# 

## (11) EP 3 210 784 A1

(12)

## **EUROPEAN PATENT APPLICATION**

(43) Date of publication:

30.08.2017 Bulletin 2017/35

(51) Int Cl.:

B41J 2/165 (2006.01) C11D 11/00 (2006.01) C11D 7/50 (2006.01)

(21) Application number: 17156288.7

(22) Date of filing: 15.02.2017

(84) Designated Contracting States:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

**Designated Extension States:** 

**BA ME** 

**Designated Validation States:** 

MA MD

(30) Priority: 23.02.2016 EP 16156981

(71) Applicant: OCE Holding B.V. 5914 CA Venlo (NL)

(72) Inventor: PELZERS, Ronald J.H.M.C. 5914 CA Venlo (NL)

(74) Representative: OCE IP Department St. Urbanusweg 43 5914 CA Venlo (NL)

## (54) MAINTENANCE LIQUID FOR PRINTERS

(57) The present invention relates to the use of an aromatic compound having a carbonyl group in a maintenance liquid for use in an ink jet printer, wherein the aromatic compound has a molar weight of below 200 g/mol. Particular examples of aromatic ester compounds are methyl benzoate and benzyl formate.

Such maintenance liquids provide efficient cleaning of printer parts that are contaminated with cured or semi-cured ink residues, without damaging the printer parts that have been in contact with the maintenance liquid.

EP 3 210 784 A1

#### Description

5

10

15

20

#### FIELD OF THE INVENTION

**[0001]** The present invention relates to a maintenance liquid in particular for cleaning (inkjet) printers, the maintenance liquid comprising an aromatic ester compound. The present invention further relates to the use of an aromatic ester compound in a maintenance liquid in particular for cleaning printers.

#### **BACKGROUND ART**

[0002] Maintenance liquids for cleaning print heads are known in the art.

US 2007/0132807 discloses a maintenance liquid for ink jet recording containing water, a resin solvent and a moisturizing agent. US 2007/0132807 further discloses that the resin solvent comprises at least one selected from the group consisting of alcohols, ethers, ketones, esters, nitrogen-containing compounds, and sulfur-containing compounds and that the amount is preferably less than 10 wt% because otherwise cleaning properties are deteriorated by reduction in fluidity caused by increase in viscosity of the maintenance liquid and because of reactivity with ink flow passage members that may get damaged during cleaning.

EP 2 796 516 discloses a maintenance liquid of inkjet printers including at least 50 wt% of at least one ether solvent. US 2007/0225185 discloses an ink washing liquid for a photo curable ink including at least one type of ether compound [0003] It is however a disadvantage of such maintenance liquids that the resin solvent used may form peroxides, which renders the cleaning liquid unsuitable for use in printers wherein radiation curable inks are used.

[0004] It is another disadvantage that many resin solvents are not HS&E friendly compounds.

**[0005]** It is yet another disadvantage that many resin solvents are aggressive towards materials used in printers, in particular in ink handling systems of printers including print heads, such that high concentrations of the resin solvent must be avoided in order to prevent damage to the printers, which adversely affects the efficiency of the maintenance liquid and hence requires long maintenance actions.

It is therefore an object of the present invention to provide a maintenance liquid that overcomes or at least mitigates said disadvantages and provides efficient cleaning and which is mild to commonly used materials in printers.

#### 30 SUMMARY OF THE INVENTION

**[0006]** This object can be partly achieved by providing a maintenance liquid comprising a low molar weight aromatic compound comprising a carbonyl group. In particular the molar weight is below 200 g/mol, preferably below 175 g/mol, more preferably below 150 g/mol.

[0007] Therefore, in a first aspect the present invention relates to the use of an aromatic compound comprising a carbonyl group in a maintenance liquid for use in an ink jet printer, wherein the aromatic ester compound has a molar weight of below 200 g/mol.

[0008] In an embodiment, the aromatic compound is a compound according to formula 1:

$$Q_m$$
-( $C_6H_5$ )-( $C_{n1}H_{2*n1}$ )-R-( $C_{n2}H_{2*n2}$ )-H Formula 1

wherein:

40

45

50

55

 $Q_m$  represent optional substituents present on the benzene ring, wherein m is between 0 and 5 and wherein Q may be independently of one another selected from the group consisting of -NH<sub>2</sub>; -OH; -OCH<sub>3</sub> and-CH<sub>3</sub>

R = -O-(C=O)-; -(C=O)-O-; -(C=O)-

n<sub>1</sub> is 0, 1, 2 or 3;

n<sub>2</sub> is 0, 1, 2 or 3;

and  $n_1 + n_2 \le 5$ , preferably  $n_1 + n_2 \le 4$ , more preferably  $n_1 + n_2 \le 3$ , more preferably  $n_1 + n_2 \le 2$ .

**[0009]** In an embodiment, m = 1 and Q is located at a para-, meta, or ortho position with respect to the  $-(C_{n1}H_{2*n1})-R2-(C_{n2}H_{2*n2})-H$  group.

[0010] In an embodiment,  $n_1 + n_2 = 1$ .

[0011] In an embodiment, the aromatic compound comprises an aromatic ester compound.

**[0012]** In an embodiment, the maintenance liquid comprises at least one aromatic ester compound selected from the group consisting of methyl benzoate, ethyl benzoate, methyl salicylate, methyl phenylacetate, methyl anthranilate and benzyl formate. Due to their cleaning efficiency, methyl benzoate and benzyl formate are preferred and benzyl formate is most preferred.

[0013] Inventors have surprisingly found that the maintenance liquid according to the present invention are able to efficiently remove cured or semi-cured radiation (e.g. UV) curing ink residues from printer parts, in particular from printer parts that are difficult to access (such as the interior of print heads and clogged nozzles). Because of efficient removal of (semi) cured ink residues, low residence times of the maintenance liquid in the printer parts are required, such that damaging the printer parts due to contact with aggressive resin solvents present in the maintenance liquid. The required low residence time also improves the down-time of the printer for maintenance actions and therefore improves the overall productivity of the printer. The aromatic ester compounds present in the maintenance liquids are non peroxide forming, therefore initiating of further polymerization reactions of the radiation curable inks is prevented. The aromatic ester compounds selected in this invention are also HS&E friendly.

**[0014]** In an embodiment the resin solvent compound has a flash point that is higher than 40 °C, preferably higher than 70°C. Such resin solvent compounds will not easily self-ignite when used under normal environmental conditions.

[0015] In an embodiment, the maintenance liquid is substantially free of water

**[0016]** In an embodiment, the aromatic compound is present in an amount of more than 50 wt%, preferably more than 75%, more preferably more than 90%

**[0017]** Typically methyl benzoate or benzyl formate are used as maintenance liquid in their pure form (100 wt%, disregarding impurities of the components as such), or a mixture of x wt% methyl benzoate and y wt% benzyl formate wherein x+y = 100 wt%.

[0018] In an embodiment, the maintenance liquid comprises organic solvents that are inert towards materials used in a printer and are miscible with the aromatic ester resin solvent.

In a second aspect the present invention relates to a method for maintaining a printer comprising the step of applying a maintenance liquid using an aromatic compound having a carbonyl group and having a molar weight of below 200 g/mol, in accordance with any embodiment of the first aspect of the present invention.

A method for maintaining a printer may be a method for cleaning the printer or parts thereof. The printer may be configured to eject droplets of an ink composition, in particular a radiation curable ink composition use of a low molar weight aromatic esters compound as described above in all aspects in a maintenance liquid, in particular a maintenance liquid for cleaning printers, more particular printers for printing radiation curable inks.

#### **DETAILED DESCRIPTION**

[0019] In a printer wherein radiation curable inkjet ink is jetted to form an image onto a recording substrate, the formed ink image needs to be radiated in order to initiate a polymerization reaction between reactive monomers present in the ink, such that the ink image is cured. Radiation sources, e.g. UV-lamps or UV-LEDs are used to radiate a freshly printed image. Due to e.g. scattering of the radiation, the radiation curable ink may be partly and accidently cured in the printer, for example in the ink tubes that supply and transport ink to and in the printer; the print head; the nozzle plate. Such cured or semi-cured ink residues are difficult to remove from printer parts.

[0020] Curing (polymerization) of ink inside the printer may cause all kinds of print problems:

- malfunctioning of the print heads: e.g. non-jetting (clogged) or misdirecting (partly clogged) nozzles;
- clogging of: filters, ink tubes, etc.

**[0021]** Cured or semi-cured ink residues may be successfully removed with a maintenance (cleaning) liquid comprising a resin solvent which dissolves and/or causes the (semi) cured ink residues to swell.

**[0022]** In order to be able to work safely with organic solvents the flash point of the used solvents should be above the operating temperature of the printer, or at least above the maintenance temperature of the printer.

The Flash Point of a volatile chemical is the lowest temperature at which it can ignite in either liquid or vapor form. In general, chemicals which have a flash point that is higher than the environment (e.g. room temperature) will be at low risk of catching fire.

For example a solvent with a flash point of 2 degrees Celsius is prone to ignition in almost any normal workplace. In contrast a product with a flashpoint above 40 degrees Celsius would only be an ignition risk under quite extreme conditions.

#### **UV-curable ink compositions**

[0023] UV-curable ink compositions comprise:

- an ink vehicle comprising one or more radiation curable compounds (monomers), for example acrylates;
  - a colorant, for example a dye, a pigment, or a mixture of dyes and/or pigments;
  - an initiator, which is a compound that can easily form a reactive species when radiated. The reactive species starts a polymerization reaction (curing) of the reactive monomers;

3

45

40

20

50

55

 additives such as: inhibitors (preventing spontaneous reaction of the reactive monomers and/or reaction under influence of e.g. oxygen); viscosity modifiers; gelling agents; etc.

[0024] Examples of such compounds and examples of radiation curable inks are well known in the art.

#### Maintenance liquid

**[0025]** The maintenance liquid according to the present invention comprises an aromatic ester compound as a resin solvent.

**[0026]** Suitable aromatic ester compounds are: methyl benzoate(Flash point = 82°C), ethyl benzoate, methyl salicylate, methyl phenylacetate, methyl anthranilate and benzyl formate.

**[0027]** The maintenance liquid may further comprise additives such as surfactants, dispersants, inhibitors etc, which are known in the art. Specific additives are not limited to any kind, as long as the effect of the present invention is maintained.

#### Maintenance (e.g. cleaning) method

[0028] Ink residues in and on printer parts may be removed with a maintenance liquid according to the present invention, which maintenance liquid may be applied in various ways, also depending on the location of the contamination with ink residues. Examples are: spraying, application with a cloth (wiping), (off-line) soaking, flushing via liquid (ink) handling system of the printer, etc. The methods may be performed manually or (semi) automatically.

#### **EXAMPLES**

## 25 Comparative example A

**[0029]** Prints were made comprising full cover areas of each color from a UV-curable CMYK ink set comprising standard curable ink vehicles (i.e. an acrylate monomer composition comprising acrylates commonly known in the art of UV-curable inkjet inks). The used print medium was IJM608 which is a polyester fiber reinforced paper obtained from Canon. The prints were made on a printer set-up comprising an Océ printhead adapted for being used in combination with UV-curable inks and cured with a UV-LED curing device. The ink layers are cured such, that just non-tacky ink layers are obtained

Then a drop of benzyl alcohol as maintenance liquid was placed on the print and left to soak for 1 min and for 3 min. When the maintenance liquid is effective the ink layer will wrinkle and swell. After set time we remove in one rub as much as swelled ink layer from the medium with a AlphaWipe TX1004 tissue. When the liquid is effective all swelled ink is removed from the medium (0% ink layer remaining), when not effective no ink is removed from the media (100% ink layer remaining). This was repeated for all colored inks in the set.

For the black inks two printing modes were used, a production mode (printed with 4 passes of the printhead) and a presentation mode (printed with 8 passes of the printhead), which are printer settings. The difference between said modes is that in a presentation mode a print with a higher quality (denser ink layer) is obtained. It is expected that due to a denser ink layer, penetration of the solvent into said layer is more difficult.

For the cyan, magenta and yellow inks, prints are only made in the presentation mode and only 3 min soaking tests are. **[0030]** The results for the black ink in the production and presentation mode are shown in Table 1. The results for the complete CMYK ink set made in the presentation mode and tested at 3 min soaking are shown in Table 2 (n.d. = not determined).

## Examples 1-6

[0031] Comparative Example A was repeated for all solvents shown in Tables 1 and 2.

Table 1 : results black ink in production and presentation mode at 1 and 3 min soaking

		production mode		presentation mode	
	soak time (min)	1	3	1	3
Ex	Solvent				
Α	Benzyl alcohol	>80%	>80%	60-80%	>80%

20

15

5

10

35

40

30

50

55

45

#### (continued)

		production mode		presentation	mode
	soak time (min)	1	3	1	3
Ex	Solvent				
1	Benzyl formate	>80%	>80%	40-60%	60-80%
2	Methyl benzoate	60-80%	>80%	20-40%	40-60%
3	Ethyl benzoate	40-60%	60-80%	<20%	n.d.
4	Methyl salicylate	40-60%	>80%	n.d.	n.d.
5	methyl phenyl acetate	40-60%	60-80%	n.d.	n.d.
6	methyl anthranilate	40-60%	60-80%	20-40%	n.d.

Table 2: results CMYK ink set in presentation mode and at 3 min soaking

		Cyan	Magenta	Yellow	Black
Ex	Solvent				
Α	Benzyl alcohol	>80%	n.d.	n.d.	>80%
1	Benzyl formate	>80%	>80%	>80%	60-80%
2	Methyl benzoate	>80%	>80%	>80%	40-60%
3	Ethyl benzoate	40-60%	40-60%	>80%	n.d.
4	Methyl salicylate	<20%	n.d.	n.d.	n.d.
5	methyl phenyl acetate	20-40%	n.d.	n.d.	n.d.
6	methyl anthranilate	>80%	>80%	>80%	n.d.

#### [0032] From Table 1 it can be concluded that:

- all selected solvents are able to remove black ink from prints made in production mode (in particular at longer soaking);
- the selected solvents are less effective on prints made in presentation mode;
- benzyl formate is the most efficient (non peroxide forming) alternative for benzyl alcohol;
- methyl benzoate is a good runner up.

## 40 [0033] From Table 2 it can be concluded that:

- the tested solvents are more efficient on colored ink layers than on black ink layers;
- for colored inks (CMYK), benzyl formate, methyl benzoate and methyl anthranilate are efficient alternatives for benzyl alcohol;
- considering the entire ink set (CMYK), benzyl formate is the most efficient alternative for benzyl alcohol;
- Methyl benzoate is a good runner up.

#### Example 7

5

10

15

20

25

30

35

45

[0034] A print head nozzle plate is on purpose exposed with UV-light which results in a clogged (i.e. non-jetting) print head. After soaking the nozzle plate in Benzyl formate for 12 minutes the print head showed complete recovery for all nozzles. No damage to the print head was found.

[0035] Detailed embodiments of the present invention are disclosed herein; however, it is to be understood that the disclosed embodiments are merely exemplary of the invention, which can be embodied in various forms. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limiting, but merely as a basis for the claims and as a representative basis for teaching one skilled in the art to variously employ the present invention in virtually any appropriately detailed structure. In particular, features presented and described in separate dependent

claims may be applied in combination and any advantageous combination of such claims is herewith disclosed.

[0036] Further, the terms and phrases used herein are not intended to be limiting; but rather, to provide an understandable description of the invention. The terms "a" or "an", as used herein, are defined as one or more than one.

**[0037]** The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

**[0038]** It will, for example, be obvious to the skilled person that the maintenance liquid according to the present invention may also be suitable for use in printers using other ink types that may suffer from accumulation of resinous compounds and/or pigments in printer parts. For example aqueous latex ink or pigmented ink compositions.

#### Claims

10

15

20

25

40

45

50

- 1. Use of an aromatic compound having a carbonyl group in a maintenance liquid for use in an ink jet printer, wherein the aromatic compound has a molar weight of below 200 g/mol.
- 2. The use according to claim 1, wherein the aromatic compound is a compound according to formula 1:

$$Q_{m}$$
-( $C_{6}H_{5}$ )-( $C_{n1}H_{2*n1}$ )-R-( $C_{n2}H_{2*n2}$ )-H Formula 1

wherein:

 $Q_m$  represent optional substituents present on the benzene ring, wherein m is between 0 and 5 and wherein Q may be independently of one another selected from the group consisting of -NH<sub>2</sub>; -OH; -OCH<sub>3</sub> and-CH<sub>3</sub>

R = -O-(C=O)- or -(C=O)-C-

 $n_1$  is 0, 1, 2 or 3;

n<sub>2</sub> is 0, 1, 2 or 3;

and  $n_1 + n_2 \le 5$ .

- 30 **3.** The use according to claim 2, wherein m = 1.
  - **4.** The use according to any one of claims 2-3, wherein  $n_1 + n_2 = 1$ .
- 5. The use according to any one of the preceding claims, wherein the maintenance liquid comprises an aromatic ester compound.
  - **6.** The use according to claim 5, wherein the maintenance liquid comprises at least one aromatic ester compound selected from the group consisting of methyl benzoate, ethyl benzoate, methyl salicylate, methyl phenylacetate, methyl anthranilate and benzyl formate.
  - 7. The use according claim 6, wherein maintenance liquid comprises benzyl formate and/or methyl benzoate.
  - **8.** The use according to any one of the preceding claims, wherein the aromatic compound has a flash point that is higher than 40 °C.
  - 9. The use according to any one of the preceding claims, wherein the maintenance liquid is substantially free of water
  - **10.** The use according to any one of the preceding claims, wherein the aromatic ester compound is present in an amount of more than 50 wt%, relative to the total maintenance liquid composition.
  - **11.** A method for maintaining a printer comprising the step of applying a maintenance liquid comprising an aromatic compound having a carbonyl group and having a molar weight of below 200 g/mol.
- 12. Method according to claim 11, wherein the maintenance liquid comprises at least one aromatic ester compound selected from the group consisting of methyl benzoate, ethyl benzoate, methyl salicylate, methyl phenylacetate, methyl anthranilate and benzyl formate.
  - 13. Method according to claim 12, wherein the maintenance liquid comprises at least one aromatic ester compound

selected from methyl benzoate and benzyl formate.



#### **EUROPEAN SEARCH REPORT**

**DOCUMENTS CONSIDERED TO BE RELEVANT** 

**Application Number** 

EP 17 15 6288

10	

	DOCUMENTS CONSID	ERED TO BE RELEVA	<u> </u>		
Category	Citation of document with ir of relevant pass	dication, where appropriate, ages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)	
X	W0 2013/083413 A1 ( 13 June 2013 (2013- * page 6, line 18 - claims 1,5,8,12,14 * page 7, lines 3-6 * pages 12-13 *	06-13) page 7, line 15; *	1,2,5,8,9,11	INV. B41J2/165 C11D7/50 C11D11/00	
X,D A	EP 2 796 516 A1 (AG 29 October 2014 (20 * page 5, paragraph	14-10-29)	1,2,4 5,8-11		
Α	US 2013/141501 A1 (6 June 2013 (2013-6 * page 3, paragraph claims 1,5 * * page 1, lines 4-6	6-06) s 39-40,44,46,47;	6,7,12,		
А	10 February 2010 (2	3-5; claims 1,3-8 h 4-5 *	13	TECHNICAL FIELDS SEARCHED (IPC)	
Α	EP 1 550 556 A1 (KO INC) 6 July 2005 (2 * paragraphs [0192] * paragraphs [0085] [0090], [0105], [	, [0244], [0297] , [0086], [0089],	13	B41J C11D	
Α	WO 2005/091771 A2 (INC) 6 October 2005 * page 25, line 15;		LAB 6,7,12,		
	The present search report has I	peen drawn up for all claims  Date of completion of the se	arch	Examiner	
	The Hague	13 June 2017		nbier, Titia	
X : part Y : part docu A : tech O : non	ATEGORY OF CITED DOCUMENTS icularly relevant if taken alone icularly relevant if combined with anotiment of the same category nological background written disclosure mediate document	E : earlier pa after the f ner D : documen L : documen	principle underlying the tent document, but publi ling date to ited in the application to ited for other reasons of the same patent family	invention shed on, or	

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

EP 17 15 6288

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 The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

13-06-2017

	Patent document cited in search report		Publication date		Patent family member(s)	Publication date
	WO 2013083413	A1	13-06-2013	EP JP US WO	2788194 A1 2015507550 A 2014283879 A1 2013083413 A1	15-10-2014 12-03-2015 25-09-2014 13-06-2013
	EP 2796516	A1	29-10-2014	AU CA CN EP JP KR US WO	2014257792 A1 2902893 A1 105164215 A 2796516 A1 2016516118 A 20150138274 A 2016068790 A1 2014173727 A1	10-09-2015 30-10-2014 16-12-2015 29-10-2014 02-06-2016 09-12-2015 10-03-2016 30-10-2014
	US 2013141501	A1	06-06-2013	JP JP US	6003050 B2 2013116603 A 2013141501 A1	05-10-2016 13-06-2013 06-06-2013
	GB 2462410	A	10-02-2010	CN DE GB JP JP KR US WO	102124588 A 112009001788 T5 2462410 A 5667563 B2 2011528861 A 20110031984 A 2011269255 A1 2010010337 A1	13-07-2011 09-06-2011 10-02-2010 12-02-2015 24-11-2011 29-03-2011 03-11-2011 28-01-2010
	EP 1550556	A1	06-07-2005	AU CN EP KR TW US WO	2003264553 A1 1684834 A 1550556 A1 20050054963 A 1299306 B 2006017782 A1 2004028815 A1	19-04-2004 19-10-2005 06-07-2005 10-06-2005 01-08-2008 26-01-2006 08-04-2004
	WO 2005091771	A2	06-10-2005	AT CA EP US US US	485360 T 2551855 A1 1723224 A2 2005197267 A1 2013133694 A1 2015152363 A1 2005091771 A2	
ORM P0459						

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

#### REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

## Patent documents cited in the description

- US 20070132807 A **[0002]**
- EP 2796516 A **[0002]**

• US 20070225185 A [0002]