(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
24 July 2014 (24.07.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/111267 A1

(51) **International Patent Classification**:
C11D 7/36 (2006.01) *C11D 7/26* (2006.01)

(21) **International Application Number**:
PCT/EP2014/000129

(22) **International Filing Date**:
17 January 2014 (17.01.2014)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
13000245.4 17 January 2013 (17.01.2013) EP
137/2013 7 March 2013 (07.03.2013) PK

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

WO 2014/111267 A1

(54) **Title**: SYSTEM FOR THE REMOVAL OF IRON OXIDE FROM SURFACES

(57) **Abstract**: A system for the removal of heavy metal oxides from surfaces comprises the treatment with a composition comporising at least ethane-1-hydroxy-1,1'diphosphonic acid (HEDP) and water and an organic reducing agent. The invention is also relevant for a process for the removal of iron oxide from textiles or fabrics by treatment with a solution of the composition over a certain time period at a certain temperature in a stirred vessel.

SYSTEM FOR THE REMOVAL OF IRON OXIDE FROM SURFACES

Specification

The instant invention pertains to a new and more effective system for the removal of heavy metal oxides, especially of iron oxide, from textiles or fabrics.

Catalytic degradation of hydrogen peroxide in the presence of iron catalyst is well known and is used as Fenton's reagent for variety of applications. Cotton fabric usually has to be bleached by treatment with hydrogen peroxide under alkaline conditions in order to achieve a satisfactory level of whiteness through oxidation of coloured impurities. The trapped rust residues in the fabric acts as catalyst in this process. The oxycellulose thus produced becomes visible in form of tiny holes commonly addressed as iron pin-holes in the industry. Fabrics comprising pinholes are rejected, however, as waste and are cause of major concern to textile processing organizations.

Current art practiced in the industry is to dissolve iron oxide (rust) using oxalic acid at concentrations exceeding 4 g/l at temperatures upto 50 °C. The contaminated fabric after singeing process, which is a process to remove undesirable protruding fibers, is padded (pick-up 100 %) with oxalic acid and batched for 4 to 6 hours under rotation. The treated fabric is then washed to remove impurities that may have been dissolved as a result of the treatment. The washed fabric is then padded with alkaline solution of hydrogen peroxide to get a bleached fabric with varying degree of whiteness.

Although such a treatment reduces the probability of pin-holes, it is not a guarantee of avoidance. In addition, calcium oxalate formed as a consequence of the treatment has a number of undesirable effects. Calcium oxalate being insoluble in water gets deposited on parts of the fabric and machines. Calcium oxalate on the fabric act as resist spots in subsequent processes. Calcium oxalate deposited on the machine parts have to be removed mechanically which has negative impact on machine production and effective life. In addition, uneven transfer of heat from the metallic rollers with varying degree of calcium oxalate layers, lead to variations across the length of the fabric.

US 278,176 describes oxalic acid in combination with terpentine or benzene for removing rust spots or stains from fabric.

US 4,828,734 describes the use of oxalic acid together with ferrous ions and mineralic acids to remove rust from sold surfaces like toilet bowls, tubes, sinks etc.

GB 2,157,322 describes the removal of iron oxide particles from surfaces by treatment with a solution of sequestring agent at pH of from 1 to 7.5, whereby the sequestring agent is an organic or inorganic phosphor compound.

The object of the instant invention was to find a system for a better protection against iron pin holes during the peroxide bleaching of cellulosic fabric and simultaneously to find a suitable way to eliminate the formation of undesirable insoluble salt.

Such object is surprisingly achieved according to the instant invention by a system as mentioned initially, wherein the textiles or fabric are treated with a composition comprising Ethane-1-hydroxy-1,1'diphosphonic acid (HEDP) and water and an organic reducing agent.

The organic reducing agent is thereby selected from the group consition of ascorbic acid and glucose. The composition for the treatment comprises at least 50 wt.-% of HEDP, preferably at least 60 wt.-% and more preferred at least 70 wt.%, based on dry content of the composition, and the reducing agent in an amount of from 5 to 50 wt.-%, preferably from 10 to 40 wt.-%, based on dry content of the composition.

The instant invention pertains additionally to a method for the removal of heavy metal oxides, especially of iron oxide, from surfaces, especially from textiles or fabrics, in which the surface or the textile or fabric is treated with a solution of Ethane-1-hydroxy-1,1'diphosphonic acid (HEDP) in combination with an organic reducing agent in water.

The method of the instant invention is preferably a one step process which replaces traditional desizing process. However, it may be performed also in two or more steps. In the process of the instant invention the surface or textile or fabric is treated with the solution of Ethane-1-hydroxy-1,1'diphosphonic acid (HEDP) and an organic reducing agent in water at a temperature in the range of from 20 to 100 °C, preferably from 60 to 100 °C, most preferred from 80 to 100 °C.

The time period for the treatment depends upon the contamination of the surface with heavy metal impurities. Preferably, the treatment is maintained over a time period of from 3 to 10 hours, more preferred from 4 to 8 hours.

The method of the instant invention is carried out at a pH-value in the range of below 7, however, for optimum results a pH-value of below 5 is suitable and more preferred below 4 is to recommend. The treatment according to the instant invention may take place in an open stirred vessel.

In addition to the HEDP other inorganic reducing agents like sodium dithionite or sodium sulphite, may be present during the treatment. However, especially the pungent and irritating smell of some sulfur containing additives is not favourable for open production areas.

Although HEDP performed very well with a number of reducing agents, ascorbic acid is the best choice according to the invention. Fabric treated with HEDP and ferrous sulphate was not able to yield the desired level of whiteness upon bleaching and hence the effectiveness is limited. Similary, being an open system for treatment, the use of sodium dithionite and sodium sulphite is restricted due to the unpleasant, penetrating odor. Fabric treated with HEDP and ascorbic acid yields the desired level of whitenss in the subsequent bleaching process. The bleached fabric yields the desired level of whiteness without localized catalytic damage.

Other sequesterants based on methylene phosphonic acids such as DTPMP (Diethylene-triamine pentamethylene phosphonic acid) and ATMP (Amino-trimethyl phosphonic acid) have been found less effective.

Oxalic acid (analytica grade) was taken as a reference as it is widely reported to be effective in iron oxide dissolution.

Ethane-1-hydroxy-1,1'diphosphonic acid (HEDP) is commercially available in liquid with 60 % active content and as 98 % white crystalline powder. Both forms were experimented and found effective in the current study.

By the subsequently following experimental part the invention will be disclosed and illustrated in more detail for the artisan without to establish any limitation to the specified embodiments.

Working examples 1 to 6

Certain quantities of complexing agent (oxalic acid or HEDP) and different reducing agents were added to a ferric oxide suspension (0.05gm/1000ml) in glass bottles. The bottles are then kept in an oven at different temperatures and varying duration. Physical appearance of the Ferric Oxide suspension after the storage was used to determine the efficacy of the respective combination of complexing and reducing agent. The results of examples 1 to 6 with 6 hours exposure at 95 °C are given in Table 1 herein-below.

Table 1

	Bottle 01	Bottle 02	Bottle 03	Bottle 04	Bottle 05	Bottle 06
Ferric Oxide Suspension 0.05 gm / 1000 ml	100 ml	100 ml	100 ml	100 ml	100 ml	100 ml
Oxalic acid powder	0.5 g	0.5 g				
HEDP (60%)			0.5 g	0.5 g	0.5 g	0.5 g
Ascorbic Acid		0.2 g	0.2 g			
Ferrous Sulphate				0.2 g		
Sodium Sulphite					0.2 g	
Sodium Dithionite						0.2 g
Time (hours)	6	6	6	6	6	6
Temperature (°C)	95	95	95	95	95	95
Result observed	Poor Dissolution	Conversion but lot of precipitate	Full conversion with clear solution	Conversion but very little precipitate	Convers n. but little precipita te	Convers n. but little precipit ate

It is to observe that example 3 comprising the combiantion of HEDP with ascorbic acid as the reducing agent did approach the best result.

Working examples 7 to 12

Certain quantities of different complexing agents in combination were added to a ferric oxide suspension (0.05gm/1000ml) in glass bottles. The bottles are then kept in an oven at different temperatures (°C) and varying duration (h). Physical appearance of the

Ferric Oxide suspension after the storage was used to determine the efficacy of the respective combination of complexing and reducing agent. The results of examples 7 to 12 are given in Table 2 below.

Table 2

	Bottle 07	Bottle 08	Bottle 09	Bottle 10	Bottle 11	Bottle 12
Ferric Oxide Suspension 0.05 gm / 1000 ml	100 ml	100 ml	100 ml	100 ml	100 ml	100 ml
HEDP Liquid (60%)	0.5 g					
Ascorbic Acid	0.2 g	0.2 g	0.2 g	0.2 g	0.2 g	0.2 g
DTPMP		0.5 g				
ATMP			0.5 g			
Sodium Gluconate				0.5 g		
Nitrotriacetic acid					0.5 g	
polyacrylic acid, sodium salt						0.5 g
Time (hours)	6	6	6	6	6	6
Temperature (°C)	95	95	95	95	95	95
PH	Adjusted to 2	Adjusted to 2	Adjusted to 2	Adjusted to 2	Adjusted to 2	Adjusted to 2
Result observed	Full conversion with clear solution	Iron Oxide residues at bottom	Few Iron Oxide residues at bottom	Undiss. Iron Oxide particles	Significant undissd. Iron Oxide particles	Significant undissd. Iron Oxide particles

The results of examples 7 to 12 clearly show that the result of example 7 comprising HEDP in combination with ascorbic acid reflects the best performance. Unlike oxalic acid, the novel system using HEDP in combination with ascorbic acid was most effective in the reduction of iron oxide into water soluble salts. On the contrary, conventional systems, even if they were able to partly reduce iron oxide, resulted into residual water-insoluble salts.

Working examples 13 to 15

A highly rust contaminated cotton sheeting fabric with 30x30/76x68 construction was padded with oxalic acid (taken as reference) and two different rust remover formulations in accordance with Table 3 following herein-below.

Table 3

Rust Remover	*Example 14*	*Example 15*
HEDP Powder	90 g	90 g
Ferrous Sulphate	10 g	--
Ascorbic Acid	--	10 g

The fabric impregnation was carried out at 70 °C with 90 % pick-up (see Table 4). The impregnated fabric was then batched for 6 hours followed by washing.

Table 4

PRODUCT		**Acid Treatment**		
		13	**14**	**15**
HOSTAPAL MRN liq. Conc.*	g/l	3.0	3.0	3.0
oxalic acid	g/l	8.0	-	-
RUST REMOVER (Trial #1)	g/l	-	4.0	
RUST REMOVER (Trial #2)	g/l			4.0

* HOSTAPAL MRN liq Conc. is a non-ionic wetting agent to improve fabric pick-up. It is a mixture of 75 to 85 % ethoxylated fatty alcohols and 4 to 8 % diethylene glycol monobutyl ether with 1 to 2 % cloud point anti-foam.

After such acid treatment the fabric was subjected to alkaline hydrogen peroxide bleaching using recipe mentioned in Table 5. Pickup was adjusted to 90 % and the fabric after impregnation was steamed at 102 °C for 20 min. Fabric was then washed at boil and at room temperature. CIE Whiteness of the bleached fabrics (Table 4) was determined using Datacolor Spectrophometer.

Table 5

PRODUCT		**A**	**B**
HOSTAPAL MRN liq. Conc .	g/l	4.0	4.0
STABILIZER SIFA liq.**	g/l	-	4.0
CAUSTIC SODA 48 °Be	g/l	20.0	20.0
HYDROG. PEROXYDE 50%	g/l	25.0	25.0

STABILIZER SIFA liq** is a modified polyacrylate and is used to stabilize the depletion of hydrogen peroxide under alkaline conditions.

Table 6

RECIPES	BLEACHED TEGEWA***	CAPILLARY ****TEST Cm	CIE WHITENESS[1]
13 (A)	5	3.1	66.57
13 (B)	5	3.0	68.11
14 (A)	5-6	2.3	35.09
14 (B)	5-6	2.7	48.11
15 (A)	5	3.1	70.34
15 (B)	5	3.4	71.98

TEGEWA*** is a mesure to access the presence of starch on the fabric.[2]
CAPILLARY **** is an indicative of fabric absorbancy (a desired feature after bleaching)[3]

Above illustration is an illustrative confirmation that the system and method of the instant invention (example 15) is able to achieve or surpass the performance of conventional processes using oxalic acid (example 13). System based on Ferrous Sulphate and HEDP (example 14) is not able to achieve the desired level of whiteness. This is attributed to poor stability of hydrogen peroxide in presence of ferrous ions.

[1] AATCC (2005), AATCC Test Method 110-2000, Whiteness of Textiles, AATCC Technical Manual
[2] C.K. Au and I. Holme, **The Alkali Desizing of Woven Cotton Fabrics**. Research Journal of Textile and Apparel, Volume 3, Issue No.1., May 1999, Pages 16-30
[3] AATCC (2011), AATCC Test Method 197, Vertical Wicking of Textiles, AATCC Technical Manual

SYSTEM FOR THE REMOVAL OF IRON OXIDE FROM SURFACES.

CLAIMS

1. System for the removal of heavy metal oxides, especially of iron oxide, from surfaces, especially from textiles or woven or nonwoven fabrics, wherein the textiles or fabrics are treated with a composition comprising at least ethane-1-hydroxy-1,1'diphosphonic acid (HEDP) and water and an organic reducing agent.

2. System according to claim 1, wherein the organic reducing agent is selected from the group consisting of ascorbic acid and glucose.

3. System according to claim 1 or 2, wherein the composition comprises at least 50 wt.-% of HEDP and 5 to 50 wt.% of the organic reducing agent based on the dry content of the composition.

4. Process for the removal of heavy metal oxides, especially of iron oxide, from surfaces, especially from textiles or woven or nonwoven fabrics, wherein the surface, especially the textiles or woven or nonwoven fabrics are treated with a solution of Ethane-1-hydroxy-1,1'diphosphonic acid (HEDP) and an organic reducing agent in water.

5. Process according to claim 4, wherein the treatment is performed at a temperature within the range of from 20 to 100 °C, preferably from 60 to 100 °C.

6. Process according to claim 4 or 5, wherein the treatment is maintained over a time period of from 3 to 10 hours, more preferred from 4 to 8 hours.

7. Process according to any of claims 4 to 6, wherein the treatment is carried out at a pH-value in the range of below 7, preferably at a pH-value of below 5.

8. Process according to any of claims 4 to 7, wherein the treatment is carried out in the presence of an organic reducing agent like ascorbic acid or glucose.

9 The use of ethane-1-hydroxy-1,1'diphosphonic acid (HEDP) in combination with ascorbic acid for the removal of heavy metal oxides, especially of iron oxide, from surfaces, especially from textiles or woven or nonwoven fabrics.

10. The use according to claim 9 for the removal of iron oxide contaminations from cellulosic woven fabrics.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/000129

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D7/36 C11D7/26
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02/36504 A2 (HERCULES INC [US]) 10 May 2002 (2002-05-10) examples 1-4	1-10
X	EP 0 313 335 A1 (DEARBORN CHEMICALS CO [CA] GRACE DEARBORN INC [CA]) 26 April 1989 (1989-04-26) claims 1-4; example 1; table VI	1,2,4,5, 8,9
X	EP 1 652 969 A1 (HENKEL KGAA [DE]) 3 May 2006 (2006-05-03) paragraph [0046]; example 2	1,5,7,9
A	GB 2 157 322 A (DIVERSEY LIMITED) 23 October 1985 (1985-10-23) cited in the application example 1	1-10

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
31 March 2014	04/04/2014

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1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/000129

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2003/004073 A1 (EVERSON TERRENCE P [US] ET AL) 2 January 2003 (2003-01-02) claims 1-20 -----	1-10

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2014/000129

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