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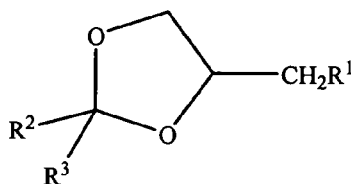
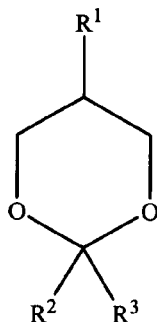
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(54) **Compositions for degreasing hard surfaces**

(57) Suggested are degreasing compositions comprising at least one glycerol acetal or ketal according to general formula (Ia) or (Ib)



(Ia) (Ib)

in which R¹ stands for hydrogen or an hydroxyl group, and R² and R³ independently from each other mean hydrogen, an hydrocarbon radical having 1 to 22 carbon atoms, and 0 or up to 3 double bonds - optionally substituted by an amine, hydroxyl, phenyl or hydroxyphenyl group.

Description**Field of the invention**

[0001] The present invention is related to the area of metal treatment and refers to new degreasing compositions, a method for degreasing hard surfaces and the use of green solvents for degreasing operations.

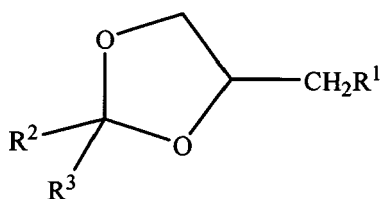
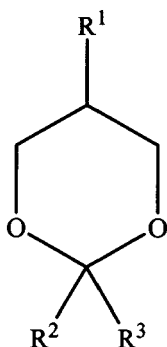
Background of the invention

[0002] In ordinary metal processing metal parts are greased to avoid the corrosion process during their manufacture, storage and transport. Since the degreasing agent is incompatible with subsequent metal processing stages, a cleaning step to remove the metal protector is inevitable. Over the past few years, one of the major challenges in the area of metal degreasing has been the transition from fully emissive open-top systems based on the use of chlorinated solvents to closed-loop metal-degreasing systems based on low VOC emission, low toxicity solvents. Alternative chlorinated solvents such as trichloroethanol, chloroform, methyl chloride, CFC-113, HFCs, HCFCs, CO₂ jets, scCO₂ semi-aqueous solvents, alkaline cleaning agents, emulsifying detergent-based cleaners, and aliphatic hydrocarbon based solvents and azeotropic mixtures have been proposed to replace the widely used current industrial standard, namely trichloroethylene. However, none of the proposed alternatives fully satisfy the key industrial needs of the metal finishing sector.

[0003] Therefore the object of the present invention has been to develop new compositions allowing to perform metal degreasing operations in highly variable settings, with metal parts of different size and shape, minimizing diffuse emission, release of contaminated air during loading and unloading, and solvent release from cleaned metal parts. The use of these compositions should also avoid the generation of large waste streams, allowing to establish an easy and cost effective process in order to recycle solvent and rinsing water and ultimately delivering parts adequately conditioned for immediate use in subsequent steps of the metal finishing process. More particularly the present invention intends to replace commercial degreasing solvents known from the market by new compositions being more efficient, safer and friendlier to the environment.

Detailed description of the invention

[0004] The present invention refers to new degreasing compositions comprising at least one glycerol acetal or ketal according to general formula (Ia) or (Ib)



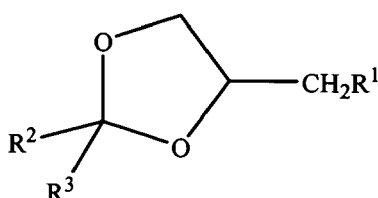
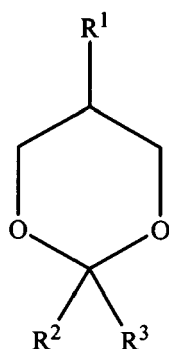
(Ia) (Ib)

in which R¹ stands for hydrogen or an hydroxyl group, and R² and R³ independently from each other mean hydrogen, an hydrocarbon radical having 1 to 22 carbon atoms, and 0 or up to 3 double bonds - optionally substituted by an amine, hydroxyl, phenyl or hydroxyphenyl group.

[0005] Surprisingly it has been observed that cyclic acetals or ketals based on glycerol or its partial hydrogenation product propandiol, regardless whether the metal surfaces have been protected by solvent based or cerous metal preservatives containing antioxidants and other additives show a high degreasing efficacy compared with improved ecotoxicological behaviour. In addition, the solvents can be easily rinsed off with water, collected and then recycled without any additional purification. Replacing well known chlorinated organic degreasing solvents (e.g. trichloroethanol, trichloroethylene, perchloroethylene) by glycerol acetals and ketals leads to a more environmentally friendly process without losing performance.

Degreasing process

[0006] Another object of the present invention relates to a method for the degreasing of hard surfaces, characterised in that said surfaces are brought into contact with at least one organic solvent selected from the group consisting of glycerol acetals or ketals according to general formula (Ia) or (Ib)



(Ia) (Ib)

in which R¹ stands for hydrogen or an hydroxyl group, and R² and R³ independently from each other mean hydrogen, an hydrocarbon radical having 1 to 22 carbon atoms, and 0 or up to 3 double bonds - optionally substituted by an amine, hydroxyl, phenyl or hydroxyphenyl group.

Glycerol acetals and ketals

[0007] In order to avoid ambiguities it is stated that the phrase "glycerol" as used according to the present invention includes also hydrogenation products of glycerol as propandiol-1,2 and propandiol-1,3. This is reflected in general formulae (Ia) and (Ib) for the case R¹ = hydrogen.

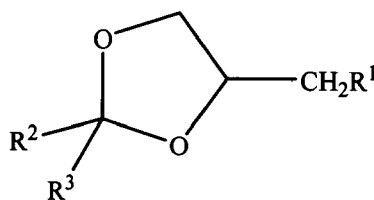
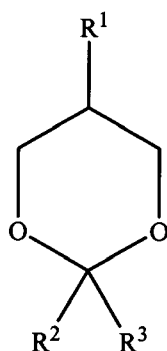
[0008] Acetals and ketals are obtained by condensation of alcohols and aldehydes or ketones respectively. In case the alcohol is a diol the formation of cyclic, 6-membered or 5-membered structures takes place.

[0009] Typical examples for suitable acetals or ketals are those obtained from the condensation of glycerol, 1-2,propandiol or 1,3-propandiol with lower aldehydes like for example formalin, acetaldehyde, propanal, butanal, pentanal, or fatty aldehydes comprising 6 to 22 carbon atoms, like capronal, laurylaldehyde, myristylaldehyde, palmitylaldehyde, stearylaldehyde, oleyl aldehyde, behenyl aldehyde, erucylaldehyde and the like. Suitable ketals are obtained from lower aliphatic ketones like for example acetone or fatty ketones like distearyl ketone. The preferred products are glycerol acetals, in particular those obtained from aliphatic aldehydes having 1 to 6 carbon atoms, more in particular the ones with 3 to 6 carbon atoms like glycerol propanal or glycerol iso-butyral.

[0010] As explained above, typically the hard surfaces represent metal surfaces, such as those used in the manufacture of automotive and building components. The glycerol acetals or ketals, which are used as so-called "green solvents" serve as degreasing agents in order to remove all greases and stains, in particular the preservatives from the surfaces. This can be done either by tipping the parts into the solvent or - more convenient - by spraying. Once degreasing has taken place, the acetals or ketals are collected and reused several times without purification.

Industrial application

[0011] As outlined above, glycerol acetals and ketals show excellent performance in removing stains, grease and especially preservatives from hard surfaces. Another object of the present invention is therefore directed to the use of glycerol acetals or ketals according to general formula (Ia) or (Ib)



(Ia) (Ib)

in which R^1 stands for hydrogen or an hydroxyl group, and R^2 and R^3 independently from each other mean hydrogen, an hydrocarbon radical having 1 to 22 carbon atoms, and 0 or up to 3 double bonds - optionally substituted by an amine, hydroxyl, phenyl or hydroxyphenyl group, as degreasing agents for hard surfaces.

[0012] The degreasing process consists of the following phases:

- (i) Immersion or spraying of the metal parts coated with the preservative at room temperature;
- (ii) Drain off the excess solvent in the metal part;
- (iii) Rinsing with water by immersion or spray; and
- (iv) Recovery of the solvent and water for further use in subsequent cycles.

[0013] The solvent can be reused several times without loss of efficacy. At the end of its useful life, the solvent can be recycled by distillation with yields higher than 80%. Figure 1 shows the fundamental aspects of the degreasing process.

Examples

Metal degreasing procedure

[0014] For our evaluation, a comparative method was used, in which removal efficacy (RE) of several alternative solvents are compared with RE value obtained for the industrial standard degreaser, trichloroethylene.

[0015] Removal Efficacy (RE) measures the degree of removal of organic materials (grease and/or solvent) from the surface of metal parts. Removal efficacy screening test, remove the grease of ten metallic greased pieces by degreasing process. The standard procedure was done by bringing the solvent into contact with the metal surface, more particular by immersion without agitation during 10 minutes in one volume of fresh solvent followed by three consecutive washing cycles by immersion in clean water. The amount of organic material (grease and/or solvent) that was not eliminated by the assayed procedure was determined by direct weight after removal of organic residues from the metallic parts by standard cleaning procedure with trichloroethylene.

[0016] The removal efficacy (RE) for a standard degreasing solvent in industry $CHCl=CCl_2$ is between 94-98 % depending on the nature of the preservative (Table 1). These RE values were used to compare with the results obtained by assayed solvents and to determine their effectiveness compared with trichloroethylene.

Table 1:

Removal Efficacy (%) value for trichloroethylene		
Preservative	A (solvent-based)	B (cereous-based)
RE (%)	94.2	98.1

Example 1

Degreasing studies with acetal and ketal solvents.

[0017] The removal efficacy of the glycerol acetal and ketal solvent family was studied. These experiments remove the grease of ten greased pieces according to the procedure described before. This experiment was carried out for two different greases and the obtained results are described in table 2.

Table 2

RE (%) value normalized to trichloroethylene for acetals and ketals solvents		
Solvent	Solvent-based preservative	Cereous preservative
Trichloroethylene	100	100
Glycerol propanal	34	72
Glycerol isobutyral	57	78
Glycerol formal	21	53

Example 2**Recovery and regeneration of solvent**

[0018] In order to have an economically viable process, the degreasing solvent must be able to be used several times without any prior purification. For this reason reusability of the solvent glycerol formal has been studied in both preservatives. The results are outlined in Table 3.

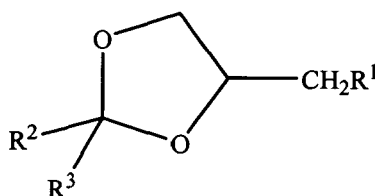
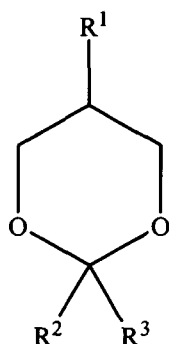
Table 3

Reusability of glycerol formal. Figures indicate percentage reduction of maximum efficacy.		
Number of cycles	Solvent based preservative	Cereous preservative
1	99.21	99.01
2	98.05	98.70
5	96,11	98,13
9	89.97	97.49

[0019] After 5 cycles with the solvent-based preservative the loss in efficiency was less than 4% for both solvent based and cereous preservatives.

Claims

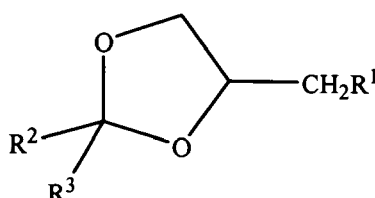
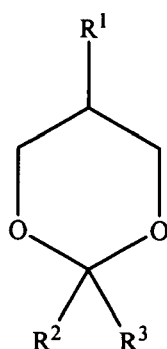
1. Degreasing compositions comprising at least one glycerol acetal or ketal according to general formula (Ia) or (Ib)



(Ia) (Ib)

in which R¹ stands for hydrogen or an hydroxyl group, and R² and R³ independently from each other mean hydrogen, an hydrocarbon radical having 1 to 22 carbon atoms, and 0 or up to 3 double bonds - optionally substituted by an amine, hydroxyl, phenyl or hydroxyphenyl group.

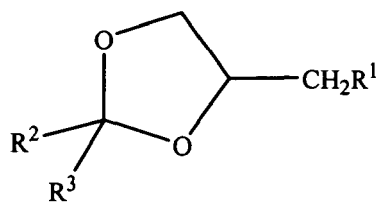
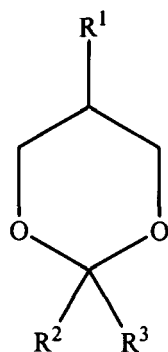
2. Degreasing compositions according to Claim 1, **characterised in that** they comprise glycerol acetals according to formula (Ia) or (Ib) in which R¹ stands for a hydroxyl group, R² means hydrogen and R³ stands for an hydrocarbon radical having 1 to 22 carbon atoms, and 0 or up to 3 double bonds - optionally substituted by an amine, hydroxyl, phenyl or hydroxyphenyl group.
3. Degreasing compositions according to Claim 1, **characterised in that** they comprise glycerol acetals according to formula (Ia) or (Ib) in which R¹ and R² both mean hydrogen and R³ stands for an hydrocarbon radical having 1 to 22 carbon atoms, and 0 or up to 3 double bonds - optionally substituted by an amine, hydroxyl, phenyl or hydroxyphenyl group.
4. A method for the degreasing of hard surfaces, **characterised in that** said surfaces are brought into contact with at least one organic solvent selected from the group consisting of glycerol acetals or ketals according to general formula (Ia) or (Ib)



(Ia) (Ib)

in which R¹ stands for hydrogen or an hydroxyl group, and R² and R³ independently from each other mean hydrogen, an hydrocarbon radical having 1 to 22 carbon atoms, and 0 or up to 3 double bonds - optionally substituted by an amine, hydroxyl, phenyl or hydroxyphenyl group.

5. A method according to Claim 4, **characterised in that** said acetals according to formula (Ia) or (Ib) are used, in which R¹ stands for a hydroxyl group, R² means hydrogen and R³ stands for an hydrocarbon radical having 1 to 22 carbon atoms, and 0 or up to 3 double bonds - optionally substituted by an amine, hydroxyl, phenyl or hydroxyphenyl group.
6. A method according to Claim 4, **characterised in that** said acetals according to formula (Ia) or (Ib) are used, in which R¹ and R² both mean hydrogen and R³ stands for an hydrocarbon radical having 1 to 22 carbon atoms, and 0 or up to 3 double bonds - optionally substituted by an amine, hydroxyl, phenyl or hydroxyphenyl group.
7. A method according to any of the preceding Claims 4 to 6, **characterised in that** said acetals are used, representing condensation products of either glycerol, 1,2-propanediol or 1,3-propanediol with aliphatic alcohols having 1 to 18 carbon atoms.
8. A method according to Claim 7, **characterised in that** said acetals are used which are derived from propanal, butanal, isobutylal pentanal, hexanal or dodecanal.
9. A method according to any of the preceding Claims 3 to 8, **characterised in that** after degreasing has taken place, said glycerol acetals or ketals are collected and reused without purification.
10. Use of glycerol acetals or ketals according to general formula (Ia) or (Ib)



(Ia) (Ib)

in which R¹ stands for hydrogen or an hydroxyl group, and R² and R³ independently from each other mean hydrogen, an hydrocarbon radical having 1 to 22 carbon atoms, and 0 or up to 3 double bonds - optionally substituted by an amine, hydroxyl, phenyl or hydroxyphenyl group, as degreasing agents for hard surfaces.

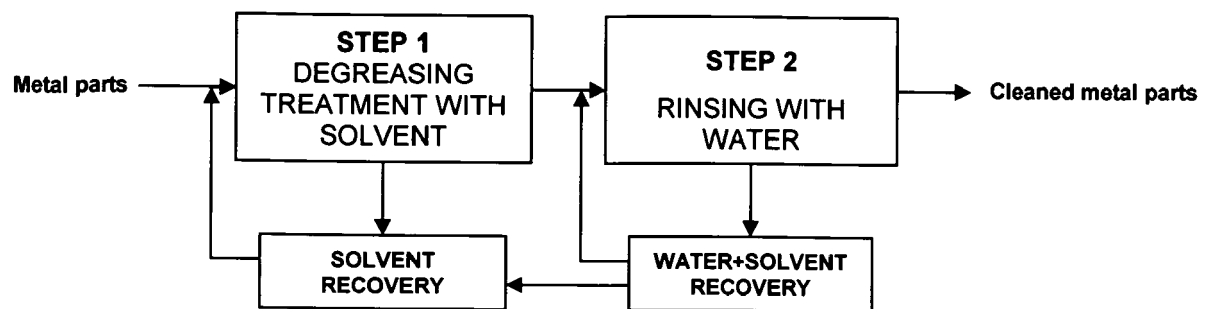


Figure 1
Degreasing process using acetals and ketals



EUROPEAN SEARCH REPORT

Application Number
EP 08 02 1577

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	JP 06 346093 A (KAO CORP) 20 December 1994 (1994-12-20) * paragraphs [0006] - [0020]; claims; examples *	1-10	INV. C23G5/032 C11D7/26
X	EP 1 905 767 A (COGNIS IP MAN GMBH [DE]) 2 April 2008 (2008-04-02) * paragraph [0004] *	1,2	
X	SOKOLOWSKI A ET AL: "ACETALS AND EHTERS. 11. SOLUBILITY OF ALKYL-SUBSTITUTED 1,3-DIOXOLANES AND 1,3-DIOXANES IN WATER" JOURNAL OF PHYSICAL CHEMISTRY, AMERICAN CHEMICAL SOCIETY, US, vol. 88, no. 4, 16 February 1984 (1984-02-16), pages 807-809, XP000646189 ISSN: 0022-3654 * page 807; table 1 *	1,3	
			TECHNICAL FIELDS SEARCHED (IPC)
			C23G C11D
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 30 April 2009	Examiner Mauger, Jeremy
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 08 02 1577

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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30-04-2009

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