RESEARCH REVIEW No. 52

THE OPPORTUNITIES FOR USE OF ESTERS OF RAPESEED OIL AS BIO-RENEWABLE SOLVENTS

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by

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Abstract

This study reviews the market opportunities for use of esters of rapeseed oils as solvents. Potential market uses and requirements are reported, along with a discussion of the technical properties required of vegetable-based solvents for comparison with conventional organic solvents.

This report examines the opportunities as well as the constraints and barriers affecting uptake and further development of bio-solvents. There is increasing legislative pressure encouraging change and these driving forces such as legislation to reduce use of volatile organic compounds (VOC's) and measures to control the use of hazardous substances in the workplace are reviewed and discussed. Estimates of market costs, and, where available, costs of commercially available products are used for comparison with conventional organic solvents.

Vegetable oil derived fatty acid esters have a number of characteristics which suit their use in the solvent sector. Rape methyl ester has a high solvating capacity, due to its small ester group, but conversely, its long carbon chain length (predominantly C18) leads to relatively high viscosity and its high levels of unsaturation restricts the natural life of the oil through oxidative degradation. The latter is only of concern where long term recycling and re-use are considerations (i.e. in cleaning dip baths).

In the solvent market, there appears to be limited opportunity for use of rape fatty acid esters in the surface coating sector, which is increasingly converting to use of water-based formulations. Other vegetable oils predominate in this sector because of technical advantages in terms of drying time or ability to cost effectively produce alkyl resins.

The second most important industrial user of solvents in the UK is the printing industry, both in ink formulations and in wash down solutions. Progress has been made in developing ink formulations and significant volumes are produced and used in the UK and Northern Europe, but use in the UK probably accounts for no more than 20% of the market. Vegetable oils have been used for some time in the ink sector with no reported problems and few technical obstacles or barriers exist to further adoption. Rape methyl ester is commonly used in ink formulations. Significant market penetration has been achieved in some sectors, but is limited by significant drivers to change.

There is a significant opportunity for use of rape methyl ester in print cleaning solvents. There are a number of misconceptions in the industry currently preventing greater uptake. Benefits in terms of the working environment for print operators and reduced use of solvent come at a cost, in terms of high initial price and increased labour in the cleaning process. Fears over problems with swelling of rubber components appear to be unfounded with current formulations, and there appears to be no greater fire risk with rape than coconut based fatty acid ester products. Further education and demonstration is required to try and overcome some of the current misconceptions and to prove the technology to the industry. There is also a need to prove the worth of vegetable esters against the recently introduced hydrocarbon based high boiling point solvents. The printing industry has adopted these latter materials to comply with increasing legislative and health and safety pressures, as they generally involve little change to current working practice. However, to

date there have been few conclusive studies to quantify the cost benefits against vegetable oil based technologies. The view of the health and safety industry is that vegetable based esters are safer to the working environment than high boiling point solvents, but vegetable- based solvents will have to prove their worth in this respect to encourage further uptake.

Of the remaining industrial sectors, there are opportunities for use of rape methyl ester products in the metal cleaning sector, but much of the industry relies on recycling and re-use of solvent materials which results in a preference for coconut based products with greater oxidative stability. The key opportunities for rape derived fatty acid esters as metal cleaners are in one-off cleaning operations, tar and bitumen removal and in polishing operations for vehicles, however the demand in this sector is likely to be limited.

Other niche areas of interest include development of treatments for oil spill clean up, and formulations for removal of graffiti. Rape methyl ester has significant technical potential in both these areas, but the demand in the former case is likely to be sporadic, and further work would be required to ensure no significant environmental damage would result from the use of the solvent itself, current evidence suggests it is more benign than current solvents used for oil clean up.

Further work is required to develop suitable, effective formulations of vegetable fatty acid esters and working practices in the UK. There is a need for close working relationships between solvent users, suppliers and machinery manufacturers to ensure there are no problems with use of vegetable esters, which can affect rubber, plastic and epoxy materials.

The development of these potential markets is dependent upon certain driving forces (e.g. banning of hazardous products, government or EU policies, health and safety legislation and public opinion). Although, currently they cannot be seen as a total substitute for petrochemical based solvents, predictions suggest there could be at least a 12.5% market share for vegetable oil-based solvents by 2010 in a total market of 4-4.5 million tonnes per annum.

The key barriers identified by industry to adoption of vegetable based bio-solvents includes cost of materials, costs of capital investment required to introduce new technology and lack of recognition of the potential damage to workers health which can potentially arise from conventional volatile solvent use. In the metal cleaning sector, solvent use has been shown to be significantly reduced in some cases by adopting vegetable based esters, leading to significant costs savings. There are a number of other cost benefits which need to be taken into consideration including reduced risk to workers health, lower risk of fire and explosion and reduced level of hazardous waste to dispose of. All of these costs benefits need to be balanced in order to help users weigh up the costs of converting to vegetable based solvents.

It is estimated that in the most promising sector, development of print washes based on rape methyl ester could lead to an ongoing demand for around 50,000 tonnes of rape oil per annum in the UK if at least half of the print wash solvent use was derived from rape oil. Niche markets in other sectors could add to this demand.

1.0 Introduction

This report reviews the opportunities for use of esters of rapeseed oil and their derivatives as solvents in the UK as a means of potentially adding value to UK produced oilseed crops. This builds on related previous HGCA-funded work examining means of adding value to oilseed rape meal, and a number of other reviews and research projects which identified alternative and added value uses for oilseed rape.

The potential industrial uses of vegetable oils include opportunities in the polymer, lubricant, solvent and surfactant markets (see section 4.1 and Carruthers *et al.* 1995). The potential for use of rapeseed in the manufacture of polymer (Clarke et al., 2001) lubricant and surfactant markets has been studied in previous HGCA studies (Kasterine and Batchelor, 1998). In the surfactant market, demand for renewable materials is anticipated to grow, but is likely to be predominantly met by tropical oils such as palm and coconut, due to the predominance of short chain fatty acids in these crop oils. However, the solvent market exhibits significant potential for further growth and expansion in utilisation of materials derived from renewable resources (section 4.1) for which rape oils appear particularly suited. This study specifically focuses on assessing the potential for use of rape-derived oils in the solvent market place.

The following sections assess the current solvent market, potential uses for vegetable oil based solvents in this market, the technical requirements in these markets and the chemical and physical properties of bio-solvents. The drivers and barriers affecting uptake and use of bio-solvents production are analysed and discussed. The estimates of market potential are used to derive an estimate of the potential demand for oilseed rape that could be developed by increasing the use of vegetable-based solvents in key sectors.

1.1 Solvent nomenclature

A solvent is a liquid, which has the ability to dissolve, suspend or extract other materials, without chemical change to the material or solvent. Hence, solvents make it possible to process, apply, clean or separate materials. Solvents can be divided into two main groups, organic and inorganic solvents (i.e. water or salt solutions).

1.2 Organic solvents

Within the organic solvent sector two key categories are identified according to their chemical structure as either chlorinated/halogenated or non-chlorinated solvents. Non-chlorinated solvents are further classified as either hydrocarbon solvents (e.g. toluene and paraffin) or oxygenated solvents (e.g. alcohols, ethers and esters).

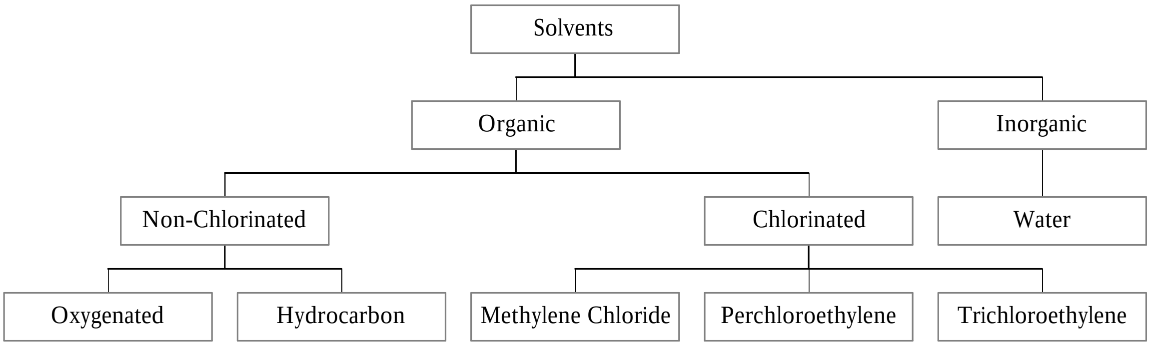

Figure 1. Solvent classification

Oxygenated solvents, as the name suggests, contain oxygen. This class of solvents is chemically synthesised and they possess a broad range of physical properties that makes them particularly suitable for use in paint and surface coating formulations. Hydrocarbon solvents are derived from the refining of crude oil (aliphatics) or coal tar (aromatics). Again, the main areas of use for hydrocarbons are in the paint and surface coating industry.

Organic solvents, and chlorinated hydrocarbons (CHCs) in particular, are highly regarded for their cleaning and solvating abilities. However, increasing concern over occupational health impacts has reduced their popularity and the demand for less harmful replacements has increased. Currently the use of chlorinated hydrocarbons is severely limited. Mainstream chlorinated solvents include methylene chloride, perchloroethylene, and trichloroethylene. Methylene chloride is used as a solvent in the pharmaceutical industry, chemical processing, electronics, aerosols, urethane foam blowing and paint stripping. Perchloroethylene is used in dry cleaning (80% of use) and in metal cleaning. Trichloroethylene is used for metal cleaning (80% of use) and speciality adhesives.

1.2.1 Technical problems associated with organic solvents

The volatility of many organic solvents means they pose a number of technical problems to industry, which leads to requirement for special handling and/or storage etc. There are fire and explosion risks in use, transport and disposal which increase costs to users. Some materials may also be affected by prolonged contact with organic solvent, for example rubber-based products can harden and become brittle. There are also environmental risks arising from volatilisation of organic solvents (section 2.0), and risks to operatives (section 2.2).

1.3 Inorganic solvents

Water is the main substance used as an inorganic solvent, but other acidic or caustic liquids are also used in industry. In many cases acidic or alkaline solutions can cause caustic and irritant effects on the skin and mucous membranes. There are limited opportunities for vegetable based cleaning agents in this sector of solvent use.

2.0 Environmental impacts of organic solvents and legislation affecting use

A major concern affecting conventional use of organic solvents is their contribution towards emissions of volatile organic compounds (VOC's) and impacts on thinning of the ozone layer and their contribution to photochemical smog. The concern is such that there is now legislation to either remove VOC's or restrict the use of materials responsible for their emission (section 2.1). Solvents are still one of the major routes of VOC contamination despite the decline in emissions seen in this and other emission sectors (Figure 1). Solvents currently account for 10% of the EU VOC contribution to ground level ozone. Substitution with vegetable-derived bio-solvents can facilitate the reduction of VOCs.

2.1 Legislation to reduce VOC's and limit impacts on occupational health

Legislative change, particularly that designed to tackle pollution or other environmental issues, is commonly seen as key driver influencing the recognition by industrialists of the advantages of materials derived from renewable resources. Recognising the impact that VOC emissions from solvent use were having on elevation of ground ozone levels (as a result of UV-decomposition), the EC introduced a Solvent Directive that came into force on 11 March 1999 (*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 VOCs from industrial processes by approximately 66% in 2007 (from a baseline of VOC emissions in 1990).

This Directive requires preventive actions to protect public health and the environment against the consequences of harmful emissions from the use of organic solvents. The Directive defines organic solvents of concern as "any VOC which is used alone or in combination with other agents, and without undergoing a chemical change, to dissolve raw materials, products or waste materials, or is used as a cleaning agent to dissolve contaminants, or as a dissolver, or as a dispersion medium, or as a viscosity adjuster, or as a surface tension adjuster, a plasticiser, or as a preservative". This legislation affects new industrial development and any new installation must comply with monitoring requirements and emission limits. Existing installations must comply with the legislation no later than 31 October 2007.

The Directive also states that substances classified as carcinogens, mutagens or toxic to reproduction under Directive 67/548/EEC which need to carry the risk phrases R45, R46, R49, R60, R61 (see definitions in Table 1), should be replaced by less harmful substances in the shortest possible time.

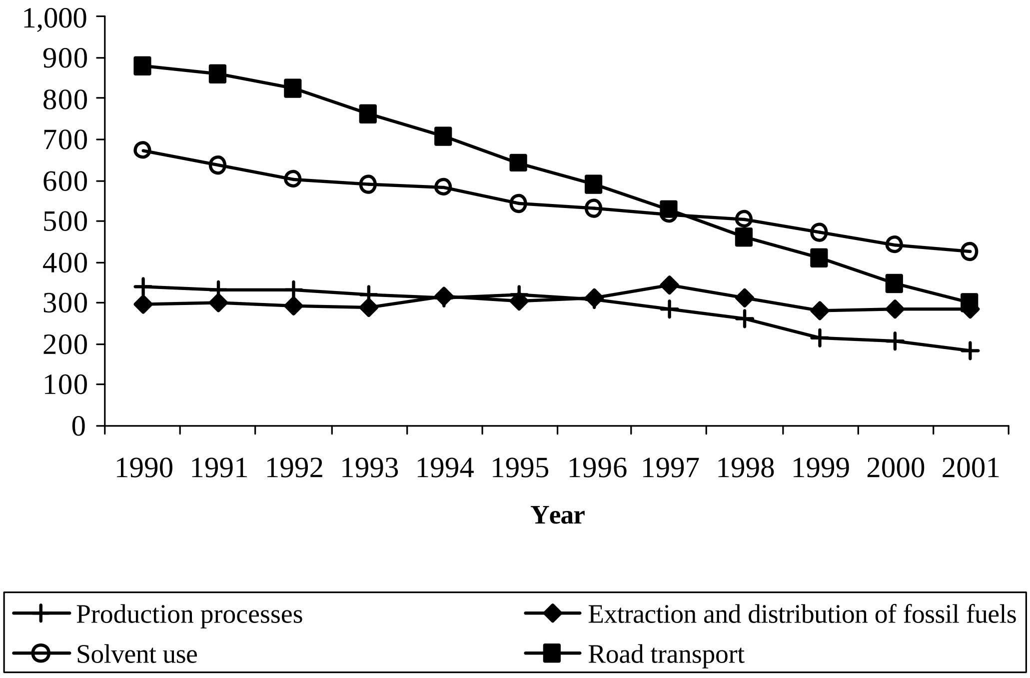

Figure 1. Major sources of VOC emissions in the UK (‘000 tonnes) (1990-2001) (Defra)

Table 1. Risk phrases under EU Directive 67/548/EEC

	Risk Phrases
R45	May cause cancer
R46	May cause heritable genetic damage
R49	May cause cancer by inhalation
R60	May impair fertility
R61	May cause harm to unborn children

The Directive requires industry to either

a) Meet an emission limit value for VOC's in waste gases and fugitive emissions[1];

b) To meet the total emission limit value, or

c) Implement solvent reduction schemes to reduce emissions.

An emission limit value is proscribed of 2 mg/Nm³, which refers to the total mass sum of the individual compounds released. The above legislation is enforced through the Environmental Protection Act and through Local Authority Air Pollution Control and Integrated Pollution Control regimes.

UK industry accounts for 35% of total UK VOCs emissions. Between 1990 and 2001 VOC emissions from industry were reduced by approximately 38% (Defra). To comply with the 66% reduction target, by 2007 UK, VOCs emissions from industry will need to be reduced to 291,000 tonnes or less. VOC emissions are currently falling at a rate of around 6% per annum. If this trend continues, a 62% reduction should be achieved by 2007. However, the UK Government has given an undertaking to cut VOC emissions to 72% of 2000 levels by 2010 (UK Environment Agency[2]). which would require an annual decrease of 7.2% per annum.

The decline in VOC emissions in the UK had started before the EU Directive 1999/13/EC came into force in 1999. In part this was due to other international commitments. The UK is a signatory to the 1991 UN ECE Protocol (Convention on long-range transboundary air pollution (CLRTAP)) on control of emissions of VOCs which required signatories to cut VOC emissions by 30 per cent by 1999 (relative to 1988 levels). Legislative measures therefore have been effective drivers in reducing VOCs emissions by UK industry.

2.2 Occupational health and environment

In some occupations such as printing, operatives are exposed to inhalation of solvents for prolonged periods. In the printing industry occupational exposure to organic solvents has been linked to liver damage, kidney damage and mild and reversible effects on the nervous system as well as problems such as degreasing of the skin and dermatitis (GPMU, 1997). Bio-solvents can reduce odour and fume problems, benefiting workers' health and safety (see section 8.1). Adoption of biosolvents could therefore reduce the requirement for costly exhaust ventilation systems.

Many organic solvents are hazardous to soil and water. Biosolvents like rape methyl ester (RME) are biodegradable and may therefore reduce the risks of water and soil pollution in sensitive situations.

[1] Fugitive emissions includes emissions of VOCs into air, soil and water as well as solvents contained in any products.
[2] http://www.environment-agency.gov.uk

2.2.1 Control of Substances Hazardous to Health Regulation, 2002[3]

The main legislation in the UK covering occupational exposure to solvents is the Control of Substances Hazardous to Health Regulations 2002 (COSHH). All solvents are subject to a COSHH assessment in the workplace, but certain solvent compounds are proscribed. The substances listed in Table 2, and any substance containing one or more of those substances are prohibited for use at work in diffusive applications such as in surface cleaning. COSHH regulations specifically require employers to seek less hazardous materials for use in the workplace to reduce risks to employees. This should be enforced through Health and Safety Inspections.

Table 2. Prohibited substances list under COSHH

Chloroform
Carbon Tetrachloride
1,1,2 Trichloroethane
1,1,2,2 Tetrachloroethane
1,1,1,2 Tetrachloroethane
Pentachloroethane
Vinylidene chloride
1,1 Dichloroethylene
1,1,1 Trichloroethane

Source:http://www.hmso.gov.uk/si/si2002/20022677.htm

3.0 Vegetable oils as solvents

Given the above concerns and drivers for change, there is increasing interest in development of solvents that will reduce the emission of VOC's and associated risks to operators (Layman Report, 2001). Modified vegetable oils have very good solvating properties and use of such materials would be compatible with many areas of current solvent use.

Vegetable oils are composed of triglycerides, large branched molecules comprised of glycerine and three associated fatty acid chains. High levels of polyunsaturation (i.e. double bonds) in the associated fatty acids commonly lead to instability and increased susceptibility to oxidation (degradation). These large, branched molecules result in the characteristic high levels of viscosity in unrefined oils, an undesirable trait for solvent applications. Fatty acids can be separated from glycerine through simple esterification reactions with alcohols to form fatty acid esters. This reduces viscosity and improves technical performance for the solvent market. Synthetic mineral esters are produced by the same process whereby mineral oil acids are esterified with alcohol.

[3] http://www.hmso.gov.uk/si

Rape Methyl Ester (RME) is one of the most well known vegetable derived esters and has attracted significant commercial interest as a substitute for diesel (commonly referred to generically as biodiesel). The current interest in developing a UK-based biodiesel industry which would, at least in part, use UK produced rape, could provide significant quantities of rape methyl ester for which higher value market outlets could be sought. This increase in availability could help reduce costs of raw material for specific niche industrial uses of rape methyl ester. However, it is currently not clear whether rape methyl ester (supplied as a blend of fatty acid esters from biodiesel plants) is the most appropriate ester, or whether further refining would be required to produce products capable of competing in the solvent market. Rapeseed oil and coconut esters currently dominate the European market for technical applications, while soya based esters dominate in the US market place. These vegetable esters will compete in sectors of the solvent market place, so price is an important factor affecting use.

The matching of both vegetable oil and alcohol, and method of esterification has an impact on the characters and properties of the resulting ester formulation. Fatty acid esters are generated be either trans-esterification or a more extensive esterification process.

Trans-esterification is a “single-stage process” in which a vegetable oil is transformed into a technical ester mixture (i.e. reflecting the composition and mix of each fatty acid in the original vegetable oil) with glycerol produced as a by-product. The quality of the ester obtained therefore depends upon the fatty acid composition of the original vegetable oil.

Esterification is a “two-stage-process” where the vegetable oil is split into its respective free fatty acids and glycerine (hydrolysed), then before esterification the individual fatty acids are separated out using fractionated distillation before being esterified individually or in tightly controlled mixtures (as 100% purity is rarely achieved). This allows ester manufacturers to produce fatty acid esters with specific properties.

Once esterification or transesterification processes have taken place and any further additives have been included (i.e. to prevent oxidation or improve performance etc) the oil technically becomes a chemical product and therefore subject to appropriate safety instructions for correct handling, storage, use and disposal etc.

Rape methyl ester is a comparatively low-cost ester but requires further ‘cleaning’ and processing for use in cleaning operations or other special applications. Unfortunately low cost products like pure rape methyl ester can have some technical disadvantages. For instance, it can cause rubber materials to swell, although this can be compensated to a certain extent by formulation additives. Oxidation of RME can lead to intensification of oil colour, and an increase in odour and viscosity, reducing mobility and making it less suitable for cleaning geometrically complex machine parts (Stautz, 2002). However this is not a problem in solvating or cleaning operations requiring single use, where RME is well suited due to its high solvating power.

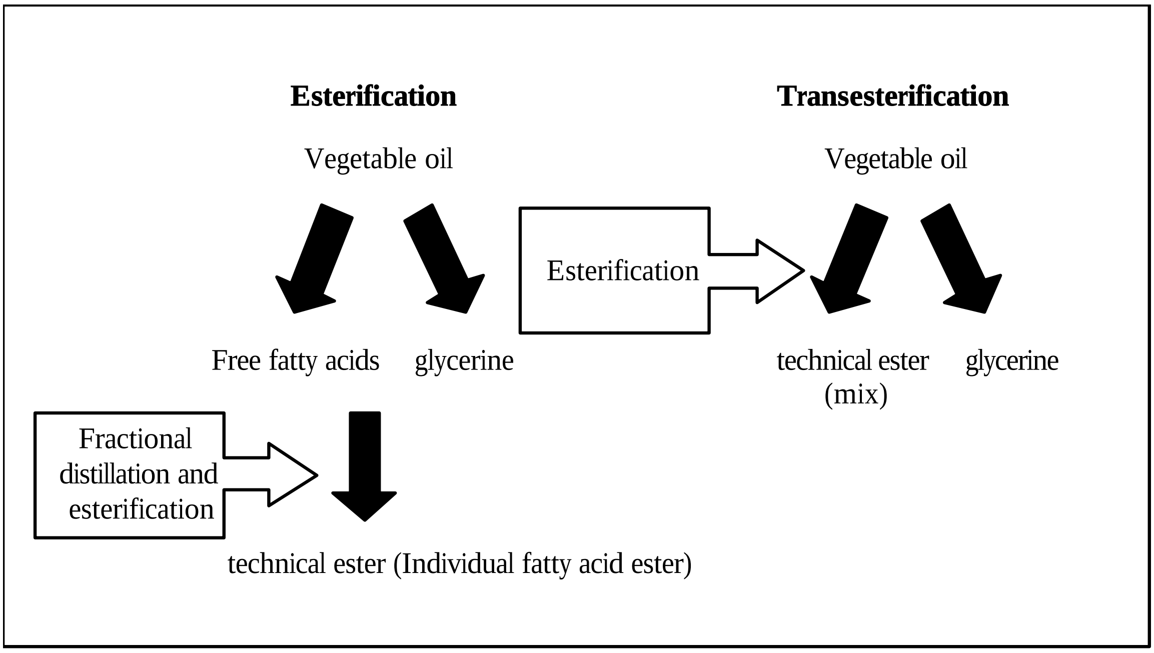

Figure 2. Esterification and transesterification of vegetable oils

The attraction of using vegetable oil esters are their technical properties, which are already recognised in some industries. Vegetable oils are already used as additives to improve the action of other mineral oil cleaners. In the printing industry some solvent manufacturers add ester components to their mineral oil-based products to enhance the results of cleaning offset printing presses.

3.1 Efficacy of vegetable based solvents

Tests have been carried out in order to generate information on the performance of bio-solvents in the metal cleaning sector[4]. These demonstrated that their cleaning capability in many cases is better than that of conventional mineral oil-based cleaners (Stautz *et al.* 2002). Rape methyl ester also shows a high solvating power for clear or white and pale coloured inks. Rape methyl ester also provides corrosion protection for metal components in contact with the solvent. These are discussed in more detail in later sections dealing with individual market sectors. Examples of the type of soiling that vegetable-based esters can remove (Stautz *et al*., 2002) includes-

Animal and vegetable oils and fats

Mineral oils and fats

Drawing oils (viscous lubricants) and fats (e.g. stearates), lubricants

[4] Within the SUBSPRINT project more than 130 metal companies tested the fatty acid ester as new cleaning agents for their purposes.

Waxes

Corrosion inhibitor oils and protective coatings (typically applied to metals)

Lapping and polishing agents

Graphite and pigments

Bitumen and tar

Abrasive dust

3.2 Properties of vegetable oil esters

3.2.1 Physical properties

The cleaning performance and environmental impact of a solvent is determined by its physical and chemical parameters. The key parameters of concern include,

- Boiling point. The temperature at which the liquids pass into the vapour state. Vegetable oil esters have a very high boiling point in comparison to mineral based solvents, which is reflected in a low vapour pressure. The boiling point for common pure vegetable derived fatty acid esters ranges between 211-365ºC. The larger the molecule the higher the boiling point. Increased levels of branching in the ester group lower the boiling point.

- Vapour pressure[5]. The higher the vapour pressure, the more volatile the substance. At room temperature vegetable oil esters have a very low vapour pressure.

- Flash Point. The lowest temperature at which sufficient vapours can be liberated by a combustible solvent to cause ignition (according to a defined test method). This is the most important parameter determining the hazard potential for fire and explosion. The lower the flash point, the faster the rate of evaporation will be and the higher the risk of fire or explosion.

- Density. Unsaturated vegetable oils have a high density relative to conventional solvents. The longer the carbon chain and/or the larger the ester group, the lower the density. Pure C_{10}-C_{18} fatty acid esters have densities (at room temperature) ranging from 0.853 to 0.876 g/cm^3, the unsaturated oleates having the highest densities. Commercially available products based on vegetable-based fatty acid esters tend to have slightly higher densities. Esters derived from rapeseed oil, which contains high levels of long-chain unsaturated fatty acids, tend to produce the highest density bio-solvents.

- Viscosity. Is a measure of flow characteristics, the higher the viscosity, the less mobile the liquid. Cleaning agents with low viscosity are suitable for machine parts with complex geometry. An increase in the length of the carbon chain or size of the ester group leads to an

[5] The Solvents Directive of the European Union provide for a limit to vapour pressure of 0.1mbar/20°C (Stautz, 2002).

increase in viscosity. The viscosity of vegetable oil esters is high compared to many conventional organic solvents, but still well within the required range for a number of cleaning applications. Chlorinated solvents tend to be more suitable for cleaning parts with complex geometry due to their low viscosity.

- Surface tension. The lower the surface tension, the less energy will be required to increase the surface area of a drop of liquid (i.e. the easier it is to wet a surface). Vegetable oil esters have similar surface tension values to organic solvents. Increasing the chain length increases the surface tension, which again does not favour rape-derived esters.

- Solubility. The Kauri-Butanol (KB) value is a measure of solvency power. The KB value of a solvent must at least match that of the contaminant to be removed while at the same time be safe to the underlying material. Generally high KB value solvents are used for heavy organics such as oils and greases. The KB value of vegetable oils esters is usually between 47 and 66. Conventional solvent values range between 10 and 350. Methylene chloride, perchloroethylene and trichloroethylene have KB values of 136, 129 and 90, respectively. Vegetable oils based solvents are therefore best suited to removal of substances that match their spectrum of KB values. The solubility characteristics of fatty acid esters are comparable to those of ethers and unsaturated aliphatics. The length of the fatty acid carbon chain has little effect on solubility characteristics, which are determined by the size of the ester group. The larger the ester group the lower the solvating ability. The small ester group associated with Rape methyl ester results in very good solvating characteristics.

The first three of these parameters give an indication of evaporative loss, which is important for valuing the potential impact on human health and the environment. The lack of volatility of vegetable esters means that an oily residue is left on the surface after any cleaning operations. This can be removed by wiping or heating (though in this case this would increase emission of volatile components).

A comparison of the properties of commonly available solvents is given in Table 3. Low viscosity and wetting ability which is comparable to conventional solvents, matched to good solvating ability means that vegetable fatty acid esters have significant potential in the cleaning sector.

3.2.2 Effects on treated surfaces

It is unusual for fatty acid esters to have a corrosive effect on metal as they are not inherently corrosive. VOFApro[7] (Stautz *et al.* 2002) reported on a test of 4 vegetable fatty acid ester products; one product with a high acid value was noted to corrode metals containing zinc (zintec, galvanneal, hot-dipped galvanised steel and brass) (VOFApro Bulletin[7]). The effect on zinc was attributed to the emulsifier included in the formulated product. In contrast, mild corrosion of steel occurred following exposure to a

Table 3. Comparison of chemical/physical properties of common cleaning agents[6]

	Flash Point (°C)	Vapour pressure (mbar 25°C)	Boiling point (°C)	Density (g/cm3) (20°C)	Viscosity at 20°C (*25°C*)	Surface Tension (Dynes/cm)	Solubility (KB)	HAP (Hazardous Air Pollutant)
Vegetable oil esters	>100	0.1-0.5	211-366	0.86-0.90	2.3-9.8	22-31	47-66	no
Trichloroethylene	None	93	87	1.40	0.57	28.7	129	yes
Perchloroethylene	None	27	121	1.60	*(0.84)*	32.3	90	yes
Methylene Chloride	None	467	40	1.30	0.44	27.2	136	yes
n-Propyl Bromide	None	148	71	1.30	0.49	25.3	125	no
Acetone	64	305	56	0.79	0.36	22.7	-	no
Cyclohexane	-20	127	81	0.78	1.00	24.9	58	no
Isopropyl Alcohol	0.6	53	82	0.79	2.40	21.7	-	no
N-Methyl Pyrrolidone (NMP)	93	0.3	204	1.02	*(1.67)*	40.7	350	no
D-Limonene	49	2.7	154	0.83	*(3.50)*	25.0	67	no
Trans-1, 2-Dichloroethylene	2.2	440	48	1.42	-	27.5	117	no

[6] Data obtained from Stautz *et al*. (2002) and http://www.cleantechcentral.com/Magazine/Past-Issues/oct2003/2.asp. (1 Millimetre mercury = 1.33 mbar)

synthetic ester. One of the advantages of vegetable-based esters is their natural anti-corrosion properties which is of value in the metal cleaning sector.

Fatty acid esters can have an effect on non metallic materials. Vegetable-based fatty acid esters may cause rubber to swell and can leach plasticises from plastics (though those derived from rape have less effect than other fatty acid esters). Teflon, Viton, fluoropolymer and polypropylene are reported to be unaffected by vegetable-based fatty acid esters (VOFApro Bulletin[7]).

Vegetable oil fatty acids can solubilise, or mix with alkyds and chlorinated rubber. Methyl and ethyl esters can solubilise binders (used in composite materials) such as phenolic rosin and low molecular weight epoxys. Clearly such characteristics need to be examined before use to protect machinery from damage.

4.0 The market for solvents

4.1 The European market for vegetable oil derived renewables and potential for market development

A review of the European market potential for use of oil crops for industrial use (Askew, 2002) indicated that there is considerable scope for further expansion in the use of vegetable oils in polymer production, but that potential in the bio-lubricant market is limited due to problems with price and performance compared with non-vegetable oil-based lubricants.

The potential for growth in the markets for renewables as a whole from oil crops has been reviewed by Ehrenberg (2002), who forecasts an EU potential consumption in 2010 of 500,000 tonnes of polymers derived from renewable oil resources. For the lubricants, solvents and surfactants markets, consumption of 200,000 tonnes, 235,000 tonnes, and 1,450,000 tonnes, respectively from renewable oil resources is forecast for 2010. However, expansion of surfactant production from EU grown bio-renewable oil sources is limited by the inability of the EU to produce vegetable derived short chain fatty acids, e.g. lauric acid[8]. Consequently, apart from the limitations for surfactants, given the appropriate drivers for change, realisation of these potential markets would represent a significant market expansion given levels of uptake seen in recent years in these sectors (Table 4 and Figure 3).

[7] www.rrz.uni-hamburg.de/kooperationsstelle/praxis/vofapr/bulletin
[8] A common constituent of coconut oil

Table 4. EU Consumption of polymers, lubricants, solvents and surfactants and proportion of each market accounted for by materials derived from renewable oil resources in 1998.

Market Sector	Total Consumption ('000 tonnes)	Renewable Consumption ('000 tonnes)	Share held by renewables (%)
Polymers	33,000	25	0.07
Lubricants	4,240	100	2.4
Solvents	4,000	60	1.5
Surfactants	2,260	1,180	52.2

Source: Ehrenberg (2002)

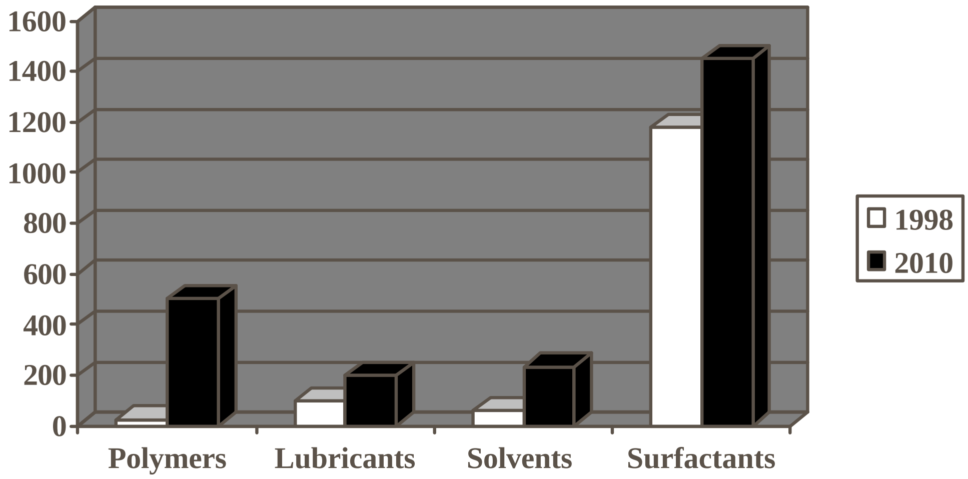

Figure 2. Estimated potential for growth in use of materials derived from renewable raw materials[9] ('000 tonnes) (Ehrenberg, 2002)

[9] Based on Ehrenberg (2002) forecasting data.

4.2 European solvent market

The EU solvent market currently uses between 4 and 4.5 million tonnes per annum of solvents (Johansson, 2000). In the non-chlorinated solvent market, 1.9 million tonnes of hydrocarbon solvents and 2.3 million tonnes of oxygenated solvents are typically used per annum. Sales of chlorinated solvents have steadily declined over the last ten years as users have switched to either alternative industrial processes using smaller volumes or alternative solvents. The chlorinated solvent market accounted for only 300,000 tonnes of product in 1998. In the chlorinated solvent market, methylene chloride accounts for around 50% of use and perchloroethylene and trichloroethylene account for 25% each of the remaining uses (Johansson, 2000). The trend towards more environmentally friendly solvents is expected to accelerate the use of oxygenated solvents.

Due to the impacts of environmental and health legislation discussed earlier, it has been predicted that total solvent production in the EU could fall to 1.9 million tonnes in the EU-15 by 2010 (Patel, 2002). However, use of vegetable oil-based solvents is expected to increase in volume and as a proportion of the market. The IENICA[10] market report (IENICA, 2000) estimated that at least 12.5% (app. 250,000 tonnes) of the solvent market could be partly or totally substituted with vegetable oil derived solvents in the EU-15, which is in agreement with estimates by Ehrenberg (2002) (see Figure 2) of 235,000 tonnes by 2010. Other estimates have predicted that the potential for vegetable based solvents will be "in excess of 100,000 tonnes" (Legrand 1998).

The surface coatings sector (paints etc) and the printing industry are two of the most important end users of solvents in the EU (Table 5). There is also a heavy reliance on organic solvents in the metal cleaning sector, which accounts for c. 280 thousand tonnes of organic solvent use in the EU and there are opportunities for vegetable derived esters in all of these market sectors.

4.2.1 Solvent use in the surface coating sector

Most (>60%) of the solvents used in the EU surface coatings sector are hydrocarbon based. Of the remaining solvents used, 15% are ester based, 10% ether based, <8% are alcohol based and 7% are based on ketones or other solvent molecules. Virtually no chlorinated solvents are used in the industry. Building and home applications account for 40% of use, the auto industry 20% and wood and timber treatments for nearly 20% of solvent use.

The paint industry has deliberately moved away from organic solvent formulations in recent years and typically towards water-based or non-solvent formulations. Around 70% of the decorative paints used within the EU today are water-based (Johansson, 2000), this along with the requirement for solvents with low boiling points, limits the potential for introduction of vegetable oil based solvents into the market place.

[10] IENICA: Interactive European Network for Industrial Crops and their Applications.

Vegetable oils are still used in gloss paints (predominantly linseed and tung oils). Alkyl resins, derived from vegetable oils, can also used in paint and surface coating formulations because of their film-forming properties. These alkyl resins are predominantly derived from soya, but also more recently from sunflower oil. Attempts have been made to use vegetable derived ethyl lactates as solvent replacements but there have been compatibility problems[11] and ethyl lactates are an occupational health risk in their own right. The opportunities for rape derived materials in the paint solvent market currently appears to be limited.

Table 5. Percentage of solvent shipments (i.e. usage) in the EU by end user sector (1997)

	% of shipments by end-user sector
Coatings	43
Inks	12
Pharmaceuticals	8
Adhesives	7
Extraction Agent in Food	3
Rubber/Polymer Manufacturing	3
Cosmetics	2
Metal Cleaning	2
Dry Cleaning	1
Agrochemical	1
Others	18

Source: Frost and Sullivan Market Report - 1998

4.2.2 The Solvent market in the printing industry

In the graphical industry, solvents are used both in printing inks, and cleaning solutions to clean up printing machinery. The UK hosts one of Europe's largest printing industries.

Solvent use in the printing industry accounted for 14% of manufacturing solvents demand in 2000, a share that is expected to increase slightly in 2005. Solvents are used in ink formulations and in washes to clean print machinery.

Solvents are used in printing inks to solubilise the ink resins to allow the ink to be applied and to facilitate flow of liquid inks. Soya oils, esters and alcohols have increased their presence in the market, while ethers and chlorinated solvents have declined. Use of hydrocarbons, the largest product type used in printing inks, remains comparatively flat. A number of vegetable oil based ink formulations have been developed. The current EU market for vegetable-based printing inks is reported to be in excess of 120,000 tonnes per annum (Johannson, 2000), with a market value in excess of £2 billion. (Weeks, 1998). There is a

[11] EU FAIR Programme project CT98-9588 "Bio-liquid mixtures for solvent and/or detergent applications" (www.nf-2000.org/secure/Fair/F901.htm)

focus on use of vegetable based inks in Belgium, the Netherlands, Germany and Scandinavia. Within the Belgian market, 80% of the printing ink market is vegetable-based. (Trenal, a Belgian printing ink manufacturer produces and sells around 17,000 tonnes of vegetable oil-based (rape and sunflower oil) printing inks to the newspaper industry (Weeks, 1998). These figures suggest significant levels of market penetration by vegetable based inks have already been achieved.

The area where further substitution could occur is in print washes. Renewable solvents with high boiling points are used as cleaning agents. Currently the cleaning process for offset printing machines, using conventional solvents, is estimated to account for 1% of the total VOC emissions in Europe.

4.3 Solvent markets in the United States

Outside Europe, the US has taken significant steps towards use of renewable solvents. Demand for solvents in the USA is forecast to rise by nearly 1% per annum to reach over 5 million tonnes by 2007 (Table 6). Sales of "green" solvents are increasing and are expected to account for an increasing proportion of the market. Demand for solvents in the paint and coatings sector is forecast to remain stable or fall slightly by 0.1% per annum in the period 2000-2005, with consumption estimated at 1.05 million tonnes in 2005. Consumption of solvents in printing inks is forecast to rise by 1.6% per annum to 472 thousand tonnes in the same period. As in Europe, the move towards "green" solvents has been prompted by environmental and regulatory concerns that have prompted end users to replace traditional solvents with more benign alternatives.

Table 6. Conventional and 'green' solvent demand in the United States and predicted growth (thousand tonne)

				% Annual Growth	
	1997	**2002**	**2007**	**1997/2002**	**2002/2007**
Total solvent use	4794	4745	5073	-0.2	1.4
Conventional solvents use	4432	4286	4468	-0.7	0.8
Conv. % of total use	92.4	90.3	88.1		
Green solvent usage	363	458	607	5.2	6.5
Green % of total use	7.6	9.7	12.0		
Solvents demand (million £)	815	807	913	-0.2	2.6

Source: Based on US data from the Freedonia Group

Soya is the dominant oil-bearing crop in the US from which methyl soyate is derived. As with rape methyl ester, it has good potential as an industrial solvent for use in machine part cleaning, paint and ink removal and as a carrier solvent. The potential solvent markets available to methyl soyate in the US are estimated at 270,000 tonnes (Table 7). It has potential as a replacement (at least in part) for solvents such as trichloroethylene, methylene chloride, methyl ethyl ketone,, toluene and xylene which have already been severely restricted in their use or are soon likely to be. Vegetable based esters are anticipated to provide the longer term solutions to loss of these chemicals.

Table 7. Solvents markets in the USA (2002) where methyl soyate and its derivatives could potentially substitute (at least in part)

Solvent	Tonnes	% of total
Methylene Chloride	54,000	20.2
Trichloroethylene	54,000	20.2
Perchloroethylene	16,000	5.9
Methyl Ethyl Ketone	32,000	11.8
d-Limonene	23,000	8.4
Other solvents	91,000	33.6
Total	270,000	100

Source: United Soybean Board (2002)

Clearly in a number of cases US soya-derived ester products could end up competing in the European market place with esters derived from European rape oil. All other issues being equal, factors affecting the comparative costs of the base oils will therefore have an impact on the competitiveness of European produced rape methyl ester. In such cases, rape methyl ester based solvents will need to demonstrate advantages over their soya-based equivalents. Clearly work to develop tailor made ester products and/or formulations could help secure market advantage as well as increase confidence in the industry in use of products supplied as speciality products rather than as bulk solvents.

5.0 Solvent use in the printing industry

5.1 EU and UK printing industry

The printing industry was one of the first industrial sectors to introduce vegetable oil derived esters as substitutes for conventional cleaning products. Use of solvents of all types in the printing industry amounts to around 270,000 tonnes per annum in the EU-15 (European Solvent Industry Group). The UK reportedly uses 40,000 tonnes of solvents per annum for cleaning printing machinery (Table 8).

Table 8. Consumption of solvents in the EU and UK printing industry in 2000 (tonnes)

Market	**EU**	**UK** (% of EU)
Printing Ink Solvents	270,000	52,000 (19%)
Cleaning Solvents	100,000	40,000 (40%)

Data: British Coatings Federation and GIFNFC, 2003

Vegetable oil based cleaning agents for offset-printing presses were developed in Denmark in 1988/1989. After successful technical tests in 1989 this technology was introduced into around a third of Danish printing shops either as the major technology or as an alternative to existing cleaning technologies (SUBSPRINT, 1997). In Germany this technology was adopted in around 5-10% of offset-printing businesses[12].

It has been estimated that offset printing companies in the EU use about 100 million litres of organic solvents per year and between 60-90% of the petroleum-based solvents evaporate into the atmosphere.

5.1.1 Print processes used in the in UK and opportunities for use of vegetable solvents.

The majority of the UK commercial printing industry is based upon lithographic flat-bed printing. Offset printing is the most common flat bed printing technology. In offset printing the ink is not directly transferred to the substrate (i.e. paper) but to a rubber blanket. The rubber blanket transfers the image to the substrate. Within the offset process there are a number of options for use of bio-solvents in inks and ink wash solutions (The following information on ink usage and wash systems was provided by Tony Kington, BASF),

- Sheet-fed offset printing –this process utilises the bulk of the vegetable oil currently used within the industry. This is used for low volume production of magazines and packaging, and accounts for use of up to 10,000 tonnes of ink per annum. Between 20 and 50% of the presses involved will have automated cleaning systems.
- Heat-set printing –used for magazines, books and publications. The solvent portion of the ink is driven off by heat; this system therefore depends on volatility of inks. The ink must dry very quickly, and as vegetable oils dry relatively slowly, they have limited applications in this process. This process accounts for use of up to 28,000 tonnes of ink per annum, and most presses have automatic cleaning systems.
- Cold-set printing –mostly used to produce newsprint. The ink dries by absorption only, therefore a very absorbent substrate is required. There are good opportunities for use of vegetable oils in this

[12] Information (updated 2000) obtained from SUBSPRINT http://www.rrz.uni-hamburg.de

process. This process accounts for use of 35,000 tonnes of ink per annum (35% colour, 65% black). Very few of the presses in this category have automated cleaning systems

- Waterless printing –a very small, new industry, similar to the sheet-fed process.

Currently vegetable based inks are being developed for the above offset industries, but current use accounts for less than 20% of the available market in the UK (British Coatings Federation personal communication).

5.1.2 Use of cleaning agents in the printing industry

After the print run, machines have to be cleaned of ink and paper dust must be cleaned from the machine. Areas to be cleaned include the rubber blanket, the inking system, the printing plate and impression cylinder. The substrate materials involved include steel, aluminium and rubbers of different types, so any replacement solvent must be compatible with these materials.

Hand cleaning is done with paper or cotton rags plus solvent. In automated cleaning systems, solvents are sprayed onto rollers and/or the rubber blanket and allowed to act for a short period before ink and paper dust is removed with squeegees, brushes or webs. Conventional cleaning agents are predominantly petroleum based and contain materials such as mineral spirits; naptha (in various forms); dimethyl benzine; 1,2,4-trimethyl-benzine; 1,1,1 trichloroethane; trichloroethylene; methyl ethyl ketone, toluene and xylene. In automated systems, most of the solvent evaporates after cleaning leaving a solid waste to dispose of.

With conventional cleaning, aliphatic or aromatic hydrocarbons are used to 'pick up' and solubilise any remaining ink. In contrast, fatty acid esters clean by make inks less viscous and easier to remove. Five major groups of product are currently marketed for offset cleaning (SUBSPRINT, 1997) (Table 9).

Table 9. Classification of solvent groups, based on volatility.

Print cleaning agents	Boiling point (ºC)	Flash point (ºC)	Vapour pressure mBar @ 20ºC
Extremely volatile (AI)	<100	<21	30-800
Highly Volatile (AII)	115-190	<55	0.5-40
Medium volatile (AIII)	180	>55	0.5-4
High boiling point	>235	>100	0.01-1
Vegetable	>250	>150	<0.1

A European funded project SUBSPRINT, (SUBSPRINT, 1987) examined the potential for use of vegetable derived solvents in the cleaning of print machinery. SUBSPRINT's aim was to build on the experiences gained in Denmark with alternative cleaning agents based on vegetable fatty acid esters. The SUBSPRINT project aimed to demonstrate the technology to a wider audience to encourage uptake across the EU.

At the outset of the SUBSPRINT project in 1992, a number of opinions were prevalent in the printing industry about vegetable-based fatty acid cleaners, which included;

- ? Vegetable based fatty acid cleaners are not suited to automatic cleaning systems
- ? There is a danger of slippage through discarded cleaner
- ? Higher workload required to remove due to higher viscosity
- ? Bad odour from a few products
- ? Swelling, shrinkage and hardening of rubber blankets
- ? Reduction in print quality (tone)
- ? Suspicions of corrosion effects,
- ? Risk of self ignition and toxicity.

In some cases these effects were related to the quality of the early pilot materials available at the time. The SUBSPRINT project was able to demonstrate that vegetable based cleaning agents could be used with automated wash systems without harm to machinery. The project also confirmed the benign impact of vegetable derived cleaning agents on the environment and print operatives. However, vegetable cleaning agents contaminated with waste ink must be disposed of as hazardous waste due to metals in the ink formulations. Virtually all print machinery manufacturers insist on the addition of corrosion inhibitors and or emulsifiers in vegetable-based cleaning formulations.

In response to curbs on VOC emissions and health and safety concerns, the printing industry is currently substituting volatile organic solvents with high boiling aliphatic hydrocarbons. However, in terms of operator safety they are ranked below vegetable-based solvents (see 8.1.2 and Table 11).

5.2 Solvent use in printing industries outside the EU

In South America, the Far East and the Middle East mineral oil-based inks continue to be used for the most applications, but in the US significant steps have been made to introduce vegetable based solvents.

5.2.1 Renewable solvent use in the US printing industry

The US has developed a significant vegetable oil printing ink industry, based on soya. Soya-based inks account for 9.1% of the total ink market in the USA (ILSR, 1997). 25% of commercial printers and 33% of newspapers (dailies, weeklies and monthlies) use soya ink and 45% of the USA ink manufacturers produce at least one soya ink product (ILSR, 1997).

Legislation has been a key factor driving the development of the US soya ink market. The US Clean Air Act has been an important driver for environmental legislation. In 1994, the US Congress passed the Vegetable Ink Printing Act, which mandates printers for government contracts to use vegetable-based inks whenever possible. As a result, the use of soya ink by the US Government Printing Office has nearly quadrupled (ILSR, 1997).

The advantages of soya-based inks are reported as

- Brighter colours (a result of the greater translucency in soya inks) (American Soybean Association).
- A 5 to 50% increase in transfer efficiency (i.e. larger number of impressions per print run due to greater translucency) (Hilts, 1991).
- Reduction in paper waste, reducing disposal costs[13]
- Lower VOC content (The VOC content of soya based inks ranges from 2-5% compared to 30-35% with petroleum based products).

The only disadvantage reported was in relation to situations where durability was a key requirement where traditional solvent-based formulations continue to be favoured.

The development of the US soya ink market is influenced by small differences in price. The cost of the carrier oil solvent has the greatest effect on ink price, since this accounts for up to 80% of the formulation. The higher cost of the soya bean solvent means black soya inks are around 38% more expensive than petrochemical derived alternatives (Table 10). However, because of the improved performance of coloured soya inks, the higher cost of the soybean oil solvent is offset by a reduction in the amount of hard resin required in the coloured ink formulation (ILRS, 1997), so the price for coloured inks are very similar.

Despite the above reported advantages, this difference in price does affect the market. In the newspaper industry, the level of substitution by soya based products is lower with black inks (up to 25% market share) than coloured (up to 80% market share) (Weeks, 1998). This differential is not observed in the European market (Weeks, 1998).

Table 10. Price comparison of soya and petroleum based inks in the United States

	Price
Black offset lithography news ink – petroleum based	£0.8/kg
Black offset lithography news ink – soya based	£1.1/kg
Coloured – petroleum based	£3.9-4.7/kg
Coloured – soya based	£3.9-4.7/kg

Source: ILSR (1997)

[13]Information from Solid Waste Management Coordinated Board. http://www.swmcb.org/about/index.html

5.3 Experiences in the printing industry gained from use of vegetable derived solvents

To date, the performance of vegetable esters washes have been rated as good as conventional petroleum-based wash solvents (US EPA, 1997; SUBSPRINT, 1997). This is representative of responses across the industry from large newspaper print rooms to small individual print businesses (SUBSPRINT 1996b). Generally use of vegetable cleaning agents has slowed the cleaning process, due to the need to remove the oil film left after automated cleaning (in one case this was quantified to an extra 2.5 minutes), but this has more than been outweighed by reductions in solvent use or specific improvements in operator health in some cases (SUBSPRINT, 1996b).

Varn Products Ltd, who produce vegetable ester print wash formulations cite the main barriers to use of rape ester products by the industry as cost and acceptance by the printing industry. Clearly issues over impacts on rate of solvent use and better performance of new products are not widely appreciated by the printing industry and there is a need to communicate these messages to build confidence and encourage change. The print solvent industry anticipated that increasing environmental pressure and health and safety legislation will be a driving force towards increased use of bio-solvents.

5.3.1 Experiences in the printing industry – field test

To gain more information on the performance of rape-methyl esters, a print cleaning agent containing predominantly oilseed rape-oil and its esters (Vegra Rapid Wash 220 224 (further details in Table 14)) was obtained from Germany via Pomeroy Pressroom Products Ltd. The product is recommended as suited for both automatic rubber blanket washers and for washing by hand. It contains a mixture of 38% rape oil and 35% rape methyl ester along with an emulsifier and added corrosion protection compounds. Unlike earlier vegetable based cleaning agents that reportedly damaged printing machinery parts, new products like Vegra Rapid Wash have very high cleaning power but do not cause embossing or shrinking of rubber blankets or rollers and as such carry approved for use by offset printing machine manufacturers.

The vegetable cleaner was supplied to a local printer (Best Print & Design Ltd, Malton, N Yorks) for use on a lithographic offset printer using a black oil-based ink. The cleaning agent was used at a dilution ration of 1:1 (300ml of water to 300ml of cleaning agent) and applied to print rollers manually using a wash bottle.

After a conventional print run, the printing press was set to clean as normal, and the Vegra Rapid Wash solution was applied. There were no problems with the cleaning run and cleaning took approximately the same amount of time as the conventional solvent cleaning programme.

The plates were then re-inked up again and the print quality tested on a further print run. No noticeable problems were observed with the test print. The cleaning process was repeated using the Vegra Rapid Wash. The performance was deemed to be as good as conventional practice and no problems were envisaged with further use. The print operator was impressed with the re-inking achieved after washing, no diminution in print quality was observed, and no marbling of the image was observed despite the initial reservations of the print operator.

Overall the rape-methyl ester performed as well as conventional solvents with no noticeable problems. However a longer term trial would be required to ascertain whether there were any potential long term problems.

5.3.2 Inks and de-inking of recycled paper

The experience with vegetable-based inks in Europe has been favourable (Weeks, 1998), with lower levels of spoilage, 10-15% less ink use and greater colour intensity while minimising odour and use of carcinogenic materials found in conventional ink formulations. At least 17 million tonnes of vegetable based ink has been supplied for use in the newspaper industry with no reported problem.

Inks based on vegetable oils were thought to be responsible for problems with de-inking of paper for recycling, resulting in discolouration etc. However, a study by ADEME in France demonstrated that vegetable inks caused no additional problems[14].

5.4 Ability of the UK printing industry to invest in change

The value of annual sales in the UK printing industry is approximately £13 billion, and accounts for 1.7% of UK GDP. The industry employs 170,000 people in more than 12,000 companies. The industry is therefore dominated by a large number of small companies, and only 500 employ more than 50 people (approximately 90% employ less than 20 people). In its latest survey of its members, the British Printing Industries Federation (BPIF) has found increased overcapacity and lower margins across all sectors. Profits in the UK printing sector are expected to fall again this year after declining last year to provide an average pre-tax sales margin of 4.5 percent. The industry is increasingly competitive and margins rely on increasing volume.

All of the above puts increasing pressure on printers at a time when change in working practice is expected. The fragmented nature of the industry also makes communication more difficult and there is less impetus to change and adopt new working practices without a significant health and safety or legislative driver.

[14] www.ademe.fr/partenaires/agrice/htdocs_gb/research_solvents.htm

6.0 Vegetable solvent use in the metal cleaning market

Organic solvents and aqueous cleaners are currently used in the metalworking industry. Organic solvents are very effective cleaning agents but the risks associated with their use are well recognised. The industry is slowly phasing out the use of organic solvents but is looking for 'green' replacements that are more cost effective than aqueous cleaning processes.

The physical and chemical parameters of vegetable oil fatty acid esters indicate that they should be capable of removing contaminants commonly found in the metal industry – lubricants, greases, oils, dust, swarf and grinding agents etc.

The European funded Vegetable Oils and their Fatty Acid Esters Products (VOFAPro) project (Stautz *et al.*, 2002) studied the use of vegetable oils within the metal cleaning industry and examined the practical and technical implications for use. This study found a number of uses for vegetable oil fatty acid esters. Vegetable oil fatty acid esters are very efficient at removing mineral oil from metal surfaces, when applied as a wipe, spray or via immersion, at room temperature and without the need for any specialist equipment. Lanolin is a more difficult substance to remove. Vegetable oil fatty acid esters can remove lanolin using manual cleaning techniques, but spray and immersion methods require longer periods and dipping requires elevated temperatures to achieve the best effect. Vegetable fatty acid esters can remove mixtures of contaminants from metals, but longer cleaning times may be required than with single contaminants. Where dirt is baked on, vegetable fatty acid esters are as effective as conventional cleaning agents, though neither are very effective in this case.

Key applications of vegetable oil esters in the metal industry are in maintenance; cleaning; removal of protective coatings and protection against corrosion. As use of vegetable oil fatty acid esters leaves a slight oily residue, this can be a problem in some metal working industries where further surface treatments are to be applied, i.e. paints, and the oily film has to be removed.

VOFApro examined the impacts of use of vegetable-based ester cleaning agents in 40 factories in the metal industry in Germany (Stautz *et al.*, 2002). These included

Pirelli Cable Factory, Schwerin (Germany)

Vegetable oil esters (coconut based) were tested on soiled gear components, casings, bearings and shafts made of ordinary steel, stainless steel, brass, aluminium and cast iron. Following a nine month test period, a considerable saving in costs of solvent purchase was reported.

Heikenberg Drehtechnik GmbH

Vegetable oil esters (coconut based) were used to replace an AIII organic solvent for washing of engineering parts following complaints with skin disorders amongst the workforce. No problems were encountered and there was a significant odour reduction.

Feiler agricultural machinery repair shop, Gross-Enzesdorf (Austria).

To reduce risk to workers, organic solvent baths were replaced with vegetable oil esters (coconut based) to clean oils and fats from engines and engine parts of agricultural and horticultural machinery.

Aluminium Ranshofen Service GmbH (Austria)

Vegetable oil esters (coconut based) were used in the automobile repair workshop for dip and manual cleaning of machinery parts. Performance was as good as with previous organic solvents.

Aluminium Menziken Industries AG (Switserland)

Commercially available vegetable oil based esters cleaning solutions (Symbiol Clean) were used to replace perchloroethylene in the process of stripping viscous drawing grease, swarf and graphite from aluminium pipes and moulded profiles for aircraft, cars and machinery manufacture. A new 2-stage dipping procedure was established (lasting 10 minutes) and the residual film left by the cleaning agent was removed by evaporative drying using warm air circulation. The dipping baths have a working life of 6-8 months, after which the solvent is filtered and recycled by distillation. This approach has led to a 6-8 fold reduction in solvent demand. There was no effect on the aluminium base metal.

Thyssen Nordseewerke shipyard, Emden (Germany)

Vegetable oil esters were used for removing protective layers (Tectyl) from imported marine diesel engines, a laborious manual, time consuming process. Soaking in vegetable ester (composition not defined) enabled the coating to be simply wiped off. However, there are a number (at least 15) of different Tectyl formulations and problems were encountered with removal an another Tectyl formulations. Further work is in progress to solve the problem.

Ven der Giessen-de Noord Ship yard

Used a coconut ester paste formulation to help remove Tectyl from ship machinery. The gel was applied and left for a few hours then washed off. Although the ester product was more expensive, labour costs were cut by 80%, and solvent emissions cut.

Bloom & Voss Industrie (Germany)

A vegetable oil fatty acid ester product (Esticlean 298) is used for cleaning small metal parts, and replaces an AIII group cleaning agent. As a result, incidents of skin complaints have been reduced. The solvent is filtered and re-used and the company now routinely uses the new vegetable-based solvent.

Bus Danmark A/S

Twice a year, in addition to regular washing, Bus Danmark uses a rape methyl ester product (Raps-cleaner) to clean bus exteriors. It is sprayed on the exterior, left for 2 hours while the interior is cleaned (normally 10 minutes is sufficient) then washed off with water in an auto washer. Asphalt and bitumen is removed by this process. This product cleans better than the original aqueous cleaner, by removing asphalt etc, and the cleaning process is less arduous as no manual scrubbing is required.

Bitumen/tar removal

VOFAPro also tested vegetable oil-based products for removal of bitumen from lab equipment and from industrial signs during manufacture. In addition in the UK, Biochem Wales Ltd. are at an advanced stage with development of a number of solvents based on rapeseed oil. Current products include a water washable engine degreaser; a bitumen solvent for tarmac contractors and a tar spot remover for cars.

In general, all users appreciated the good cleaning action (which in some cases was better than that achieved by conventional methods), skin compatibility, mild smell and the additional temporary protection against corrosion afforded by vegetable-based esters.

In order to clean successfully, the type of contamination, surface purity, material compatibility and condition of the cleaning facilities have to be taken into account (Stautz *et al.*, 2002). Based on a wide range of experiences there were some problems reported with use of vegetable oil fatty acid esters which included;

Comparatively high cleaning costs

Compatibility with current cleaning facilities

Extended cleaning times (due to increased handling requirement and longer drying time)

Dealing with waste disposal/recycling issues

These problems are not insurmountable and reflect reliance on entrenched existing practices. The experiences at Pirelli also show that over an extended period, savings in costs are possible through reductions in evaporative loss etc, or through reduced labour demand as a result if increased efficiency.

Many of the smaller dip baths use filtering and recycling to add to bath life etc. However, at the end of useful life it may be possible to use the waste materials as fuel oil to minimise the problem of disposal.

7.0 Miscellaneous uses of vegetable oil based solvents

7.1 Oil spill remediation

Formulations containing methyl esters derived from vegetable oil can be used to dissolve and remove crude or fuel oil from shorelines (Von Wedell, 1998). The U.S. Environmental Protection Agency has listed a methyl soyate (soya methyl ester) bio-solvent (CytoSol[16]) on the National Contingency Plan product schedule for oil spills. It is also licensed by the state of California for shoreline use (USB[15], 2002). .

Methyl soyate can extract heavy petroleum fuel oils from shoreline habitats, mussel-encrusted breakwaters or pilings, and estuary vegetation without major disruption to these ecosystems (it has a half life

[15] The United Soybean Board (USB) comprises 62 US soybean farmers appointed by the Secretary of Agriculture to invest soybean checkoff funds.

of 4 days in such conditions). It has less environmental impacts than alternative cleaners such as petroleum derived solvents or acidic citrus oils used in cleanup operations. It has also been used successfully in sensitive mussel beds. In laboratory efficacy tests and field trials, the CytoSol bio-solvent released 50 to 98% of the oil adhering to or trapped in various shoreline sediments ranging from coral beach sand to coarse beach sand and gravel[16].

The soya methyl ester dissolves petroleum oil and decreases its viscosity by dilution and it decreases oil adhesion. In practice the ester is sprayed onto contaminated surfaces as the tide recedes and is left for two hours. Water (fresh or sea) at ambient temperature is then used under low or high pressure (depending on sensitivity of the ecosystem present) to remove the oil. The loosened oil floats in water and consolidates as globules of oil for collection by conventional boom and skimming techniques. The recovered oil can be recycled as boiler fuel. In addition, it enhances the natural biodegradation of oil residues. The efficiency of oil removal depends upon ambient temperature, the condition of the spilled oil, the volume of product applied, the time allowed for contact with the oil, and the amount of rinse water applied. This bio-solvent is now commercially available worldwide with distribution points in North America, Europe and Japan.

A problem with this technology is the ratio of solvent to oil required. Typically application rates are 0.5:1 and 1:1 with water, so likely best use is in cleaning up residual oil after the main cleaning operation, or for cleaning up relatively small spills.

Rape Methyl Ester is just as effective as soya methyl ester in removing oils. Preliminary work undertaken at Bangor University has demonstrated the ability of rape methyl ester in this respect. There is only likely to be a sporadic demand for such uses of rape methyl ester and therefore it is unlikely that UK companies would invest much research and development funding in this area, which will remain a potential niche market for use of rape methyl ester. The increasing development of the UK biodiesel industry at least means that stocks of vegetable-based esters are available which could be diverted to such use in an emergency situation. However field trials and environmental evaluations would be required under UK conditions to promote confidence in its use. In this respect there would be advantages in using material from a common defined feedstock etc to gain Environment Agency approval (based on efficacy and ecotoxicology studies) which from a logistics basis is most likely favour rape methyl ester in the UK.

7.2 Graffiti removal

A US company (Vertec) produces bio-solvents based on ethyl lactate formulations (lactate esters are also produced through reaction of an alcohol with a fatty acid). These are used in paint stripping, textile machinery cleaning and adhesive removal. A blend of maize and derived ethyl lactate and soya oil methyl esters has been developed for the purpose.

[16] www.cytoculture.com

This represents a novel though niche use for vegetable derived solvents and there appears to be no technical reason why similar products could not be developed from rape oils.

8.0 Overview of factors affecting adoption and use of vegetable-based solvents

The above overview of opportunities for vegetable-based esters identifies several factors affecting ability of rapeseed-based feedstocks to substitute for petrochemical-based feedstocks within the solvent industry.

8.1 Health and safety

Concerns have been raised in the printing industry following misconception of the risks posed by vegetable-based solvents. Evidence to date suggests vegetable based solvents are much safer overall to operators than most existing organic solvents by virtue of their lower volatility. A study of dermatological risks arising from use of vegetable oil esters was carried out by the German Berufsgenossenschaften (Institution for Statutory Accident Insurance and Prevention) in 1999, which found that handling of vegetable oil based agents could cause a slightly increased dermatological risk compared with mineral oil based agents, but no significant skin penetration was found[17]. However, because vegetable oil based cleaning agents may affect the skin, gloves[18] should be worn when handling and safety instructions followed (e.g. GMPU 1997). It is thought that the provision of gloves for use in trials of vegetable-based cleaning solvent actually caused workers concern, particularly in the printing industry, as traditionally they were not used to using gloves with conventional solvents despite the risks (see below).

Long chain methyl esters derived from vegetable oils have been demonstrated to be very mild to the human skin and eye. Tests conducted by Procter & Gamble on human subjects, found that virtually no irritation was observed for C8-C10, C12-C14 and C16-C18 methyl esters applied to the skin. Test of C16-C18 (palm methyl ester) on 68 human subjects did not induce skin sensitisation (P&G unpublished data).

8.1.2 Impact of current solvents on occupational health

There is contention over the impact of current VOC solvents on the health of users. Trade Unions and Occupational Health Workers have expressed concern at what is seen as a lack of recognition of the serious damage, which it is claimed, may occur to the brain and nervous system from workplace exposure to VOC solvents[19]. VOC induced neurotoxicity is still not recognised as an occupational problem in the UK.

[17] Information obtained from http://www.hvbg.de/e/bia/pro/pro1/pr9187.html
[18] In practice protective gloves made of nitrile rubber have proved the best type and should be replaced regularly. (Stautz, 2002)
[19] Hilda Palmer, Greater Manchester Hazards Centre

However in Germany, Denmark, other Scandinavian countries and the US, the condition has been accepted as related to solvent use and compensation has been awarded. In Denmark, between 1980 and 1990, 596 printers were compensated for brain damage associated with use of organic solvents.

Other problems arising from exposure to organic solvents include liver damage, kidney damage and mild and reversible effects on the nervous system, degreasing of the skin and dermatitis (GPMU, 1997). The high level of evaporation associated with conventional organic solvents means that users such as print workers are exposed to solvents for extended periods which are inhaled, the highest risk being during the print cleaning operation.

High boiling point solvents have been developed in response to pressure to reduce VOC emissions and these products reduce inhalation exposure and risks to workers. German data indicates that workers could typically inhale 5.5 litres of vapour in a day from an AI class solvent, 1.7 litres from an AII class solvent, 0.025 litres from a high boiling point solvent and 0.007 litres form a vegetable oil based cleaning agent (Coates Lorilleaux, personal communication). Despite the above figures, high boiling point solvents are not considered to be as safe to 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 11), which highlights that one of the key benefits of using vegetable-based solvents is their low risk to operators.

In Germany, in the offset printing industry, a voluntary agreement for solvent substitution agreed between manufacturers, solvent suppliers, trade associations and users, was introduced in 1995 and led to a 50% reduction in VOC emissions. The current aim is to half this again. The UK Health and Safety Executive is also trying to promote a similar agreement. Although it has no basis in law, the aim is to reduce the use of low boiling point solvents and encourage substitution, by providing health and safety inspectors with benchmark standards for good practice in ink and solvent use. Some of the key agreements include:

? All new printing machines must be compatible with solvents having a flash point above 55ºC (Type AIII).

? Cleaning solvents with flash points less than 21ºC (Type AI) should not be used for routine wash operations.

? All in the industry should work to promote use of alternatives to organic solvents, including higher boiling point solvents.

? Solvents in ‘blanket revivers’ and ink stripping formulations will not contain chlorinated solvents, terpenes, n-hexane, secondary amines or amides.

? The percentage of isopropyl alcohol or low boiling point organic solvent used in fount solution will be reduced to 5-10%

This voluntary agreement has already been given support by a number of print federations and associations, the print Trade Union (GMPU) and Newspaper Publishers Association. This could prove to be an important driver in the print industry that traditionally has been reluctant to change. The HSE has also started to build a dossier on impacts of organic solvent use on the central nervous system (which remains a contentious issue in the industry) in support of potential court cases. Any move in this direction is likely to push the printing industry into rapid action and uptake of the voluntary agreement.

Table 11. Hierarchy of safety to operators based on exposure to solvents used in the print cleaning industry

Least risk to operators	Vegetable based cleaning agents (VCA's)
	Synthetic esters (mineral based)
	Mixtures of VCA's/high boiling point solvents (HBS)
	High boiling point solvents (HBS)
	Mixtures of VCA/HBS
	Mixtures of VCA/terpenes
	Aromatic free solvents
	Terpenes
Highest risk to operators	Traditional petroleum based volatile products (kerosene or white spirit)

Source: SUBSPRINT

8.2 Changes to working practice

Vegetable derived based solvents may need somewhat different work place practices than traditional solvent materials, which can lead to reluctance to change. However, such barriers can be overcome through education in new working practices designed to optimise performance and efficiency of use of vegetable-based solvents

There may be cost barriers to implementing changes in working practices. For example a need to replace rubber based seals and washers etc where methyl esters are used, and a need to shut down while replacements are made. Original Equipment Manufacturers (OEM's) also need to support the use of new products, to avoid negating warranties etc, particularly where expensive machinery is involved. However, any threat of actions in relation to compensation for impacts on workers health could easily outweigh such costs.

The costs of change and ensuring that information gets to the appropriate decision makers to support change to vegetable-based solvent are a particular problem for small and medium sized enterprises (which represents the majority of businesses in the UK printing sector). For such enterprises, finding suppliers, obtaining samples for trial demonstrations, and undertaking work to optimise use and efficiency of new products is much more difficult.

The physical characteristics of vegetable-oil based solvents e.g. high viscosity means that machinery or operating procedures have to be modified to deal with the new product.

8.3 Costs

Based on information available to the authors, the cost of producing biodiesel in the UK as a raw bulk product is estimated at between £0.42 and £0.46 per litre (£0.47/kg and £0.52/kg) depending on efficiency of esterification and variation in cost of feedstock (the above figures assume an average price of £149/tonne (± £2.7) for oilseed rape over the last three seasons. These figures are in a similar range to those for soy-based methyl-esters in the USA, which in turn are comparable with the cost of other organic solvents used in the US market (Table 12). However, cost is very sensitive to feedstock prices, since raw material cost account for 76-79% of the final cost. Efficiency of oil extraction and transesterification will also affect final cost. Formulation costs, packaging and marketing etc will add to these basic raw material costs.

The choice of alcohol used in producing the ester will also have an impact on price, methanol is commonly used because it is relatively cheap compared to other alcohols (Table 13). Methanol has the added advantage in that it results in an ester with relatively low viscosity. At current prices, rape methyl ester has a price advantage over other vegetable-derived esters (Varn Products, personal communication).

Table 12. Typical cost of solvents in the US and likely price range for UK produced rape methyl ester

Solvent	Price
Rape Methyl Ester	£0.47/kg-£0.52/kg*
Soya Methyl Ester	£0.4/kg-£0.6/kg †
N-Methyl Pyrrolidone	£2/kg-£2.4/kg †
d-Limonene	£0.5/kg †
Methylene Chloride	£0.4/kg †
Triclhoroethylene	£0.9/kg †
Perchloroethylene	£0.5/kg †
Methyl Ethyl Ketone	£0.6/kg †
Typical hydrocarbon solvent	£0.4-0.46/kg

*Estimated raw material cost in the UK.

† Data from United Soybean Board 2002

Table 13. Comparative cost of alcohols (based on 5000 litre purchase)

Alcohol	£/tonne (purity %)
Methanol	250 (99.9)
Ethanol	520 (99.9)
Propanol	500 (99.8)

Source: Alcohols Ltd (www.alcohols.co.uk)

In the printing industry, both vegetable based products and the newer low boiling point hydrocarbons are more expensive than the conventional organic solvents typically used in the industry (i.e. type AII solvents) (Table 14). However, as detailed in this report, there is increasing legislative pressure and industry agreements to phase out commonly used volatile hydrocarbon solvents which is likely to force printers to use these more expensive products. Factors such as rates of use also need to be taken into consideration. In the case of both vegetable based products and low boiling point hydrocarbon solvents, less solvent is actually used during cleaning (up to 80% less), so overall costs to the industry should be reduced. Based on data obtained from industry (Table 14), vegetable based print wash cleaners are between 22 and 95% more expensive than high boiling point hydrocarbon cleaners. However, vegetable-based washes (like Vegra's rapid wash) are commonly applied as an emulsion in water (as a 50:50 mix). Conventional solvent print wash formulations are commonly applied as an emulsified solution with water to remove paper waste, followed by a neat solution to remove any ink contamination. Overall use of vegetable-based cleaning agents is therefore likely to be lower than for high boiling point organic cleaners, but unfortunately there is currently little information available in the printing industry to quantify this. The SUBSPRINT (1997) project reported that after operator training, the volume of vegetable-derived solvent used in printing was a third to a quarter less than that used with traditional organic solvents, but comparisons with high boiling point solvents were not made. US experience was that additional time required to remove the oil film left after cleaning added to the overall costs (US EPA 1997), but this was not balanced against savings in solvent cost.

8.3.1 Consumption/bath lives and costs of disposal

This above problem is not confined to the printing industry, in many industries in the metal cleaning sector information on consumption of cleaning agents is not well recorded (Stautz *et al.* 2002). High prices for alternative vegetable-derived products may put off purchasers, but consideration of impacts on total costs, particularly over a protracted period can reveal significant savings. In the VOFApro project (Stautz *et al.* 2002), reported that use of vegetable oil ester cleaning agents at a cable works significantly extended cleaning bath life over that achieved with conventional organic solvent (an AIII group solvent). This resulted in savings in cost of hazardous waste disposal and solvent use was significantly reduced from 800 to 20 litres per annum resulted in a 95% cost saving. In the same project, in a shipyard using solvents for maintenance applications, solvent use was reduced from 400 to 60 litres per annum by using vegetable based esters, saving up to two thirds on previous costs. In the printing industry, the cost of recycling vegetable oil esters is reportedly costly when compared to high boiling aliphatic hydrocarbons[20]. This arises primarily from the residues of inks, which contain heavy metals. Development of solutions to the problem may

[20] Christopher Searle (Hydro-dynamic Products).

Table 14. Comparison of properties and costs of commercially available vegetable based and organic high-boiling point (AIII group) print washes

(costs based on 25 litre batches (typical for deliveries to small printers in the UK))

Product/Solvent Group (see Table 9)		**Boiling Point (^{o}C)**	**Flash Point (^{o}C)**	**Vapour Pressure (kPa @ 20^{o}C)**	**Cost per litre**
Vegetable -based					
Binol Vegeol CEG	A mix of alkyl esters of coconut, palm-kernel and rape-seed with vegetable based emulsifiers (25 - 50% rapeseed oil).	210	> 150	Negligible under normal conditions	£2.70
VEGRA Rapidwash 220 224	38% Rapeseed oil, 38% rapeseed fatty acid ester and 10% mineral oil	> 260	135	< 0.01	£2.87
AII Group					
HDP; Eagle Blanket & Roller Wash	Naptha (petroleum), & light aromatics	150 - 210	40	0.19	£0.68
AIII Group (high boiling point)					
Ultrachem Prima Autowash FX	Naptha (petroleum)	175 - 194	> 62	0.1	£1.58
Ultrachem Prima Autowash GX	Naptha (petroleum) & heavy aromatics	180 - 217	62	0.1	£1.47
Ultrachem PrimaLogic Autowash 50:50	Petroleum distillates	220 - 315	> 62	< 0.01	£2.20

currently be limited by the relatively small volumes involved. Wider adoption of the technology could result in less costly solutions for disposal, for example through incineration. Work in the Netherlands examined the potential for recovery of rapeseed and coconut esters from solvent emulsions by vacuum distillation[11] with high recoveries (91-94%) and only marginal effect on composition, but further work is required to refine the method.

Clearly taking into account all the relevant costs associated with disposal, rates of use and working lifetime may help outweigh the initial high costs of vegetable-based solvents at the time of purchase, but many industries will need persuasive data and examples to encourage change.

8.4 Longevity of vegetable-based cleaning agents

Concerns over the long term stability of vegetable based solvents have been raised. Gumming-up (polymerisation) of vegetable esters has been examined by Vegra Ltd (personal communication). After 5 months storage at room temperature, rape methyl ester and coco iso-octyl ester (used in commercial solvent formulations) both alone and in mixtures (with other hydrocarbon solvents) showed no evidence of build up of gum polymers. This is as expected as oils like rape, soya, coconut and palm can be stored in sealed containers for longer than 5 months without deterioration. However, when formulated with drying agents, addition of cotton waste (as used in cleaning rags) to rape methyl ester does stimulate formation of gum polymers, which could affect the ability to recycle such solvents.

8.5 Competitor feedstocks to rape

Raw oil feedstock price can be a barrier to the development of bio-solvents in the absence of other overriding pressures to change working practices. Given that there is likely to be competition between esters derived from rape, soya and coconut in many of the markets highlighted in this report, the competitiveness of feedstock price and exchange rates are important variables which, all other factors being equal, could affecting the ability of rape-based materials to compete in the market. As far as manufacturers of vegetable-based solvents are concerned, the only advantage rape methyl ester has over other vegetable esters is its price (Chris Searle, Hydrodynamic Products personal communication). The lower the exchange rate with respect to other currencies, the more competitive UK rape-based products would be in the market place.

There has been some debate in the German printing industry over preference for coconut based esters because of their higher self ignition point (136ºC for rape methyl ester v 168ºC for coco fatty acid iso-octylester). The flash and smoke points of rape methyl ester and coconut fatty acid esters are very similar (flash point of 192ºC for rape methyl ester v 184ºC for coconut iso-octanyl ester, and smoke point of 118ºC for rape methyl ester v 121ºC for coconut iso-octanyl ester[21]) and these do not differ sufficiently to warrant separation on this basis alone. However, problems arise where vegetable esters are mixed with cotton residues (for example from wipes). Cotton acts as a substrate in the presence of oxygen to facilitate oxidation of the vegetable ester leading to spontaneous ignition under certain extreme circumstances. Due to higher levels of unsaturation, this is a potentially greater problem for rape-based products. Formulation with drying agents and other additives commonly lowers the flash point increasing the risks of ignition. However, Tests by Vigra[21], on formulated print wash solvents mixed with cotton residues, found no difference in flash and smoke points between products based on rape methyl ester and coconut methyl ester (flash point ranged from 120-122ºC and smoke point was 50ºC in both cases for products based on a) 38% rape methyl ester + 38% rape oil and b) 50% coconut iso-octyl ester). Clearly the presence of cotton residues significantly increases the risk of combustion, by lowering the flash and smoke point. However, the flash point of rape methyl ester formulations mixed with cotton residues is still regarded as high (>100ºC) and expert opinion suggests that there should be no problem with self ignition under normal working conditions. It is recommended working practice in the printing industry that when using vegetable ester print washes, soiled wipe rags are stored in a lidded metal container to reduce fire risk.

Solvents for printing inks are commercially available based on rape, coconut and soya fatty acid esters and there appears to be no technical barrier to rape base products in this market in terms of performance or removal for recycling.

The problem of unsaturation in rape oils and its impact on long-term stability is cited as a reason why most commercially available vegetable-based metal cleaners use coconut esters. This arises from the use of dip baths, where the cleaning solution is filtered and recycled leading to extended bath lives. For example, Esticlean 298, based on a 70-90% coconut ester fomulation, has been used in work bench recycling cleaners for at least nine months without significant deterioration in efficacy (Stautz *et al.*, 2002). There appear to be no comparative studies to validate whether rape-based esters could have a role in the dip solvent market. By their very nature, these markets tend to use relatively conservative amounts of solvent through recycling which keeps costs down (8.3.1). There would be no such limitations in use of rape-based esters in one-off cleaning operations, such as those involved in vehicle cleaning etc. A few commercial metal cleaning formulations based on rape oils are available e.g. Rumanol Bio (>90% rape methyl ester).

The predominance of C18 fatty acid chains in rape-derived oils means that compared to coconut with predominantly C8 to C16 chains, formulation of esters with higher alcohols is more difficult without significantly increasing viscosity, which could limit the opportunities for specialist uses.

Impacts on machinery components can also influence product choice. The problem of swelling of rubber caused by fatty acid esters has been highlighted previously. However all solvents affect rubber and terpenes (i.e. white spirit, commonly used in print cleaning) cause most swelling. Silicon and butyl rubber

[21] Unpublished tests for Vegra Ltd by Institut Für naturwissenschaftlich-technische Diense GmbH

are actually affected more by traditional hydrocarbon solvents than vegetable esters, conversely neoprene is most strongly affected by vegetable esters. Of the fatty acid esters, methyl esters cause most swelling and those based on octyl alcohol the least. Octyl esters are most commonly represented by coconut-based esters. However recent experiences in the printing industry suggest that with current solvent formulations formulations any swelling of rubber materials caused by rape methyl ester is within design limits and does not affect the printing process.

Most vegetable oil esters can dissolve binders, adhesives and resins which could affect applications to machinery. Alkyds, chlorinated rubber and hexa-methoxy-methyl melamine are known to be subject to solvation by vegetable esters. Methyl and ethyl esters can also solvate phenolic and epoxy resins with low molecular weights. Nitrocellulose is particularly susceptible to vegetable esters. It is for this reason that machinery manufacturers need to be consulted when considering any changes to solvent use. The formulation and types of ester involved will significantly influence its solvating properties. Much of the relevant information is not readily accessible in the public domain, but should be available through solvent and machinery manufacturers.

9.0 Discussion and conclusions

Likely markets for growth in use of rape-based esters

Vegetable oil derived fatty acid esters have a number of characteristics which suit their use in the solvent sector. Rape methyl ester has a high solvating capacity, due to its small ester group, but on the downside, the long carbon chain length (predominantly C18) leads to relatively high viscosity and the high levels of unsaturation restricts the natural life of the oil through oxidative degradation. The latter is only of concern where long term recycling and re-use are considerations (i.e. in cleaning dip baths).

Of the solvent markets available, there appears to be limited opportunity for use of rape fatty acid esters in the surface coating sector, which is increasingly converting to use of water-based formulations. Other vegetable oils predominate in this sector because of technical advantages in terms of drying time or ability to cost effectively produce alkyl resins.

The second most important industrial user of solvents in the UK is the printing industry, both in ink formulations and in wash down solutions. Progress has been made in developing ink formulations and significant volumes are produced and used in the UK and Northern Europe. Use in the UK probably accounts for no more than 20% of the market. Vegetable oils have been used for some time in the ink sector with no reported problems and few technical obstacles or barriers exist to further adoption. Rape methyl ester is commonly used in ink formulations. Significant market penetration has been achieved in some sectors, but is limited by significant drivers to change. There is no significant additional cost to users, though as the US experience, described earlier, shows, small difference in price significantly affects consumption trends in favour of the cheaper option in the absence of other drivers.

There is a significant opportunity for use of rape methyl ester in print cleaning solvents. There are a number of misconceptions in the industry that currently prevents greater uptake. In addition, the advent of high boiling point solvents as a solution to problems with VOC emissions is distracting attention from what may be greater benefits from use of vegetable derived cleaning agents. Benefits in terms of the working environment for print operators and reduced use of solvent comes at a cost, in terms of higher initial price and increased labour in the cleaning process. Fears over problems with swelling of rubber components appear to be unfounded with current formulation, and there appears to be no greater fire risk with rape than coconut based products. Further education and demonstration is required to try and overcome some of the current misconceptions and to prove the technology to the industry. There is also a need to prove the worth of vegetable esters against the recently introduced hydrocarbon based High Boiling Point Solvents (AIII materials). The printing industry has adopted these materials to comply with increasing legislative and health and safety pressures, as they generally involve little change to current working practice. However, to date there have been few conclusive studies to quantify the cost benefits against those of vegetable oil based technologies. The view of the health and safety industry is that vegetable based esters are safer to the working environment than High Boiling Point Solvents, but vegetable- based solvents will have to prove their worth in this respect to encourage further uptake.

Of the remaining industrial sectors using solvents, there are opportunities for use of rape methyl ester products in the metal cleaning sector, but much of the industry relies on recycling and re-use of solvent materials which means there is a preference for coconut based products with their greater oxidative stability. Anti-oxidants can be formulated with rape-based esters, but this adds to costs, and the additives may increase problems with recycling or may negate the environmental benefits being sought by use of such renewable raw materials. The key opportunities for rape derived fatty acid esters as metal cleaners is in one-off cleaning operations, tar and bitumen removal and in polishing operations for vehicles, however the demand in this sector is likely to be limited.

Other niche areas of interest include development of treatments for oil spill clean up, and formulations for removal of graffiti. Rape methyl ester has significant technical potential in both these areas, but the demand in the former case is likely to be sporadic, and further work would be required to ensure no environmental damage would result form the use of the solvent itself. In the latter case there would be a small but ongoing demand for solvent. Further work is required to develop suitable, effective formulations and working practices in the UK.

Drivers for change

Currently vegetable derived solvents do not currently figure in the business plans of the major petrochemical solvent manufacturers. A barrier to interest and development of bio-solvents is seen as the large initial capital investment requirement. Most development to date in this sector has been undertaken by small companies and specialist solvent suppliers working in conjunction with users. This is an important relationship as the previous sections have shown that different problems and materials may require quite different formulations of fatty acid esters, either to prevent damage to equipment, or to ensure the most efficient cleaning. It is difficult to include larger companies in such developmental work unless significant returns are envisaged.

There is plenty of spare manufacturing capacity within the chemical industry to undertake esterification/transesterification of vegetable oils in the UK. The development of a biofuel industry in the UK, even though currently based on used vegetable oil, has also created an increased demand for such facilities, and new-build is planned in both the North East and East of the UK which could provide additional capacity. This increased capacity could help reduce costs of production and make rape methyl ester based products more competitive. It is likely that these ventures, as well as smaller entrepreneurs in the chemical industry, could take advantage and develop a vegetable based solvent market, given the appropriate drivers for change.

Organisations like the British Coating Federation (BCF) see few driving forces currently acting to encourage the greater use of bio-solvents in the surface coatings sector. Factors such as cost, efficiency, fitness for use, and the changes that are likely to be required in manufacturing processes etc. are seen as barriers to change. However practical results from the VOFApro project, reported in earlier sections, show that there can be significant savings in solvent costs and labour costs in some systems. However, the opportunities for rape-based esters to achieve such savings are limited.

Legislation and cost of non-compliance

One key area that would significantly increase the rate of change is legislation. Implementation of measures based upon international agreements and national legislation to reduce VOC's and solvent use to protect the environment and protect workers health have been significant drivers towards market adoption of solvent reduction schemes and new technology and this can help overcome non-technical financial barriers.

In other European countries (e.g. Austria, Denmark, Germany, Sweden) positive legislation has been implemented, designed to encouraging the substitution of hazardous solvents with vegetable based alternatives. In Denmark, in 1994 the Environmental Protection Agency of Copenhagen ordered offset printing companies to change to non-volatile cleaning agents. Germany has also implemented legislation restricting the use of volatile cleaning agents. As a result solvent replacement has been more rapid in Scandinavian countries and Germany.

The British Printing Industry Federation (BPIF) in the past has lobbied to exempt as much of the printing industry as possible from environmental legislation to protect what it sees as the large number of small printers form the burden of costs of compliance. The BPIF managed to get the threshold of solvent use for compliance with the 1990 Environmental Protection Act raised from 5 to 25 tonnes per year for small and medium sized companies, which exempted up to 95% of the UK printing industry from Local Authority Air Pollution Control regimes. However, as VOC emissions decline from other industries and other significant

VOC emission sources like road transport, there will be increasing pressure put on solvent users to help the government meet its targets for VOC reduction.

Voluntary agreements between parties can also stimulate change. These can include agreements on chemical criteria for products used in industry, and procedures for testing in relation to health and technical aspects. In Germany in 1995, printing press manufacturers, solvent supply companies and the Association of Printing Ink Manufacturers reached an agreement on chemical criteria for the cleaning agents to be used in the German printing industry (Stautz, 2002). Hopefully the current agreement being brokered by the UK Health and Safety Executive will reduce the use of low boiling point solvents and encourage substitution with vegetable based products where economically viable, by providing health and safety inspectors with benchmark standards for good practice in ink and solvent use. The EU Solvent Directive and voluntary agreements in place or in development means that all new presses must be capable of use with AIII solvents (i.e. flash point >55ºC), which will facilitate changeover in new developments.

The US Federal Government has opted for legislation to ensure government stationary is printed using vegetable based inks and cleaning solution and has significantly increased market use of such products. The UK Government is under increasing pressure to lead by example in is procurement policies in a range of sectors. The UK Government has a large dedicated printer in the shape of Her Majesties Stationary Office (HMSO). The HMSO has trialled vegetable-based products as cleaning agents and favoured a part vegetable oil formulation, but further extended trials are planned. If successful, the fact that such technology is adopted should be advertised on Government publications.

Health and Safety

Workers exposed to organic solvent vapours commonly complain of headaches and other ailments. Substitution of vegetable solvents for fossil based materials should help reduce worker absenteeism and reduce costs to the workplace. Substitution with less volatile materials should also reduce Employers Liability Insurance, and some insurance companies, particularly in Germany, are already insisting on such substitutions. Regulations (Hazard Information Packaging for Supply) in development to increase use of risk and hazard warnings on packaging will raise awareness of the potential risk of materials previously considered ‘safe’ in the workplace. In addition, moves by the Health and Safety Executive to carrying out an evaluation of the relationship between solvents and neurotoxicity is also likely to increase awareness of the issues and risks both in industries using solvents and in their associated insurance providers.

Vegetable-based solvents do have some potential health impacts. Skin and mucous membranes can be irritated (Bartlett, 2004) but these are relatively minor and can be overcome by wearing gloves during use. In addition, more physical effort may also be required to remove oil films left after cleaning, and care is required to avoid spillage and the risk of slippage.

The inherently low volatility of predominantly vegetable-ester formulated products should reduce fire and explosion risks to workers and this should be reflected in insurance premiums. Costs of storage and associated paperwork for storage of hazardous materials should also be lessened. The lower volatility of vegetable esters also reduces the need for installation of expensive ventilation systems in closed environments. The only down side in relation to fire risk is with unsaturated vegetable esters, where contamination with cotton or other flammable materials can lower the ignition point. This is a risk in areas like printing where re-usable cotton wipes are used. However, even in this situation rape methyl ester solvents are no worse than conventional hydrocarbon solvents and it is expected that they should pose no problem under normal working conditions. However for safety reasons discarded wipes, or those awaiting recycling, should be stored in sealed containers.

Other costs savings

The reduction in volumes of solvent used in the metal cleaning industry should reduce costs of disposal for manufacturers opting to substitute with vegetable derived esters which should help cover increased purchase costs, in some cases resulting in significant savings for use in dip baths etc, but this application does not suit rape methyl ester formulations.

Disposal and recycling

Given that solvents based on vegetable esters do not evaporate, this can mean that they become a disposal problem at the end of their useful lifespan. This is an area of current research and development and vacuum distillation techniques have been evaluated as a means of recycling inks etc. In other cases, collection and recycling schemes have not been established so materials are currently disposed of as waste, which is becoming increasingly expensive. Depending on the contaminants, vegetable esters could be used as fuels at the site of use, or through collection schemes.

Likely impacts of renewable solvents on future demand for oilseed rape

Current oilseed rape production in the UK over the last 5 years (1998-2002) has averaged 1.4 m tonnes (± 0.11 m tonne)[22] of which between 73 and 379 thousand tonnes were produced on set-aside land for industrial end uses. Current market forecasts suggest that renewable 'green' solvents could account for 12.5% of EU bio-solvent market by 2010. This equates to a demand for approximately 250,000 tonnes of solvent.

Under current best practice, and efficiency of extraction, a tonne of rapeseed yields 0.415 tonne of rape methyl ester (Turley and Ceddia, 2003). Refining costs for industrial use are low, as only degumming and neutralising (removal of any free fatty acids) are required and for food use expensive deodorising is required.

Based on the above levels of efficiency, approximately 602,500 tonnes of rapeseed (equivalent to c. 172,000 ha of OSR @ 3.5 t/ha) would be required in the EU to meet a demand for 250,000 tonnes of 'green' renewable solvents derived entirely from rape oil. However, 'green' solvents derived from materials

[22] Defra Statistics (provisional data for 2002)

other than rape are likely to account for significant proportions of this market where they show particular technical or cost advantages.

Given that the 52,000 tonne UK market for printing inks is already relatively well represented by vegetable-based inks, the potential for growth in this sector is limited compared to the potential for use in print cleaning solvents, which represents a market currently of c. 40,000 tonnes in the UK. Replacing all of this with rape methyl ester based solvents would require c. 96,000 tonnes of rapeseed, equivalent to c. 27,500 ha of UK oilseed rape which could be easily accommodated within current farm practices. However, it is likely that only a fraction of this would be achieved in practice, given that there are competing synthetic products and rape methyl ester is commonly be formulated with other materials, including synthetic compounds in commercial solvent formulations. Demand in the metal cleaning sector is difficult to quantify, but is likely to represent only a relatively small proportion of current solvent use for the reasons outlined above. Other niche markets such as oil spill remediation will create sporadic demand and there could be a small additional demand for use in graffiti removal. The volumes directed towards print wash solvents currently appear to be the most promising outlet.

Close working of solvent manufacturers, users and machinery manufacturers

Most problems in printing industry have been overcome with perseverance to match vegetable fatty acid products to machines and by trial and error testing to optimise the system. A close working relationships with all involve din the supply chain is essential to successful uptake and development.

Summary of benefits of vegetable ester solvents

A summary of the key technical advantages that vegetable based esters offer in the solvent market is provided in Table 15.

All of the above costs and benefits need to be taken into consideration and weighed against the additional costs of vegetable derived products to build a persuasive case for change, particularly in the print wash sector which could lead to an ongoing demand for around 50,000 tonnes of rape oil per annum in the UK if at least half of the print wash solvent use was derived from rape based esters. Niche markets in other sectors could add to this demand.

Table 15. Summary of key advantages of vegetable oils for use in solvent markets

Health and safety at work and environmental impacts	**Application and technology**	**Profitability**
Elimination of polluting emissions	Good solvating/cleaning performance in many sectors	Reduced consumption
Reduced risk to operatives	Temporary corrosion protection	Extended cleaning bath life
Reduced odour	High flash point (reduced fire/explosion risk)	Reduction in costs for issues connected to fire and explosion risk (i.e. storage and insurance etc)
Reduced hazard risk	Use of defined fatty-acid esters rather than complexity found with mineral oil compounds	Reduction in need for safety apparatus and fume extraction
Biodegradable	Tailor made products to suit applications	Image advantage

Source: Modified from original developed by Stautz *et al.*, 2002

10.0 Recommendations for further work

There is a need for ongoing demonstrations with industry, particularly the printing industry to dispel existing misconceptions and facilitate confidence in the use of vegetable fatty-acid based ester solvents. Information in support of use of vegetable based cleaning agents in the printing industry have been produced (SUBSPRINT, 1996a; US EPA 1997), there needs to be further efforts to build on these initiatives in the UK to help encourage change. The US printing industry has received significant support with information and training aids from the US Environmental Protection Agency (EPA). These have been developed from investment in research and development to providing information to help companies substitute for conventional practices. A similar approach is required in the UK to raise industry awareness and cope with change. To this end, building on this current review, Defra has just embarked on a demonstration project within the printing industry to demonstrate the efficacy of vegetable derived print washes based on rape derived oils.

A real problem with any technology transfer programme to the printing industry will be getting information to the large number of small enterprises involved in the industry. This would be best achieved through dialogue with the Printing Industry Federation and Print Unions to agree a suitable approach.

To support change there is a need to generate information on the long term cost benefits of using vegetable derived fatty acid esters, especially in competition with high boiling point solvents. Both approaches can help meet targets for Volatile Organic Compound reduction, but there could be additional benefits from use of vegetable derived esters for operators and in rates of use which need to be quantified.

There is a need to study disposal/recycling options for vegetable fatty acid esters to optimise both the life cycle analysis, and to minimise on costs of disposal for users.

Currently it is difficult to get comparative information on the chemical properties of fatty acid esters, much of the information is held by industry and is not public available. Access to such information would help in the development of new uses and in development of formulations, which is likely to form an important part of the industry to ensure solvents are compatible with a wide range of machinery and applications.

A real drive to development would be positive pressure to adopt the technology. Government and other organisations with environmental concerns need to be persuaded to demand less polluting technologies through their procurement policies driven by positive supporting information on the case for change.

The use of rape methyl ester as an oil spill clean up agent is an interesting niche. Some ecotoxicological and field studies are required to provide information in support of its wider development for use in any emergency situation.

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