a further 10% by weight water was added to the mixture. The product so obtained was used at a 0.5% dilution level in water. The ARHR reading was 58 (average of two results).

Claims

1. A liquid industrial hard surface cleaning composition **characterised in that** it is water dilutable and comprises a mixture of three surfactant types consisting of (a) from 5 to 50% by weight of an anionic surfactant, (b) from 5 to 50% by weight of a first non-ionic surfactant comprised of both ethoxy and propoxy groups and having the general formula $R'-(AO)_n-OH$ wherein R' is C_9 to C_{20} alkyl, each AO unit is either $-OCH_2CH_2-$ or $-OCH_2CH(CH_3)-$; the molar ratio $[-OCH_2CH(CH_3)-]/[-OCH_2CH_2-]$ is in the range up to 8 and n is greater than 6 and (c) from 5 to 50% by weight of a second non-ionic surfactant having the general formula, $R'-(OCH_2CH_2)_n-OH$ wherein R' is C_9 to C_{20} alkyl, and n is less than 6 each of said weight percentages being with respect to the total weight of (a), (b) and (c).
2. An industrial hard surface cleaning composition as claimed in claim 1 **characterised in that** the first non-ionic surfactant has a cloud point in water in the range 50-90°C
3. An industrial hard surface cleaning composition as claimed in claim 1 or claim 2 **characterised in that** the second non-ionic surfactant has a cloud point in butyl diglycol solution in the range 30-70°C.
4. An industrial hard surface cleaning composition as claimed in any one of claims 1 to 3 **characterised in that** (1) the anionic surfactant has a $\log_{10}P$ value (in the unionised, acid form) in the range 5 to 7 and/or (2) the first non-ionic surfactant has a $\log_{10}P$ value in the range 0.1 to 3 and/or (3) the second non-ionic surfactant has a $\log_{10}P$ value in the range 0.1 to 3.
5. A industrial hard surface cleaning composition as claimed in any one of claims 1 to 4 **characterised in that** the molar ratio $[-OCH_2CH(CH_3)-]/[-OCH_2CH_2-]$ in the first non-ionic surfactant is in the range 0.1 to 4.
6. An industrial hard surface cleaning composition as claimed in any one of claims 1 to 5 **characterised in that** the AO units are arranged in blocks.

7. An industrial hard surface cleaning composition as claimed in claim 6 **characterised in that** the end block is made of $-OCH_2CH(CH_3)-$ units.
8. An industrial hard surface cleaning composition as claimed in any one of claims 1 to 7 **characterised in that** it is produced by water dilution of a corresponding concentrate.
9. An industrial hard surface cleaning composition as claimed in any one of claims 1 to 8 **characterised by** further including an anti-foam.
10. An industrial cleaning composition as claimed in any one of claims 1 to 9 **characterised by** having a pH in the range 6 to 9.
11. Use of the industrial hard surface cleaning composition of any one of claims 1 to 10 to remove vegetable oil from metal surfaces which are either coated with a corrosion-resistant layer or have become profiled by use or corrosion.
12. Use of the industrial hard surface cleaning composition of any one of claims 1 to 10 to clean marine cargo tanks or holds.

Patentansprüche

1. Flüssige industrielle Reinigungszusammensetzung für harte Oberflächen, **dadurch gekennzeichnet, dass** sie wasserverdünnbar ist und ein Gemisch aus drei Tensidtypen umfasst, bestehend aus (a) ab 5 bis 50 Gew.-% eines anionischen Tensids, (b) ab 5 bis 50 Gew.-% eines ersten nichtionischen Tensids, das sowohl Ethoxy- als auch Propoxygruppen umfasst und die allgemeine Formel $R'-(AO)_n-OH$ aufweist, worin R' C_9 -bis C_{20} -Alkyl ist, jede AO-Einheit entweder $-OCH_2CH_2-$ oder $-OCH_2CH(CH_3)-$ ist; das molare Verhältnis $[-OCH_2CH(CH_3)-]/[-OCH_2CH_2-]$ im Bereich bis zu 8 liegt und n grösser als 6 ist, und (c) ab 5 bis 50 Gew.-% eines zweiten nichtionischen Tensids mit der allgemeinen Formel $R'-(OCH_2CH_2)_n-OH$, worin R' C_9 - bis C_{20} -Alkyl ist und n kleiner als 6 ist, wobei sich jede der genannten Gewichtsprozentangaben auf das Gesamtgewicht von (a), (b) und (c) bezieht.
2. Industrielle Reinigungszusammensetzung für harte Oberflächen nach Anspruch 1, **dadurch gekennzeichnet, dass** das erste nicht-ionische Tensid einen Cloudpoint in Wasser im Bereich von 50-90° C hat.
3. Industrielle Reinigungszusammensetzung für harte Oberflächen nach Anspruch 1 oder Anspruch 2, **dadurch gekennzeichnet, dass** das zweite nicht-ionische Tensid einen Cloudpoint in Butyldiglycollösung im Bereich von 30-70 °C hat.
4. Industrielle Reinigungszusammensetzung für harte Oberflächen nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, dass** (1) das anionische Tensid einen $\log_{10}P$ -Wert (in der unionisierten, sauren Form) im Bereich von 5 bis 7 hat und/oder (2) das erste nichtionische Tensid einen $\log_{10}P$ -Wert im Bereich von 0,1 bis 3 hat und/oder (3) das zweite nichtionische Tensid einen $\log_{10}P$ -Wert im Bereich von 0,1 bis 3 hat.
5. Industrielle Reinigungszusammensetzung für harte Oberflächen nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, dass** das molare Verhältnis $[-OCH_2CH(CH_3)-]/[-OCH_2CH_2-]$ in dem ersten nichtionischen Tensid im Bereich von 0,1 bis 4 liegt.
6. Industrielle Reinigungszusammensetzung für harte Oberflächen nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** die AO-Einheiten in Blöcken angeordnet sind.
7. Industrielle Reinigungszusammensetzung für harte Oberflächen nach Anspruch 6, **dadurch gekennzeichnet, dass** der Endblock aus $-OCH_2CH(CH_3)-$ Einheiten besteht.
8. Industrielle Reinigungszusammensetzung für harte Oberflächen nach einem der Ansprüche 1 bis 7, **dadurch gekennzeichnet, dass** sie durch Wasserverdünnung eines entsprechenden Konzentrats hergestellt wird.
9. Industrielle Reinigungszusammensetzung für harte Oberflächen nach einem der Ansprüche 1 bis 8, **dadurch gekennzeichnet, dass** sie ausserdem einen Entschäumer enthält.
10. Industrielle Reinigungszusammensetzung nach einem der Ansprüche 1 bis 9, **dadurch gekennzeichnet, dass** sie einen pH-Wert im Bereich von 6 bis 9 hat.
11. Verwendung des industriellen Reinigungsmittels für harte Oberflächen nach einem der Ansprüche 1 bis 10 zur Entfernung von Pflanzenöl von Metalloberflächen, die entweder mit einer korrosionsbeständigen Schicht überzogen sind oder durch Gebrauch oder Korrosion profiliert wurden.
12. Verwendung der industriellen Reinigungszusammensetzung für harte Oberflächen nach einem der Ansprüche 1 bis 10 zur Reinigung von Schiffsladentanks oder Laderäumen.

Revendications

1. Composition liquide de nettoyage industriel de surfaces dures, **caractérisée en ce qu'elle** est diluable à l'eau et comprend un mélange de trois types de tensioactifs consistant en (a) de 5 à 50 % en poids d'un tensioactif anionique, (b) de 5 à 50 % en poids d'un premier tensioactif non ionique comprenant à la fois des groupes éthoxy et propoxy et ayant la formule générale $R'-(AO)_n-OH$ dans laquelle R' est un groupe alkyle en C_9 to C_{20} , chaque unité AO est soit $-OCH_2CH_2-$ soit $-OCH_2CH(CH_3)-$; le rapport molaire $[-OCH_2CH(CH_3)-]/[-OCH_2CH_2-]$ est dans la gamme allant jusqu'à 8 et n est supérieur à 6 et (c) de 5 à 50% en poids d'un second tensioactif non ionique ayant la formule générale $R'-(OCH_2CH_2)_n-OH$ dans laquelle R' est un alkyle en C_9 to C_{20} , et n est inférieur à 6, chacun desdits pourcentages en poids étant par rapport au poids total de (a), (b) et (c). 5
2. Composition de nettoyage industriel de surfaces dures selon la revendication 1, **caractérisée en ce que** le premier tensioactif non ionique a un cloud point dans l'eau dans la gamme de 50 à 90 °C. 10
3. Composition de nettoyage industriel de surfaces dures selon la revendication 1 ou la revendication 2, **caractérisée en ce que** le second tensioactif non ionique a un cloud point dans une solution de butyl diglycol dans la gamme de 30-70 °C. 15
4. Composition de nettoyage industriel de surfaces dures selon l'une quelconque des revendications 1 à 3, **caractérisée en ce que** (1) le tensioactif anionique a une valeur $\log_{10}P$ (sous la forme non-ionisé et acide) dans la gamme de 5 à 7 et/ou (2) le premier tensioactif non ionique a une valeur $\log_{10}P$ dans la gamme de 0,1 à 3 et/ou (3) le second tensioactif non ionique a une valeur $\log_{10}P$ dans la gamme de 0,1 à 3. 20
5. Composition de nettoyage industriel de surfaces dures selon l'une quelconque des revendications 1 à 4, **caractérisée en ce que** le rapport molaire $[-OCH_2CH(CH_3)-]/[-OCH_2CH_2-]$ dans le premier tensioactif non ionique est dans la gamme de 0,1 à 4. 25
6. Composition de nettoyage industriel de surfaces dures selon l'une quelconque des revendications 1 à 5, **caractérisée en ce que** les unités AO sont disposées en blocs. 30
7. Composition de nettoyage industriel de surfaces dures selon la revendication 6, **caractérisée en ce que** le bloc terminal est constitué d'unités $-OCH_2CH(CH_3)-$. 35
8. Composition de nettoyage industriel de surfaces dures selon l'une quelconque des revendications 1 à 7, **caractérisée en ce qu'elle** est produite par dilution dans l'eau d'un concentré correspondant. 40
9. Composition de nettoyage industriel de surfaces dures selon l'une quelconque des revendications 1 à 8, **caractérisée en ce qu'elle** comprend en outre un anti-mousse. 45
10. Composition de nettoyage industriel selon l'une quelconque des revendications 1 à 9, **caractérisée en ce qu'elle** a un pH dans la gamme de 6 à 9. 50
11. Utilisation de la composition de nettoyage industriel de surfaces dures de l'une quelconque des revendications 1 à 10 pour éliminer l'huile végétale de surfaces métalliques qui sont revêtues d'une couche résistante à la corrosion ou qui ont été profilées par l'utilisation ou la corrosion, 55
12. Utilisation de la composition de nettoyage industriel de surfaces dures de l'une quelconque des revendications 1 à 10 pour nettoyer des réservoirs ou cales de cargaison marine.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 6716804 B [0004]
- US 20120277140 A [0005]
- WO 9621712 A [0006]
- GB 2259518 A [0007]
- US 5707948 A [0008]

Non-patent literature cited in the description

- *Ecotoxicology and Environmental Safety*, 1986, vol. 11 (3), 251-260 [0015]