EVALUATION OF VEGETABLE-BASED BIOSOLVENTS FOR USE AS CLEANING AGENTS IN THE PRINTING INDUSTRY

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The Graphical, Paper and Media Union (GPMU) provided information on the UK printing industry and other general support to the project.

Karlshamns Binol AB and VEGRA GmbH helpfully supplied relevant technical support and literature pertaining to the vegetable-based print wash solvents.

The project was administered and facilitated through the National Non-Food Crop Centre and support from Jeremy Tomkinson and Warren Smith is gratefully acknowledged.

The support of the HGCA in funding a review which preceded this report and which provided a significant amount of information and experience in support of this demonstration project is also acknowledged.
Aims and objectives

The main aim of this 3-month project was to assess the performance and cost effectiveness of vegetable-based cleaning solvents in the UK printing industry, and to assess the potential hazards and risks associated with their use. A key objective was to use products in a commercial environment to assess the scale of barriers to wider uptake, and use of vegetable-based solvents by the UK printing industry.

- The aim was to demonstrate the potential for use of vegetable derived solvents as cleaning agents in the UK printing industry, focusing on the performance, handling issues and cost to the industry.

- The project assessed the performance of commercially available predominantly rape-based/vegetable-based cleaning solvents in a commercial printing environment.

- The project will validate the efficacy, suitability for use, cost effectiveness, compatibility with existing equipment and practices and impacts on labour requirement.

- This project represents the first steps towards a wider demonstration and dissemination programme that will be developed in light of the conclusion of the test results and findings from this study. Based on the results of the trials work, a strategy will be devised to identify the best means of disseminating the results of the work.

- The Health and Safety Executive (HSE) and the British Printing Industries Federation (BPIF) were consulted and their concerns raised over use of vegetable-based cleaning agents were addressed as far as time and resources permitted.
INTRODUCTION

In its first annual report (2002), the Government-Industry Forum on Non-Food Uses of Crops (GIFNFC) highlighted the potential for use of vegetable oils as biosolvents in the printing industry. GIFNFC recommended that support was required to increase awareness and gradual uptake of bio-based cleaning materials across the industry, which is disproportionately represented by a large proportion of small businesses.

More recently, work funded by HGCA\(^1\) highlighted a range of technical opportunities for the use of vegetable based esters as solvents. One key area of potential highlighted by the review was that of using vegetable-based esters in the printing industry as print washes for removing ink from offset printing presses. This work built on earlier EU funded work in the SUBSPRINT and VOFApro projects.

The UK printing industry is the second largest user of solvents in the UK. There is significant potential for further growth and expansion in utilisation of materials derived from renewable resources in the solvent sector. Vegetable oils including rapeseed, soya and coconut and their derivatives have excellent solvent properties that match the technical requirements of the printing sector.

Many organic hydrocarbon solvents traditionally used in the industry contain high levels of volatile organic compounds (VOC’s) that are associated with ozone depletion. As such there is legislative pressure to curb their use and reduce emissions in the workplace. The European Commission introduced a Solvent Directive, which came into force on 11 March 1999 \(\text{European Directive 1999/13/EC}\) (Directive on the limitation of emissions of VOCs due to use of organic solvents in certain activities and installations). The Directive aims to reduce the emissions of VOC’s from industrial processes by approximately 66% in 2007 (from a baseline of VOC emissions in 1990). As a result the printing industry is currently looking for alternative low VOC, low-hazard solvents as replacements for conventional petroleum-based solvents such as isopropyl alcohol and the alkyl-aromatics. It is estimated that only 8% of printing companies have an Environmental Management System (EMS) in place, but roughly 67% of companies are working to improve environmental performance on their site\(^2\).

Conventional solvents used in the UK printing industry can be classified as low boiling point hydrocarbon (Group AII) solvents. These volatilise very quickly leaving little need for further treatment and so they have been used for many years. Much of the printing industry is currently converting to the use of high boiling aliphatic hydrocarbons (Group AIII), developed to replace traditional high VOC solvents. Esters of vegetable oils have a very high boiling point compared with mineral based solvents, which is manifest as a low vapour pressure.

High boiling point solvents have been developed in response to pressure to reduce VOC emissions. However, although these products reduce inhalation exposure and risks to workers, they are not considered to be as safe for workers as vegetable-based solvents. SUBSPRINT developed a hierarchy of wash solvents for use in the print industry, based on minimising risks to operators (Table 1), which highlights one of the key benefits of using vegetable-based solvents.

\(^1\) The opportunities for use of esters of rapeseed oil as bio-renewable solvents, Turley, Areal & Copeland (2004).
\(^2\) Attitudes 2003, Data Build, Research & Solutions.
Table 1: Hierarchy of safety to operators based on exposure to solvents used in the print cleaning industry

<table>
<thead>
<tr>
<th>Least risk to operators</th>
<th>Vegetable based cleaning agents (VCA’s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Synthetic esters (mineral based)</td>
</tr>
<tr>
<td></td>
<td>Mixtures of VCA’s/high boiling point solvents (HBS)</td>
</tr>
<tr>
<td></td>
<td>High boiling point solvents (HBS)</td>
</tr>
<tr>
<td></td>
<td>Mixtures of VCA/HBS</td>
</tr>
<tr>
<td></td>
<td>Mixtures of VCA/terpenes</td>
</tr>
<tr>
<td></td>
<td>Aromatic free solvents</td>
</tr>
<tr>
<td></td>
<td>Terpenes</td>
</tr>
<tr>
<td>Highest risk to operators</td>
<td>Traditional petroleum based volatile products (kerosene or white spirit)</td>
</tr>
</tbody>
</table>

Source: SUBSPRINT

In addition to impacts on VOC’s, health and welfare in the workplace and the impacts of long-term solvent inhalation is also an issue that concerns the printing industry. Naphtha is one of the most commonly used products for print washing and other solvent-based tasks. Naphtha is a hydrocarbon solvent with a low boiling point and high vapour pressure. There is a potential risk to health from such physical characteristics. In addition, many Naphtha products are classified under the CHIP Regulation as being carcinogens, primarily Category 2 carcinogens. Any product containing over 10% should carry the warning letter T = Toxic and the material safety data sheets should carry the appropriate risk phrase (45 ‘May cause cancer’).

The UK printing industry

In the EU-15, the graphic industry consists of approximately 80,000 companies employing an estimated workforce of 962,000 people with a turnover of about €80 billion. The UK printing industry employs approximately 160,000 people in over 12,000 companies; which reflects a high proportion of companies with small workforces (only 500 employers have more than 50 people in their workforce). The UK printing industry has a turnover in the region of £13 billion. As the UK printing industry is characterised by small printing companies, the fragmented and small scale of individual operators in the UK industry presents challenges to information dispersal and in encouraging change to existing tried and tested methods.
UK printing processes

The lithographic process

The lithographic process is the most commonly used printing process. This involves the application of ink onto the printing plate via rollers. The plate is dampened with a solution (normally water and propan-2-ol plus additives) before inking. The image is then transferred to the rubber blanket cylinder and onto the printing material. ‘Offset’ is the term used to describe this process of double transfer of an image from the plate to the blanket roller, then to the printing material.

Common print processes:

Heatset Web Offset

This process is on a continuous reel "web", and is primarily used for magazines and coated papers when printing large numbers of copies, and gives richer colours than cold set printing. This industry uses approximately 28,000 tonnes of ink per annum in the UK.

Coldset Web Offset

Cold set printing is also based on a continuous reel "web". This process is typically used for newspapers printed on absorbent uncoated paper and uses approximately 35,000 tonnes of ink per annum in the UK. The inks dry by absorption of the substrate or oxidation. Cleaning of blanket rollers and print rollers is a more frequently required during this process.

Sheet Fed Offset

Sheet Fed Offset is used for low volume magazine and packaging and uses approximately 10,000 tonnes of ink per annum. The inks dry as a result of absorption by the substrate or oxidation.

Blanket and roller washes

To maintain a high quality image with offset printing process the blanket and rollers must be cleaned. Blanket and roller washes, remove ink, dust, paper and other debris from the blankets and rollers that would otherwise damage the machinery and impact on image quality. There are many different factors that affect the number of washes carried out during a print run. These can include build up of debris, a change in ink colour, reduction in image quality or change of print run.

Blanket and roller cleaning can be undertaken manually or automatically, both systems are used in the UK. Most of the Heat Offset industry uses automatic cleaning systems, 25-50% of the Sheet-fed offset industry uses automatic cleaning systems, but only a few cold set systems are fitted with automatic cleaning systems.

With manual cleaning, the cleaning solvent is applied to print rollers by hand using a squeeze bottle with a pipette tip (the operator estimating the amount needed to clean the roller through experience). The blanket cylinder is then wiped down with a solvent soaked cloth (cloth wipe or disposable wipe).
Automatic blanket and roller cleaners are mechanical devices that clear the blanket of debris by applying cleaning solvent and/or scrubbing the blankets mechanically. Excess wash is either removed automatically, or paper is run through the press to absorb excess ink and solvent.

Different washes can be used for the blankets and the rollers. A water miscible wash can be used to remove debris, then a non-water miscible wash applied for cleaning and drying the blanket and rollers. Each technique used, varies from pressroom to pressroom and with conditions at the time of cleaning.

This project concentrated attention on the sheet-fed offset printing process as representing the majority of small and medium sized print companies in the UK.

Although new vegetable based cleaning solvents are available in Europe, few have been adopted in the UK. The demonstration project aims to provide information relating to the performance, cost and risks associated with these vegetable-based cleaning solvents.

**Industry concerns**

A key objective of this project was to work with the printing industry itself to provide a comparative assessment of vegetable-based and conventional (traditional and new low-boiling point hydrocarbon solvents) blanket and roller washes used by the lithographic industry. The aim was to provide printers with information to assist them in decision making when purchasing blanket and roller washes, by providing an independent appraisal of cost, performance and hazards associated with vegetable-based solvents, supplied as alternatives to current commercial print washes marketed in the UK.

At the outset of the project, representatives of the printing industry (Dale Wallis of British Printing Industry Federation & Maureen Kingman of the Health and Safety Executive) were approached to ascertain attitudes towards the use of vegetable derived solvents and areas of concern. The following areas of concern and questions were highlighted.

1. Has any assessment been made of any possible inter-reactions with other chemicals used in printing, e.g. pigments?
2. Can solvents affect metal components or blankets used on printing presses? (e.g., could they cause hardening of blanket?)
3. Do the vegetable-based solvents leave any residue that could build up or which could attract dust/debris?
4. How much longer does it take for the vegetable-based cleaning agents to flash off (dry) compared with conventional petroleum-based solvents?
5. What is lifespan of vegetable-based solvent? (i.e. how many times can it be used in an automatic wash up facility on a printing press?)
6. Magazine printers are moving to single fluid printing – is there any information available on the suitability of biosolvents for this use?
7. Would bio-solvents be suitable for cleaning machines used for printing on food-grade packaging?
8. Has the problem of slipperiness been addressed in more recent formulations?
9. What is the recommended glove type to be worn when handling the vegetable-based cleaning agent?
10. What is the break-through time for the recommended glove type?
11. Can bio-solvents be absorbed through skin?
12. How easy is it to remove the vegetable-based cleaning agents off the hands?
13. How would a spillage of the bio-solvents be contained and cleaned up?
14. What percentage of solvent is vegetable oil/vegetable ester based?

As far as possible, and within the constraints of the project, an attempt was made to answer as many as possible of the above concerns.
**METHODOLOGY**

Two vegetable-based print wash solutions were sourced from European Suppliers. The aim was to obtain wash solutions based solely on vegetable derived oils or with a high vegetable oil-based content (Table 2) and which satisfied the criteria of a type III solvent (i.e. low VOC content). Preference in selection was for blanket and roller wash solvents derived from rape (as the UK could supply raw materials for such products), rather than those based on coconut, soya or palm oils.

Table 2: Details of vegetable-based solvents used in the trials

<table>
<thead>
<tr>
<th>Product</th>
<th>Characteristics</th>
<th>Ingredients</th>
<th>Boiling Point (°C)</th>
<th>Flash Point (°C)</th>
<th>Vapour Pressure (kPa @ 20°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vegeol CEG; Karlshamns Binol AB, Sweden.</td>
<td>Recommended as a graphic cleaner for rubber rollers and blankets in the Off-set industry.</td>
<td>A mix of different alkyl esters of coconut, palm-kernel and rape-seed fatty acids with vegetable based emulsifiers (25 - 50% rape-seed oil).</td>
<td>210</td>
<td>&gt; 150</td>
<td>Negligible under normal conditions</td>
</tr>
<tr>
<td>VEGRA Rapidwash 220224; VEGRA GmbH, Germany. (Supplied by Pomeroy Pressroom Products Ltd, UK.)</td>
<td>A vegetable based, water miscible cleaning agent suitable for automatic rubber blanket washers and for washing by hand.</td>
<td>38% Rapeseed Oil, 38% Rapeseed fatty acid ester and 10% Mineral oil</td>
<td>&gt; 260</td>
<td>135</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Printclean; BASF Printing Systems.</td>
<td>A microemulsion cleaning agent suited for manual and automatic washing systems</td>
<td>Formula is based on water, 40% Rapeseed and Coconut ester mix and surfactants</td>
<td>&gt; 100</td>
<td>&gt; + 99</td>
<td>&lt; 24.0 Hpa</td>
</tr>
</tbody>
</table>

Generating solvents specifically for the project would have been difficult within the available project timescale. Commercial products were used for two main reasons:

a) Hazard data sheets were already available for the products to satisfy the health and safety concerns for employees and the environment.

b) The products were already approved for use on printing equipment thereby reducing the risk of significant damage to expensive printing presses.

As a result of initial trials and some problems with automated wash systems the third solvent was secured during the final test phase of the project as a product approved for use within a automatic cleaning systems.

The solvents were evaluated and compared on two lithographic printing presses.

The trial at BestPrint used a 2 colour Komori Sprint S228, Lithographic printing press that uses manual cleaning processes.
The trial at DocQwise used a 4-colour Heidelberg QM46.4DI, lithographic printing press fitted with an automatic cleaning systems. Solvents can be used either manually or with the automatic system.

In each test two vegetable based cleaning solvents were evaluated against a conventional high boiling point solvent (group AIII solvent) or, as at BestPrint, against a group AII solvent (Table 3).

Table 3: Details of conventional wash solvents used in print trials

<table>
<thead>
<tr>
<th>Product</th>
<th>Operation</th>
<th>Characteristics</th>
<th>Ingredients</th>
<th>Boiling Point (°C)</th>
<th>Flash Point (°C)</th>
<th>Vapour Pressure (kPa @ 20°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eagle Blanket &amp; Roller Wash; Hydro-Dynamic Products, UK.</td>
<td>Manual</td>
<td>A general purpose non-water miscible blanket and roller wash.</td>
<td>Naphtha (petroleum), Hydrodesulfurized Heavy &amp; Solvent Naphtha (petroleum) Light Aromatic</td>
<td>150 - 210</td>
<td>40</td>
<td>0.19</td>
</tr>
<tr>
<td>Heidelberg Saphira Blanket &amp; Roller Wash 60</td>
<td>Automatic</td>
<td>A high boiling point lithographic blanket and roller wash</td>
<td>Tetraoxotetracosan &amp; Naphtha (petroleum) Hydrodesulfurized Heavy.</td>
<td>180 - 217</td>
<td>62</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Assessments

Efficacy and Performance
Each print operator was asked to record parameters relating to visual interpretation of roller and blanket cleaning performance, and the impact on printing quality. Finally they were asked for their opinion of the solvents used.

Labour input
The time taken to clean the blanket and rollers was recorded for each print wash operation for each wash product during the trial. Barring any technical problems, the aim was to undertake 2-3 print washes over 2-3 days of printing (typically machinery is washed once a day on large print runs or between new print jobs).

Quantity used
The quantity of solvent used in each wash operation was recorded for each solvent using measuring bottles. All wash solutions were applied according to manufacturers recommendations and were diluted as appropriate. In this report reference to volume of solvent use refers to total volume of actual solvent used rather than volume of wash solution.

Cost
An estimate of the costs of use of each solvent was obtained using information from the supply industry on raw material cost, plus information derived from the trial on rates of use during normal operation etc. Based on DocQwise estimates of annual consumption of conventional print wash solvent use (approximately 520 litres per annum) and assuming that vegetable-based solvents would be used as often as conventional solvents, an estimate of total consumption of vegetable-based solvents was made.
BestPrint - Komori Sprint S228 (manual wash procedure)

The conventional solvent Eagle Blanket and Roller Wash, was compared with the performance of VEGRA 220/224 (76% rape-oil based) and Vegeol CEG (25-50% rape oil based in a fully vegetable oil based product). Each product was tested for three successive wash operations. Between vegetable solvent washes, a conventional solvent was used for one wash cycle.

Print quality and cleaning performance

After cleaning using vegetable-oil-based products there was no noticeable impact on print quality. Yellow can be a difficult colour to maintain but no problems were encountered with a yellow and black ink run. Re-inking of the rollers appeared to improve after use of the vegetable based solvents.

It was reported that the VEGRA wash solution performed particularly well as a blanket wash.

Solvent use and cost

Data on volumes of each solvent used during print washing is given in Table 4 and Figure 1. Significantly less solvent was used during mechanical cleaning when using vegetable-based wash solutions. Compared to the conventional cleaner, volumes of solvent use were reduced by 30% with Vegeol and 59% with VEGRA.

Although using vegetable based solvents reduced the volumes of solvent used, they cost significantly more than conventional products (Table 5). The cost per wash overall was higher with vegetable-oil-based materials. Cost per wash operation was 75-78% higher with vegetable-based products. However, as these vegetable-based products had to be imported from Europe they incurred significant haulage costs. The raw material cost is in the region of half the retail price, which would bring the cost of use into line with that of conventional solvents.

Labour input

With the Komori Sprint S228, the wash solvent is applied to the rollers from squeeze bottles and solvent is collected in trays. The solvent is then applied to a cloth to wipe the blanket and remove any remaining ink and debris from the rollers.

Although the recorded data shows little difference in time taken to wash the rollers and blankets with each wash product (Table 4), print operators reported that both vegetable based products appeared to take longer to wash off. VEGRA 220/224 was reported to take slightly longer to wash off, but Vegeol left a greasy residue that took much longer to remove.

Other comments

It was reported that there was a noticeable strong odour when using the conventional Eagle wash solvent, but none with either of the vegetable-based products.

Following the initial trial carried out by BestPrint, they continue to use the VEGRA Rapidwash 220/224. This solvent is used in combination with their conventional solvents (which are used as a follow-on cleaner to optimise cleaning action in conditions of heavy soiling). BestPrint are looking to continue to use the VEGRA Rapidwash 220 224 and will consider purchasing this product in the future.
Table 4: Estimates of solvent use, solvent costs and time taken for individual print wash runs on the Komori Sprint S228 (manual wash procedure)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Observations</th>
<th>Mean</th>
<th>Std. Deviation</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total solvent use per wash (ml)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eagle (Conv.)</td>
<td>3</td>
<td>200.0</td>
<td>10.00</td>
<td>190.0</td>
<td>210.0</td>
</tr>
<tr>
<td>VEGRA 220</td>
<td>3</td>
<td>83.3</td>
<td>7.63</td>
<td>75.0</td>
<td>90.0</td>
</tr>
<tr>
<td>224</td>
<td></td>
<td>140.0</td>
<td>5.00</td>
<td>135.0</td>
<td>145.0</td>
</tr>
<tr>
<td>Vegeol</td>
<td></td>
<td>0.136</td>
<td>0.007</td>
<td>0.13</td>
<td>0.71</td>
</tr>
<tr>
<td>VEGRA 220</td>
<td>3</td>
<td>0.239</td>
<td>0.022</td>
<td>0.22</td>
<td>0.26</td>
</tr>
<tr>
<td>224</td>
<td></td>
<td>0.378</td>
<td>0.014</td>
<td>0.36</td>
<td>0.39</td>
</tr>
<tr>
<td><strong>Total time taken per wash (minutes)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eagle (Conv.)</td>
<td>3</td>
<td>19.3</td>
<td>0.57</td>
<td>19.00</td>
<td>20.00</td>
</tr>
<tr>
<td>VEGRA 220</td>
<td>3</td>
<td>19.0</td>
<td>2.64</td>
<td>17.00</td>
<td>22.00</td>
</tr>
<tr>
<td>224</td>
<td></td>
<td>22.0</td>
<td>2.00</td>
<td>20.00</td>
<td>24.00</td>
</tr>
</tbody>
</table>

Table 5: Solvent costs/litre (supplier costs [including UK import cost for VEGRA and Vegeol])

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eagle (Conv.)</td>
<td>£0.68</td>
</tr>
<tr>
<td>VEGRA 220 224</td>
<td>£2.87*</td>
</tr>
<tr>
<td>Vegeol</td>
<td>£2.70*</td>
</tr>
</tbody>
</table>

* Prices would reduce if UK produced (e.g. basic cost for Vegeol = £1.70/l)
Figure 1: Comparison of volumes (ml) of conventional (Eagle) and vegetable-based solvent used during mechanical cleaning of a Komori Sprint S228 printer.

(Boxes denote mode, max and min values, and bars represent 95% confidence interval).

**DocQwise - Heidelberg QM46.4DI 4-colour lithographic printing press with automatic cleaning system**

The conventional solvent Saphira 60 (Group AIII) was compared with the performance of VEGRA 220/224 (76% rape-oil based) and Vegeol CEG (25-50% rape oil based in a fully vegetable oil based product). The plan was to test each product for three successive wash operations. However, due to problems with use of the automated system with vegetable-based products, manual tests were also undertaken for evaluation purposes.

**Print quality and cleaning performance**
All products cleaned the blankets and rollers to a satisfactory level and maintained print quality.

**Vegeol**
Vegeol was the easiest product to apply as it has a very oily viscous nature and does not drip easily. It cleaned fairly well in terms of ink removal especially when used as a manual cleaning wash, but the product had a tendency to leave a greasy residue on the blanket and rollers. Removing the solvent itself became a major, and frustrating process.
When the product was finally removed from the rollers, and after a prolonged drying time, it was felt that it left the rollers greasy, but this did not affect ink transfer rates.

When used in the automatic wash system Vegeol caused significant problems. Viscosity was an important shortcoming of this wash as it clogged parts of the automatic wash system.

The wash solvent is transferred to the blankets via a wick felt contained within a holding tray; this became blocked with oil and began to deteriorate. The felt wicks had to be removed and replaced and the machine stopped for a day. Cost of damage to such systems can be significant. Had the solvents had any serious effect on the automatic print wash system devices themselves this could have resulted in a replacement bill of £12,000 (on a larger press this would move towards £45,000).

The solvent was deemed to be too oily to continue to use and so its use was terminated.

**VEGRA**

Technical material supplied with VEGRA indicated that is was deemed suitable for automatic blanket washing.

The product was recommended to be mixed with water in a one to one ratio. This was found to separate out when mixed with tap and distilled water. It was then mixed at a ratio of two parts solvent to one part water, but this did not increase the separation time. The problem of separating out of the emulsion was a difficulty encountered for automated washing systems, where the wash solvent is held in a reservoir prior to use. Re-mixing the product before each wash would significantly add to labour demand.

VEGRA was very good at removing ink and debris from the blanket and rollers but did so very slowly. VEGRA had no detrimental impact on ink transfer rates to printing plates or blankets. However, the VEGRA product was felt to be too greasy, and, it was not considered for use in the automatic wash devices.

Given the problems with the automated wash system a further vegetable–based solvent was sought which was approved for use in automatic wash systems. Printclean formula is based on water, fatty acid ester (rapeseed and coconut) and surfactants (40% vegetable oil based).

The Print Clean product was less viscous than VEGRA or Vegeol. It was used as recommended and applied neat, and then cleaned off with water, which initially worked well on the rollers. However it was found to take some considerable effort to clean the blankets. The product was easy to handle, but the evaporation time was again a concern. Based on these initial results there was reluctance to try this with the automated wash system.

For manual cleaning the product is recommended to be applied by spraying the wash on while the machine is running. However, it was considered that this would mist the inner workings of the press with wash and may pose a Health and Safety risk during cleaning operations.

**Solvent use and cost**

Given the problem with the automatic wash system it is difficult to draw firm conclusions. All data for the vegetable based solvents in Table 6 elates to manual application. Though it appears more Print Clean was applied, the product is applied neat as an emulsion (only 40% oil content), so actually the volume of solvent applied is similar to that of the other two vegetable solvents. The price of the product was unavailable at the time of writing.
Table 6: Estimates of solvent use, solvent costs and time taken for individual print wash runs on the Heidelberg QM46.4DI 4-colour lithographic printing press

(Saphira – automatic wash system, all other solvents applied manually)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Observations</th>
<th>Mean</th>
<th>Std. Deviation</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solvent use per wash</td>
<td>Saphira (Conv.) 2</td>
<td>230.0</td>
<td>14.14</td>
<td>220.0</td>
<td>240.0</td>
</tr>
<tr>
<td>(ml)</td>
<td>Vegra 220 224 1</td>
<td>246.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Vegeol CEG    1</td>
<td>260.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Print Clean   1</td>
<td>440.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cost of Solvent used per wash</td>
<td>Saphira (Conv.) 2</td>
<td>0.39</td>
<td>0.024</td>
<td>0.38</td>
<td>0.41</td>
</tr>
<tr>
<td>(£)</td>
<td>Vegra 220 224 1</td>
<td>0.71</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Vegeol CEG    1</td>
<td>0.70</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total time taken per wash</td>
<td>Saphira (Conv.) 2</td>
<td>33.5</td>
<td>6.36</td>
<td>29.0</td>
<td>38.0</td>
</tr>
<tr>
<td>(minutes)</td>
<td>Vegra 220 224 1</td>
<td>48.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Vegeol CEG    1</td>
<td>89.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Print Clean   1</td>
<td>37.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Labour input

The less viscous nature of the Printclean solvent made it easier to remove from the rollers and re-inking (make ready time) was improved. The greasy film left by Vegeol was much more difficult to remove and added significantly to the time required to clean the rollers (up to 1 hour).

Other comments

All the vegetable-based solvents tested were considered unsuitable for use in the current automatic printing system environment. The main reason for this was the failure of all three products tested to clean as quickly as conventional solvents. Evaporation time (how quick the blanket and rollers dried after application) was deemed to be too long.

Other concerns related to the handling of the oily products, with oily residues spread via contamination of the working area from protective equipment. When trying to clean off some of the solvent, damp cloths proved unsuitable, and the product was only finally removed with a large quantity of dry wipes that would affect cost effectiveness.

General comments

The print operators using the two vegetable-based solvents found that they had to use more effort to get the blanket and rollers clean, but there was variation in opinion as to how much more effort was required. It was seen to be unacceptable when used on the automatic system, but on the manual cleaning system it was accepted that some extra effort would be needed in order to effectively clean the blanket and rollers.

As expected, both printers found that the vegetable-based solvents required a change in their application and cleaning methods. Modification such as wiping the blanket and rollers with a dry or damp wipe was required to remove excess oily residues.

Of the vegetable-based solvents used, it was clear that they did not suit all printing systems. The fully (100%) vegetable-based cleaning agent (Vegeol) was found to be too oily when used on both machines, but the water miscible vegetable (80%) and hydrocarbon mix (VEGRA),
was found to work well with manual cleaning system. This highlighted that vegetable-based washes have potential to work well when matched to appropriate machinery and print technologies.

**Hazard and health and safety assessment of conventional and vegetable-derived solvents**

Material Safety Data Sheets (MSDS) on two commonly used group AII and AIII solvents were obtained from manufacturers, and similar data sheets were obtained from manufacturers of two vegetable-based print wash solvent formulations. These were supplied to the Health and Safety Executive (HSE) and the Greater Manchester Hazards Centre (GMHC), without identifying the manufacturer or product name for review, and to compare the potential risks posed to workers from each group of chemicals. A summary of the relevant data extracted from the MSDS’s is presented in Annex 1. A summary of comments from the HSE and GMHC is presented in Annex 2. The guidance sheets referred to under the COSHH heading in the Annex 2. refer to COSHH control guidance sheets produced by the Health and Safety Commission for the printing industry.

Naphtha is a common constituent of commonly used group AIII and AII print wash solvents. The volatility of naphtha makes it a risk to health via inhalation in addition to risks from adsorption through the skin. Many naphtha products are classed as carcinogens (risk phrase R45), which arises from the Benzene component of naphtha. If the Benzene component is >0.1% then the product should be labelled with the letter ‘T’ (denoting toxic) and R45. Many pressroom solvent suppliers claim the benzene component of their products is below 0.1% and so the product does not require the R45 or T labels. This is something that, as yet, needs to be verified by the HSE. Therefore, in many cases conventional print wash solvents containing Naphtha do not carry the above hazard markings and risk phrases.

In any assessment of risk in the workplace, account would be taken of volumes of use, ventilation mechanisms in place, and reports of ill health. However, the present exercise of comparing MSDS’s, though limited in scope, serves as a rough comparator between products. This allowed them to be classified to existing hazard groupings from A (least hazardous) to E, and indicates what control measures would be required to protect employee health. For the benefit of this exercise, products containing Naphtha were assessed both including and excluding the R45 risk phrase.

The presence of Naphtha and the R45 risk phrase significantly elevates the hazard grouping for many Group II and III solvent formulations, compared with vegetable based solvents (Table 4). In most cases, vegetable-based solvents offer advantages in terms of COSHH hazard group ratings over conventional print room wash solutions. All wash products except for the second vegetable-based solvent (F) would be subject to COSHH assessment. The second of the two vegetable-based solvents (F) contains only vegetable esters and emulsifiers (this product was 100% vegetable oil based) and carries no warning signs or risk factors. The other predominantly vegetable-based solvent contained some ingredients in the formulation with risk hazard warnings (product E was only 80% vegetable oil based).

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3 Control of Substances Hazardous to Health Regulations 2002 impose a duty of due diligence on employees to reduce risk to employees from chemicals and other hazards in the workplace.
Arguments over carcinogenicity aside, the main risks assessed as being associated with the products reviewed were:

*Group II*
Irritation to exposed tissues
Risk of drowsiness through skin or inhalation exposure.
Dangerous to the environment
Fire risk or highly flammable

*Group III (Low boiling point)*
Irritant
Damage to lungs if swallowed
Risk of drowsiness through skin or inhalation exposure.
Dangerous to the environment
Highly flammable

*Vegetable-based solvents*
Potential fire risk
Some potential for skin damage

Clearly the vegetable-based product appear to offer much lower risk in the workplace based on disclosed information in MSDS’s
Table 7: Hazard group rating of commonly used print wash solvents

(A to E; A, least hazardous, E, special measures required)

<table>
<thead>
<tr>
<th>Solvent Type</th>
<th>+ R45 risk phrase</th>
<th>(carcinogen)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A III – 1</td>
<td>A</td>
<td>E</td>
</tr>
<tr>
<td>B A III - 2</td>
<td>D</td>
<td>E</td>
</tr>
<tr>
<td>C AII – 1</td>
<td>C</td>
<td>E</td>
</tr>
<tr>
<td>D AII – 2</td>
<td>D</td>
<td>-</td>
</tr>
<tr>
<td>E Vegetable-based 1</td>
<td>A</td>
<td>-</td>
</tr>
<tr>
<td>F Vegetable-based 2</td>
<td>A</td>
<td>-</td>
</tr>
</tbody>
</table>

A II – 1
Rating E - Special measures required (G400)
Rating C - Engineering control required (G200/202)

AII - 2
Rating D Special measures required (G400 plus S100 and S101)

A III – 1
Rating E – Special measures required (G400)
Rating A – General ventilation required

AIII – 2
Rating D & E – Special measures required (G400)

Vegetable based - 1
Rating A - General ventilation required

Vegetable based - 2
Rating A - General ventilation required

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G 400  Specific and specialist advice required in design of control measures
G 200/G 202 Engineering controls required to reduce exposure
S 100/101 Risk of harm via skin or eye contact (protective equipment required)
General ventilation Powered wall or window mounted fan required (5 air changes per hour)
DISCUSSION AND AREAS OF FURTHER RESEARCH AND DEVELOPMENT

Vegetable-based cleaning agents have been used for over 10 years with no reported negative reactions associated with mixing with other printing chemicals. However vegetable esters can affect some materials, particularly natural rubber causing swelling, but this problem is well documented and formulations are designed to eliminate this problem. The fully (100%) vegetable-based cleaning agents used in this study has been shown not to cause shrinkage or swelling of the blankets and rollers made of Nitrile and NBR rubber, but there is the potential for swelling of natural rubber components. The vegetable-based (80%) and hydrocarbon mix cleaning agent is formulated with corrosion inhibitors and so does not attack metal components. It is unusual for fatty acid esters to have a corrosive effect on metal as they are not inherently corrosive. In many cases the anti corrosive nature of fatty acid esters is valued in the metal cleaning sector as it provides a protective coating.

Vegetable based solvents do not evaporate, and so required removing from the machinery by mechanical means or by hand. Also some can leave oily residues that are difficult to remove. Such oil-based residues are unacceptable to the printing industry and therefore have to be removed as part of the cleaning process. Water miscible products help remove both dust and debris from the blanket and rollers.

This project was too short to evaluate the lifespan of vegetable based products, but they do have a limited shelf life once exposed to the air through oxidation, though formulation with anti-oxidants would provide adequate protection for most normal uses. In most cases wash solutions are used on a one-off basis, with waste collected for disposal, so continuous reuse of the solvents would not be an issue. Problems were experienced in this study with settling out of vegetable-based emulsions held in reservoirs for automated print washes, despite the fact that they were approved for automatic use. The whole area of formulation and recommendation for use needs careful study to avoid misleading printers into using unsuitable formulations.

Waste from vegetable based solvent use should be disposed of in accordance with local regulations. Large amounts should be handled as special waste and incinerated. Due to the high quantities of oils contained in the solvent, it is not possible to readily recover the solvent.

Care is required when dealing with vegetable-based cleaning agents. Any spilled material on floors or surfaces needs to be contained to avoid accidents. Spills can be contained and collected with binding material, e.g. sand, silica gel, universal binding materials or sawdust. Once absorbed, affected areas should be cleaned with an appropriate cleaning material. In many cases risks of spillage can be reduced by modifying the way a printer handles the vegetable-based cleaning agents, for example by use of a squeeze bottle to apply a specified amount of solvent to the area required. Use of appropriate storage containers can prevent accidental spillage. All application and cleaning equipment used must be disposed of to prevent the spread of oil and stored in suitable containers. Handling and storage of the vegetable solvents requires care to prevent the unwanted spread of any spilled material.

When handling any solvent, appropriate protective equipment must be worn. This is covered on product information sheets and the material safety data sheet that accompanies all products (CHIP regulations). As a minimum it is advised that operators should wear Nitrile gloves. However it appears there is little or no data available on glove break through times. This is an area that needs attention, though the risks are considerably less than those associated with use of conventional hydrocarbon wash solvents.
If use of vegetable-based solvents leads to the products being left in contact with the operators hands, then there is a possibility of absorption through the skin for the vegetable-based (80%) and hydrocarbon mixed cleaning agent used in this study (Acute toxicity: LD₅₀ (oral, dermal) > 200mg/kg LC₅₀ >5mg/l). The fully (100%) vegetable-based cleaning agent reportedly does not pose any risk of dermal toxicity. However, if contact with the skin occurs it is advised to clean the area with soap and warm water.

In this study vegetable-based esters proved to be technically very effective in removing ink and print debris from commercial printing machines. But current formulations appear only to be suited to manual cleaning, unless the technical problems associated with maintaining emulsions and with automatic wash systems are resolved. The problem with automatic wash systems in the trial relates to clogging of the wiping/application system by viscous materials. This could be overcome by redesigning the solvent application system, perhaps use rubber applicators rather than felt pads. The prolonged drying time with vegetable based solvents, due to oily residues, also causes delays in the printing process. Again additional wash systems (a detergent wash) or a rubber blade wiper system could perhaps help speed up the process of roller and blanket cleaning. With manual washing this is not a series problem, as the amount of time taken is similar with conventional and vegetable based cleaning agents, though more physical effort is required to remove the residue left by vegetable based solvents. This becomes an increasing problem with more complex printers (where access may be more difficult), which increases the cleaning time.

The experiences from the manual cleaning test on the two-colour Komori Sprint printer were very promising and offer opportunities for further development. Clearly cost is an issue and costs should be reduced if the products were more widely available in the UK. Costs for vegetable solvents could be comparable to those of conventional washes. Volumes of solvent for disposal should also be reduced due to the lower rates of use.

Based on known and declared hazards on product data sheets, vegetable based wash solvents should offer a lower level of risk in the workplace and reduce the requirement for installation of ventilation equipment and volatile vapour containment etc in many UK printing businesses. In addition they could also help the printing industry work towards reducing VOC emissions, but further technical development in relation to wash formulations and printer wash design will be required to have a significant impact on further uptake and use in the UK, particularly with medium and large print companies.
Annex 1: Information derived from Material Safety Data Sheets supplied with commonly used print wash solvents and two vegetable oil based solvents.

<table>
<thead>
<tr>
<th>Product</th>
<th>High Boiling Point (Group AIII) Solvent</th>
<th>High Boiling Point (Group AIII) Solvent</th>
<th>Highly Volatile (Group AII) Solvent</th>
<th>Highly Volatile (Group All) Solvent</th>
<th>Vegetable Solvent</th>
<th>Vegetable Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
<td>E</td>
<td>F</td>
</tr>
<tr>
<td><strong>Information on Ingredients</strong></td>
<td>Tetraoxatetracosan &amp; Naphtha (petroleum)</td>
<td>Tetraoxatetracosan &amp; Naphtha (petroleum)</td>
<td>Naphtha (petroleum), Hydrodesulfurized Heavy, Solvent Naphtha (petroleum)</td>
<td>Contains Dichloromethane, Propane-2-ol and Toluene</td>
<td>A mix of n-,l- and Cycloaliphats</td>
<td>Composition based on vegetable esters.</td>
</tr>
<tr>
<td><strong>Hazard Symbols</strong></td>
<td>Xn = harmful, Xi = irritant, N = dangerous for the environment</td>
<td>Xn = harmful, Xi = irritant, F = Highly Flammable, N = dangerous for the environment</td>
<td>Xn = harmful, Xi = irritant, N = dangerous for the environment</td>
<td>Xn = harmful, Xi = irritant, F = Highly Flammable,</td>
<td></td>
<td>No data</td>
</tr>
<tr>
<td><strong>Appearance</strong></td>
<td>Liquid</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Liquid</td>
</tr>
<tr>
<td><strong>Colour</strong></td>
<td>Blue</td>
<td>Colourless</td>
<td>Colourless</td>
<td>Colourless</td>
<td>Yellowish</td>
<td>Yellow</td>
</tr>
<tr>
<td><strong>Odour</strong></td>
<td>Hydrocarbon</td>
<td>Hydrocarbon</td>
<td>Hydrocarbon</td>
<td>Characteristic</td>
<td>Typical</td>
<td>Bland</td>
</tr>
<tr>
<td><strong>Boiling Point (°C)</strong></td>
<td>180 - 217</td>
<td>98-140</td>
<td>150-210</td>
<td>39-111</td>
<td>250</td>
<td>&gt; 260</td>
</tr>
<tr>
<td><strong>Flash Point (°C)</strong></td>
<td>62</td>
<td>2</td>
<td>40</td>
<td>n/a</td>
<td>135</td>
<td>&gt; 150</td>
</tr>
<tr>
<td><strong>Vapour Pressure (kPa) @ 20°C</strong></td>
<td>0.05</td>
<td>11.1</td>
<td>0.19</td>
<td>37.8</td>
<td>&lt; 0.01</td>
<td>Negligible under normal conditions</td>
</tr>
<tr>
<td><strong>Water Solubility</strong></td>
<td>Forms an emulsion with water</td>
<td>Immiscible with water</td>
<td>Immiscible</td>
<td>Partial</td>
<td>Emulsive</td>
<td>Emulsify</td>
</tr>
</tbody>
</table>
### Annex 2: Comments from HSE and GMHC on risks and hazards associated with solvents in Annex 1 (based on information and data derived from Material Safety Data Sheets)

<table>
<thead>
<tr>
<th>Product</th>
<th>Active Ingredients</th>
<th>Warning Signs</th>
<th>Risk Phrase</th>
<th>Comments</th>
<th>COSHH Assessment</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Boiling Point (Group AII) Solvent A</td>
<td>Tetraoxatetrasan &amp; Naphtha (petroleum) Hydrodesulfurized Heavy.</td>
<td>Xn = harmful, Xi = irritant, N = dangerous for the environment (Could be a fire risk)</td>
<td>R-36/38, 50 and 65</td>
<td>Naphtha which is 60-100% of the product, is classified by CHIP as a category 2 carcinogen and hence anything containing over 10% should carry a T= toxic and R45 'May cause cancer' phrase. Main health risk - damage to lungs if swallowed.</td>
<td>Hazards Group E, (Special). Guidance Sheets G400</td>
</tr>
<tr>
<td>High Boiling Point (Group AII) Solvent B</td>
<td>A mix of n-Hexane, n-Heptane, Cyclohexane, Methylcyclohexane, Octane, Naphtha (petroleum) Hydrotreated Light, &amp; Solvent Naphtha (petroleum) Heavy Aromatic</td>
<td>Xn = harmful, Xi = irritant, F = Highly Flammable, N = dangerous for the environment</td>
<td>R-11, 38, 48/20, 50/53, 51/53, 62, 65, 67, Rep3</td>
<td>Naphtha which is 10-30% of the product, is classified by CHIP as a category 3 carcinogen (but at very low concentration) and hence anything containing over 10% should carry a T= toxic and R45 'May cause cancer' phrase. Main health risk - drowsiness by skin or inhalation exposure.</td>
<td>Hazards Group E, (Special). Guidance Sheets G400</td>
</tr>
<tr>
<td>Highly Volatile (Group AII) Solvent C</td>
<td>Naphtha (petroleum). Hydrodesulfurized Heavy &amp; Solvent Naphtha (petroleum) Light Aromatic</td>
<td>Xn = harmful, Xi = irritant, N = dangerous for the environment (Could be a fire risk)</td>
<td>R-10, 20, 36/37/38,37, 51/53, 65,66</td>
<td>Both the Naphtha's are classified under CHIP as category 2 carcinogens and therefore the label should carry T = Toxic sign and R45 'May cause cancer risk phrase' as they each make up over 10% of the product. Main health risk - irritation to all exposed tissues.</td>
<td>Hazards Group E, (Special). Guidance Sheets G400</td>
</tr>
<tr>
<td>Highly Volatile (Group AII) Solvent D</td>
<td>Contains Dichloromethane, Propane-2-ol and Toluene</td>
<td>Xn = harmful, Xi = irritant, F = Highly Flammable,</td>
<td>R-11,20, 36 40, 67</td>
<td>Dichloromethane is a category 3 carcinogen and is labelled as R40 - 'May cause irreversible effects'. Main health risk - drowsiness by skin or inhalation exposure.</td>
<td>Hazards Group D, (Special). Guidance Sheets G400</td>
</tr>
<tr>
<td>Vegetable Solvent E</td>
<td>A mix of n-J- and Cyclo-aliphats</td>
<td>Xn = harmful (Could be a fire risk)</td>
<td>R-65,66</td>
<td>Main health risk - low risk of lung damage if swallowed.</td>
<td>Hazards Group A, (General ventilation)</td>
</tr>
</tbody>
</table>

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- **With Risk Phrase 45** - Hazards Group E, (Special). Guidance Sheets G400
- **Without Risk Phrase 45** - Hazards Group A, (General ventilation)
- **COSHH Assessment** - Both require Guidance Sheets S100 and S101