Identification of Unknown Photo-initiators in offset UV-inks and prints
1 Abstract

More advertising is being personalized every day, digital printers are encounter problems related to the use of offset printed materials (pre-printed). For better understanding of these problems it is necessary to better understand the formulation of these offset UV-inks.

In this study a method has been developed for the identification of photo-initiators in offset UV inks and in printed materials. It is concluded that methylene chloride is the best extraction solvent for the different photo initiators in the different inks. Analysis using a DB-5MS column gives good separation for all the initiators identified.

For the identification of the unknown initiators a combination of normal electron ionization (EI) and chemical ionization (CI) has been used. Most of the photo initiators do not give any information about the molecular mass, chemical ionization is being used. It is concluded that a combination of CH$_4$-Cl and iC$_4$H$_{10}$-Cl gives valuable information towards the identity of the unknown photo-initiator. Many initiators have methoxy or acids groups which become visible using CH$_4$-Cl, which results in the loss of water or methanol. For determination of the molecular ion iC$_4$H$_{10}$-Cl results in the most abundant molecular signal. In comparison to CH$_4$-Cl, iC$_4$H$_{10}$-Cl gives simple chromatogram without additional signals from addition reactions.

In total 11 different photo-initiators have been identified in 29 different inks from 5 different suppliers. It was found that different photo initiators were used in different colours from a single brand of ink.

In the final step this method is being used on printed media, from which the extracted photo initiators are being compared to the pure ink. A print with 4 different inks and two different cure settings has been used. In all the prints all the photo initiators could be identified. Showing that the developed working method can also be used for identification of photo initiators when printed, regardless of curing degree or offset printer.
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2 Introduction

More mail, like advertising and personal bills, is being personalized today than 10 years ago. To create this personal mail, a digital process is needed like printing. However digital colour printing is more expensive in comparison to offset printing. Therefore the market in which both techniques are combined is growing. First the colour print is made using offset printing (called pre-printed), after which it is personalized using a digital printer.

For offset printing there are two main types of inks available, oxidative drying inks and UV curable inks. In this report the composition of these UV inks is being investigated. The main components in UV inks are reactive acrylates (monomers) and initiators. There are two main applications areas in which UV offset inks are being used. One of the main applications of UV inks is for offset printing off food packaging (i.e. milk packaging), because of the relative high quality and low residue of these prints, in comparison to oxidative drying inks. Some of these components are being labelled as having a health risk. Within Europe there are regulations towards the use of these initiators and the maximal concentration present in the food is being regulated\(^1\). Recent awareness of photo-initiators (especially ITX) in food by the European Food Safety Authority (EFSA)\(^2\), has led to an increase in the analysis of photo-initiators in food.

The use of UV inks in can also give problems when a digital printer is being used to personalize offset printed media. Most printers use a warm fusing step in which the toner is fused to the media. During this process remaining components deriving from the UV inks are transferred to the digital printing system. When these compounds deposit on critical parts of a printer, these can result in a service call and repairs. Therefore the composition of different offset inks used is of interest for the printing industry to better understand the mechanisms responsible for these failures.

In this report, the photo-initiators used in different UV inks are being identified. The difference in the type of photo-initiators used by different manufactures is being investigated, as well as the possible differences between colours of the same ink.

In literature different LC-MS methods\(^3\)\(^\text{4}\)\(^5\)\(^6\)\(^7\)\(^8\) are being described, in which the presence of these initiators is measured. Most of these methods need a clean-up before analysis like; solid phase, or liquid liquid extraction. Similar methods are being described using GC\(^9\)\(^10\), in which also the samples are pre-treated using SPE. Only limited amount of effort has been taken in the analysis of the packaging. But still a clean up and purification of the sample is required\(^6\)\(^11\). One of the goals of this research is to develop a simple method without extensive cleanup for direct analysis.

All described methods are based on pre-selected photo initiators. In this research the focus is on the identification of the photo-initiators. A simple gas chromatographic method combined with mass spectrometric detection is being developed for the identification of photo-initiators in the ink. Because of the reactive nature of photo initiators, EI ionization mass spectra usually only gives limited information about the molecular mass. For confirmation about the identity also chemical ionization is used.

\(^1\) Schweizerische Eidgenossenschaft, Verordnung des EDI über Bedarfsgegenstände (SR 817.023.21) vom 23. November 2005, Anhang 6
\(^3\) Cuilian Sun, Sheot Harn Chan, Dan Lu, Hui Min Wendy Lee, Bosco Chen Bloodworth, Journal of Chromatography A, 1143 (2007) 162-167
3 Principle

3.1 UV-inks

For the hardening of a UV-curable offset ink a mixture of different photo-initiators are being used. An ink usually consists of multiple photo-initiators, because of the different lamps used by different offset printers. The effective absorption spectrum is different for each initiator. Because of the use of different pigments (colours), other photo-initiators are needed which are effective in a different spectral region than the pigment.

Photo-initiators can be divided into two main groups according to their working principle. Norrish type I: which are initiators who decay after being exposed to UV light, through homogenic splitting into radicals, and are build into the polymer. Norrish type II: These initiators need a synergist (hydrogen donator) to produce radicals, and the initiator does not react into the polymer.

The type I initiators are the most reactive, because of the use of a benzoyl radical. The disadvantage of some of these initiators is their colour, which turns yellow after reacting. An example of a Norrish type one photo-initiator is Irgacure 651 (also know as photocure 51) as shown in Figure 3.1.1. The primary reaction is the Norrish type I splitting, in which a benzoyl and a benzyl radical are being formed. The benzyl radical can split into a highly reactive methyl radical and the stable methyl benzoate. This reaction is temperature depended, and is the main mechanism at room temperature but will not happen at 0°C.

![Figure 3.1.1. Example of Norrish type I initiation of Irgacure 651 (Photocure 51)](image)

Other examples of the Norrish type I photo-initiators are the α-amino alkylphenonen, such as Irgacure 369 and Irgacure 907, see figure 3.1.3. Because of the benzoyl group the absorption spectra of these initiators is shifted (towards the 300-322 nm) see Figure 3.1.2, while smaller photo-initiators have their absorption well below the 300nm (i.e. benzophenone, 240-250 nm). This is an advantage in pigmented inks, which partial block the UV light.

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12 IR 97322.022, Literatuurstudie naar foto-initiatoren voor UV uitharding, J van de Reek
13 Ciba, Photoinitiators for UV curing, key product selection guide 2003, g-48/2003 October
The Norrish-type II photo initiators consist of a benzophenone or thioxantone group in combination with a hydrogen donor (synergist). The reaction mechanism consists of 4 steps:

1. Absorption of UV light, crating a single state electron at the keton.
2. Transition from the single state to the triple state (inter system crossing).
3. Creating of radical's trough hydrogen splitting from a synergist or hydrogen donor (usually a tert-amine).
4. Initiating through addition of the radicals with a monomer.

For the working of a type II photo-initiator the transfer of a proton is needed\textsuperscript{14}. The active protons are located at the $\alpha$-position of the tert-amine or alcohol. This results in ketyl radical and an $\alpha$-amino-alkylradical. The ketyl radicals are not used in the initiaton, and are being terminated by recombination or by transition back into the initial state. The $\alpha$-amino-alkylradicals are used in the initiation as shown in Figure 3.1.4.

One other problem when using radical initiation is oxygen inhibition. The use of Norrish type II initiators, are less sensitive towards oxygen inhibition. Therefore usually a mixture is used in the ink receipt.

\textsuperscript{14} H.F. Gruber/ Photo initiators for free radical polymerization / Prog. Polym. Sci. / Vol. 17 / 953-1044 / 1992
A second example of the Norrish-Type II initiator is the reaction of benzophenone with Michler’s ketone (4,4-bis-(dimethylamino)benzophenone), and is one of the most reactive initiators. Because of combination of the benzophenone with the amino groups, a very reactive system is created, in comparison to the normal amine.

However the Michler’s ketone is prohibited, because of its carcinogenic properties. As substitute other initiators are being used with similar properties. As replacement a photo initiator with only one dimethyl amino group 4-(dimethylamino)benzophenone (DMAB), or with the methyl groups replaced by ethyl groups 4,4-bis-(diethylamino)benzophenone (BDEAB), is being used.
3.2 Gas Chromatography

The most common GC\textsuperscript{15} analysis starts with the injection of a volatile sample into a hot injector for evaporation, and transfer to the column (there are many different injection techniques for GC analysis available, which shall not being explained in this thesis). The components are separated based on their difference in boiling point and interaction with the stationary phase of the column giving the components retention. At the end of the column the separated components are detected using a detector. In this research a single quadrupole mass detector has been used.

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\textbf{Column type}

The purpose of the column is to give the components with similar boiling points different retention, resulting into separation. The most simple is the HP-1 (or DB-1) column, of which the packing material is made of dimethylpolysiloxane. One of the most widely used columns is HP-5 column, in which the packing material is also made of dimethylpolysiloxane of which 5\% of the methyl groups have been replaced by phenyl groups. To reduce bleeding of the column, the methyl group situated at the other side of the phenyl group is replaced by a second phenyl group. This makes the polymer more ridged and lowers the possibility to create cyclic siloxanes (which mainly causes the bleeding).

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\textsuperscript{15} M.C. McMaster, GC/MS A Pratical User’s Guide 2\textsuperscript{nd} edition, Wiley Interscience, 2008, pag. 25-28
3.3 Mass Spectrometry

3.3.1 Electron Ionization

The most commonly used ionization technique in GC-MS is EI (Electron Ionization). Using this technique an electron is knocked off a molecule, leaving behind a molecular ion with a positive charge. This ion is directed towards the entrance of the mass analyser by a repeller. The electrons are produced by a filament, which are repelled with 70 eV to produce a stream of electrons. The energy of the electrons is high enough not only to produce molecular ion, but also to produce fragments of these ionized molecules. The fragmentation pattern of the sample ions formed is related to the energy by which the electrons are being repelled (70eV), resulting in a specific fingerprint of ions. As result it is possible to create commercially available libraries. Because EI is a relatively hard ionization technique often the molecular ion is not detected.

3.3.1.1 Fragmentation using EI

If sufficiently excited the M⁺ ion can form a variety of product ions depending on their stability and formation energy by which rearrangement can occur. During fragmentation using electron ionization the most important factor for ion formation is the stability of the product ion. The stability of the ion can be increased by separating the charge over the ion. Two of the main mechanisms are electron sharing (in which the charge is devided over two atoms by a nonbonding orbital i.e carbonyl group) and resonance stabilization (in which the charge is located over the π-electrons i.e. benzyl cation).

To most simplistic way to predict the fragmentation is to assume that the reactions are initiated at the favoured site of the unpaired electron. The most favored molecular ion is arising from the loss of an electron with the lowest energy, which is generally σ- < π- < n-electrons.

<table>
<thead>
<tr>
<th>Sigma (σ)</th>
<th>Pi (π)</th>
<th>Non-bonding (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH₂C:CH₃R’</td>
<td>RHC::CHR’</td>
<td>R-O-R</td>
</tr>
</tbody>
</table>

Cleavage of a single bond results into an odd-electron (OE⁺⁺) molecular ion should result into an even-electron fragment ion (EE⁺⁺) and the loss of a neutral radical fragment. The formation of each ion should be equally based on coincidence.

\[ \text{CH₃CH₂CH₃} \rightarrow \text{CH₃CH₂⁺ + CH₃} \]
\[ \text{CH₃CH₂⁺} + \text{CH₃} \]

Formation of the OE⁺⁺ ion from an EE⁺⁺ ions involve energetically favourable rearrangement and charge retention.

\[ \text{CH₃CH₂-O⁺=CH₂} \rightarrow \text{CH₃CH₂⁺ + O=CH₂} \]
\[ \text{CH₂=CH₂ + HO⁺=CH₂} \]

Reactions initiated at the radical sites from free electron pair, arises from their tendency for electron pairing to form a new bond with an adjacent atom. This is followed by the homolytic cleavage of the second bond to that α-atom, and is therefore called α-cleavage.

<table>
<thead>
<tr>
<th>Saturated site:</th>
<th>Unsaturated hetero atom:</th>
</tr>
</thead>
<tbody>
<tr>
<td>R─CR₂=Y⁺⁺→R⁺⁺</td>
<td>R─CR=Y⁺⁺→R⁺⁺</td>
</tr>
</tbody>
</table>

An unpaired electron can also be donated from an adjacent atom through space, so called β-cleavage. This is one of the most familiar rearrangements and is also called the McLafferty

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For components containing an unsaturated carbonyl group, the unpaired electron can be donated from a hydrogen atom to form a new bond. As part of the driving force is the strong O-H bond, followed by the rearrangement which is favoured by a six-membered-ring transition state. For this rearrangement to occur the third position from the carbonyl group should consist of a hydrogen atom (see Figure 3.3.1).

**Figure 3.3.1** McLafferty trough γ-H rearrangement with a carbonyl group.

An second example is the rearrangement of the fragmentation of Escalol 507, resulting in the stable m/z 165.

**Figure 3.3.2** McLafferty rearrangement on Escalol 507

### 3.3.2 Chemical Ionization

Using Chemical ionization (CI) a large amount of reagent gas is introduced into the ion source. Since there is much more reagent gas than sample, most of the emitted electrons ionize the reagent gas forming reagent ions instead of the sample molecules. These reagent ions react with each other and with the sample in various ways. The energy of the reagent gas is transferred to the sample by transferring a proton. The amount of energy transferred is therefore based on the difference in the proton affinity between the reagent gas and the sample.

Many different chemical ionization reagent gasses have been investigated, with each their own specific purposes. The energy of the reactant ions are based on their proton affinities.
Table 3.3.1. Overview of some reagent gases\textsuperscript{18}.

<table>
<thead>
<tr>
<th>Reagent gases</th>
<th>Proton affinities ([\text{kcal/mol}])</th>
<th>Reactant ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2)</td>
<td>423</td>
<td>(\text{H}_3^+)</td>
</tr>
<tr>
<td>(\text{CH}_4)</td>
<td>551</td>
<td>(\text{CH}_5^+) and (\text{C}_2\text{H}_6^+)</td>
</tr>
<tr>
<td>((\text{CH}_3)_2\text{CHCH}_3)</td>
<td>816</td>
<td>(\text{C}_4\text{H}_5^+)</td>
</tr>
<tr>
<td>(\text{CH}_3\text{OH})</td>
<td>761</td>
<td>(\text{CH}_3\text{OH}_2^+) and ((\text{CH}_3\text{OH})n\text{H}^+)</td>
</tr>
<tr>
<td>(\text{NH}_3)</td>
<td>854</td>
<td>(\text{NH}_4^+) and ((\text{NH}_3)_n\text{H}^+)</td>
</tr>
</tbody>
</table>

There are four basic ionization processes that take place during (positive) CI.

- Proton Transfer
- Hydride Abstraction
- Addition
- Charge Exchange

Charge exchange ionization processes are not often used, and require noble gasses as reagent gas. These shall not be used in this study, and shall therefore not be further explained.

**Proton Transfer**

The majority of the ionization occurs by proton transfer to species of a higher proton affinity (Brönsted acid reagent system)\textsuperscript{18}. The proton affinity is the energy change when a proton is added to neutral molecule to form a protonated cation.

\[ A + H^+ \longrightarrow AH^+ \]

The proton affinity is defined as:

\[ PA = -\Delta H^0(298) = \Delta f H^0(A) + \Delta f H^0(H^+) - \Delta f H^0(MH^+) \]

When a molecule with a higher affinity is found, the proton will be transferred.

\[ AH^+ + M \longrightarrow A + MH^+ \]

Therefore the choice of the reagent gases is of influence on the amount of protonated molecular ions formed, especially for instable molecules.

One of the most used reagent gases is methane. When methane\textsuperscript{19} is ionized using electron impact (EI) three major ions are formed; \(\text{CH}_4^+\), \(\text{CH}_3^+\) and \(\text{CH}_2^+\). This result in three major ions, \(\text{C}_4\text{H}_9^+\), \(\text{C}_2\text{H}_6^+\), and \(\text{C}_3\text{H}_5^+\), as shown below.

\[ \text{CH}_4 + e^- \longrightarrow \text{CH}_4^{**} + 2e^- \]
\[ 2\text{CH}_4^{**} \longrightarrow 2\text{CH}_3^+ + \text{H}_2 \]
\[ \text{CH}_4^{**} + \text{CH}_4 \longrightarrow \text{CH}_5^+ + \text{CH}_3^+ \]
\[ \text{CH}_3^+ + \text{CH}_4 \longrightarrow \text{C}_2\text{H}_5^+ + \text{H}_2 \]

A second frequently used reagent gas is isobutane, with a higher proton affinity in comparison to methane. Isobutane yields mainly \(\text{C}_4\text{H}_9^+\) as reagent ion with a minor yield of \(\text{C}_3\text{H}_5^+\) (3%), as a result isobutane generally yield more simple spectra in comparison to methane. Using isobutane as reagent gas the main ionization shall occur through proton transfer. In comparison to methane almost non addition reaction shall occur.

\[ i - \text{C}_4\text{H}_{10} \longrightarrow i - \text{C}_4\text{H}_{10}^{**} \]
\[ 2i - \text{C}_4\text{H}_{10}^{**} \longrightarrow 2\text{C}_4\text{H}_9^+ + \text{H}_2 \]

\textsuperscript{18} A.G. Harrison, Chemical Ionization Mass Spectrometry, CRC press, 1983
Hydride abstraction
The created reactant ions using CI can have relative high hydride-ion (H-) affinities. In methane-CI both CH$_5^+$ and C$_2$H$_5^+$ are capable of hydride extraction, which results in the loss of H$^-$ according to the general reaction:

\[ \text{CH}_5^+ + M \longrightarrow [M - H]^+ + \text{CH}_4 + H_2 \]

This reaction is often seen at long chain alkanes. When using CH$_4$-CI it is possible both MH$^+$ by proton transfer and M-H$^+$ by hydride extraction can occur in one spectrum (i.e. methyl-esters).

Addition
Besides proton transfer and hydride abstraction also addition reactions can occur. Often reagents gasses are reactive enough to combine with the analyte molecules by condensation or association (addition reactions) in so called adduct ions. These adduct ions are often seen when using Methane as reagent gas, forming [M+C$_2$H$_4$]$^+$ and [M+C$_3$H$_6$]$^+$ ions. Addition reactions are also very important when using ammonia as reagent gas, as ammonia has a very high proton affinity and only few organic compounds will undergo proton transfer as main ionization step. Using ammonia as reagent gas the mayor ions formed are NH$_4^+$, [NH$_2$NH$_3$]$^+$, and [NH$_4$(NH$_3$)$_2$]$^+$. This will give rise to an intense [M+NH$_4$]$^+$ peak by the addition reaction.

Because of the relative small difference in energy between the reagent gas and the sample, CI is a so called soft ionization technique which results in high abundant molecular ion. However still fragmentation and rearrangement can occur, driven by the stability of the formed product. One of the mechanisms seen is hydrogen shift, especially when oxygen of nitrogen groups are present in the analyte. A very often seen rearrangement is the loss of water in the analysis of alcohols, aldehydes, ketones, and acids, see Figure 3.3.3.
The mechanism for alcohols is driven by the relative instable MOH$_2^+$ ion for alcohols higher than C$_4$. For acids higher than C$_4$ this is usually followed by the loss of CO, strongly seen with aromatic acids like benzoic acid or phenyl acetic acid in which the ion is stabilized in the aromatic ring.

![Figure 3.3.3 Example of the chemical ionization using CH4 reagent gas](image-url)
4 Experimental

4.1 Materials

All solvents used are purchased from Merck: Methylene Chloride (>99.8%), 2-butanol (>99.9%), Cyclohexane (>99.5%), Methanol, (>99.5%). For chemical ionization gasses are used from Air Products with research quality. All inks are obtained through different ink suppliers. Because of the confidential nature in the collaboration of Océ Technologies and offset ink suppliers the exact name and type of the analyzed inks can not be published.

4.2 Sample preparation

4.2.1 Inks

Extraction of the inks was performed in a 25ml vial with screw silicon caps coated with PFTE. About 100mg of the ink is extracted using about 5g of extraction solvent. For extraction the vials are shaken for 2 hours using an automated vortex shaker from Scientific Industries. To remove the pigments from the ink the extract was transferred in 4 ml vial with screw silicon caps coated with PFTE, and centrifuged for 15 minutes at 5000G using a Microcentrifuge 154 from the firm OLE DICH. The clear supernatant was transferred in a 2 ml GC vial for analysis.

4.2.2 Pre-printed media

The pre-printed media were cut using a punch of 5cm x 2 cm. The punched out piece of paper were cut into small strokes of about 2mm*20mm and transferred into a 4 ml vials with screw silicon caps coated with PFTE. The papers were extracted for 2 hours in 1.5 g of MC. To perform blank references a piece of unprinted paper was extracted according to the same procedure. The vials are centrifuged for 15 minutes after which the supernatant was transferred in a 2ml GC vial.

4.3 Apparatus and method

4.3.1 GC-MS (EI)

All experiments have been conducted using an Agilent 7890A GC with an Agilent 5975C EI/CI MSD detector. The columns used are both from Agilent, DB-1MS, 128-0112, 12m x 0.2 mm x 0.33µm, and DB-5MS, 122-5532, 30m x 0.25 mm x 0.25µm. For analysis 1.0 µl of sample is injected using a 5 µl syringe into a glass liner filled with glasswool. Sample injections are performed using a split of 25:1. The GC inlet temperature is 325°C. The oven temperature is programmed from 80°C, held for 2 minutes, raised with a rate of 8°C/min to 325°C, held for 5 minutes. The total duration of the analysis is 37.6 minutes. The MSD transfer line is set at a temperature of 325°C. The ion source is set at 230°C and the quad at 150°C. Before analysis the MSD is automatically tuned using PFTBA with an “atune”. The MS data is collected in scan mode from m/z 14 to 600, at 70 eV electron energy. The solvent delay is set to 3 minutes.

4.3.2 GC-MS (CI)

For CI analysis the same Agilent 7890A GC and 5975C MSD has been used. For CI analysis only the Agilent DB-5MS, 122-5532, 30m x 0.25 mm x 0.25µm column has been used. For CI analysis the same GC instrument parameters are as for EI analysis. Ionization has been performed using a high pressure CI ion source. The MS Source temperature is set at 250 °C, and the Quad at 150°C. Before CH₄-CI analysis the MSD has been automatically tuned using PFTBA with a "pcich4.u" tune. The gas flow is set at 14%. The MS data is collected in scan mode from m/z 14 to 600, at 40 eV electron energy. The solvent delay is set to 1.5 minutes. Performing iC₄H₁₀-CI the same GC instrument parameters are used as for CI analysis using CH₄. Before iC₄H₁₀-CI analysis the MSD has been automatically tuned in CH₄-CI mode using
PFTBA with a “pcich4.u” tune. The MSD is switched to iC$_4$H$_{10}$-Cl mode, and the gas-flow is optimized using the reagent ions m/z 43 and m/z 57, the tune file is saved as “PCIC4H10.U”. The gas flow for iso-butane has been optimized and set on 13% (see § 5.1.3.).

5 Results and discussion

5.1 Method optimization

Before starting with the identification of the photo initiators in the different inks, the working method has been optimized.

The optimization consists of:
1. Choice of column
2. Choice of Solvent
3. Optimization of the CI parameters

5.1.1 Column

In the first step, two different column types have been investigated, both from J&W Scientific. The column which is most frequently used is the HP-5MS$^{6,11}$ column. This column shall be compared to normal DB-1MS column.

1. DB-1MS 12m x 0.2mm x 0.33µm
2. DB-5MS 30m x 0.25mm x 0.25µm

Three different reflex blue inks have been used in the comparison.

1. Ink A-1
2. Ink B-1
3. Ink B-3

The Samples have been dissolved in methyl ethyl keton (MEK), with a concentration of 20-30 mg/g, using identical GC parameters both columns are being evaluated.

A comparison between two types of columns has been made, by differences seen in the peak shape, and the retention of the components. Because the DB-5MS column is 30m while the HP-1MS is only 12m long, the retention times are a higher using the DB-5MS column, as shown in Figure 5.1.1.

Figure 5.1.1. Ink A-1 measured on the HP-1 column
The components analyzed using the HP-1 column clearly show non-symmetric peak shape, and most peaks show an extensive tailing. The in red en bleu highlighted parts are given in Figure 5.1.2 and Figure 5.1.3.

Figure 5.1.2. Ink A-1 measured on the DB-5 column

When the same sample is being analyzed using a DB-5 column, the peak shape has significantly improved, see Figure 5.1.2. Possibly there is more column interaction on the HP-5 column resulting in a more stable chromatography, as most of the initiators have aromatic groups.

Figure 5.1.3. Comparison between some components.
The DB-5 column consists of 5% phenyl groups, which results in more retention for some of the components. The
In the chromatogram using the DB-5 column the Irgacure 907 has more retention than Escalol 507, while on the HP-1 column the Escalol has more retention, (see Figure 5.1.3). This is most likely caused by the double ring structure in Irgacure 907 (see Figure 5.1.4), which has more column interaction with the DB-5 stationary phase.

![Figure 5.1.4. Structure of Escalol 507 and Irgacure 907.](image)

Similar results are seen with ITX and 4-phenyl-benzophenone, in relation to an acrylate present in the chromatogram (see Figure 5.1.3). Using a HP-1 column the acrylate is has got the more retention time, however on the DB-5 column both initiators have more retention in comparison to the acrylate. This extra retention is caused by the interaction between the aromatic groups of the initiators with the phenyl groups of the stationary phase. This interaction results in better chromatographic separation, and therefore better peak shape. The DB-5 column is therefore the preferred column for the analysis and therefore used in this study. More examples are given in the appendix 8.3.

![Figure 5.1.5. Structure of ITX and 4-phenyl-benzophenone.](image)

### 5.1.2 Solvent

The inks will be analyzed by simple direct dissolving of the ink and direct analysis. Therefore four different solvents have been compared.

1. Cyclohexane (CH)
2. Methanol (MeOH)
3. Methylene Chloride (MC)
4. 2-butaneone (MEK)

To ensure that enough different initiators are being evaluated, four different reflex blue inks have been used in the comparison.

1. Ink A-1
2. Ink B-1
3. Ink B-3
4. Ink C-1
The solvents are being compared by calculating the response of each photo-initiator in the different solvents.

Table 5.1.1. Calculated response \([\text{Area} \times 10^6 / \text{mg}]\) in the 4 solvents

<table>
<thead>
<tr>
<th>Ink</th>
<th>CH</th>
<th>MeOH</th>
<th>MC</th>
<th>MEK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ink B-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzophenone</td>
<td>5.6</td>
<td>11.0</td>
<td>22.1</td>
<td>12.5</td>
</tr>
<tr>
<td>Irgacure 184</td>
<td>3.6</td>
<td>10.5</td>
<td>19.7</td>
<td>10.8</td>
</tr>
<tr>
<td>EDB</td>
<td>3.4</td>
<td>9.0</td>
<td>18.5</td>
<td>9.7</td>
</tr>
<tr>
<td>Photocure 51</td>
<td>3.8</td>
<td>11.0</td>
<td>21.9</td>
<td>12.2</td>
</tr>
<tr>
<td>Ink C-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-methyl-benzophenone</td>
<td>3.9</td>
<td>11.8</td>
<td>29.4</td>
<td>18.2</td>
</tr>
<tr>
<td>Acrylate ([m/z = 55/113])</td>
<td>3.1</td>
<td>23.8</td>
<td>56.0</td>
<td>30.9</td>
</tr>
<tr>
<td>Ink A-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Photocure 51</td>
<td>0.6</td>
<td>7.9</td>
<td>16.5</td>
<td>9.5</td>
</tr>
<tr>
<td>Escalol 507</td>
<td>1.0</td>
<td>14.0</td>
<td>28.3</td>
<td>15.7</td>
</tr>
<tr>
<td>Irgacure 907</td>
<td>0.8</td>
<td>10.7</td>
<td>20.5</td>
<td>11.5</td>
</tr>
<tr>
<td>ITX</td>
<td>0.4</td>
<td>4.5</td>
<td>9.4</td>
<td>5.1</td>
</tr>
<tr>
<td>4-phenyl-benzophenone</td>
<td>0.3</td>
<td>4.5</td>
<td>9.7</td>
<td>5.2</td>
</tr>
<tr>
<td>Ink B-3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDB</td>
<td>1.0</td>
<td>6.2</td>
<td>14.1</td>
<td>8.3</td>
</tr>
<tr>
<td>Photocure 51</td>
<td>0.8</td>
<td>7.2</td>
<td>15.0</td>
<td>8.5</td>
</tr>
<tr>
<td>Unknown Acrylate</td>
<td>0.3</td>
<td>5.6</td>
<td>14.0</td>
<td>8.3</td>
</tr>
<tr>
<td>Irgacure 907</td>
<td>0.5</td>
<td>5.4</td>
<td>11.8</td>
<td>6.6</td>
</tr>
<tr>
<td>Unknown Acrylate</td>
<td>0.3</td>
<td>6.4</td>
<td>20.5</td>
<td>12.3</td>
</tr>
<tr>
<td>DETX</td>
<td>1.5</td>
<td>15.0</td>
<td>32.9</td>
<td>19.2</td>
</tr>
</tbody>
</table>

The responses of the different photo-initiators have been calculated for each solvent. Extraction using cyclohexane results in the lowest response and ethylene chloride gives the highest response. An example of the difference between cyclohexane and methylene chloride is given in Figure 5.1.6 below.

Figure 5.1.6 Chromatogram of a extract using MC and CH for ink C-1.

Using MC as extraction solvent, the highest response for all of the different initiators is
generated. Also some acrylates which shall not been identified, give the highest response using MC. Because all samples have been extracted for 2 hours using an automated vortex, it is expected that not all of the initiators are dissolved in all of the investigated solvents. Possibly some components could be better dissolved when using longer extraction times, this is not further investigated. Therefore MC has been used as extraction solvent for the inks in the identification of the photo-initiators. Using the DB5 column no problems with overlapping of peaks are being expected.

5.1.3 Chemical Ionization

In the next step a comparison between the identification using normal Electron Ionization (EI) and Chemical Ionization (CI) is being made. For the CI measurements methane and iso-butane are being used as reagent gas.

Using methane as reagent gas, different reagent ions are responsible for the ionization. Using methane the following ions can be responsible for the ionization:

- $\text{CH}_5^+ = m/z\ 17$
- $\text{C}_2\text{H}_5^+ = m/z\ 29$
- $\text{C}_3\text{H}_5^+ = m/z\ 41$

When using iso-butane ($i$-$\text{C}_4\text{H}_{10}$) two ions are responsible for the ionization.

- $\text{C}_4\text{H}_9^+ = m/z\ 57$
- $\text{C}_3\text{H}_7^+ = m/z\ 43$

![Figure 5.1.7 Example of the ions using CH₄-CI](image)

Using the Agilent 7890 GC in combination with the Agilent 5975C MSD the amount of reagent gas is controlled by adjusting the gas valve (set in %), as shown in the schematic overview below. When using methane, the system can be tuned using PFTBA (Perfluor-tributaneamine). Because of the high proton affinity of isobutane PFTBA can not be used for tuning the MS.

![Schematic overview](image)
Figure 5.1.8 Schematic overview of the CI installation of the Agilent 5975C MSD.

Table 5.1.2. Setting the gas valve for methane

<table>
<thead>
<tr>
<th>Valve setting [%]</th>
<th>Area in 10^5</th>
<th>m/z 17</th>
<th>m/z 29</th>
<th>m/z 41</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>470</td>
<td>779</td>
<td>133</td>
<td></td>
</tr>
<tr>
<td>10%</td>
<td>640</td>
<td>1090</td>
<td>262</td>
<td></td>
</tr>
<tr>
<td>14%</td>
<td>660</td>
<td>1140</td>
<td>303</td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>642</td>
<td>1098</td>
<td>287</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.1.3. Setting the gas valve for iso-butane

<table>
<thead>
<tr>
<th>Valve setting [%]</th>
<th>Area in 10^5</th>
<th>m/z 57</th>
<th>m/z 43</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>1379</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>10%</td>
<td>2067</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>13%</td>
<td>2110</td>
<td>103</td>
<td></td>
</tr>
<tr>
<td>16%</td>
<td>2082</td>
<td>101</td>
<td></td>
</tr>
</tbody>
</table>

Using methane the valve is set on 14%, and for iso-butane the valve is set on 13% resulting in the maximum amount of regent ions.

The ink A-1 has been analyzed for comparison of both chemical ionization modes and electron ionization. The total ion chromatograms are shown in Figure 5.1.9 (because of some small differences in the initial oven time, the response times are all shifted for 1 minute, this has no influence on the results). All the methods of ionization result in similar chromatograms, with only small differences in response.

Looking at the EI spectrum of Irgacure 184 no molecular ion can be detected, see Figure 5.1.10. Therefore CI is could be used to determine the molecular mass, which is helpful in the identification of unknown initiators. Using CH₄-Cl an abundant mass of 187 can be detected, see Figure 5.1.11. However in the case of Irgacure 184 this is not the molecular ion, but this ion is the molecular ion with the loss of water. This becomes clear when using iC₄H₁₀-Cl, which results in an abundant mass of 205, which is the MH⁺ mass, as shown in Figure 5.1.11. Using iC₄H₁₀-Cl still an abundant signal of 187 can be detected, but the protonated molecular mass is clearly 205.
Figure 5.1.9 Comparison of the TIC with El, CH₄-Cl and iC₄H₁₀-Cl.

Figure 5.1.10 EI spectrum of Irgacure 184

Figure 5.1.11 CI spectra of Irgacure 184

A disadvantage of using methane as reagent gas is the possibility to form ions by addition reactions of C₂H₅⁺. As example this is shown when analyzing ITX (2-Isopropyl-thioxanethone). ITX is a relative stable molecule which already gives the molecular ion during EI. Using CH₄-Cl besides the ionization by proton transfer, also ionization by addition of C₂H₅⁺ is seen. When using iC₄H₁₀-Cl only the MH mass is detected, as shown in Figure 5.1.12.
It can be concluded that using methane as reagent gas, does not ensure visibility of the protonated molecular ion. However this can also be an advantage as it gives extra structural information about the possible presence of acids- or methoxy-groups. Besides more fragmentation also addition reactions can occur. Using isobutane as reagent gas results in more clean spectra as less fragmentation and no addition reactions have been seen. Furthermore the use of isobutane results in a clear protonated molecular ion. Therefore isobutane is more suitable as additional reagent gas in addition on normal EI analysis.

5.1.4 Conclusions method optimization

For identification of the photo-initiators in the inks, the inks shall be dissolved in MC for direct analysis. Analysis shall be performed using a 30m DB5 column. For identification a combination of EI and CI has been used. Normal EI mode gives structural information about the initiator. The use of CH₄-CI can be to identify the presence of acids, alcohol, or methoxy groups. These are often not clearly visible in EI because of the very high fragmentation. Therefore CH₄-CI gives additional information about the structure of the initiator. Using IC₄H₁₀-CI only the MH mass is detected for confirmation about the molecular weight. In comparison to CH₄-CI no addition reactions are observed which results in more simple mass spectra, and clear confidence about the molecular weight.
5.2 Inks

The method as described in §3.1 has been used in the identification of unknown photo-initiators in UV inks. Several inks shall be investigated.

5.2.1 Ink A

The first ink of which the photo-initiators are being examined is UV Ink A-1. There are different colours available of this ink.
- Reflex Bleu
- Red032
- Black
- Cyan
- Yellow
- Magenta

5.2.1.1 Reflex Blue ink

The first colour investigated is the Reflex Blue. One of the first unknown initiators has fragments at m/z 105, 77, and 51 reveal the presence of an aromatic group. The high abundance of m/z 151 reveals the presence of an aromatic di-methoxy group. Most likely this is the most abundant signal because the carbonyl group is stabilizing the free radical, and the charge is set on the aromatic di-methoxy group. Most likely this is the photo-initiator Irgacure 651/Photocure 51.

![EI spectrum of Irgacure 651/Photocure 51](image)

**Figure 5.2.1** EI spectrum of Irgacure 651/Photocure 51

The identity of this initiator is being verified using CH₄-CI. The M+H mass (m/z = 257) can be found, however this component is too reactive to form an abundant M+H signal. The loss of a methanol from one of the methoxy groups, giving mass m/z 225 as the most abundant ion. When the identity is unknown, this signal could be mistaken as being the M+H signal. However the loss of methanol confirms the presence of the methoxy groups.

In the next step, CI is performed using isobutane (iC₄H₁₀) as reaction gas. Using iC₄H₁₀-CI, only the M+H mass of m/z 255 is found without the loss of water as shown with CH₄-CI. The presence of m/z 255 is confirming the identity as Irgacure 651/Photocure 51.
Figure 5.2.2. CI-Spectra (CH$_4$ and iC$_{4}$H$_{10}$) Irgacure 651 / Photocure 51

For the next initiator, similar fragmentation using EI measurement is observed, see appendix 8.2.10. Using Cl with methane as reaction gas the dominant mass is m/z 209, which results from the loss of m/z 31 from the presence of a methoxy group. As expected with CH$_4$-Cl also a large amount of addition reactions take place, resulting in masses higher that the M+H mass. As final confirmation of the structure the molecular mass is being verified using iC$_{4}$H$_{10}$-Cl, resulting in an abundant m/z 241 peak, see appendix 8.2.10.

Figure 5.2.3 CH$_4$-Cl spectra of methyl benzoylebenzoate
The next initiator at Rt 27.9 in the ink has very characteristic EI spectra. This EI spectra consists of an abundant molecular ion and a clear McLafferty rearrangement, see Figure 5.2.4. Therefore this component can be identified as being Escalol 507. The molecular mass is verified using iC_4H_10CI, resulting in an abundant m/z 278 peak as the protonated molecular ion, see appendix 8.2.9.

Figure 5.2.4. EI spectra of Escalol 507.

Very close to Escalol 507 the initiator is located in the chromatogram at Rt 28.1, see Figure 5.2.7. This initiator gives no molecular ion using EI mode but mainly a high abundant fragment at m/z 128. Chemical ionization using iC_4H_10 results in a clear M+H ion at m/z 280, confirming that m/z 128 is not the molecular ion, see Figure 5.2.6. Looking at the EI spectrum also m/z 151 can be found. The combination of m/z 128 and m/z 151 results in a total molecule mass of 279. Therefore it is concluded that this component is Irgacure 907, in which the radical is located on the carbonyl site, resulting in a stable m/z 128 ion.

If Methane is being used as ionization gas, already an abundant M+H peak can be identified, however more fragmentation and addition reactions are shown as well.

Figure 5.2.5. EI spectra of Irgacure 907
Figure 5.2.6. iC₆H₁₀-CI spectra of Irgacure 907

The next two initiators at Rt 29.2 and Rt 29.9 (ITX and 4-phenyl benzophenone) are easily identified using EI mass spectra, see appendix 8.2.5. and 8.2.11. In total 6 initiators and one synergist could be indentified in the Reflex Blue ink of Ink A-1.

Figure 5.2.7 Total ion chromatogram of Ink A-1 Reflex blue.
5.2.1.2 Black ink

In the next step the A-1 Black ink is compared to the Reflex blue ink. In addition to the reflex blue ink an extra component has been identified in the black ink. This mass spectrum is characterized by mass 99 and 81, as shown in Figure 5.2.9. The mass 99 is identified as the cyclohexanol fragment. The mass of 81 is the cyclohexanol with the loss of water. This is normally seen with straight aliphatic chain with easy excess of hydrogen. However the loss of water is also seen in the direct analysis of cyclohexanol, shown in spectrum from the NIST library, see Figure 5.2.10.

![Figure 5.2.8 Total ion chromatogram of ink A-1 Reflex blue in comparison to ink-A1 black.](image)

![Figure 5.2.9 EI spectra of Irgacure 184](image)
The EI spectrum also reveals the presence of an aromatic group, but does not give any information about the molecular mass. The CH$_4$-Cl spectrum gives a large mass at m/z 187, which is the result of the loss of water from the hydroxyl group. Using iC$_4$H$_{10}$-Cl the protonated molecular ion could be identified as being m/z 205, and still an abundant peak of m/z 187 could be found. The combination of an aromatic group, a cyclohexane group, and a hydroxyl group this initiator could be identified as being Irgacure 184.

**Figure 5.2.11** i-C$_4$H$_{10}$-Cl spectra of Irgacure 184.
5.2.1.3 Yellow Ink

In the Yellow ink dimethyl benzenamine is being identified, see appendix 8.4.1. This could be an extra synergist, however this amine could also be deriving from the yellow pigment. The yellow pigment is most likely a diarylide yellow pigment (see Figure 5.2.13), which is widely used in offset printing inks because of their transparency and temperature resistance during grinding. The diarylide pigments are classified as the bis-azo pigments. These are characterized by the azo bond (-N=N-). The synthesis of these pigments involves the coupling of di- (or tetra-) substituted diamino-diphenyls as diazonium salts with acetoacetic aryldyes as coupling components. The resulting pigments vary from greenish yellow to reddish yellow by changing the groups of the bi-phenyl with Chloride (X and Y), and replacing the end groups with methyl or methoxy groups (R$_1$-R$_3$), see figure below.

**Figure 5.2.12** Overlay of the chromatogram of Reflex blue and yellow

**Figure 5.2.13** Basic chemical structure of diarylide yellow pigments.

Using IR analysis the presence of such a pigment is being verified. The pigment has been isolated by extraction using MEK and MC. Between each step the sample is being centrifuged to precipitate the pigment, and removal of the solvent. The dried residue has been analyzed using transmission IR, and compared to possible pigments from the library. This resulted in a good match with pigment Yellow 13, see appendix 8.5.1. This pigment has di-methylphenyl groups at both sides as end groups. The presence of dimethyl-aminobenzene components in the yellow ink are therefore most likely deriving from the pigment. Especially because there are only encountered in the yellow ink.

---

5.2.1.4 Red032 ink

In the red ink also some extra peaks were found in comparison to the Reflex Blue ink (see Figure 5.2.14), which are di- and tri-chlorobenzene with in two causes also an amine group, see appendix 8.4.2 for the EI spectra. These could, similar to yellow, be deriving from the red pigment. One group of commercially used red pigments are the Naphthol AS pigments\textsuperscript{21}. These are obtained by coupling of a substituted aryl diazonium salts with arylides of 2-hydroxy-3-naphtoic acids (Naphtol AS). By changing the aromatic end groups, the color differences between medium red to brown and violet.

Similar to yellow, the pigment has been isolated from the ink, and is being identified using transmission IR and identification using a library, see appendix 8.5.2.

For the red032 ink pigment red 112 could be identified as the pigment used in the ink. This pigment contains trichloro-benzene end groups. One of the most abundant peaks in the chromatogram is of trichloro-benzeneamine. The chloride atoms are very specific in the mass spectrum, as they have a clear isotope pattern with 2 Da difference. The presence of this component also verified the pigment as being Pigment Red112, as being the only red pigment known from literature with 3 chloride groups.

![Figure 5.2.14 Overlay of the chromatogram of the ink A-1 Red032 with the ink A1 Reflex Blue.](image)

5.2.1.5 Sub-conclusion

Using GC-MS with EI as ionization technique some of the photo initiators could already be identified. However due to the reactive nature of some of these initiators the molecular mass could not be determined using EI.

For determination of the molecular mass CI has been used. However when using methane as reagent gas still fragmentation can occur. Because many initiators have a carbonyl or methoxy groups, the loss of water or methanol is being observed giving extra structural information.

When using isobutane as reagent gas during CI, the most abundant mass is for the initiators always the $M+H^+$ peak. For some component still small amount of fragmentation can be observed, which were dominant in methane-CI.

Table 5.2.1. Molecular ion clearly visible using different ionization techniques.

<table>
<thead>
<tr>
<th>Photo-initiator</th>
<th>EI</th>
<th>CH₄-Cl</th>
<th>iC₆H₄Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl-benzoylbenzoate</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Irgacure 184</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Irgacure 651</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Escalol 507</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Irgacure 907</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Quantacure ITX</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>4-phenyl benzophenone</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

The A-1 reflex blue ink consists of 6 different photo-initiators, as shown in Figure 5.2.7. In the Cyan and Magenta ink, no other initiators were found in comparison to the reflex blue ink. However in the black ink also Irgacure 184 could be indentified. Most likely the initiator mix is being adapted because of the absorbance of a part of the UV-light spectrum by the black pigment.

Table 5.2.2. Overview of the photo initiators identified in the A-1 ink.

<table>
<thead>
<tr>
<th>Photo-initiator</th>
<th>Reflex Blue</th>
<th>Red032</th>
<th>Black</th>
<th>Cyan</th>
<th>Magenta</th>
<th>Yellow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl-benzoylbenzoate</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Irgacure 184</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Irgacure 651</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Escalol 507</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Irgacure 907</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Quantacure ITX</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>4-phenyl benzophenone</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

5.2.2 Ink B

5.2.2.1 Ink B-1 reflex Blue

In the Ink A-1 in total 7 photo initiators could be identified. To check the working method using GC-MS, this method is being applied to a second ink supplier.

From the Ink B-1, three colours are available for analysis, namely Reflex Blue, Black and yellow. In reflex blue ink B-1 some photo-initiators could be identified, which were also present in the A1 ink.

The first component at Rt 20,1 is Benzophenone, which gives a simple EI spectra which can easily be used for the identification, see appendix 8.2.2. The molecular mass can be verified using Cl, which gives mainly an M+H peak.

Besides Benzophenone two other initiators could be identified: EDB and DETX. These are also easily identified using their EI spectra and an abundant molecular ion using Cl, see appendix 8.2.3 and 8.2.4. In total 7 different photo initiators could be identified in the Ink B-1.
Figure 5.2.15 Overview of the B-1 Reflex Blue ink

5.2.2.2 Ink B-1 Black

In the black ink, some differences were found in comparison to the Reflex Blue ink. The photoinitiator ITX has been replaced by a larger amount of DETX. However the amount of DETX looks lower than the amount of ITX which has been removed. Because the

Figure 5.2.16 Overview of the Ink B-1 black ink
Figure 5.2.17 Overlay of the B-1 Black and Reflex Blue inks.

Similar as measured in the A-1 inks, the recipe of the black ink is different than the reflex blue ink. The black ink is characterized by the absence of ITX, and a higher concentration of DETX in comparison to the Reflex Blue ink.

5.2.2.3 Ink B-1 Yellow

Similar to the black ink, in the yellow ink the ITX has been replaced by a larger amount of DETX in comparison to the reflex blue ink. Furthermore a dimethyl-benzene amine has been found, which is most likely deriving from the pigment as shown in the analysis of the Yellow A-1 ink.

Figure 5.2.18. Overlay of the B-1 Yellow and the Reflex Blue ink.
5.2.2.4 B-2 Cyan

From the B-2 ink, only the Cyan, Magenta and yellow inks were available for analysis. Similar to the B-1 ink the B-2 ink contains Irgacure 907 and DETX, and very small amount of Irgacure 651/Photocure 51. In comparison to the ink B-1 the B-2 also contains Escalol 507, 4-phenyl-benzophenone. These were already identified in the A-1 inks. In the cyan ink also N-(toluyl)-N-ethylanaline (NTEA) and Bisphenol A could be indentified (as shown in the figure below).

The NTEA is probably deriving from the pigment, because this amine could not be found in yellow or magenta. The Bisfenol A is most likely deriving from the use of Bisphenol A acrylate, and is found in all the three colours.

![Figure 5.2.19 EI-TIC of the B-2 cyan ink](image)

5.2.2.5 Sub-Conclusions

In total seven photo initiators could be identified in the B-1 ink. In total 3 new initiators could be identified. All these photo/initiators already give an abundant molecular ion, which can easily be verified using CI. Comparable to the A-1 ink, in the B-1 ink differences were found in the initiator mix of each colour. In the Reflex Blue ink ITX was identified as extra initiator.
Table 5.2.3. Photo initiators present in the B-1 ink.

<table>
<thead>
<tr>
<th></th>
<th>Reflex Blue</th>
<th>Black</th>
<th>Yellow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irgacure 184</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Quantacure EDB</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Irgacure 651</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Quantacure ITX</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irgacure 907</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>DETX</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

In the B-2 ink differences from the B-1 ink, as it contains a complete difference mix of photo-initiators. However no new initiators were identified, as Escalol 507 and 4-phenyl-benzophenone were already identified in the A-1 ink.

Table 5.2.4. Overview of the photo-initiators in the B-2 ink.

<table>
<thead>
<tr>
<th></th>
<th>Cyan</th>
<th>Magenta</th>
<th>Yellow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photocure 51</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Escalol 507</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>4-phenyl-benzophenone</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Irgacure 907</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>DETX</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

5.2.3  Ink E

5.2.3.1  Ink E-1

From Ink E-1 only the Reflex blue ink is available. But besides the already know initiators, a unknown photo-initiator was found.

The EI spectrum already gives an abundant molecular ion at m/z 304. Chemical ionization using i-C4H10 yields confirms 304 as the molecular ion.

The EI spectrum shows different positive ions, which are caused by structural rearrangements caused by the phenyl-thiol group\(^ {22}\). Also an abundant m/z of 77 and 105 could be identified as benzoyl group. This photo-initiator could be identified as being Quantacure BMS.

Figure 5.2.20  EI and \(iC_6H_{10}Cl\) of Quantacure BMS.

Furthermore Irgacure 184, Quantacure ITX and Escalol 507 could be identified in the E-1 ink, see Figure 5.2.21.

\(^{22}\) F.W. McLafferty / F. Turčiček, Interpretation of mass spectra, University Science Books, 1993, 268-269
Figure 5.2.21. Chromatogram of ink E-1.

5.2.4 Conclusions ink analysis

Using a combination of EI and CI all of the photo-initiators in inks from different suppliers and colours could be identified. All the identified photo-initiators gave an abundant M+H ion when using isobutane as reagent gas in CI. Using methane as reagent gas, results in the loss of water or methanol as most of the initiators contain hydroxy or methoxy groups. An overview of the most abundant ion and the presence of the molecular ion is given in Table 5.2.5. Other components present in the inks are acrylates or smaller molecules deriving from the pigments used. Isolation of the pigment and IR analysis can be used to identify the pigment used, and the source for these smaller molecules.

Using this method also some other inks have been analyzed, but only known initiators were identified. For a complete overview of all the photo-initiators present in the inks, see appendix 8.6. In total 11 different photo-initiators have been indentified in 29 different inks. Large differences have been found between the inks, varying from 2 photo-initiators in an ink, up to a mixture of 7 photo-initiators in one ink.

Table 5.2.5. Overview of the most abundant ion and the presence of the molecular ion.

<table>
<thead>
<tr>
<th></th>
<th>EI</th>
<th>Mol. Ion</th>
<th>CH₄·Cl</th>
<th>Mol. Ion +H</th>
<th>iC₆H₁₀·Cl</th>
<th>Mol. Ion +H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irgacure 184</td>
<td>99</td>
<td>No</td>
<td>105</td>
<td>No</td>
<td>205</td>
<td>Yes</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>105</td>
<td>Yes</td>
<td>183</td>
<td>Yes</td>
<td>183</td>
<td>Yes</td>
</tr>
<tr>
<td>Quantacure EDB</td>
<td>148</td>
<td>Yes</td>
<td>194</td>
<td>Yes</td>
<td>194</td>
<td>Yes</td>
</tr>
<tr>
<td>DETX</td>
<td>268*</td>
<td>Yes</td>
<td>269</td>
<td>Yes</td>
<td>269</td>
<td>Yes</td>
</tr>
<tr>
<td>Quantacure ITX</td>
<td>239</td>
<td>Yes</td>
<td>255</td>
<td>Yes</td>
<td>255</td>
<td>Yes</td>
</tr>
<tr>
<td>Irgacure 907</td>
<td>128</td>
<td>No</td>
<td>280</td>
<td>Yes</td>
<td>280</td>
<td>Yes</td>
</tr>
<tr>
<td>Photocure 51</td>
<td>151</td>
<td>No</td>
<td>225</td>
<td>Yes**</td>
<td>255</td>
<td>Yes</td>
</tr>
<tr>
<td>Quantacure BMS</td>
<td>304*</td>
<td>Yes</td>
<td>305</td>
<td>Yes</td>
<td>305</td>
<td>Yes</td>
</tr>
<tr>
<td>Escalol 507</td>
<td>165</td>
<td>Yes</td>
<td>166</td>
<td>Yes</td>
<td>278</td>
<td>Yes</td>
</tr>
<tr>
<td>Methyl-Benzoylbenzoate</td>
<td>163</td>
<td>Yes</td>
<td>209</td>
<td>Yes**</td>
<td>241</td>
<td>Yes</td>
</tr>
<tr>
<td>4-phenyl-benzophenone</td>
<td>181</td>
<td>Yes</td>
<td>259</td>
<td>Yes</td>
<td>259</td>
<td>Yes</td>
</tr>
</tbody>
</table>

* Molecular ion
** Very low abundancy
5.3 Pre-printed media

In the next step, the method used to identify the different initiators in the inks has been applied to pre-printed media. Because of the very low amount of ink present on the media followed by a curing step, it is investigated whether still all the initiators from the ink could still be found.

There can be a large difference between different offset printers, and the UV lamps used. As the amount of ink set on the media can vary per offset printer, and the intensity of the lamps used can differ. Therefore the prints with different cure settings and from two different offset printers are being investigated.

![Example of the test print](image)

**Figure 5.3.1.** Example of the test print

The test print consist of 4 different inks, together with 2 lamp setting and 2 different offset printers giving in total 16 different samples which are being investigated. The sample has been made on a offset printer using 2 UV lamps and 3 UV lamps. All the strokes have been printed using Reflex blue ink, as the mix of photo-initiators can differ per colour.

For the analysis a piece of the print has been cut out using a punch of 6 cm². This piece of the media has been cut into small pieces and is extracted using 2 ml of MC. The MC has been analyzed directly using the GC method which was also used in the analysis of the inks.
5.3.1 Comparison between print and ink

The first sample is printed using the Ink A-1 ink. In the print all the photo-initiators which are present in the ink could be found, see Figure 5.3.2.

![Comparison between ink and pre-print](image)

**Figure 5.3.2.** Comparison between ink and pre-print

The extract of the pre-print has been analyzed in normal EI mode and using iC₄H₁₀Cl. All the 6 photo-initiators could be identified using both ionization techniques. All of the Spectra are given in appendix 8.7.

The relative amount of photo initiator does not change after printing and curing. The relative amounts for the 4 prints is given in Table 5.3.1. The differences measured could be due to batch differences, this is not further examined.

The exception is the print with ink B-1 in which not all of the photo initiators present in the ink could be found (see Figure 8.8.1., in §8.8). The ITX which is clearly present in the ink is not found in the print. Instead a larger amount of DETX is measured in the print. Most likely this is caused by differences in ink batches, as the ink analysed is not from the same batch as the batch which has been used for the print. This could not be verified as the ink used for the print was not present. To investigate whether different photo initiator mixtures are being used in one type of ink more batches need to be analyzed.
Table 5.3.1. Relative amount of photo initiator in the print and ink.

<table>
<thead>
<tr>
<th>Ink A-1</th>
<th>Print</th>
<th>Ink</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photocure 51</td>
<td>18%</td>
<td>17%</td>
</tr>
<tr>
<td>Methyl-benoylbenzoat</td>
<td>11%</td>
<td>11%</td>
</tr>
<tr>
<td>Escalol 507</td>
<td>28%</td>
<td>30%</td>
</tr>
<tr>
<td>Irgacure 907</td>
<td>19%</td>
<td>22%</td>
</tr>
<tr>
<td>ITX</td>
<td>12%</td>
<td>11%</td>
</tr>
<tr>
<td>4-phenyl-benzophenone</td>
<td>12%</td>
<td>10%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ink B-1</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Photocure 51</td>
<td>20%</td>
<td>20%</td>
</tr>
<tr>
<td>Irgacure 184</td>
<td>15%</td>
<td>18%</td>
</tr>
<tr>
<td>EDB</td>
<td>12%</td>
<td>17%</td>
</tr>
<tr>
<td>Photocure 51</td>
<td>22%</td>
<td>20%</td>
</tr>
<tr>
<td>Irgacure 907</td>
<td>4%</td>
<td>5%</td>
</tr>
<tr>
<td>ITX</td>
<td>0%</td>
<td>17%</td>
</tr>
<tr>
<td>DETX</td>
<td>27%</td>
<td>2%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ink D-1</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Irgacure 184</td>
<td>51%</td>
<td>43%</td>
</tr>
<tr>
<td>EDB</td>
<td>15%</td>
<td>24%</td>
</tr>
<tr>
<td>DETX</td>
<td>34%</td>
<td>33%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ink E-1</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Irgacure 184</td>
<td>15%</td>
<td>12%</td>
</tr>
<tr>
<td>Escalol 507</td>
<td>39%</td>
<td>46%</td>
</tr>
<tr>
<td>ITX</td>
<td>11%</td>
<td>10%</td>
</tr>
<tr>
<td>BMS</td>
<td>35%</td>
<td>31%</td>
</tr>
</tbody>
</table>

5.3.2 Comparison between different prints

In the next step a comparisons has been made between the print cured with 2 lamps and with 3 lamps, see Figure 5.3.3. Both prints give similar amounts of initiators and no changes in the relative amounts. Larger differences are seen between the acrylates, which are not being identified in this study. Similar results were obtained in the comparison between the two offset printers, see Figure 5.3.4.

Figure 5.3.3. Comparison between the extract of the pre-print cured with 2 and 3 lamps.
Similar to the differences between the print cured with 2 and 3 lamps, the main difference is seen in the amount of acrylates. The amount of initiator has slightly lower in the print from offset printer 1, the relative amount between the initiators remain the same.

5.3.3  Sub Conclusions

For three of the four inks of the pre-print all the photo-initiators could be identified, see appendix 8.8. With the exception of one ink in which one initiator could not be found, this is possibly due to batch differences. Because of some small differences in the oven temperature program used, small differences are seen in retention time. Some differences in abundance between the initiators in the pre-print and the ink, but all were present. The relative amount of the initiator does not change by printing or curing. Some small differences were found using 2 or 3 UV lamps, but still all of the initiators could be identified without any problems.

The method used for the analysis of the inks, can also be applied for pre-printed materials. Analysis can be performed by extraction of the pre-print followed by direct analysis using GC-MS.
6 Conclusions

Different photo-initiators can be identified in UV inks, through direct analysis using GC-MS. No clean up steps are necessary before analysis, simple dissolving the ink in MC for direct analysis.

Using a combination of EI and CI all of the photo-initiators in the inks can be identified. All the identified photo-initiators gave an abundant M+H ion when using isobutane as reagent gas in CI. Using methane as reagent gas results often in the loss of water or methanol as most of the initiators contain hydroxy or methoxy groups.

Using this method, in total 11 different photo-initiators have been identified in the UV inks. Large differences have been found between different inks, were some inks only contain 2 initiators (ink B-3) up to a mixture of 7 initiators (B-1 ink). Smaller differences were found between different colours of the same ink.

Other components present in the inks are acrylates or smaller molecules deriving from the pigments used. Isolation of the pigment and IR analysis can be used to identify the pigment used, and the source for these smaller molecules.

Similar approach can be used in the analysis of pre-printed materials. After a simple extraction using MC the initiators can be identified using simple GC-MS analysis. A comparison between the inks and the pre-prints showed that all different photo-initiators could be detected. The relative amount of the photo initiators do not change by printing and curing. The differences measured are most likely due to batch differences, as the inks measured are not from the same batch as the ink used for the prints.

No significant difference between pre-prints made using different cure setting or different offset printer could be found.
7

References

12. IR 97322.022, Literatuurstudie naar foto-initiatoren voor UV uitharding, J van de Reek
13. Ciba, Photo initiators for UV curing, key product selection guide 2003, g-48/2003 October
8 Appendix

8.1 Overview of names and structures

Irgacure 184 (Ciba)
1-hydroxy-cyclohexyl-phenylketone

\[
\text{OH} \quad \text{C} \quad \text{H} \quad \text{C} \quad \text{H} \\
\text{O} \quad \text{C} \quad \text{H} \quad \text{C} \quad \text{H}
\]

Benzophenone

\[
\text{C} \quad \text{O} \quad \text{C} \quad \text{H} \quad \text{C} \quad \text{H} \\
\text{C} \quad \text{O} \quad \text{C} \quad \text{H} \quad \text{C} \quad \text{H}
\]

Quantacure EDB
Ethyl 4-(dimethylamino)benzoate

\[
\text{N} \quad \text{H} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{H} \quad \text{C} \quad \text{H} \\
\text{N} \quad \text{H} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{H} \quad \text{C} \quad \text{H}
\]

DETX
2,4-Diethyl-9H-thioxanthen-9-one (DETX)

\[
\text{C} \quad \text{H} \quad \text{C} \quad \text{H} \\
\text{C} \quad \text{H} \quad \text{C} \quad \text{H}
\]

Quantacure ITX
Isopropyl-9H-thioxanthen-9-one (ITX)

\[
\text{CH} \quad \text{H} \quad \text{H} \\
\text{CH} \quad \text{H} \quad \text{H}
\]

Irgacure 907 (Ciba)
3-Methyl-1-[4-(methylthio)fenyl]-2-(4-morfolino)-1-propanon (MMMP)
Irgacure 651 (Ciba)
Also known as Photocure 51
2,2-Dimethoxy-1,2-difenylethan-1-one (BDK)

Quantacure BMS
4-(p-Tolylthio)benzofenon (BMS)

Escalol 507
2-Ethylhexyl 4-(dimethylamino)benzoat (EHA)

Methyl-4-benzoylbenzoate (MBBZ)

4-Phenyl-benzophenone
4-Benzoylbifenyl (PBZ)
8.2 Overview of Spectra

8.2.1 Irgacure 184
8.2.2  

Benzophenone
8.2.3 Quantacure EDB

Abundance

CH<sub>2</sub>Cl

Quantacure EDB

m/z:

M+H

M+CH<sub>3</sub>
8.2.4 DETX
8.2.5  
Quantacure ITX

Abundance

CH₂Cl

Quantacure ITX

m/z→
8.2.6  

**Irgacure 907**
8.2.7  
Irgacure 651 / Photocure 51

![Diagram of Irgacure 651 / Photocure 51](image1)

![Diagram of CH₂Cl](image2)
8.2.8  Quantacure BMS

Irgacure 651 / Photocure 51

Quantacure BMS
8.2.9 Escalol 507

![Graph of Escalol 507](image1)

![Graph of CH₄Cl](image2)
8.2.10

**Methyl-Benzoylbenzoate**
8.2.11  

4-Phenyl-Benzophenone

![MS Spectrum of 4-Phenyl-Benzophenone](image1.png)

![MS Spectrum of CH₂Cl](image2.png)
4-Phenyl-Benzophenone
8.3 Column

UV ink B1
HP-1MS column

UV ink B1
HP-5MS column
8.4  Ink A-1

8.4.1  Yellow

![Graph of 2,4-dimethyl benzenamine](image1)

8.4.2  Red032

![Graph of chlorobenzene](image2)
8.5 IR analysis on Pigments

8.5.1 Yellow

IR analysis of Pigment Yellow of Ink A-1.

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>3,3’-dichlorobenzidine -&gt; acetoacetic arylide-2,4-dimethylaminidil</td>
</tr>
<tr>
<td>Source of Sample</td>
<td>Ciba-Geigy</td>
</tr>
<tr>
<td>Technique</td>
<td>KBr pellet</td>
</tr>
<tr>
<td>Mol.Weight</td>
<td>684.20</td>
</tr>
<tr>
<td>Formula (Empirical)</td>
<td>C&lt;sub&gt;36&lt;/sub&gt;H&lt;sub&gt;34&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;N&lt;sub&gt;6&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>Comments</td>
<td>HUMMEL DECIMAL NUMBER= 012221 Description= APPEARANCE=yellow solid</td>
</tr>
<tr>
<td>Synonyms</td>
<td>Irgalite Yellow BAWP</td>
</tr>
<tr>
<td>Color Properties</td>
<td>Colour Index Name= Pigment Yellow Colour Index Number= 21100</td>
</tr>
</tbody>
</table>

Figure 8.5.1. IR spectrum and library match with Pigment Yellow 13.

Figure 8.5.2. Pigment yellow 13.
8.5.2  Red 032

IR analysis of Pigment Red032 of Ink A-1.

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4,5-trichloroaniline -&gt; 2-hydroxynaphthoic arylide-2-methylanilide</td>
<td>Source of Sample</td>
<td>Hoechst</td>
</tr>
<tr>
<td>KBr pellet</td>
<td>Technique</td>
<td>Mol.Weight</td>
</tr>
<tr>
<td>(Empirical)= C_{24}H_{16}Cl_{3}N_{3}O_{2}</td>
<td>Formula</td>
<td>Comments</td>
</tr>
<tr>
<td>Permanent Rood FGR 70</td>
<td>Synonyms</td>
<td>Colour Properties</td>
</tr>
</tbody>
</table>

*Figure 8.5.3. IR spectrum and library match with Pigment Red 112*

*Figure 8.5.4. Pigment Red 112*
8.6 Overview of all inks

<table>
<thead>
<tr>
<th>Ink</th>
<th>Cyan</th>
<th>Magenta</th>
<th>Yellow</th>
<th>Black</th>
<th>Red032</th>
<th>Reflex Blue</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>B-1</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>B-2</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>B-3</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>C-1</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>D-1</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ink</th>
<th>Cyan</th>
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<th>Yellow</th>
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**Ink D-2**

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**Ink E-1**

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8.7 Spectra from pre-print

8.7.1 Photocure 51

8.7.2 Methyl-benzoylbenzoate
8.7.3  Escalol 507

8.7.4  Irgacure 907
8.7.5  Quantacure ITX

8.7.6  4-phenyl-benzophenone
8.8 Comparison Pre-print and ink

Figure 8.8.1. Ink B-1

Figure 8.8.2. Ink E-1
Figure 8.8.3. Ink D-1

Figure 8.8.4. Ink A-1.