An Investigation Of Methods To Reduce Solvent Emissions, For The Printing Of Flexible Packaging Substrates .

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ABSTRACT

The flexographic and gravure printing houses are the major suppliers of flexible packaging substrates, which are principally based on solventbased ink systems. The Environment Protection Authority (E.P.A) has issued a Code of Practice, in 1990, that targets the Victorian flexographic and gravure industry, with guidelines that suggest an 80% reduction in solvent emissions by the year 2000.

This thesis investigates the technologies available to the flexographic and gravure industries to comply with this Code of Practice.

Technologies existing for the elimination of emissions such as incineration, biofiltration and solvent recovery, once considered too expensive, are now beginning to be considered very seriously in the flexographic and gravure industries.

Methods which prevent emissions, such as the developing ink technologies of waterbased and ultra violet curing inks are growing at a rapid rate and will be compared for the advantages and disadvantages they present as a replacement to the traditional solventbased system. Logical methods to achieve cleaner production, at a minimum cost, are also investigated.

Finally one of the preventative methods has been studied in greater detail by an experimental case study. The waterbased ink system has been compared to the solventbased ink system for the printing of a typical flexible packaging substrate, the disadvantages and advantages have been analysed, and conclusions drawn on the viabilty of the use of waterbased inks as a solution to emission problems.

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DEFINITIONS/ABBREVIATIONS:

Acrylic - A general chemical term for a particular family of thermoplastic resins based on acrylic acid and its derivatives.

C_{CRIT} - Critical concentration

Cat. - Catalyst

CFCs - Chloro flouro carbons

CO - Carbon monoxide

CO_2 - Carbon dioxide

Concentration - An expression of the content of a solution

Emulsion - A type of mixture where two or more immiscible liquids are held together in homogeneous mixture by the action of a third agent (the emulsifying agent).

EPA - Environment Protection Authority

FDA - Food and Drug Authority of the United states government

Flexo-Flexographic

Gloss - The ability of a surface to reflect light.

Glossmeter - An instrument used to measure the gloss intensity (Gardner glossmeter).

H_2 - Hydrogen

H_2O - Water

HC - Hydrocarbon

KWh/m^3 - Kilo watts hour per meter cubed

LEL - Lower Explosive Limit

MEK - Methyl Ethyl Ketone

MIBK - Methyl Isobutyl Ketone

MnO_2 - Manganese dioxide

mg/l - Milligram per litre

NO - Nitric Oxide

NO_X - Nitrogen oxides

NO_2 - Nitrogen Dioxide

Nitrocellulose - A film former widely used in flexographic and gravure inks; nitrated cellulose.

O_2 - Oxygen

O_3 - Ozone

pH value - The degree of acidity or alkalinity measured on the scale from 0-14, with 7 has the neutral point. 0-7 is acid, from 7-14 is alkaline.

Pigment - Insoluble colour matter used in finely divided form to impart colour to inks, paints, coatings, etc..

Plasticisers - Materials, usually liquid but sometimes solid, that impart flexibility to an ink or coating.

ppm - Parts per million

Polyamide - Polymers containing amide groups

Shade - A colour produced by pigment or dye.

SO_2 - Sulphur dioxide

Solids content - The percentage of non volatile matter of which a compound or mixture is composed, based on weight of the entire mixture.

Substrate - A foundation material on the surface of which a substance may be deposited for a purpose such as printing, coating, etc.

Strength - Intensity of colour when printed.

Transparent - The unobstructed transmission of light; clear.

UV - Ultra violet - Radiation in the 315 to 400 millimicron range.

Viscosity - Resistance to flow.

VOC - Volatile Organic Compounds

Zahn cup - A device for measuring viscosity.

INTRODUCTION

Photochemical smog is one of modern societies major environmental concerns (Streeton, 1991). Photochemical pollution occurs mainly in urban areas as the product of several interacting factors. These include high densities of cars, trucks and other combustion sources producing nitrogen oxides (NO_x) in large quantities, plentiful sunlight, an atmosphere contaminated with hydrocarbon compounds, and a local climate which tends to concentrate the combustion products in the area rather than dispersing them rapidly.

This form of pollution presents by far the most significant threat to the air environment in Australia and more particularly in Victoria.

The primary pollutant involved is nitric - oxide (NO), which is derived directly from high temperature oxidative combustion processes such as occur in industry, cars, and power stations. Whilst nitric oxide itself appears to present no threat to human health, it serves as a basis for the production of secondary pollutants such as nitrogen dioxide (NO_2) and ozone (O_3). Other oxides of nitrogen are also produced in smaller quantities in combustion reactions.

There are also a number of natural sources of nitrogen oxides, including emissions from soils during, for example, biological nitrification-denitrification processes; nitrogen fixation by lightning ; and emissions from naturally occurring biomass burning. These sources vary considerably in proportion. They are unlikely to be of significance in highly polluted urban areas, but may well be important in rural areas.

Nitrogen oxides and hydrocarbons can accumulate and reach high concentrations, especially where continuous emissions from a stream of motor vehicles are combined with low wind speeds and limited vertical mixing in the meteorological phenomenon known as a 'temperature inversion' (Streeton, 1991). Under the influence of the ultraviolet component of sunlight, complex inter-related chemical reactions occurring over some hours produce a range of secondary compounds. Among the end-products are some highly reactive and potentially toxic substances. However, nitrogen dioxide and ozone predominate, and these two gases are regarded as the best indicators of photochemical pollution (Streeton, 1991). The environmental effects brought about by all these end-products may be compounded by the presence of hydrocarbons, all these elements combining to produce what has become known as 'photochemical smog' (Streeton, 1991).

In cleaner air (not urban air), where the only hydrocarbons present are those naturally produced, the photochemical process that can occur involves a series of chemical reactions that are generally well understood. For example, the nitric oxide produced by the morning peak traffic is converted over several hours to nitrogen dioxide. In the presence of sunlight and oxygen, a series of chemical reactions can then take place:(Strauss & Mainwaring, 1984)

1.0 $NO_2 + hv \rightarrow NO + O$
where hv is sunlight energy and O is atomic oxygen.

2.0 $O + O_2 + M \rightarrow O_3$
where M is any passive non-reacting substance such as nitrogen or even another oxygen molecule.

3.0 $NO + O_3 \rightarrow NO_2 + O_2$

Thus reactions 1 and 2 lead to the production of ozone, and reaction three to its destruction. The net effect of the three reactions in relatively clean air is that the ozone produced is degraded by nitric oxide, while nitrogen dioxide is being continually destroyed and regenerated; and so an equilibrium is established along the following lines:(Strauss, 1984)

$$[NO_2]/[NO = k$$

where [ ] indicates the concentration of a chemical species, and k is a constant.

In urban air contaminated by a wide range of reactive hydrocarbon compounds (often referred to as volatile organic compounds or VOCs), however, the reaction patterns are far more complex and less predictable. In the presence of VOCs, an alternative reaction 3.0 occurs:

Alternate 3.0 $RO_2 + NO \rightarrow NO_2 + RO^-$
where RO^- represents any reactive compound.

This alternative reaction allows for the regeneration of nitrogen dioxide without the destruction of ozone. The nitrogen dioxide is accumulated during the early part of the process, and as the process repeats itself there is also a progressive build up in ozone concentrations.

As previously stated, ozone, one of the chief species in smog can be harmful to humans, vegetation, and materials. The use of solvent based inks ,particularly in the flexographic (flexo) and gravure printing processes, results in VOCs being emitted into the environment (mainly reactive hydrocarbon emmisions) , which contribute to ozone production and photochemical smog. Thus as VOC is an important precursor to ozone formation it's reduction has rightfully been targeted by the Environment Protection Authority (E.P.A). The E.P.A. is currently working with the Gravure and Flexographic industry to reduce VOCs from this sector. The Code of Practice that is being developed would see an 80% reduction in VOC emissions by the year 2000. As well as reducing the precursors to ozone formation there is a need for local odours to be reduced. Thus printing factories which are in domestic areas have been targeted to reduce VOC emissions at a faster rate (Carabutt, 1993).

Therefore, this minor thesis will investigate the avenues available for flexographic or gravure printers to take in order to reduce VOCs. In particular low VOC coatings (waterbased coatings) will be compared with the current solvent based coatings available, when printed on a flexible packaging substrate, such as polypropylene. Conclusion will be presented indicating which technology would be the more viable alternative in the current climate in the state of Victoria (particularly in the Melbourne metropolitan area).

PART 1

THE CURRENT CODE OF PRACTICE FOR THE FLEXOGRAPHIC AND GRAVURE PRINTING INDUSTRIES

The current Code of Practice is one of a number of measures aimed at progressively improving air quality in Victoria(EPA, 1991).

Most gravure and flexographic printing industry operations use solvents which can contribute to the formation of photochemical smog. This code of practice addresses these solvent emissions with the aim of assisting in achieving the objectives of the State Environment Protection Policies.

The printing industry is the third largest Victorian manufacturing employer, with 37,500 employees and $3,500 million turnover per year (EPA ,1991). The gravure and flexo printing component contributes ten percent of this activity, but a more significant proportion of solvent usage (EPA, 1991).

Solvent usage in the gravure and flexo industry is some 4500 tonnes per year which is approximately sixteen percent of total industry hydrocarbon emissions to the Melbourne air shed (EPA, 1991). Establishments range in size, with about ten medium sized firms using each a total 100-800 tonnes per year of solvent and the majority using less than 35 tonnes per year (EPA 1991).

The Code focuses on the significant solvents and larger solvent users. It sets an achievable program which can be understoood and simply operated by both industry and EPA. An effective program has been set for the management of industry based solvent usage.

The code of practice was prepared by EPA with the assistance of a working group including representatives from the gravure and flexo printing industry, ink suppliers, consultants and EPA.

The code of practice applies throughout Victoria to gravure and flexographic printing processes and related adhesive, coating and laminating processes on webs of paper, board, flexible films, foils and combinations thereof using solvent containing materials.

The solvents used by this industry are volatile organic compounds (VOC) which are precursors in the formation of photochemical smog. Since 1 January 1990 all new flexo and gravure printing operations have been required by EPA to employ best available technology, such as solvent free coatings or emission control equipment. The Code of Practice is limited to operations established prior to 1 January 1990 and expansions of such premises. New and pre-used equipment using VOC materials comes within the scope of the code. Such a plant will be fully controlled and have minimal VOC emissions, unless emissions are offset by a greater reduction elsewhere from the premises.

The total VOC emissions from the gravure and flexographic printing industry make a small but significant contribution to the total VOC entering the Port Philip Control Region. As there is some potential to reduce this contribution, which would assist in improving air quality, the Code of Practice sets out a program for the progressive reduction of VOC emissions from the industry. While there are a number of possible approaches for VOC reductions, the preferred strategy is to use VOC-free or low VOC coatings.

The VOC emission reduction program has two components. The first component is aimed at minimising emissions of the more photochemically reactive solvents by mid-1992. The second component has the longer term aim of minimising waste and reducing solvent levels in coatings down to the levels consistent with current research and overseas legislation. The code sets minimum standards for industry and all plants must also comply with the Environment Protection Act 1970, State Environment Protection Policies and Industrial Waste Management Policies (EPA, 1991). In particular, plants which give rise to complaints may be required to meet early compliance dates and satisfy additional requirements on an individual basis as specified by a works approval, a licence or a pollution abatement notice. It is anticipated that the code will result in about an eighty percent reduction in VOC emissions by 1996 from this industry.

Emissions of the more photochemical reactive solvents such as toluene, xylene, MEK, and MIBK will be phased out and replaced by less reactive solvents such as ethanol. Where this approach is not practicable, the solvent emissions are to be captured and ducted to VOC control equipment e.g. carbon absorber, bio-filter, and catalytic or thermal afterburner.

VOC REDUCTION PROGRAM

1.0 Highly reactive solvents

From 30 June 1992, premises having uncontrolled emissions exceeding one tonne per year of any solvent listed in Schedule 1 of the EPA Code of Practice must capture and convey them to VOC control equipment.

SCHEDULE 1

(a) Methyl ethyl ketone (MEK)
(b) Methyl isobutyl ketone (MIBK)
(c) Toluene (Toluol)
(d) Xylene (Xylol)

(EPA , Code of Practice 1991)

2.0 Compliance program

All premises emitting more than 35 tonnes per year of VOC must reduce the aggregate VOC emissions from their premises progressively to within the compliance levels specified in Schedule 2 of the EPA Code of Practice. Compliance can be achieved by use of low VOC formulations, VOC control equipment or a mixture of these strategies. Where VOC control equipment is proposed, the VOC reduction will need to be at least equivalent to Schedule 2 targets. Premises proposing additional equipment installations which have the capacity to cause premises to exceed the 35 tonnes per year of VOC emission threshold must meet the compliance target for the next following target period.

SCHEDULE 2
COMPLIANCE TARGETS AND PROGRAM

Compliance date	1st July '92	1st July '94	1st July '96
VOC Material	Compliance target (1)		
Inks			
- white	39	34	30
- colours	55	40	30
- varnishes	60	45	30
Adhesives	50	40	30

(1) % mass of VOC discharged to atmosphere of total VOC materials input to process.

(EPA Code of Practice '91)

3.0 Reporting requirements

All premises must advise the EPA in appropriate written format by 31st July each year, commencing 31st July 1991, of the information for the last 12 months in Schedule 3 of the EPA Code of Practice;

SCHEDULE 3 (EPA, '91)

1.0 Quantity and type of purchased VOC materials in kilograms each 3 months during the previous year.

2.0 Mass percent and type of VOC contained in each of the purchased VOC materials. Similar formulations may be grouped.

3.0 Mass percent and type of VOC (solvent) usually added to each formulation (ink coating, etc.) to make press ready.

4.0 Quantity and type of waste VOC materials shipped from each separate premises for recycling or disposal.

5.0 Quantity and type of recycled VOC materials received into each separate premises.

6.0 The forecast compliance levels proposed to be achieved during the next 12 month period and the remainder of the current compliance period.

4.0 General requirements

All gravure or flexographic printers proposing to install or relocate equipment having potential VOC emissions must first obtain an EPA works approval prior to any works. Applicants for works approvals need to provide evidence that VOC emissions comply with this code ,indicating how wastes will be minimised and what alternative technologies are available for the proposed process. When equipment is installed in accordance with the EPA works approval and before it is operated the proponent must obtain an EPA licence for all VOC emission sources.

Approval of works and changes to licences will include consideration of EPA's recommended buffer distances for residual air emissions and the local planning scheme. For example large flexographic or gravure printers should preferably be located on general industrial zones at least 500 metres from residential areas, schools, hospitals and other sensitive areas.

5.0 Review

The Code of Practice is to be reviewed by 1996.

PART 2

BACKGROUND OF THE PRINTING PROCESSES

As discussed earlier flexographic and gravure printing contribute to ozone formation. Knowledge of the health effects of ozone comes from three sources:

- animal experimentation,
- controlled experiments with humans and
- uncontrolled studies involving humans (epidemiological and field studies)

From these studies it has been shown that ozone can affect all parts of the respiratory system(WHO, 1987). Inflammation of the respiratory system is the common response to ozone.Damage to red blood cells and components of serum, changes in enzyme activity, and decreased ability of the immune system to defend against infection, are further effects of ozone ingestion.

In general, decreases in lung performance have been found after exposure to ozone. People with obstructive lung disease or asthma have responses similar to individuals who do not have these disabilities (WHO, 1987).

Emissions of oxidant precursors, VOCs, to the Melbourne air shed are presented in Table 1.0 based on EPA data (Carnovale et al, 1991).

From Table 1.0 (Discussion paper on oxidant,'91), motor vehicles are the main source of both oxidant precursors (70-80% of the nitrogen oxides and 40-50% of the VOC's). Other sources of VOC's are surface coatings (10-15%), printing (2.6% in the grand total, 9.5% within Industry/commercial), motor vehicle manufacture and the production of petroleum.

TABLE 1.0

SOURCE OF VOC	EMISSIONS OF VOC(KG)	PERCENTAGE(%)
MOBILE		
Motor Vehicles	216040	45.6
Service Station/Refueling	13100	2.8
Other Mobile Sources	4998	1.1
Marine	4106	0.9
Aviation	1565	0.3
SUB TOTAL	239809	50.7
DOMESTIC		
Surface Coatings	20320	4.3
Lawn Mowing/Miscellaneous	18700	4.0
Natural gas leakage	1550	3.3
Waste Combustion	4500	1.0

SOURCE OF VOC	EMISSIONS OF VOC(KG)	PERCENTAGE(%)
Natural Gas Combustion	112	0.0
Oil and Kerosene Combustion	2	0.0
Wood Combustion	0	0.0
SUB TOTAL	59134	12.5
INDUSTRIAL/COMMERCE		
Surface Coatings	41680	8.8
Motor Vehicle Manufacture	22281	4.7
Petroleum Refining	18770	4.0
Printing	12425	2.6
Petrochemical Manufacture	8708	1.8
Major Fuel Storage	4210	0.9
Paint Manufacture	3863	0.8
Bitumen	3480	0.7
Can Manuf./Fbr. Metals	2806	0.6
Other transp. Relat. Manuf.	2420	0.5
Textiles /Clothing	2312	0.5
Other Chemical Manufacture	2116	0.4
Other Machinery Manuf.	1770	0.4
Dry Cleaning	1390	0.3
Hospitals/Colleges	736	0.2
Food and Beverage	600	0.1
Major Incinerators	430	0.1
Waste Combustion	300	0.1
Non-Metallic Min. Process	156	0.0
Paper Manuf./Paper Prod.	149	0.0
Commercial	117	0.0
Power Generation	53	0.0
Basic Metal Manufacture	43	0.0
SUB TOTAL	130815	27.6
VEGETATION	43,500	9.2
GRAND TOTAL	473258	100

Hence from Table 1.0 it is evident why the printing industry, flexography and gravure in particular, were one of the first likely targets of control. Although other areas such as motor vehicle emissions are much greater than printing, printing, surface coatings and other industries are easier targets to control, according to the EPA. The following figures illustrate, firstly (Figure 1.0) the sources of VOC in Melbourne (EPA, 1993), secondly the areas where printing ink is used (Figure 2.0) and Figure 3.0 shows a breakdown of the different types of packages printed with estimates of quantities of each (Printing ink handbook, 1991).

***Figure 1.0** Sources of VOCs in Melbourne*

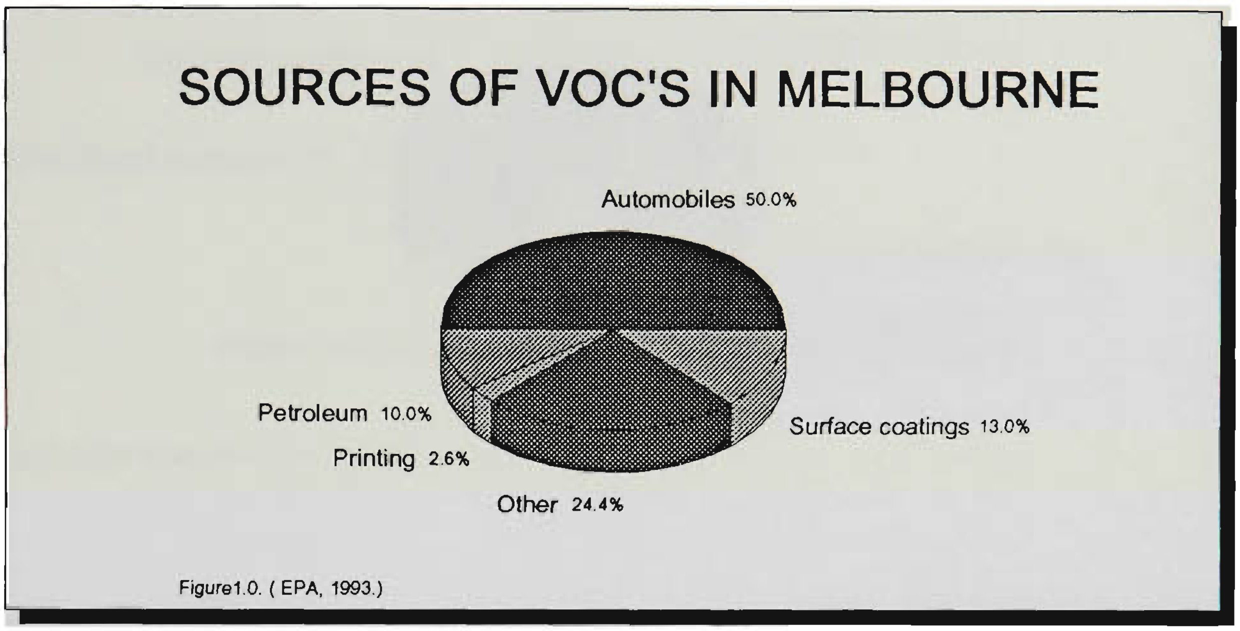


Figure1.0. (EPA, 1993.)

***Figure 2.0** The area's printing ink is used*

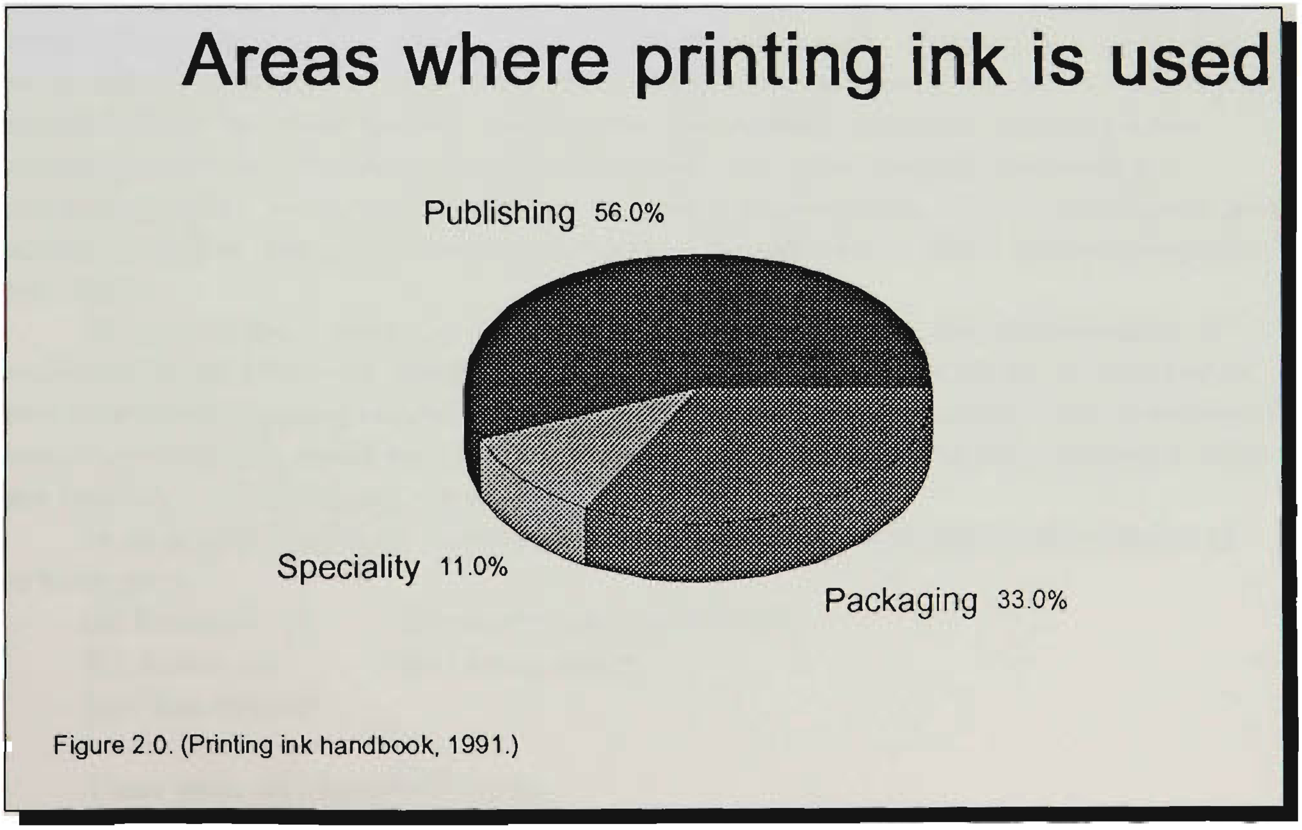


Figure 2.0. (Printing ink handbook, 1991.)

***Figure 3.0** The different types of packages printed with estimates of amounts*

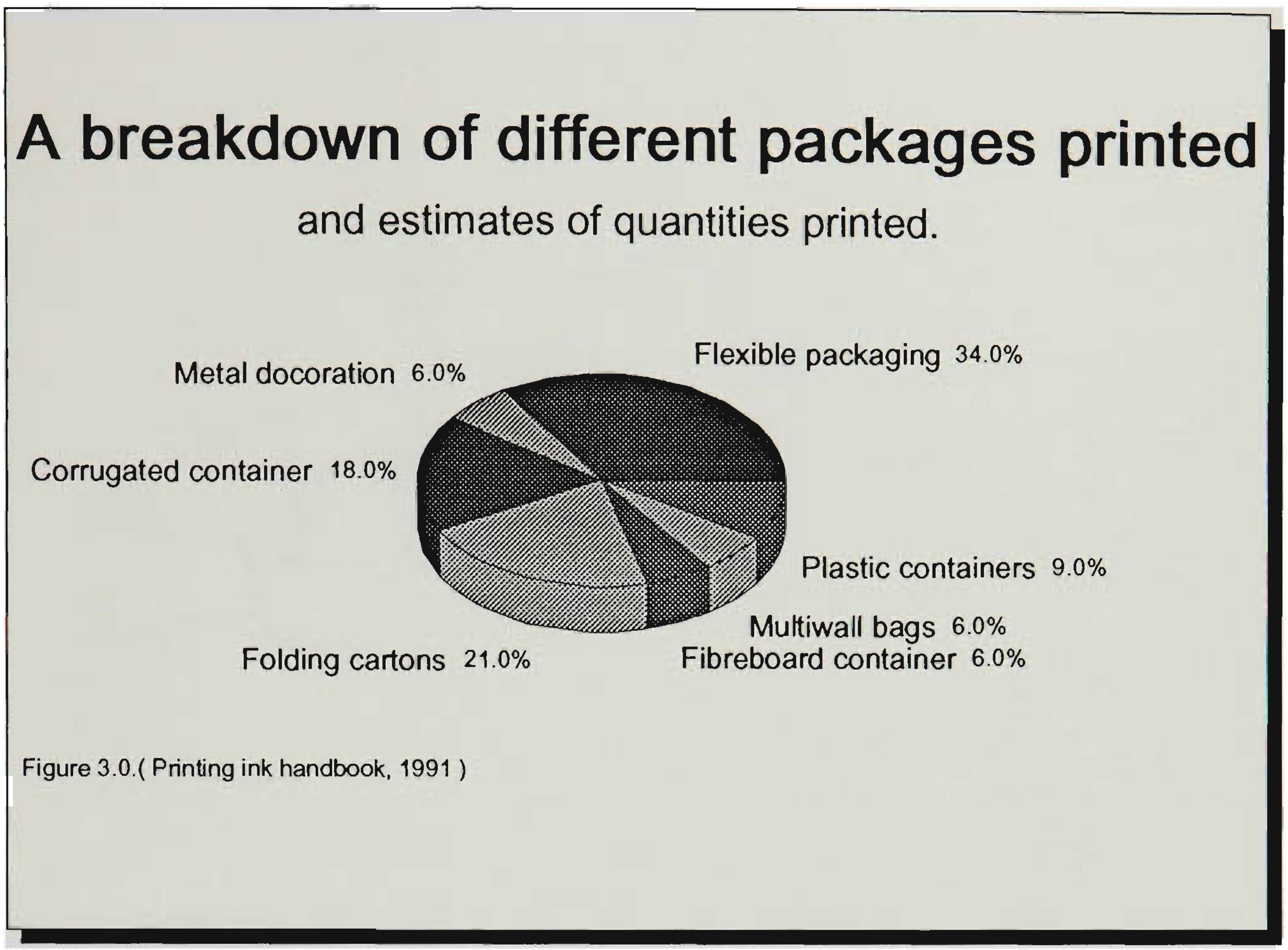


Figure 3.0.(Printing ink handbook, 1991)

1.0 Flexography

In the graphic arts field, flexography is a relatively new process, offering the ability to print on a wide range of substrates, from rough and coarse to very smooth, from absorbent tissue to glossy films and foil. Flexography is unique among other printing processes in that it was developed primarily for the printing of packaging materials,which are mostly used in roll form for feeding into form and fill, overwrapping, bag making and other continuous web processing machines. Obviously modern, flexography has grown beyond the printing of packaging materials and is now used in a wide variety of applictions, such as paperback books, magazines, textiles, newspapers, paperboard and corrugated board, labels, giftwrapping and many others.

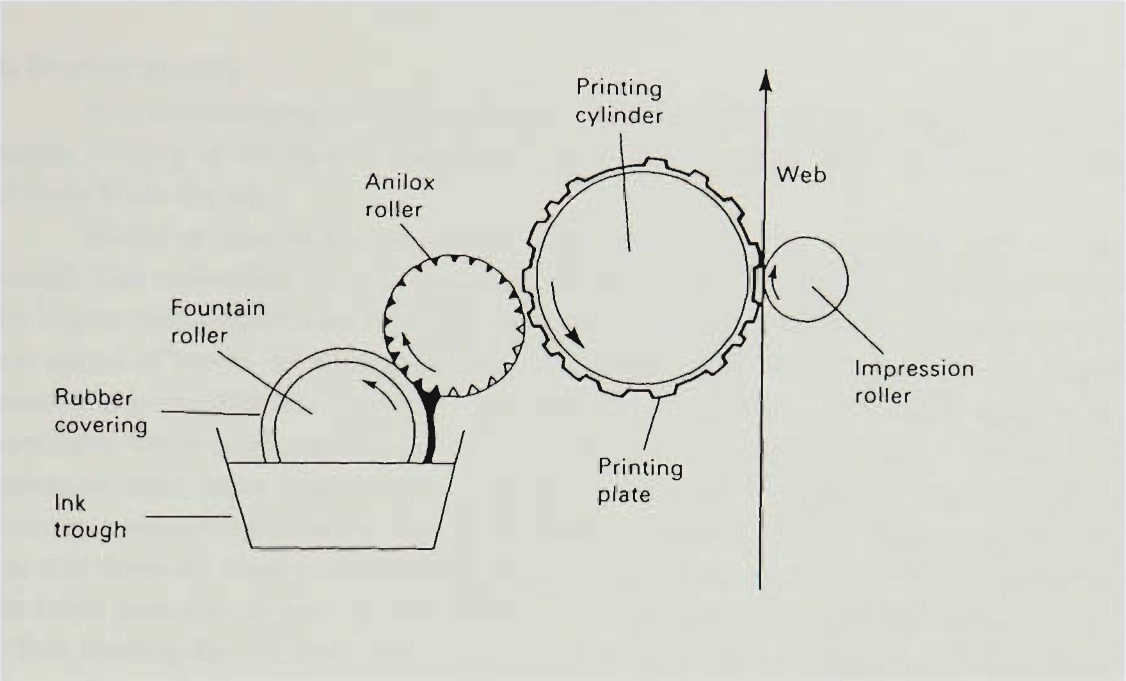
Because of the extensive growth in the technology and the scope of application of flexography in the 1980s the definition was modified as follows: Flexography is a method of direct rotary printing using resilient raised image printing plates, affixable to plate cylinders of various repeat lengths, inked by a roll or a doctor blade wiped metering roll, carrying fluid or paste type inks to virtually any substrate (FTA, 1987) .

In its simplest and most common form, the flexographic printing system consists of five basic parts:

(a) Fountain roll
(b) Anilox roll
(c) Plate cylinder
(d) Impression cylinder/roller
(e) Drying system

These parts will described briefly.

Figure 4.0 A typical flexographic printing station



(a) Fountain roll

The fountain roll is generally a rubber - covered roll of either natural or synthetic rubber. It is positioned to rotate in a reservoir of low viscosity ink. Its main purpose is to pick up and deliver a relatively heavy flow from the reservoir or fountain to the anilox roll. The fountain roll is usually driven much slower than the anilox roll in order to effect a wiping action with the anilox it presses against.

(b) Anilox roll

The anilox roll is usually a metal roll engraved over its entire surface with tiny cells numbering from 80 to 500 per lineal inch. The purpose of the anilox roll is to supply a controlled, metered fine film of ink to the printing plates affixed to the next roller in the train which is the plate cylinder.

(c) Plate cylinder

The plate cylinder is generally a steel cylinder placed between the ink transfer (anilox) roll and the impression cylinder. Printing plates are adhered to it through use of double sided adhesive tape. The ink transfer roll then transfers a finely metered film of ink to the raised surface of the plate, which in turn transfers the ink to the surface of the substrate

(d) Impression cylinder/roller

The impression cylinder is a smooth polished metal cylinder which serves to back up and support the substrate as it comes in contact with the printing plate. The surface speed of the impression cylinder must be identical to that of the plate cylinder, anilox roll and substrate.

Press frame designs are of three types, central impression, inline, and stack types. The central impression uses one common impression cylinder around which two to eight printing stations are placed. The inline design involves a tandem series of printing stations placed in a row. The stack version involves individual printing stations mounted on frames one above the other in two "stacks" generally one to four on each side of a vertical frame.

(e) Drying system

It is important to define ink drying to better understand the function of a drying system. Drying of ink on any substrate is basically the process of attempting to eliminate solvents from the ink.

Water or solvent molecules are held together by Van der Waal's forces (weak residual forces). The molecules are not static, but are always moving and colliding with each other. The higher the temperature of these molecules, the greater their kinetic energy and the faster their speed of travel. If these molecules can absorb sufficient energy from hot air or other heat sources, it is possible for them to break clear of the surface, and, at this point, start to evaporate. Once evaporation has started, a new set of conditions arise. The molecules, now in a gaseous state, must pass through a laminar layer of air that is adjacent to a moving web. These gas molecules must be removed quickly to prevent their return to the ink surface, and heat and fresh air must be continually fed to the surface to continue the evaporation process. The basic purpose of most drying systems is to induce a faster evaporation rate of the solvents by first heating the solvents, and secondly by continuously supplying a fresh supply of non solvent laden air to the ink surface in order to absorb the evaporating solvents.

Whether the flexographic press is stack, central impression, or inline type, all drying systems are designed to dry the ink between each colour station as completely as possible before the next layer of ink is applied. After the web has been printed, it travels to a final drying oven to complete the solvent removal.

2.0 Gravure

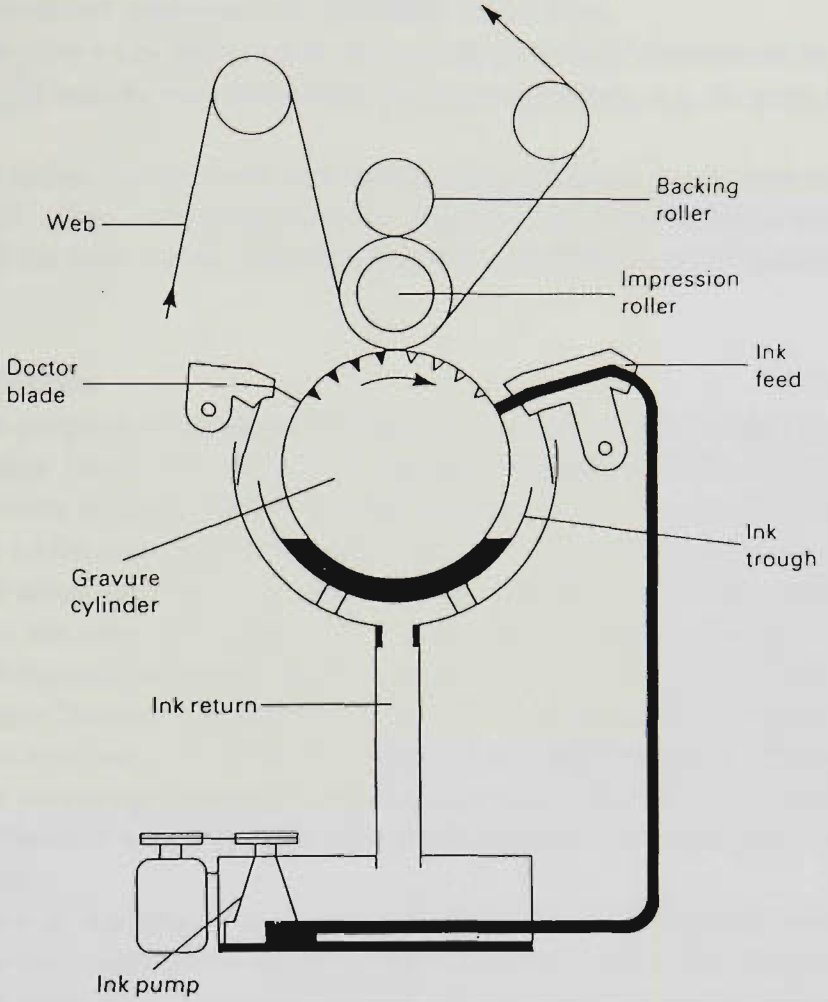
The gravure process(Figure 5.0) gives excellent quality and print definition. With very fast throughput it is best suited to long runs where the high cost of creating printing cylinders can be recovered. Economic quantities are upward of a million impressions.

This method (gravure) is the only method of printing in which there are no plates affixed to cylinder. Instead, the plate cylinder itself is machined and coated to receive the printing image photographically.

Those portions of the cylinders surface which will print are etched (usually by laser) as microscopic, cup like cells, while the non printing areas remain untouched. Ordinary line copy, such as, type and solid colour masses are etched as larger and deeper cells, while tonal values are etched as cells of varying depth or size. Inks are similar to flexo, usually solvent based.

As the image bearing cylinder is inked by a cylinder flooding applicator or rotates in the ink pan or fountain, the cells become filled with thin fluid ink. All ink clinging to the surface of the cylinder is wiped off with a doctor blade, leaving ink only in the cells beneath the surface. When the printing cylinder comes into contact with the web to be printed and backed by rubber impression cylinder, the ink in the cells is transferred to the web (substrate). Once the web is printed the ink forms a dry film by evaporation of the solvents by passing through an oven drier (usually at approximately 80^0C). The drying systems used are similar to those already described in the flexography section, where solvent is evaporated from the ink to form a dry film on the substrate. It is the solvent evaporation which is emitted into the air which is of interest in particular to the EPA.

figure 5.0 A typical gravure printing station (FTA, 1987).



3.0 Printing ink

Ingredients used in the manufacture of printing inks fall into three main classifications:

(i) fluid ingredients or vehicles;
(ii) solid ingredients or pigments;
(iii) and additives.

The function of the vehicle is to act as a carrier for the pigment and as a binder to affix the pigment to the printed surface. The nature of the vehicle determines in a large measure the flow and final properties of the finished ink. The printing process and the drying system involved determine the type of vehicle used. In the case of flexography and gravure the type of vehicle used is a solvent - resin vehicle. Flexographic and gravure type inks dry principally by evaporation of the solvent in the ink, which leaves behind a solid film of pigment and resin.

(a) Resins

It is unusual to find an individual resin that will impart all the desired properties to a flexographic/gravure ink and therefore the formulator will usually select two or possibly three resins to achieve a combination giving the desired characteristics. The essential properties to achieve are:

(1) Adequate adhesion to the substrate.
(2) Good solubility in the preferred solvent system.
(3) Combination of good solvent release properties with the ability to dry to give tack- free ink films.

(4) Capability of providing the desired level of gloss.
(5) Good pigment-wetting properties and acceptable printability characteristics.
(6) Toughness to ensure adequate rub resistance of the print.

Secondary properties of the resin system will be largely determined by the end use of the ink. These might include heat resistance, product resistance, e.g. to soap and alkali, and low odour.

The more resins that are used in a formulation, however,the greater the possibilities of incompatibility and, often, increasing need for powerful solvents to bridge the solubility requirement of all the resins used. Compatibility and solubility tests will be essential during formulation.

(b) Pigments and Dyes

The prime purpose of pigments and dyes is to confer colour. Basic dyes are rarely used in gravure packaging inks due to their reactivity and poor lightfastness (Fade in the presence of uv light). However in flexography the most widely used basic dyes are salts of cationic dye bases (commonly hydrochlorides, sulphates, etc.). Without modification they are very soluble in water and have some solubility in alcohol, the alcohol solubility being improved considerably when the dyes are ' laked' with tannic acid or synthetic mordants. Colour strength is improved by laking and dependant upon the choice of mordant, solubility in water is greatly decreased. Laking of the dye will improve lightfastness, although this remains relatively poor, and bleed resistance to wax, oil, water and glycerine will also improve. The applications of dye inks are for prints where lightfastness is not required and their tendency to bleed and migrate will cause no problems. Generally, these inks are rarely used on plastic films due to poor properties and cost.

Irrespective of the properties required by the end use of the print, suitable pigments will be chosen for their wettability and dispersion characteristics in the various solvent and resin systems which are used. Generally what is being looked for is ease of dispersion with stability on storage, good flow at high pigment concentration and maximum colour strength at reasonable cost. Properties of gloss, opacity and transparency will be important for certain applications. The flow and dispersion characteristics will be dependent upon the pigment type but pigments of similar chemical constitution vary considerably depending on the processing conditions used by the pigment makers and the various additives and treatments of the pigment during manufacture.

Flexographic inks will vary widely in the solvents used (water to aliphatic hydrocarbon) and the many resin types for the different ink ranges. While it is desirable to use the same range of pigments for all inks, the dispersion and rheological behaviour will differ with each solvent/resin system. In order to optimise the properties, the pigments selected will tend to vary somewhat for each range. Other inks may contain additives and materials which are unstable in combination with certain pigments and these factors will also have to be considered.

The choice of pigments most suited to the gravure process can be complex and their effect on the behaviour of an ink can be critical. Ideally a pigment should be resistant to the solvents in the ink, and should not give rise to adverse flow properties. Pigments which produce inks with poor flow give poor coverage, due to lack of flow into and from the gravure cells. A pigment must exhibit good printability characteristics in the chosen resin/solvent system.

As the pigment in most coloured gravure inks is the most expensive part of the formulation, the economics of pigment selection is of vital importance. The normal practice is for ink makers to have a preferred standard range of pigments against which alternatives can be assessed. Additionally to the basic requirements outlined above, consideration should be given to the tinctorial strength, ease of dispersion and gloss characteristics.

In comparison with flexography the gravure process can, when required, deposit fairly heavy film weights of ink, which are governed by the depth of engraving and hence the volume of ink held by the cells. At press viscosity the maximum pigmentation for organic pigments is unlikely to exceed 15%, most shades being matched with 5-10% of pigment (by weight). With inorganic pigments, of which titanium dioxide is the most common, higher pigment levels of 25-35% are common, particularly for backing whites on transparent films and aluminium foil.

In many areas of gravure and flexographic printing, pigments need specific properties to meet the demands made on them during the processing of the print, and in the end use of the printed material, e.g. printing of deep freeze polyethylene bag. The following is a list of the main pigments which are suitable for flexographic and gravure inks: (The Printing Ink Manual, 1988).

Pigments	*Colour Index*
Monoazo yellows	PY 3,5,98
Diaryl yellows	PY 12,13,14
Pyrazolone orange	PO 13
Permanent red 2G	PO 5
Lithol rubine 4B	PR 57
Rubine 2B	PR 48
Lake red C	PR 53
Lithol red	PR 49
Pemanent red R	PR 4
Iron oxide	PR 101
Phthalocyanine green	PG 7
Phthalocyanine blue	PB 15.3
Ultramarine blue	PB 62
Titanium dioxide	PW 6
Carbon black	PB 7
PMTA pink, green, blue, violet	PR 81, PG 1, PB 1, PV 3
Copper ferrocyanide dye complexes	PR 169, PG 45, PB 62, PV 27
Calcium carbonate	PW 18
China Clay	PW 19
Blanc fixe	PW 21
Permanent violet	PV26

NOTE: The colour index classification of pigments and dyes is the colour index, prepared by the Society of Dyers and Colourists. The index is prepared in five volumes; the first three list the colorants according to type and usage and give technical information under CI (Colour Index) generic names. For example, Lake red C is listed as CI pigment red 53. Volume 4, sometimes referred to as Part 2, lists the colorants according to their chemical constitution.The above example is listed as CI reference 15585. The final volume lists commercial names and manufacturers' code letters.

(c) Solvents

The two other main constituents of the ink, colorant and binder are both solids and therefore the prime function of the solvent is to convert the ink into the fluid form which makes it capable of being printed. The solvent is thus a carrier for other ingredients but must be easily removed from the print by evaporation and sometimes by penetration into the substrate.

The choice of solvent is governed by a number of factors. The resin used in the ink system will have specific solubility characteristics and as is often the case mixed resins with different solubility parameters will demand solvents or solvent mixtures. With flexography there will always be a restriction of choice of solvent determined by the nature of the stereo (synthetic or rubber plate located on the plate cylinder) materials used. Also with inks for food packaging certain solvents may be restricted as their presence as retained solvents in the print after drying, may represent an unacceptable risk of odour or taint even in small quantities.

Solvent choice can also be influenced by colorant and with dye inks this is obvious since the solvent must dissolve the dye. With pigmented inks the solvent can affect flow characteristics. A good example of this is the behaviour of diaryl yellows which are satisfactory in alcohol but give poor flow in ester solvents. There is also evidence that dispersion , stability and colour strength development are influenced by flow and the effect of pigment/solvent affinity. Solvents also affect adhesion to the substrates and with coated films or soluble substrates a partial solubility of the surface by the solvent will assist in ink adhesion. With nonsoluble substrates and uncoated films, solvents can also affect adhesion by increasing or decreasing wetting of the surface and adhesion is normally at its best when wetting is of a high order.

Most inks contain mixtures of solvents and care will be taken to produce a satisfactory balance for solubility of resins and for the other considerations. During printing more solvent will be added by the printer and the volume added can equal the original solvent content. Therefore the total composition must be considered when formulating and recommending diluents. During printing, solvent will be lost by evaporation from the duct and it is well known that the solvent vapours will consist of classical mixtures determined by vapour pressure, effect of solvents on each other , resin composition of the ink and atmospheric conditions. Solvent added during the run should therefore ideally be of the same mixture or imbalance can occur and the result could mean instability of the ink with possibilities of precipitation of resin, mattness of the print , increase in viscosity, loss of flow or adhesion failure. In a press unit with good coverage of the print, the rate of ink usage is such that constant replacement with fresh ink is necessary and there is little chance of the problems described . With little ink usage, however, on a unit with a small area of type or tone where the same ink constantly recirculates through the unit for many hours without fresh ink being added, special attention will need to be paid to make up solvent to ensure balance is preserved. The ink formulator should try as far as possible to use a balance of solvent with suitable evaporation rates to avoid evaporation imbalance particularly with inks for halftone printing, a classical case of low usage application. The best solution in these extreme cases is to simplify the formulation drastically and use only one solvent provided that a satisfactory ink for the substrate and end use can be made with these restrictions.

The principle solvents used in flexographic inks are: water, ethyl alcohol (methylated spirits) isopropyl and normal propyl alcohols, ethyl, isopropyl and normal propyl acetates, propylene glycol mono ethyl ether and propylene glycol mono methyl ether. In certain cases aliphatic hydrocarbon, toluene or ketone solvents (acetone , MEK, MIBK) may be used for some type of inks but the suitability of the plate composition (certain polymer plates may deform with particular solvents) must be considered.

In gravure printing the solvents above are also used, but no consideration of the printing plate is required hence the more harmful solvents such as toluene , and xylene can be used, the former often as a cosolvent with ketones in inks for use on PVC and with alcohols for inks for use on polyethylene.Aliphatic type solvents with toluene are also used commonly to give excellent printing results.It is also important that the solvents used in inks such as the above have excellent lubrication properties to reduce wear on gravure cylinders during long print runs.

(d) Additives

The overall performance of most gravure and flexographic inks can be improved by the use of additives. They perform a wide variety of functions, some of which are essential to the success of the ink , while others enhance its characteristics.

Some additives are primarily functional during the manufacturing stage, e.g. pigment-wetting aids, others perform as stabilisers and bactericides ensuring storage stability. Many resin systems require the addition of chemical plasticisers or plasticising resins, in order to prevent ink drying in the cells on the press and to ensure satisfactory adhesion and flexibility on the substrate.

The surface characteristics can be considerably modified by additives which promote rub resistance and slip. The most common and probably best additives for these purposes are polyolefin, paraffin and amide waxes.

The composition of gravure and flexographic inks varies widely dependent on the choice of the substrate, press parameters and end use of the finished print. A typical ink will, however, contain the following ingredients:

Pigment (or dyestuff)	10-15%
Resin	20-30%
Solvents	60-70%
Additives	5-10%

PART 3

DESTRUCTION OF EMISSIONS/TREATMENT OF EMISSIONS

Types of pollution control equipment to reduce VOC's can be divided into two categories, recovery and destruction.

- DESTRUCTION
- Incineration
  (a) Thermal
  (b) Catalytic
- Biofiltration
- RECOVERY
- Adsorption
- Desorption

The processes above will be discussed in greater detail indicating the advantages and disadvantages of the various alternatives.

1.0 Incineration

Incineration is the control of organic emissions by combustion. The objective is to completely oxidise the emissions to CO_2 and H_2O.

$$HC + O_2 = CO_2 + H_2O$$

In the above reaction the VOC's or hydrocarbons react with oxygen in the presence of a flame or catalyst to form carbon dioxide and water.

It should be noted that in some printing processes such as lithography and letterpress organic particles as well as vapours may need to be oxidised.

Incomplete combustion can produce more odorous and harmful pollutants than those that were present in the initial gas stream. Thus it is necessary to provide the conditions that will maximise the conversion reaction. This has seen incineration develop into three areas, namely use of flares, thermal incineration, and catalytic incineration. Flares are not applicable to the printing industry as they require enough solvent for the flame to be self-sustaining. They also have safety problems in that there is the opportunity for explosions to occur.

Thermal and Catalytic incinerators were developed to oxidise vapours at lower concentrations. These incinerators handle concentrations below 25% LEL (Lower Explosive Limit) but can handle concentrations up to 40% LEL if appropriate monitoring devices are attached. The LEL of a combustible is the concentration of the combustible below which the combustion reaction will not propagate. For safety reasons incinerators are designed such that the incoming gas must be below 25% LEL or below 40% LEL with monitors or controls (AFTA, 1990).

(a) Thermal incineration

Thermal incineration involves oxidising mixtures of solvents which have less than 40% LEL. This means that there is sufficient air in the waste gas mixture to produce complete combustion. However , for complete combustion to occur three things are required. They are commonly known as the three T's: Time, Temperature, and Turbulence (AFTA, 1990).

Sufficient time for the combustion reaction to go to completion is required. The normal residence time is 0.25 seconds to 1.0 seconds. In Victoria for solvent mixtures the residence time is 0.5 seconds. However, it should be noted that if particulates are present then 0.5 seconds is not long enough for complete combustion (AFTA, 1990).

Sufficient turbulence is required to provide good mixing between the products of combustion from the burner of the incinerator and the air solvent mixture. This is necessary to promote heat transfer. Turbulence can be achieved by baffles, or tangential entry of the waste gas to the burner. Air velocities are also used to increase turbulence and they can range from 3.50m/sec to 15.25m/sec.

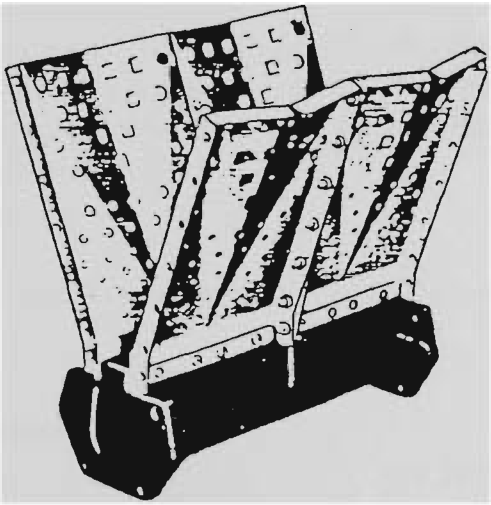
In order to cause the oxidation reaction to proceed rapidly to completion a sufficiently high temperature is required. Most thermal incinerators operate between 704^0 C and 706^0 C. It should be noted that in practice when treating fumes from lithographic presses the odour and CO levels rise when the temperature is below 760^0 C (AFTA,1990).

Burner type and arrangement have a large effect on the required residence time. The more thorough the flame contact is with the effluent gases, the shorter is the time required to achieve complete combustion. Turbulence in the combustion zone also has the desired effect. Multi-jet burners have been found to be very good in producing good flame contact (AFTA,1990).

It should be noted that although the burners take all their air required for combustion from the waste gas stream they are not capable of handling all of the contaminated stream through the burner. Thus, some of the air must be by-passed around the burner and then thoroughly mixed in the incinerator chamber.

Mixing plate burners are usually placed across the inlet section of the incineration body, and take all the air for combustion of natural gas from the contaminated gas stream. Intimate flame contact is achieved by placing the ' profile plates' to force as much contaminated air through the burner and burner flames. This type of burner involves extremely high velocities which ensure that adequate mixing occurs. Figure 6.0 is a schematic drawing of a mixing plate burner (Courtesy of Maxon Primix Burner Co.).

***Figure 6.0**. A mixing plate burner*



Nozzle mixing and premixing burners are arranged to fire tangentially into a cylindrical afterburner. Several burners are required to ensure complete flare coverage. These types of incinerators can have the contaminated gases introduced tangentially or along the major axis of the cylinder.

The high operating temperatures achieved within thermal incinerators must be considered during construction. Older style units were lined with refractory material while more modern units consist of a stainless steel shell lined with ceramic fibre modules.

The fuel used in the burners can either be gas or oil. Gas is generally favoured as the sulphur found in most oils will be oxidised to SO_2 and in turn cause an air pollution problem.

The ability to reuse some of the heat produced in the incineration process can greatly reduce energy costs.

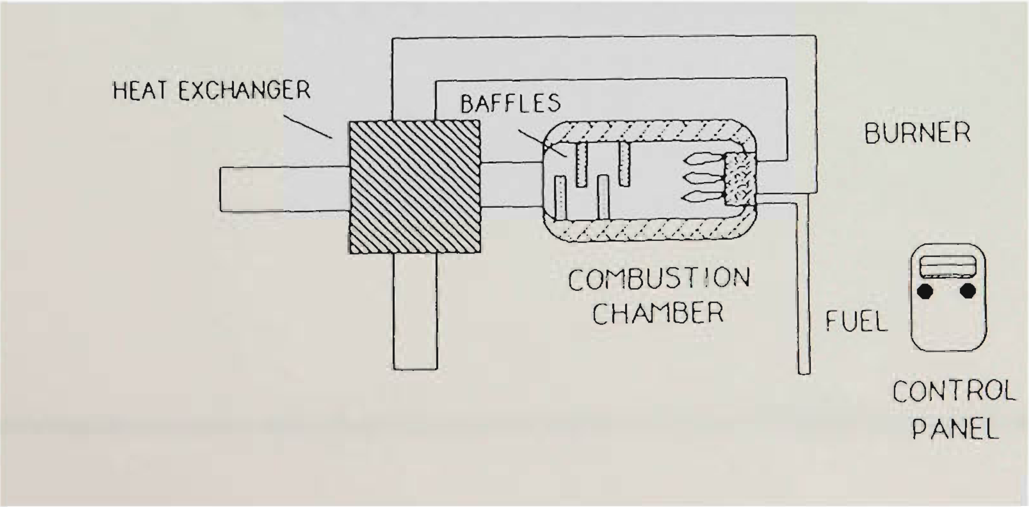
Advantages/Disadvantages of thermal incineration.

- Known and proven technology
- Can easily meet EPA regulations
- Easy to install
- Simple design
- Compact size
- Low maintenance costs
- Doesn't deteriorate over time

Thermal incinerators/afterburners have the following disadvantages;

- Long residence times (0.5 to 2.0 seconds) mean relatively large and expensive combustion chambers.
- The high temperatures involved require careful selection of materials for construction to prevent corrosion.
- Combustion chambers designed for a fixed residence time and turbulence do not operate efficiently at higher or lower flow rates. This can be compensated by operating at still higher temperatures with subsequently high energy cost.
- At the high temperatures involved in thermal combustion, the nitrogen in the air is oxidised to create NO_x, which itself is a serious and regulated pollutant.
- Can use large amounts of natural gas
- Produces large amounts of CO_2
- Require air flows to be greatly reduced from those existing on the printing press. A gravure press without recirculation will only produce a maximum of 700ppm of combustible materials, with an air flow of 60,000 m^3/hr. It is uneconomical to incinerate such low concentrations. Thus the air flow needs to be reduced resulting in an increased concentration .
- Expensive to run

Figure 7.0. *Schematic of a thermal incinerator .(Flexo, July 1991)*

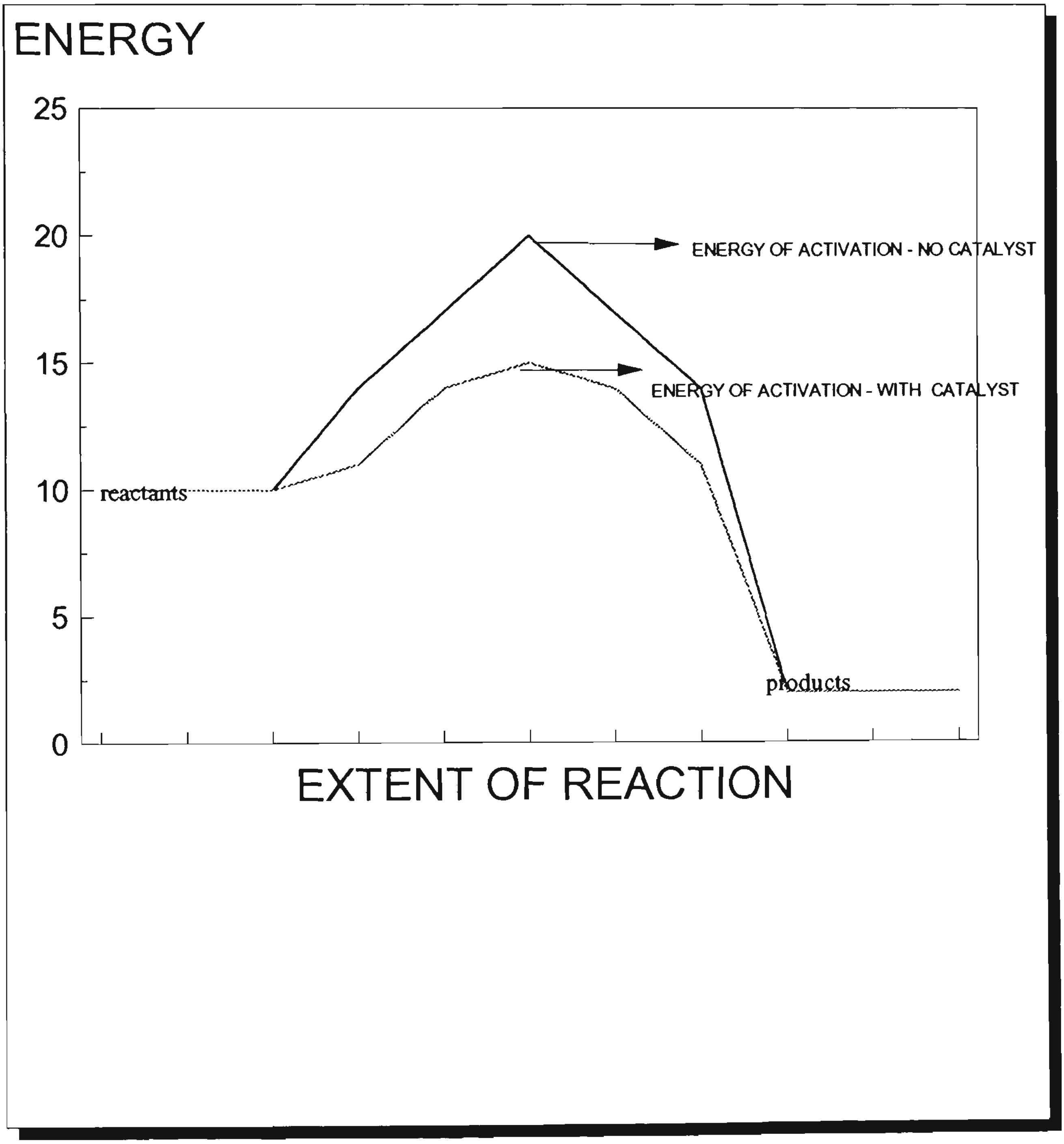


(b) Catalytic incineration

Catalysis is a process in which the rate of a chemical reaction is accelerated by a substance (the catalyst) that remains unchanged by the process. Catalysis applied to incineration or combustion of carbon monoxide is depicted in Figure 8.0. The catalyst presents an alternative route for the chemical reaction to occur, which requires lower energy and therefore can occur faster with the energy available because there are a high number of activated sites.

Figure 8.0 demonstrates this graphically.

Figure 8.0. *A catalyst lowering the activation energy for a chemical process* (Flexo, July 1991)



Catalysts are usually high surface area substances and the catalytic sites are often situated on the walls of relatively small pores.

To understand the limitations of catalysis we need a basic understanding of the process. Catalysis proceeds by several serial steps;

(a) diffusion of the reactants to the surface.

(b) diffusion of the reactants through the porous catalytic sites.

(c) adsorption onto the sites.

(d) activation and reaction.

(e) desorption of the reactants out of the porous structure and diffusion away from the catalyst proximity.

Any of these steps may be reaction- rate limited in that the process is serial. Catalysts can be tested and the data can be used to determine which step is rate determining. This data can be presented in an Arrhenius plot . The slope of the lines in an Arrhenius plot indicate the activation energy for the processes. The operating conditions determine which steps are rate-controlling. Each of the processes can become rate- determining, depending on the intrinsic activity of the catalyst, the temperature, flow rate and catalyst geometry.

Good catalyst design will ensure that the catalytic species are active, stable and presented in a geometrical shape which will ensure that mass transfer limitations (pore and bulk) occur only at very high conversions.

The apparatus for catalytic incineration is similar to that for thermal incineration with the exception that the catalyst replaces the primary and secondary incineration chambers.

In catalytic incineration the process effluent containing VOC is preheated by a heat exchanger. More heat is added if needed by a burner. The exhaust is then passed through a catalyst bed where the VOC is oxidised to CO_2 and H_2O.

Temperatures required for catalyst ignition depend on the VOC oxidised, and the nature of the catalyst composition, but can typically vary from 260^0 C to 371^0 C. The temperature required to achieve 95+ percent conversion depends on the temperature for ignition, the residence time of the effluent in the catalytic bed, and the geometry of the catalytic element. The temperature can range from 260^0C to 480^0C.

Catalytic incineration is relatively insensitive to the amount of water vapour in the effluent (in some cases water can assist in the destruction of hydrocarbons through the steam reforming reaction $C_xH_y + 2xH_2O \rightarrow xCO_2 + (2x + y) H_2$).

Catalysts rely upon their surface reactivity and very large surface area. Most catalysts consist of a noble metal such as platinum or palladium which is on support media of alumina. Common types of catalyst supports used consist of a wire grid similar to rough steel wool which has been coated with alumina and then coated with the catalyst, or alumina honeycomb which is similarly coated with a catalyst. Other shapes of coated alumina are also available. The problem with the honeycomb catalyst is that the tiles can crack very easily causing problems. The sphere type of catalyst has the advantage that if the surface is fouled for example by particles then the top five centimetres can be removed easily and replaced with fresh material. MnO_2 in the form of small worms about five centimetres long has also been used as a catalyst successfully in the U.S.A (Flexo,Vol 16 No.4, 1991).

Heat recovery can and is being used in conjunction with both catalytic and thermal incineration. It allows operating costs to be greatly reduced(Flexo, Vol 16 No.4, 1991).

Some of the heat recovery schemes that have been successful include;

1.0 Heat exchangers to heat the contaminated gases before entry into the incinerator.

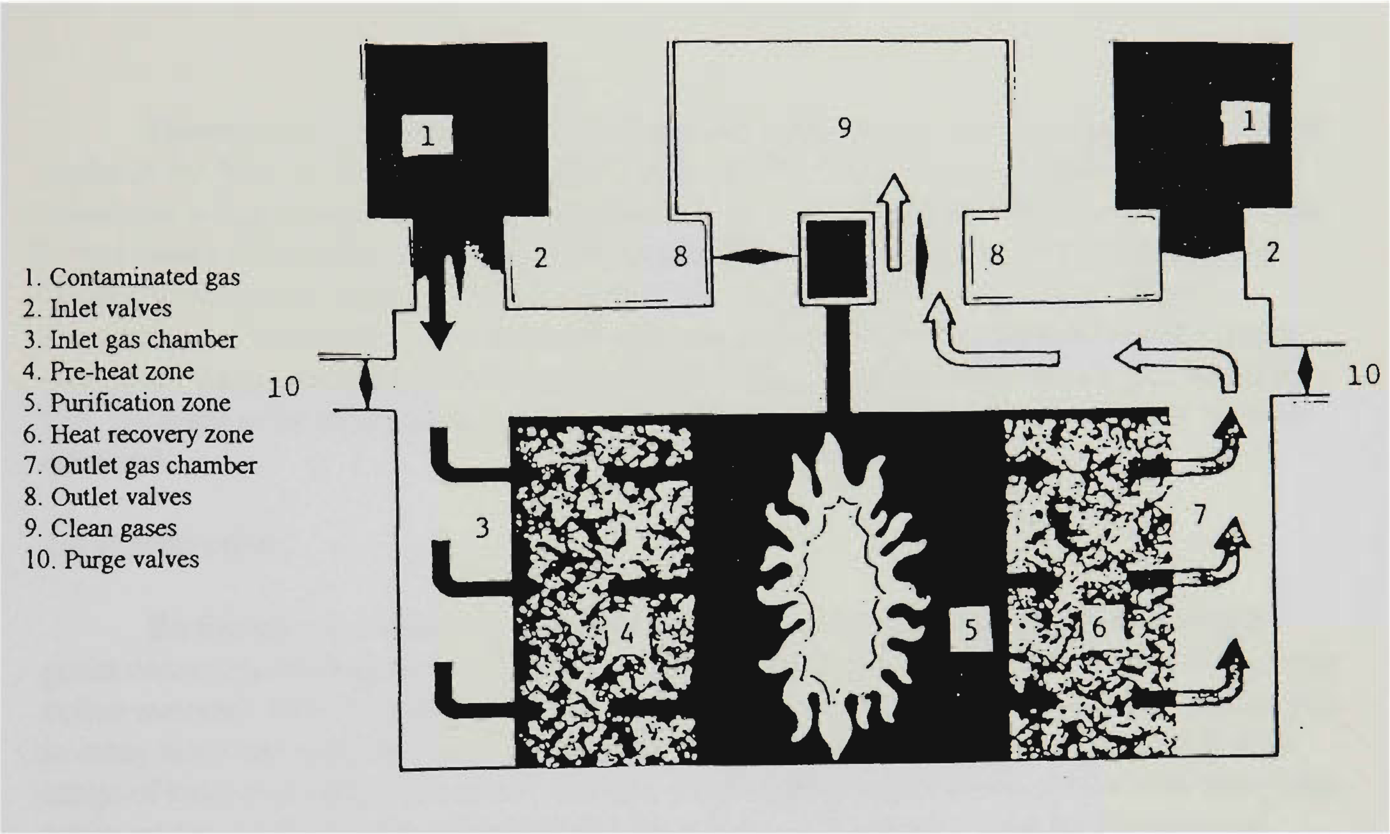
2.0 Heat exchangers to heat air as a source of heat for the equipment generating the contaminated gases.

3.0 Venting of the incinerator gases to other process equipment such as waste heat boilers.

The use of a heat exchanger to heat contaminated gases going into the incinerator is the most commonly used heat recovery system. Either recuperative or regenerative types of heat exchangers can be used. Recuperative types involve using metallic plates or tubular exchangers to preheat the incoming air.

Regenerative heat exchangers involve passing the outlet gas through a refractory material. This outlet is mechanically switched to the inlet allowing incoming gases to be heated by the refractory material.

Figure 9.0. *Thermal regenerative air purification system (Courtesy Proctor and Schwartz Inc. , 91).*



Advantages of the catalytic incinerator;

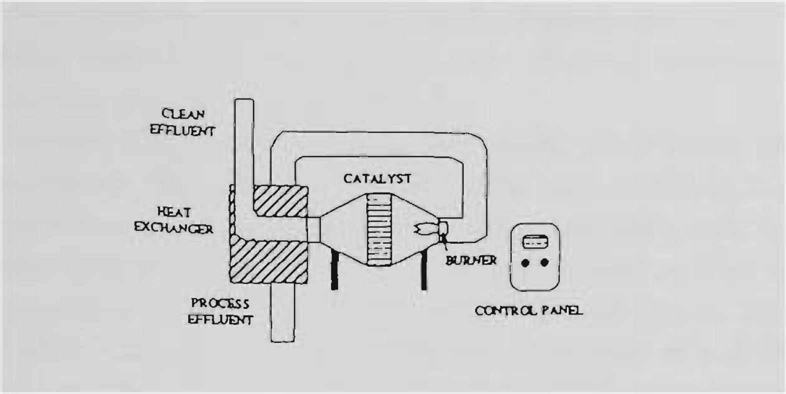
- Increased rate of reaction.
- Reaction occurs at a lower temperature.
- Lower fuel costs.
- Reaction can occur at more favourable pressures.

Disadvantages of the catalytic incinerator;

- Catalysts can be scorched by hot spots which can destroy the activity of the catalyst.
- Catalysts are easily poisoned by lead, zinc, phosphorus and other compounds.
- High maintenance cost.
- Easily fouled by particulates and dust.
- High cost of catalysts.

The schematic of a catalytic incinerator is depicted in Figure 10.0.

Figure 10.0. Schematic of catalytic incineration process. (Flexo, July 1991).



Thermal incineration and Catalytic incineration are very important and proven control methods for VOC's. They offer a relatively problem free solution to the EPA's regulations, stipulating a large reduction of VOC emissions from a printing press. However, they may not be the most cost effective solutions. They nearly always require the air flow from printing presses to be greatly reduced. This is particularly true in the gravure industry. These alterations can be expensive. Incineration also requires the use of supplementary fuel which results in a large amount of CO_2 being produced. Thus incineration would not fare well if a CO_2 tax were to be introduced. Although incineration is a proven technology it may well be outdated.

2.0 Biofiltration

Biofiltration is a relatively recent air pollution control (APC) technology in which gases containing biodegradable VOC's or inorganic air toxins are vented through a biologically active material. This technology has been successfully applied in Germany and the Netherlands in many full-scale applications to control odours, VOC and air toxic emissions from a wide range of industrial and public sector sources. Control efficiencies of more than 90% have been achieved for many common air pollutants. Due to lower operating costs, biofiltration can provide significant economic advantages over other APC technologies if applied to off-gases that contain readily biodegradable pollutants in low concentrations (Air and Waste Management, 1991).

The concept of using microorganisms for the removal of environmentally undesirable compounds by biodegradation has been well established in the area of wastewater treatment for several decades. Moreover, while bioremediation techniques are now being applied successfully for treatment of soil and groundwater contaminated by synthetic organics, at present there is very little practical experience with biological systems for the control of air contaminants among environmental professionals in Australia.The first biofiltration plant installed at a gravure printing house in Melbourne was 1992 (at Conofllex packaging, Bell Street Preston). As yet it is only controlling the emissions from one of the four gravure presses on the site.

A biofilter for control of air pollutants consists of one or more beds of biologically active material, primarily mixtures based on compost, peat or soil. Filter beds are typically 1 meter in height. Contaminated off-gas is vented from the emitting source through the filter. Given sufficient residence time, the air contaminants will diffuse into a wet, biologically-active layer (i.e., biofilm) which surrounds the filter particles. Aerobic degradation of the target pollutants will occur in the biofilm if microorganisms, mainly bacteria, are present that can metabolise them. End products from the complete biodegradation of air contaminants are CO_2, water, and microbial biomass. The oxidation of reduced sulfur compounds and chlorinated organic compounds also generates inorganic acids.

Compost, usually produced from municipal waste, wood chips, bark or leaves has generally been the basis of filter material used in recent applications in Europe, although peat and heather mixtures have also been used. The biofilters originally built in the US. were mostly "soil beds" for which biologically active mineral soils were used as filter materials.

The components needed for preconditioning of the off-gas, its transport to and distribution in the filter bed account for the other main elements of a biofilter system. Heat exchangers to cool hot off-gases or filters for the removal of particulates may be required for certain types of emissions. Radial blowers are generally used to overcome the back pressure caused by the filter. The off-gas must also be saturated with water, since it would otherwise remove moisture from the filter material, resulting in drying of the bed, the death of most microorganisms and a total loss of control efficiency. Spray nozzles usually provide the required humidity in the humidification chamber. Additional, automatic irrigation of the filter beds from the top is also used in some systems to maintain the required moisture content in the filter material. Finally the off-gas is vented, usually through slotted concrete slabs or concrete blocks with distribution canals and air nozzle into the bottom of the filter bed. Down-flow systems have also been used in several recent installations.

To date, most biofilters have been built as open single-bed systems. Open multiple story systems are also built if space constraints exist. Some European firms have developed enclosed systems, usually with stacked beds. The filter beds that are operated in parallel,are generally more expensive. The use of enclosed multiple store systems can be appropriate, in applications where minimum maintenance is required, and where space constraint prohibits the installation of a single-bed filter. Other advantages of fully enclosed systems include a lower susceptibility to changing climatic conditions and the possibility of continuous off-gas monitoring.

Mineralisation of the organic matter in biofilters will over time lead to compaction of the filter material and a corresponding increase in back pressure. In open filters, the filter material is typically turned over (e.g., by frontloaders) after two years in order to increase its porosity. After another one to two years it is replaced by fresh material. Manufacturers of enclosed systems attempt to extend the useable life of the filter material by selecting its components more carefully. A useful life for filter material of up to five years has been reported. Equipment that will eliminate the need for turnover by plowing through the filter material has also been developed. Eventual replacement of the filter material will still be required. Maintaining the porosity of the compost by turning it over, and/or replacing it entirely, once spent, are the two major maintenance requirements for biofilters with compost-based filter materials.

The Bioton-Biofilter used at Conoflex Packaging, is used to control emissions from their most recent gravure printing press, the PF12.This press is an eight colour printing press. It prints packages for Unifoods such as the Continental soup range, yogurt lidding, etc. The substrates that are printed on, include, foil, polypropylene and other flexible packaging substrates.

The exhaust gas from the PF12 can contain from about 200ppm to 800ppm of solvent. The volumetric flow rate of the exhaust is approximately 30,000m^3/hr. This high exhaust volume but relatively low concentration in Conoflex Packaging's point of view meant that incineration was not a viable option for this machine. Other control options such as solvent recovery were also investigated but found to be very expensive. It was unlikely that they would be able to reclaim solvent within their plant.

In Conoflex Packaging's case the bacteria use the hydrocarbons as a source of energy and carbon for microbial metabolism. Carbon dioxide and water vapour are produced as the byproducts. The bacteria live in media consisting of mushroom compost and polystyrene beads The polystyrene helps to maintain a porous structure through which the humidified waste gases can flow. As well as moisture content being important the bacteria prefer temperatures between 10^0C and 40^0C.

The process at Conoflex Packaging is very simple and put simply the following occurs. The exhaust from the printing press initially passes through a packed tower which humidifies the air. The water laden exhaust then passes through the filter beds where the bacteria utilize the solvent. The 'cleaned' gas then exits the process through an exhaust stack.

Some useful information on the Bioton:

- Total cost of plant and installation-$1 million
- Expected life of biological material is 4 to 5 years.
- Cost to replace biological material-$100,000
- Trace elements that the bacteria require for growth are supplied by the mushroom compost.
- Emissions can be reduced by 80%.
- The process does not require the lowering of exhaust flow rates from the printing presses.
- Examples of pollutants which can be successfully treated include solvents such as ethanol, ketones, and other hydrocarbons ranging from alcohols to aromatics.
- In the future it can be multiplied in size in order to cope with the other presses.

History of biofiltration

Suggestions to treat VOC's by biological methods can be found in literature as early as 1923 when Bach discussed the basic concept of the control of H_2S emissions from sewage treatment plants (Air and waste management, March 1991). Reports on the application of this concept dating back to the 1950's were published in the U.S. and in West Germany. Around 1959 a soil bed was also installed at a municipal sewage treatment plant in Nuremberg, West Germany for the control of odours from an incoming sewer main.

During the following two decades, several researchers in the U.S. have further studied the soil bed concept and demonstrated its usefulness in several full scale applications. Much of the knowledge about the technology is owed to Hinrich Bohn who has investigated the theory and potential applications of soil beds for more than 15 years. Successful soil bed applications in the U.S. include the control of odours from rendering plants, and the destruction of propane and butane released from an aerosol can filling operation.

It is estimated that the total number of biofilter and soil bed installations in the U.S. and Canada is currently less than 50 and that they are predominantly used for odour control. Very recently the treatment of VOC released from soil clean up operations has been addressed in several bench-scale studies. It can be inferred from the lack of literature in the U.S. and Australia during the last two decades, that little attention was paid to concurrent developments in at least two European countries, West Germany and the Netherlands. In these countries, biofiltration has developed since the early 1960's into a widely used APC technology which is now considered best available control technology (BACT) in a variety of VOC and odour control applications (Air and Waste Management, March 1991).

As noted earlier, during the 1960's and 1970's, biofilters were successfully used in West Germany to control odours from a variety of sources, including sewage treatment plants, and facilities for rendering, composting and food processing. Various designs for the air distribution system, and several filter materials with higher biological activities and lower flow resistance than soil were investigated. Compost derived from municipal solid waste was used as a filter material as early as 1966.

The basic processes determining the efficiency of a filter were understood qualitatively in the 1960's. However, the approach to designing biofilter systems was usually empirical. Mobile pilot units were often used for treatability studies and the sizing of the full scale system. Economic advantages were discussed by Jager and Jager (Ottengraf,1986). Their investigations suggested that biofilters exhibit comparatively low operating costs if used for the treatment of odorous off-gases from composting facilities for municipal waste.

Since the early 1980's, biofiltration has increasingly been used in Germany to control VOC and air toxins emitted from industrial facilities such as chemical plants, foundries, printing houses and coating operations. This development was primarily brought about by new federal regulations that required the control of emissions of VOC from new and existing sources, a well funded development program run by the West German Federal Environment Agency (EPA,1991).

The macrokinetics of the degradation processes of a great number of VOC's like alcohols, ketones, esters, aromatics, etc. have been studied in biolfilter beds. Experimental results may be summarised as follows (Ludwig,1986):

- The macrokinetics of the elimination processes in a biological filter bed can be modelled as an absorption process in a wet biolayer surrounding the constituent packing particles, accompanied by a biological degradation reaction:
- The elimination of these compounds follows zero order reaction kinetics down to very low concentrations of substrate. This has been confirmed by batch investigations of the degradation process in aqueous solutions of the compounds concerned;
- At low gas phase concentration levels or low water solubility of the compounds concerned, the elimination rate in the filter bed may become diffusion controlled in the biolayer;
- The zero order kinetics of the elimination process means that any biodegradable compound may be removed completely during a finite residence time of the gas phase in the filter bed.

Examples of the results are provided in Appendices 1.0 and 2.0. Appendix 1.0 shows that a linear concentration profile will be observed for several common VOC at higher gas phase concentrations. Appendix 2.0 demonstrates the predicted decrease in elimination rates caused by diffusion limitation at concentrations less than C_{crit} .

Microorganisms

Several groups of microorganisms are known to be involved in the degradation of air pollutants in biofilters, including bacteria, actinomycete, and fungi. Compost based filter material typically shows a significantly higher population densities of these organisms than soil and peat.

Biofiltration relies predominantly on hetrotrophic organisms that use organic off-gas constituents as carbon and energy sources. As a result, introduction of these compounds into the filter material upon start up will generally shift the distribution of existing microbial populations towards strains that metabolize the target pollutants. For common, easily biodegradable organic compounds, acclimatisation will typically take about ten days. If compounds are less biodegradable and for which suitable microorganisms are less likely to be initially present in the filter material to be treated , inoculation with an appropriate culture can reduce the acclimatisation period.

Most industrial sources of air pollutants do not operate continuously. It has therefore been of interest whether the biological activity of a biofilter could suffer during extended shut down periods. Results reported by Ottengraf (Ottengraf,1986) suggest that filter beds can survive periods of at least two weeks without significant reduction in microbial activity. If sufficient nutrients are provided by the filter material, survival periods of up to two months can be expected. In order to avoid oxygen starvation and/or dehydration in the filter, periodic aeration of the filter or operation of the blower in the turndown mode, is advisable during shutdown periods.

Off gas constituents will not always be degraded independently by microorganisms. In particular, for several chlorinated aliphatics only co-metabolism appears to be responsible for aerobic degradation. Similarly, biodegradation of benzene appears to be slow if benzene is the only off gas constituent, while presence of other organics can significantly increase its biodegradability. On the other hand , inhibition, for example, in the biodegradation of methanol due to the presence of tert-butanol, has been reported (Ottengraf, 1986).

Whether the operation of a biofilter could result in emissions of microorganisms has been investigated by several researchers(Ottengraf, 1986). One study concluded that these concentrations are only slightly higher than concentrations found in open air, and that a biofilter can actually achieve emission reductions for raw gases containing high concentrations of microorganisms. Another study concluded that maintenance or replacement of the filter material can result in an increase in emissions of fungi spores and that the use of respiratory protection should be advised for these activities. Refer to Table 2.0 for some typical organisms used in filter beds.

TABLE 2.0

Frequently identified organisms in filter beds.(Tibtech, May 1987 Vol.5 pg 135)

BACTERIA	FUNGI
Actinomyces globisporus	Penicillium sp.
Micrococcus albus	Cephalosporium sp.
Micromonospora vulgaris	mucor sp.
Proteus vulgaris	Circinella sp.
Bacillus cereus	Cephalotecium sp.
Streptomyces	Ovularia sp.
	stemphilium sp.

Filter construction and sizing

The type of construction and installation of a biofilter (e.g., open single bed, enclosed multiple bed, roof top installation, etc.) for a given application will depend primarily on the availability of space relative to the required filter volume. Other criteria include differences in capital cost and maintenance requirements between the different systems.

Since off gases from industrial processes usually contain a variety of compounds, sizing of the filter should, be based on a treatability study during which a partial off gas stream is treated in a biofilter pilot unit, typically several cubic meters in size. The required full scale filter then can be determined by scaling.

Filter material

In order for a biofilter to operate efficiently, the filter material must meet several requirements. Firstly, as mentioned earlier, it must provide optimum environmental conditions for the resident microbial population in order to achieve and maintain high degradation rates. Second, filter particle size distribution and pore structure should provide large reactive surfaces and low pressure drops. Third, compaction should be kept to a minimum, reducing the need for maintenance and replacement of the filter material.

Since it provides favourable conditions for microbes, compost derived from municipal waste, bark, tree trimmings and leaves is widely used as basic filter material. Other materials, such as porous clay or polystyrene spheres are sometimes added to increase reactive surface and durability, reduce back pressure and extend the filter material's useful life.

Typically, a compost based filter material will provide sufficient inorganic nutrients for microorganisms and addition of nutrients will not be required. In some cases, however, depending on the target pollutant and the soil of the filter material, the availability of specific nutrients might become process limiting. For example the addition of nutrients to a filter material has been shown to improve degradation of toluene significantly and was also successful in other cases.

Conditions to be maintained

- Moisture content in the filter material is a major operational requirement for a biofilter. Without providing the additional moisture, the (usually unsaturated) raw gas would quickly dry out the filter bed. Moisture is essential for the survival and metabolism of the resident microorganisms and contributes to the filter's buffer capacity. Non optimum moisture content can result in compaction, breakthrough of incompletely treated raw gas and the formation of anaerobic zones which emit odorous compounds. A moisture content of between 40% and 60% by weight is considered optimal.
- Since most microorganisms prefer a specific pH range, changes in the pH of the filter material will strongly affect their activity. The pH in compost filters is typically between 7 and 8, a range preferred by bacteria and actinomycete. In some cases the biodegradation of air pollutants can generate acidic by-products.
- In a biofilter, energy is predominantly needed by the blower to overcome the filters back pressure and, to lesser degree, by the humidifier. Typical power consumption rates for a biofilter range from 1.8-2.5kWh/1000m^3 but can vary significantly, depending on the state of compaction of the filter material.
- The routine and periodic maintenance of biofilters includes a number of operations. A daily check of the major operating parameters, such as off gas temperature and humidity, and filter temperature and back pressure, should be conducted. Periodic sampling of the filter material to detect potential failures of the humidifier or changes in pH should be conducted.
- For most biofilter installations, regulatory agencies will require a source to test the control efficiency claimed by a vendor.

Applicability of biofilters

Biofilters are best suited to low concentration VOC streams, in general between 500-1500 mg/l.

Overall biofilters can be a very effective technology if used for the correct applications. They are relatively cheaper than incineration processes and require a limited amount of maintenance.

3.0 Solvent recovery

This section will outline some of the most common types of solvent vapour recovery systems in use, namely Condensation and Adsorption. As Condensation is not widely used, I will only touch on this briefly, but I will investigate Adsorption in some depth.

Solvent vapour recovery by condensation

This technology is not seen very often in the printing industry. There is nothing dramatic in the technology itself, which relies on removing latent heat from the vapour in the air stream to the point where the solvents condense out. It operates on the same principles as the evaporator coil on an air conditioner, which on humid days will condense and drip water from the coils.

There are several reasons why this technology is not more widespread in the printing industry.

1. Energy Efficiency

For dilute vapour concentrations such as those generally encountered, the ratio of energy input to value of recovered product can be large. As a general rule, Condensation systems such as these are better applied to streams that are saturated with vapour.

2. Icing

Depending on the boiling point of the solvents involved, the temperature required on the condensing coil can be well below 0^0 Celsius. Under these conditions, water vapour in the air will freeze on the condensing coil, icing it up. If this occurs, then the system has to either be taken off line to de-ice, or if the exhaust stream is continuous, a second system needs to be installed in parallel to the first and the air flow switched to it so that emission is not interrupted while the first system is de-icing.

3. Maintenance

It has been reported by operators of such systems that the maintenance requirements are higher than they would expect for normal running maintenance (AFTA, 1990).

These and other reasons can render this technology a more expensive option than Adsorption. Also, unless there is already a refrigerant supply (normally liquid nitrogen or CFCs) on site, the cost of supplying the refrigerant must also be included in the costing. (in the case of CFCs, it must also be remembered that CFC replacements currently available do not perform quite as efficiently as CFCs, and any system previously designed to run on CFCs will therefore be derated once recharged with a CFC replacement.)

There are variations on the Condensation theme that attempt to reduce even further the volume of the exhaust stream to be treated.

One example is that of inerting the press drying zones. Instead of using air to supply the drying heat, an inert gas, normally Nitrogen, is used. A small Nitrogen stream containing relatively high concentrations of solvent vapour is then taken to the Condensation system. The governing factor on the extraction rate from the press is the drying capacity of the Nitrogen stream. As the atmosphere carrying the solvent is free of oxygen, LEL considerations only apply where there is the possibility of Oxygen leaking into the system. The system is balanced to minimise Nitrogen leakage, and requires a fair deal of modification to the press to eradicate leakage paths. To the best of the author's knowledge, the costs of modifications, and changes to operating procedures required to implement this system, are considered to outweigh the advantages of the system.

Solvent vapour recovery by activated carbon adsorption

Adsorption in general, and particularly adsorption on activated carbon, requires some definition. Firstly it is necessary to distinguish between adsorption, which is a surface phenomenon, and absorption where one substance is more or less evenly distributed throughout another, for example, water in a sponge.

Most people will have experienced adsorption (and its opposite process desorption) at some point. A good example is perfume or after shave that has been applied rather liberally. As the fragrance evaporates from the wearer, it moves about in the air, and comes into contact with solid surfaces such as clothes. Weak molecular level forces that exist on the surface of the solid, known as Van Der Waal's Forces, trap the odour molecules. The odour molecules have a<u>d</u>sorbed onto your clothes. (The phenomenon is even more noticeable with odours such as cigarette odours.)

By manipulating the conditions under which solvent molecules, are presented to a solid, and by selecting an appropriate solid surface for the molecules to deposit on, adsorption phenomena can be used to reclaim solvents.

What is activated carbon and why use it for solvent vapour recovery?

As discussed above, the solvent molecules are trapped on the surface of a solid. The higher the surface area, the more molecules can be trapped. What is needed is a solid which has a large surface area per unit volume. Activated carbon, along with other solids such as some grades of activated alumina and zeolites, have very large surface areas. To give some idea of how much, the volume of activated carbon equal to the top half of your thumb contains about the surface area of a football field.

Activated carbon is by far the most widely used adsorption material for the purification of fluid (both liquid and gas) streams. Liquid sugar and contaminated water are both purified by passing them through activated carbon. There is evidence to suggest that the ancient Egyptians, Romans and Hindus used a far less refined version of activated carbon to purify drinking water and wine. The other adsorbent materials mentioned earlier tend to be very specific in what they will adsorb, or have less capacity for a specific molecule than activated carbon.

Activated carbon is a highly refined form of elemental carbon or graphite. Carbonaceous materials such as coconut shells, peat, coal, etc. are treated chemically or in an inert atmosphere furnace, so that everything that is not pure chemical carbon is removed from the base material. The resultant activated carbon has a vast quantity of 'pores' which are mainly in the Angstrom range in diameter.

Due to the large research effort put in since World War 1, there is a large body of information on control and manipulation of pore size and distribution in activated charcoal. Appendix 3.0 shows an artist's impression of how the pores are structured.

Control of pore sizes is important since it enables appropriate grades of activated charcoal to be selected to maximise the specific adsorption of vapour.

Activated carbon comes in a variety of forms and adsorptive properties. The selection of the best activated carbon for the particular job at hand should be determined based on previous experience and relevant research data.

Manipulating the adsorption phenomenon

It is particularly useful that activated carbons have a high affinity for the solvent vapours generated by the printing industry.

Research data gathered in the laboratory and the field over many years has provided quantitative data on how various activated carbons behave with various solvents under various conditions. These performance characteristics are plotted as isotherms, which show the adsorption of a particular solvent (measured in terms of percent increase in weight of the carbon) versus the concentration of the solvent vapour in the air stream at a particular temperature. It is usual to plot multiple isotherms on the one graph to show the effect of temperature on the adsorption. Appendices 4.0 and 5.0 (AFTA, 1990) show isotherms for two different solvents on the same type of activated carbon. The percent increase in weight, or capacity, of the activated carbon for the solvents increases with increasing concentration of the solvent vapour in the air, and decreases with increasing temperature of the air carrying the solvent.

These isotherms are for equilibrium conditions, corresponding to a situation, where the activated carbon can adsorb no more, and the concentration, of the solvents in the stream leaving the Activated carbon bed is equal to the stream entering the bed. This condition is known as 'saturation'. In terms of solvent vapour recovery systems, these isotherms serve as a guide only, as in practice an Activated carbon bed would not be operating near saturation.

Appendix 6.0 (AFTA, 1990) shows the various isotherm stages typically used for the design of an activated carbon solvent vapour recovery system.

To optimise the size of the solvent vapour recovery system it is recommended that the solvent concentration in the air stream is increased. Apart from reducing the physical size of the system, these concentration lines show how increasing the concentration optimises the activated carbon's performance. As the solvent concentration decreases, so does the efficiency of the Adsorption process.

Manipulating the desorption phenomenon

In an activated carbon solvent vapour recovery system steam or hot gas is used to warm the activated carbon bed. The solvent molecules gain energy from the heat and liberate themselves from the activated carbon. The flow of steam or hot gas then sweeps the solvents from the bed. Removing the solvents in this way is known as desorption.

In Appendix 6.0 there is a line marked as 'HEEL'. When an activated carbon bed is first exposed to solvent vapours , and the bed is subsequently desorbed as described above, not all of the solvent from the initial flow of vapours onto the bed is desorbed. There are a number of explanations as to why this occurs, but the simplest explanation is that some of the molecules are taken so far down into the pore structure of the activated carbon, and lodge there so tightly, that the amount of heat supplied during desorption is not sufficient to drive them from the pores. This quantity of solvent held on the bed after a desorb is called the 'HEEL', with the difference between this HEEL and the breakthrough point being called the 'working capacity'. Working capacity is the solvent capacity of the activated carbon that works within the design of a regenerable activated carbon solvent vapour recovery system. Regenerable systems can undergo literally thousands of adsorb/desorb cycles before the HEELS need to be removed.

To remove the HEEL, or 'reactivate' the activated carbon, it is usual to send the activated carbon to a reactivation facility, which will reprocess the carbon at the original activation temperature (approx. 1,000°C) and drive off the trapped solvent molecules.

The difference between regenerative on site and reactivation off site is basically one of the temperature required. Currently there are no reactivation furnaces in Australia that accept outside activated carbon for reactivation . The typical life span of a bed of activated carbon for a regenerable system is somewhere around 10 years.

Practical application of activated carbon adsorption for solvent vapour recovery in the printing industry

Regenerable activated carbon adsorption systems are typically used in two ways:

Option 1.0 As a stand alone technology to reclaim evaporated solvents as liquid solvents for reuse or resale.

Option 2.0 as an intermediate step to concentrate the solvent vapours for treatment by some other technology.

In either case, the only difference is the fate of the desorbed solvent. In Option 1, the aim is to reclaim the solvent in a form that is suitable for reuse in the process, or which can be sold to someone else for them to use. In Option 2, the aim is to reclaim the solvents in such a condition as to optimise the size and cost of some downstream treatment, such as incineration. Appendices 7.0 and 8.0 (AFTA, 1990) show the process schematics for these 2 options.

How solvents affect the system

The range of individual solvents and the blends in which they are used in the printing industry is too diverse to explore individually in this thesis. The blends are usually dependant on the printing substrate. This blending makes it very difficult to recover the individual solvents unless further distillation takes place.

Further,these solvent blends may contain large proportions of water miscible solvents. In such cases where a steam regenerated solvent vapour recovery system is in use (by far the most popular method of regeneration), once again a distillation plant must be attached to reclaim the solvents from the condensate. This adds to the capital cost of the system.

In either case, with or without the distillation plant, the solvents recovered are normally of such quality that they can be reused in the process (Mann, 1992). However, occasionally, some top up is required because there will always be a percentage of low molecular weight solvent loss from the adsorbers.

Activated carbon systems for concentration

In some circumstances, there is the possibility that there is no need to reclaim the solvents for re-use, but it is advantageous to use the solvent in some other form. This is common where the cost of heating fuel is greater than the cost of the solvents, and where an incinerator and a heat exchanger, can be used to convert solvents to useable heat.

In these cases, a regenerable activated carbon adsorption system assists. If despite all efforts to reduce the amount of air that is carried to the vapour emission control system, the air flow is still large and the solvent concentrations are low, a relatively large incinerator is required. The capital cost of the incinerator increases with air flow and the running costs increase with decreasing solvent concentration.

Applicability of solvent recovery

To achieve the best from such a system, current work practices of the print house need to be examined to ensure that the most efficient use is being made of the drying air processes, and critical evaluation should also be made of the solvents currently in use, to ensure the most effective system can be provided for the particular application.

The major disadvantages of this method are;

- It is costly and not suited to small printing operations.
- The activated carbon is expensive and maintenance costs are high.
- Activated carbon has the potential to combust.
- The reclaimed solvent may not be pure enough to reuse.

Below is a cost, CO_2, and energy comparison of the three destruction technologies discussed (Mann, 1992).

TABLE 3.0

COMPARISON OF THE DESTRUCTION TECHNOLOGIES

(Mann, 1992)

SYSTEM TYPE	***PART A*** **Price for supply of equipment only($)**	***PART B*** **Price for installation & commisioning($)**	***TOTAL COST*** ($)	CO_2 EMISSION 0-BEST 10-POOR	ENERGY REQUIREMEN RATING 0-BEST 10-POOR
INCINERATOR (Continuous)	937,745	141,680	1,079,425	10	1
BIOFILTER	900,000	100,000	1,000,000	10	1
ACTIVATED CARBON ADSORPTION	2,324,850	381,960	2,706,810	1	10

PART 4.0

PREVENTION OF EMISSIONS

Prevention of emissions can be achieved in two ways;

1.0 Development of ink technology which eliminates/reduces the use of solvents.

2.0 Cleaner production methods.

1.0 Development of ink technology

There are many approaches available to printers to bring them into compliance with the current regulations, and any combination of them may be used to achieve this goal.

If conventional inks are to continue in use, their volatile component must be captured or destroyed. Both solvent capture/recovery, and solvent incineration /biofiltration require fairly substantial capital outlay and a further environmental burden either in terms of additional energy costs, or the emission of carbon dioxide with suspected associated greenhouse effect.

Another approach used in the USA has been to continue with solvent based inks, but to replace the ethanol with trichloroethane. This was possible because, under a strict reading of the regulations, VOC's are restricted only if they contribute to the formation of ozone, a precursor of smog. As trichloroethane does not contribute to ozone production it was considered acceptable, despite the link between chlorocarbons and destruction of the earths ozone layer! Of course, the aggressive nature of the solvent renders it unsuitable for flexographic use, but it serves to point out that compliance with one set of environmental regulations can have wider reaching impacts.

More common responses to call for the reduction of VOC's, particularly in Europe and the USA have been:

(1) To reduce or remove the solvent from the ink system, giving high solid inks.

(2) To use water as the major diluent, giving water-based inks.

High solid inks

By taking a conventional ink formulation and eliminating some or all of the solvent, it would be possible to obtain a high solid ink of sorts. However, the increase in viscosity would render such a formulation totally unsuitable for flexographic/gravure printing. Therefore a workable ink for these applications must be designed from first principles.

To obtain an appropriate viscosity with little or no solvent content, the resin must be selected to have as low a molecular weight as is possible. However, resins at low molecular weights exhibit poor properties, such as water, oil, grease, heat, scuff, and scratch resistance in the dried film. Also, it is likely that the print will remain tacky even after thorough drying, resulting in clinging and blocking.

To overcome this it is necessary to build into the ink a method of increasing the molecular weight of the resin, and thus obtaining the desired toughness of the ink film, after printing. Thus the resin used must be capable of crosslinking or polymerising.

The two major curing methods are by catalysis and radiation.

Catalysed, or 2 pack curing systems are generally polyol/aminoplast blends, to which an acidic catalyst is added on press, in much the same way as 2 pack systems are mixed for application involving contact with aggresive chemicals or demanding environmental conditions.

Radiation/Ultra violet curing inks are basically a monomer and/or oligomer mixture incorporating a small amount of photoinitiator. Immediately after printing, the ink is exposed to radiation, usually ultra violet, but sometimes an electron beam, and the photoinitiator, by absorbing the available energy, " kick starts" the crosslinking of the resin.

Because the solvent content of high solids inks is reduced or eliminated, the pigment and resin loadings of the ink can be of the order of 2 to 4 times that of conventional inks:

Flexographic Inks - Relative compositions

	Conventional	**Catalysed**	**UV curing**
Pigment	11	25	44
Resin	12		
Polyol/Aminoplast		55	
Monomer/Oligomer			47
Additives	7	10	9
Solvents/Water	70	10	

UV curing inks

The development of UV curing inks is far from new. During the 60s, UV curable resins were developed for timber coating, where indeed they are still widely used. Concurrently, lamp makers developed medium-presssure, mercury arc lamps that generated commercially useable quantities of UV, at practically manageable cost (NAPIM, 1992).

These systems were rapidly improved through the 70s, and significant areas of the paste ink market, notably flat-sheet metal decoration, self adhesive label printing, and sheetfed folding carton production became strongly dependant on UV. As a simple example, self adhesive labels pre-1980 were printed at 2-3,000 impressions per hour in up to four colours, due to the constraints of infra red drying, but currently labels are printed in up to ten colours at 14,000 impressions per hour, and the level of sophistication in design is truly remarkable.

Another area of major growth in UV technology has been the gloss varnishing of magazine and book covers, a process that has rendered virtually obsolete the slower and more costly film lamination procedure for the same application.

Over the past twenty years, there have been many attempts to extend the use of UV curing into the flexographic and gravure segments of the market. Major impediments have been the difficulty in printing on existing equipment with inks that are totally different in flow character - being 'syrupy' rather than' watery', the relatively large size of UV lamps, and the considerably higher vehicle costs of UV compared to solvent and waterbased systems. It can be said that the first two of these hurdles have been addressed, if not fully overcome, and a compromise may be emerging on the latter.

UV curing inks differ in many ways from conventional inks. Firstly, the vehicle carrier has no volatile components; everything that is applied to the substrate stays there. Secondly, unlike the low energy process of evaporation, high-energy UV causes chemical polymerisation to occur throughout the printed film.

UV inks consist of reactive resins, either acrylic functional epoxies, urethanes, or polyesters (or in the case of cationic systems, straight epoxies), dispersed into a multi-functional monomer that acts both as a crosslinking agent, and a viscosity diluent. Another vital component of the UV vehicle is a photo-initiator, a chemical that absorbs UV light, and then passes the energy onto the resins and monomers to start them reacting together to form a highly crosslinked polymeric film.

Another factor that needs consideration in UV curing is the influence of the ink colour, that is the pigment, on the rate of UV cure. The slowest colour is invariably black. Black is, by definition, a colour that absorbs all incident electromagnetic radiation, and that certainly includes UV, and the carbon pigment absorbs so much light, that little is left to promote curing of the ink vehicle.

The next slowest colours are white and gold, for the opposite reason.In the case of these colours, maximum reflection is sought, so light, again including UV is not permitted to penetrate the ink layer to easily cure the film. Thus if a system is designed to handle a black solid, all other colours will be readily accommodated.

As previously noted, efforts have been made over many years to adapt UV technology to the classical solvent ink processes. The first problem encountered was how to meter and supply ink to the plate, given the quite different rheological properties of UV 100% solids resin mixtures compared to resin solutions. A logical approach was to heat the ink. Unfortunately for many such attempts, heating UV resins over extended periods starts them slowly reacting together, much more slowly than UV exposure, but enough to turn their honey like consistency into molasses, and hence to make them unprintable. For small machines, this is not significant, as the ink can be frequently replaced with cool material, but on large presses long term recirculation of heated ink is a recipe for disaster.

Recent times have seen the development of the heated chamber-blade assembly, which has neatly addressed the problem, as only the small amount of ink in the chamber is heated, with the bulk of the ink in the circulation system acting as a heat sink.

As UV inks are 100% solids, only one-third the volume compared to conventional inks must be applied. Clearly there is greater need for accuracy.

A most important consideration in the UV system is the size and power output of UV lamps- and also one of their less desirable characteristics, their significant heat output. Lamps are now available that are very powerful, emitting up to 180 watts of energy per linear centimetre, compared to a ceiling of only 80 watts a few years ago. Mercury arc lamps have another characteristic that if switched off, they must electrically stabilise before they can be reignited; this can take up to ten minutes, a very good reason not to extinguish lamps.

For both narrow and full width presses, current upper speed limits are around 200m/min, with 150m/min being average. At this speed, two lamps of 120watt/cm for each colour are necessary to ensure complete cure. Thus for a six colour press, twelve lamps of 1.5 meters length, would require a total of 216Kw of electrical energy (Flexo, March 1991).

The range of substrates being printed by UV methods increases daily, but, to ensure optimum adhesion, in line corona treatment of plastic films is essential.

Examples currently listed in literature include:

Paper
Polyethylene
PVC
P/P and OPP
Polyester
N/C coated foil

In Australia at present, commercial operation is limited to narrow web paper, although excellent print qualities are being obtained on the above substrates.

In the flexible area, work is continuing to satisfy questions on applicability for food packaging on a wide scale, because although UV has the advantage of no retained solvent, the self odour of UV prints is different from all conventional systems and acceptance by food packagers must be obtained.

There are some questions of health and safety which should be addressed before deciding on a system. UV inks have in the past been blamed for eye and skin irritations after prolonged exposure. These risks can be minimised by the use of proper housekeeping, but the possibility should be kept in mind and an ink system with least health risk should be selected.

Summary of high solids/UV cured systems

Advantages:

◆ Reduced VOC emissions	
◆ Water resistance	Very good
◆ Solvent resistance	Excellent
◆ Chemical resistance	Excellent
◆ Heatseal	230°C/1sec/3 Bar
◆ Gloss	Very good
◆ Printability	Very good
◆ No drying on the press	
◆ Reduced washup	
◆ No need for solvent makeup	
◆ Inks more expensive but only use 1/3rd	

Disadvantages:

- Health and safety questions
- Requires strict control and better training
- Need for curing unit
- May require new aniloxes and metering systems.
- Consumer acceptance

UV curing ink will, like its lithographic counterpart, come to provide a useful tool for sections of the flexographic and gravure printing industry. It will not sweep conventional technologies aside, and companies seeing the technology as some easy way out of the environmental question will be disappointed.

Waterbased inks

The use of waterbased inks on porous substrates has been a fact of life for some years, being well established for flexo printing on Kraft media for bags and sacks, corrugated board cartons, disposable tissue products and duplex board for packaging and other food containers.

Because of this established technology, the most widespread response to VOC emission control around the world has been to extend the use of waterbased inks into areas where solvent inks have traditionally been used - particularly to impervious substrates.

American experience was that legislation required rapid reduction of VOC emissions, and in order to keep operating, converters adopted waterbased inks, (inks reduced with a water/alcohol mixture) despite some reduction in print quality (AFTA, 1990).

European governments have exerted less pressure on the printing industry in most cases, and although adoption of water reducible systems has been slower, the results are true waterbased inks containing less than 10% solvent, reduced with straight water, and able to stand on their own merits in terms of quality.

The pigmentation of water based inks is on average slightly higher than solvent inks, (not counting waterbased high solid inks of course) due to the finer aniloxes required. The resin systems are, in the vast majority of occasions, acrylic blends, although other resin types such as urethanes and polyesters have been used. Acrylics offer good compatibility, versatility of properties and cost effectiveness. Acrylics and pigments are not as a rule hydrophilic materials, and it is for this reason that the systems are formulated at high pH - to solubilise the acrylic and give a vehicle suitable to disperse and/or carry pigment to its end use. This high pH is obtained by ammonia or other amines. Ammonia is very volatile, aiding fast drying and development of adhesion, but the slower amines give better press resolubility (easier to clean the press) and pH stability - a combination usually gives a workable compromise. In addition waterbased inks contain waxes for slip and scuff requirements, antifoams and often surfactants to aid printability and print appearance.

As well as the VOC emission issue, there are other expectations of waterbased inks which have led to interest in this technology. Some of these expectations are not necessarily based on facts.

Waterbased inks are by their very nature non-flammable, rendering them safer to manufacture, transport and use. Also, storage does not require the strict precautions and facilities needed for solvent inks.

Strict standards set by food companies, restricting the acceptable levels of retained solvents in packaging materials, are easier to achieve with waterbased inks, although they are no less subject to testing for taint by resin odour and residual ammonia or amine. It is not the case that waterbased systems are ipso facto more suitable for food contact applications than solvent based. While manufacturers of waterbased inks, and their raw material suppliers, are constantly seeking FDA exempt materials, the printer must specify where an ink is to be used in such an application, as there can be no guarantee that a standard waterbased ink will be appropriate.

Because in the past the major market for these inks was for post-corrugation printing of cartons, which represented one of the less demanding applications, an image was created that waterbased inks are naturally cheap, particularly as water is virtually free compared with organic solvents. Unfortunately this is not necessarily the case because of the more demanding properties required in other applications, particularly coated boards and other impervious substrates. The harder, glossier, faster drying resins and other additives used to achieve these properties all serve to raise the cost of the higher performance waterbased ink towards, and perhaps above, the cost of the solvent based equivalent.

When opting to use waterbased inks, there are several practical points which must be considered, as it is not simply a matter of taking solvent inks out of the duct, adding the waterbased, and using the same methods and equipment to print.

Although perhaps more critical in gravure cylinders, it is important that the cells of the anilox are of the correct configuration to obtain optimum transfer to the stereo. The best results are obtained with fine screen aniloxes with a truncated pyramid shaped cell obtained by mechanical engraving. The fine screen assists in an even lay of ink, and, by reducing the amount of ink deposited, lessens the drying required. It is for this reason that waterbased inks are somewhat stronger (in colour) than solvent-based. As the usage is increased, the true cost of these inks may be lower than initially appears to be the case.

Drying can be one of the most problematic aspects of waterbased inks. The use of resin emulsions in modern inks has sped up the drying of these inks significantly, and, as previously mentioned, the use of high strength inks at low deposit weights reduces the amount of water to be removed. The volume of air from driers is of paramount importance - perhaps more important than the actual temperature of the air, particularly as overheating of polyolefin films can make them more difficult to adhere to. Thus the optimum drier is one which delivers as much air as possible at about 80^0C. This should avoid problems of dimensional changes to the film also.

A critical area for waterbased inks is that of adhesion to impervious substrates. Adhesion generally develops more slowly than with solvent based inks, so a standard tape test immediately off press may give an apparent failure to an acceptable print. Ensuring the film is not overheated, thorough drying by large air volumes and testing some time after printing all will contribute to better results.

Waterbased inks are often criticised for their tendency to foam, and indeed it is true that compared to solvent based inks, this is common. The necessity to include surfactants in waterbased formulation almost ensures some foam formation. Usually the ink manufacturer will include sufficient anti foam to prevent problems under normal conditions. Extra antifoams can be added but there is a risk that excess may cause pinholing, reticulation or "fish-eyes". A programme of prevention can avoid such problems; the use of a peristaltic pumping system will reduce agitation; return hoses delivering ink to the bottom of the tank rather than dropping it into the top will cut foaming significantly.

Because of the low evaporation rate of water, viscosity adjustment is not required as often as with solvent based inks, but pH control becomes important as the loss of volatile amine from the ink can cause changes in viscosity and print quality.

The alkaline quality of waterbased inks can exacerbate the tendency of water itself to cause corrosion. This has been successfully dealt with in the corrugated carton sector, and good housekeeping, speedy clean-up of splashes and spills and thorough washing of the press, stereos and aniloxes after a run seem to be the best ways of preventing corrosion.

The final consideration is one of waste management, Will you be swapping an air pollution problem for a water pollution problem? It is not acceptable to dump waste into the sewerage or stormwater systems. In many countries the disposal of waste is the responsibility of the generator of that waste, who cannot simply pay someone to cart it away but must ensure it is treated correctly. From the years of experience of the corrugated industry several methods of disposal have developed. Settling tanks and precipitation/coagulation vessels are common. A new process is "ultra-filtration" where practically all solids can be extracted from ink waste pumped through the filter. The filtered water is reusable, and the concentrated waste can be recycled, in a black ink for instance.

Summary of waterbased inks

Advantages:
- Reduced VOC emissions
- Eliminate reducer costs
- Low flammability
- Lessened health and safety problems
- Technology established in some areas

Disadvantages:
- Some compromise in properties, e.g. gloss
- Require efficient dryers, different aniloxes
- Foaming possibility
- Corrosion potential
- Waste disposal

Again, it can be seen that, with correct use of these inks, the advantages can be maximised, while the disadvantages are lessened or eliminated. The main requirement to make waterbased inks work is cooperation between ink makers and printers to take the most suitable ink and use it in the most effective manner. Refer to Tables 4, 5 & 6 for a comparison of formulations, their effects on the environment, and economy of the developing ink technologies against the solventbased system respectively.

TABLE 4.0

A COMPARISON OF THE FORMULATIONS OF THE DEVELOPING INK TECHNOLOGIES, AGAINST THE SOLVENT BASED SYSTEM

	SOLVENT BASED	**WATER BASED**	**UV -CURABLE**
PIGMENTS	10 to 15 %	10 to 15 %	20 to 30 %
RESINS (POLYMER)	20 to 30 % Numerous chemistries -Nitrocellulose -Polyamide -Urethane -Acrylic etc...	20 to 30 % Limited chemistry -Acrylic solutions -Acrylic emulsions -Polyurethane emulsions	50-70 % (oligomer) Numerous chemistries -Epoxy acrylate -Polyester acrylate -Polyurethane acrylate etc...
SOLVENTS	60 to 70 % -Alcohols -Acetates -Glycols -Hydrocarbons	60 to 70 % -Water -Glycols	No solvent
ADDITIVES	About 5 % -Plasticisers -Waxes -Adhesion promoters etc...	About 5 % -Surfactants -Waxes -Defoamers -Amines etc...	About 5 % -Photoinitiators/ co-initiators -Waxes -Surfactants etc...

*Table compiled from (AFTA, 1990), (FTA, 1987), (Sicpa Australia, 1993) and own knowledge.

TABLE 5.0

A COMPARISON OF THE DEVELOPING TECHNOLOGIES AGAINST SOLVENT BASED SYSTEMS AND THEIR EFFECTS ON THE ENVIRONMENT

	SOLVENT	AQUEOUS	U.V.
ATMOSPHERE	VOC	No problem if organic solvent low	No problem
INK WASTE	Incineration (with/without treatment)	Incineration Landfill after treatment	Incineration
WATER WASTE	No problem	Need appropriate treatment	No problem
USED CONTAINER	No major problem	No problem	May need particular treatment
PACKAGING RECYCLING/ DEINKING	No major problem	No major problem	No major problem
GENERAL IMPACT	Low - will need significant investment	Low - will need limited investment	Very low No investment

* Table compiled from (AFTA, 1990), (FTA, 1987), (Sicpa Australia, 1993) and own knowledge.

TABLE 6.0

INKS FOR TOMORROW vs ECONOMY

	SOLVENT	AQUEOUS	U.V.
PRINTING SPEED	HIGH	LIMITED	HIGH
CLEANING NEEDS	SIGNIFICANT	LOW	VERY LOW
INK COST	STANDARD	HIGHER	MUCH HIGHER
MILEAGE	STANDARD	BETTER	MUCH BETTER
INK STOCK	LIMITED	LARGER	LIMITED
SHELF LIFE	LONG	MEDIUM	LIMITED
INK RETURNS USE	EASY	EASY	LIMITED
INVESTMENT	STANDARD	ANILOX WATER TREATMENT DIAPHRAGM PUMPS	ANILOX INK CHAMBER DOCTOR BLADE UV DRYER DIAPHRAGM PUMPS

* Table compiled from (AFTA, 1990), (FTA, 1987), (Sicpa Australia, 1993) and own knowledge.

2.0 Cleaner production

Cleaner production is the use of better housekeeping, management practices, and production processes to minimise harmful environmental impacts from the beginning to the end of the production process. These changes not only protect the environment, but can reduce production costs through greater efficiency, less waste of material inputs, increased productivity, reductions in energy used and lower waste treatment charges.

All printing houses should work to improve the air quality for their workers. In some instances , waterbased printers have fugitive ammonia and alcohol vapours that are approaching Occupational Safety and Health Administration (OSHA) limits. Uncontrolled chlorinated fugitive vapours can get back into the gas burner, and when exposed to a flame, create a dilute form of hydrochloric acid. These vapours are corrosive and have contributed to oven deterioration and increased building maintenance.

Pollution control concerns have been a driving force for press manufacturers to improve the overall capture of fugitive emissions while reducing the net exhaust volume. Not everyone can afford a new million dollar printing press, but a great deal can be learned from what the press designers have done to machinery to meet the capture standards.

A smart farmer was once asked " What is the easiest way to catch a cow?" He responded, " Don't let the cow out of the barn in the first place." This bit of homespun logic also applies to fugitive capture in the press room. Fugitive emissions may be defined as that portion of solvents which are delivered to the printer, but are not delivered to the capture device (Capture of Fugitive Emissions, PSTC Technical seminar 1990). If the solvent vapours are not allowed to escape in the first place, the ambient air quality will be greatly improved.

New flexographic/gravure printing presses have very tight fitting ink pan covers, ink-tank covers and some innovative contaminant approaches. Anguil Environmental systems,Inc.(Printing press suppliers), have found that the two greatest areas of fugitive emissions are from the ink-tank area adjacent to the press (where inks are pumped into the pans) and after the last colour deck (where there is a long open web lead prior to going to the overhead tunnel drier). Most flexographic presses do not have a between colour drier after the last printing deck, and consequently, the wet web is being air dried prior to going into the tunnel dryer. On many jobs this results in significant generated solvent, since 100% coverage, either a back up white or an overlacquer, may be applied on the last deck. A great deal of solvent emission occurs prior to entering the overhead tunnel dryer. The new presses lack this open printed web leads.

The best way to improve air quality in the press room is to start with balancing the press ovens. Many older presses have systems severely out of balance. This means the supply air to the drier is greater than 80% of the exhaust air from the dryer. Obviously this is a large contributor to fugitive emissions.

The EPA has developed new guidelines and is emphasising maximising fugitive capture when pollution control equipment is used. They are encouraging the use of 100% capture rooms. One way they are encouraging this is by proposing capture test procedures that could be very costly and inconvenient to a production facility not using 100% capture rooms.

Consequently, many facilities have gone to the 100% capture, or in EPA terminology, "Permanent Total Enclosure(PTE)." The criteria and verification of a PTE is listed in the EPA document, Procedure T. There are various criteria, but the most important criteria is that the average face velocity of air, through all natural draft openings, shall be at least 3,600 meters per hour (200 feet per minute). Also the direction of air through all natural draft openings shall be into the enclosure.

Steps to Improve Capture

Improving the press room's ambient air conditions can be accomplished in house or with minimal outside assistance at reasonable cost. The following is a guideline for improving capture:

Balance dryers - The dryers obviously have more exhaust than supply. The average is about 20% more exhaust. If the printers can fine tune the between colour dryers, they should have a higher exhaust percentage (20 to 35 %) to better capture printing deck fugitives. Overhead tunnel dryers have the vapours in a box so they can be exhausting 10 to 20 % more than supply.

Map the fugitive vapours - A portable detection device can be applied to determine the press side hot spots. A sensitive nose can also be used but it often goes out of calibration.

Housekeeping - Open ink pans,and ink pails contribute to fugitive emissions. Safety cans, and tight pail and pump covers should be used. Ink pan covers should be examined ; new pan covers do a better job of capture. Manifold doctor blades also reduce fugitives.

Floor sweeps - Simple slotted pipe pick-ups exhaust vapours from under the press and around the ink tanks.

Flash off hoods - The highest level of fugitives is above the open web lead typically after the last printing deck and before the overhead tunnel dryer. This area is often not enclosed on older presses. A simple box extension on the overhead and hinged hood after the last colour deck can dramatically reduce fugitives. Involve the operator in hood design for webbing access. Fugitives are higher where a wet web makes a turn.

Wash-up - Run the between-colour dryer exhaust and floor during wash-ups. Solvents are heavier than air and are concentrated along the floor.

PART 5.0

AN EXPERIMENTAL CASE STUDY OF SOLVENT BASED vs WATER BASED INKS

Under the current economic climate and conditions most of the flexographic/gravure printing houses within the Melbourne metropolitan area are small in size compared to those in the USA, Japan, and Europe. Due to the size of these printing houses, it is difficult to expect these companies to adopt one of the destruction technologies, because of the high costs involved. Hence it is more likely and feasible that either water based inks, or U.V. curable inks will eventually overtake solvent based inks in the future.

At this point in time it appears that water based inks will play a bigger role in the lowering of VOC emissions than UV inks due to the similarities of the former with solvent based inks. The printer/operator will accept the use of water based inks more readily than U.V. inks, because water based inks appear to be similar to solvent based inks in flow/viscosity and other characteristics already mentioned in part 4.0, Tables 4.0, 5.0, and 6.0. Hence, in this section waterbased versus solvent based inks will be compared experimentally in the laboratory of the Liquid Ink Division of Sicpa Australia. These experimental results will indicate where the deficiencies lie in the water based system and the extent of development required to obtain a standard equal to solvent based inks.

Aim:

To investigate the use of waterbased ink technology in lowering VOC's in Polypropylene film printing where traditionally solvent based inks are used. Some of the major properties that are required by solvent based polypropylene inks will be compared to the developing technology of water based inks. It will be possible to draw conclusions as to the limitations and areas that need to be improved in waterbased ink technology for this application.

Experimental procedure:

Samples of water based and solvent based inks were supplied by Sicpa Australia. the colour chosen for testing was cyan blue. The standard test methods used are from Sicpa Australia's Quality Control Manual, Liquid inks Section 13, dated 25/5/93. Sicpa Australia's test methods were chosen because they are the most up to date test methods available for the subject of interest.

The ink samples were reduced to a printing viscosity of 30 seconds on the Zahn 2 cup, according to Standard Test Method 13-10A (see Appendix 9.0). The ink samples were then printed by the flexographic method, according to Standard Preparation of Proofs Method, Test Method 13-0 (see Appendix 10.0). The ink samples were at all times printed side by side at equal viscosity in order to obtain an equal comparison at equal printing speeds and comparable dry film weights.

The substrate printed was Polypropylene, supplied by Shorko Australia, (grade of polypropylene was Shorko B20). The level of treatment the film was supplied at was 38/39 dynes/cm. This treatment level is carried out by the film supplier in order to promote good ink adhesion, as polyolefin films result in adhesion difficulties otherwise. Therefore surface treatment of the film is required. The most common of these treatments is corona discharge, where high voltage electrodes oxidise the substrate surface (Flexo, Sept. 1990 Pg 38). Corona treatment is also used by the printer usually prior to printing. The treatment level was also estimated prior to laboratory use using "dyne solutions". These solutions were prepared by mixing quantities of formamide and ethyl cellosolve as outlined in ASTM Procedure D2578. Once again a dyne level of 38/39 was confirmed using this test method. This test method was chosen since it is the monitoring technique most commonly used by converters.

Once the test samples were printed, they were allowed to dry at 80°C for 10 seconds, then the following tests were carried out:

1. Standard Test Method 13-15 for VOC content (see Appendix 11.0).
2. Standard Test Method 13-2 for Gloss (see Appendix 12.0).
3. Standard Test Method 13-3 for Adhesion (see Appendix 13.0).
4. Standard Test Method 13-5 for Flexibility (see Appendix 14.0).
5. Standard Test Method 13-4 for Scratch resistance (see Appendix 15.0).
6. A comparison of visual appearance was carried out, that is the quality of the printed samples were compared for any visual defects.
7. A cost comparison was also made, based on the cost of the formulation.

As stated on the previous page, the samples were at all times printed at equal viscosity using a 180 anilox roll (see page 13), and side by side not allowing for any discrepancies in film weight, which will vary from printed sample to printed sample, due to the variation in printing speed. Each test was repeated 10 times, with the exception of 1.VOC results were obtained as an average of three readings.

Results :

1.0. The formulation for the water based and solvent based samples cannot be disclosed for confidentiality reasons. However, a simplified formulation, without specific additives is shown below in Table 7.0.

TABLE 7.0 FORMULATIONS AND VOC CONTENT RESULTS

RAW MATERIAL	*SOLVENTBASED (% BY Wt)*	*WATERBASED (% BY Wt)*
PHTHALOCYANINE BLUE PIGMENT	10	10
RESIN	25	
ACRYLIC SOLUTION/EMULSION		30
SOLVENTS ALCOHOL/ACETEATE	60	10
WATER		42
ADDITIVES	5	8
SOLIDS	37.5	29
VOC	62.5	12
% REDUCER REQUIRED FOR PRINT VISCOSITY	20 (100%Alcohol)	15 (80:20, Water:Isopropanol)

2.0. the gloss test results were measured visually and instrumentally as per Standard Test Method 13-2 (see Appendix 12.0). All of the instrumental measurement results for each sample are an average of 5 readings.

TABLE 8.0 GLOSS COMPARISONS OF BOTH SOLVENT AND WATER BASED PRINT SAMPLES, MEASURED VISUALLY AND INSTRUMENTALLY.

	SOLVENT-BASED	**WATER-BASED**	**SOLVENT-BASED**	**WATER-BASED**
sample No.	*VISUAL*	*VISUAL*	*INSTRUMENT*	*INSTRUMENT*
1	greater	lower	58	50
2	greater	lower	60	55
3	greater	lower	61	53
4	greater	lower	59	52
5	greater	lower	61	51
6	greater	lower	59	54
7	greater	lower	60	51
8	greater	lower	60	54
9	greater	lower	60	56
10	greater	lower	65	52
Average	greater	lower	60	52

NB; All prints printed on polypropylene film.
Instrument range 0 - 100.

3.0. The adhesion tests as per Standard 13-3 were carried out immediately after printing, 24 hours after printing and 7 days after printing the substrate. The results are as follows (Table 9.0).

TABLES 9.0 PERCENTAGE INK RETAINED AFTER CARRYING OUT STANDARD TAPE TEST AT;

(a) immediate
(b) 7 hours
(c) 24 hours

Refer to page 54 for adhesion results.

table 9.0(a)

sample No.	solventbased (%)	waterbased(%)
1	95	45
2	90	40
3	90	45
4	90	50
5	95	45
6	90	45
7	95	50
8	95	30
9	95	50
10	95	30
average	93	43

table 9.0 (b)

sample No.	solventbased(%)	waterbased(%)
1	100	70
2	100	75
3	100	70
4	95	70
5	95	70
6	100	75
7	100	75
8	100	75
9	90	70
10	100	75
average	98	72

table 9.0 (c)

sample No.	solventbased(%)	waterbased(%)
1	100	100
2	100	100
3	100	100
4	100	100
5	100	100
6	100	100
7	100	100
8	100	100
9	100	100
10	100	100
average	100	100

4.0. Flexibility of the printed substrate was tested according to the Standard Test Method 13-5 (see Appendix 14.0). The samples were tested immediately (@ t = 0), after 7 hours and after 24 hours. An average result of the 10 samples tested is shown below (Table 10).

TABLE 10.0 RESULTS OF FLEXIBILTY COMPARISONS BETWEEN SOLVENT AND WATER BASED INKS ON POLYPROPYLENE.

Time tested (hours)	Solventbased	Waterbased
t = 0	standard	inferior to standard
t = 7	standard	inferior to standard
t = 24	standard	Equal to standard

NB; 10 Samples were tested in each time interval.

5.0. Scratch resistance of the printed substrate was tested according to the Standard Test Method 13-4 (see Appendix 15.0). Once again the samples were tested over the same intervals as previously. The average of ten samples tested are tabulated below in Table 11.0.

TABLE 11.0 RESULTS OF SCRATCH RESISTANCE OF SOLVENT AND WATER BASED INKS PRINTED ON POLYPROPYLENE.

Time tested (hours)	Solventbased	Waterbased
t = 0	Standard	Equal to standard
t = 7	Standard	Equal to standard
t = 24	Standard	Equal to standard

NB; 10 samples were tested at each time interval.

6.0. A comparison of visual appearance was made as per Standard Test Method 13-1 (see Appendix 16.0). Shade, strength and any visual differences between the solvent based and water based were noted.

TABLE 12.0 COMPARISON OF PRINT QUALITY BETWEEN SOLVENT AND WATERBASED INKS, PRINTED ON POLYPROPYLENE.

Property	**Solventbased**	**Waterbased**
Strength	Good	Very good
Shade	Standard	Equal
Print laydown	Good	Slightly inferior

7.0. The cost of the ink samples tested, that is the cost to manufacture the ink samples from raw materials is as follows;

	SOLVENTBASED	**WATERBASED**
COST ($A)/Kg	4.00	6.00

TABLE 13.0 SUMMARY OF TEST RESULTS

PROPERTY TESTED	SOLVENTBASED	WATERBASED
VOC content (%)	62.5	12
Reducer content (%)	20	15
Gloss (i) Visual (ii) Instrument	greater gloss 60	lower gloss 52
Adhesion % ink retained		
(a) t = 0 hours	93	43
(b) t = 7 hours	98	72
(c) t = 24 hours	100	100
Flexibility		
(a) t = 0 hours	standard	D< standard
(b) t = 7 hours	standard	= standard
(c) t = 24 hours	standard	= standard
Scratch resistance	standard	= standard
Shade/strength	standard	= standard
Print lay/Quality	good	inferior
Cost ($A)/kg	4	6

Discussion of results:

From the ink samples compared and the results obtained a number of observations can be made. Firstly and most obviously, the aim of this technology is to lower VOC emissions at the printer/converter. This requirement has been attained. The reduction in VOC is by approximately 80% if the waterbased ink is introduced, which is more than adequate to comply with EPA regulations.

Secondly, the properties obtained by reducing the VOC this amount has had an effect on the performance of the waterbased ink against the solvent based ink for polypropylene printing.

The gloss of the dry waterbased ink film against the solventbased counterpart appeared to be much lower visually, the difference was observable immediately. However when using the Gardner Glossmeter the difference was not so great. Reference to Table 13, indicates that the average results are similar. One possibility for the visual difference to appear greater than that obtained by the instrument, may be due to the lay (coverage) of the water based print. The lay as is pointed out in Table 13.0 is inferior to the solventbased print. This poor lay may give the waterbased print an appearance of lower gloss, visually, where in actual fact instrumentally it is somewhat better, as indicated.

The gloss is an important aspect when printing on a flexible packaging substrate, such as polypropylene: the greater the gloss the more attractive the package appears. Hence, the lowering of the gloss is an important consideration when choosing water based ink.

The gloss is obtained through the polymer components in the formulation. In the water based ink the acrylic emulsion gives the gloss characteristic. Hence, increasing the polymer content would increase the gloss in the final print obtained. Increasing the emulsion content will also improve other characteristics, such as adhesion and flexibility as will be discussed later.

The adhesion of an ink to the substrate must be adequate. If the adhesion of an ink is not sufficient to withstand the normal demands anticipated, then the ink is of no value for the proposed application. From the test results it can be seen that the immediate adhesion to the polypropylene is not as good as the solvent based system, but with 24 hours of allowing the dry film to cure, the adhesion of the water based print improves to an equivalent level to that of the solventbased print. Therefore the printer/converter should keep this in mind, when substituting to water based technology. Ideally the print should be allowed 24-48 hours to cure before being converted to a package.

Once again, in water based ink formulations the key to obtaining adequate adhesion is dependent on the polymer or in this case the acrylic emulsion. If the emulsion has good adhesion to the substrate then the water based ink will also have good adhesion. Unlike the solvent based ink additives available for adhesion promotion, the waterbased additives for adhesion promotion are not as effective, as yet. With further development from the additive suppliers, adhesion promoting additives will improve.

The flexibility, like the adhesion, improves with time, has can be seen from the results obtained (Table 10.0). Flexibility is an important property and one which must be satisfied for the printing on polypropylene. Once the polypropylene is converted to a package it will require good flexibility characteristics due the nature of the package, its handling conditions and final application. The flexibility properties are obtained from the polymers present in the ink formulation.In the case of the water based ink formulation, this is from the acrylic solution/emulsion. Hence increasing the content of acrylic emulsion will improve the flexibility of the finished dried print. This is a possibility since there is plenty of water that can be substituted for emulsion, and viscosity will not be greatly increased. This is something that can be kept in mind for future improvements.

The Scratch resistance of the water based ink tested was found to be equal to the solvent based ink when printed on polypropylene. The scratch resistance of an ink is obtained by the additives placed in the formulation. In this case the water based formulation contains approximately 8% additives, of which 2-3% of the additives is most likely a wax or wax dispersion. These additives give the desired lubrication required to give the adequate scratch resistance. The introduction of too much of a wax or additive may have drastic effects on the ink properties before or during printing. Moderation is the key when additives are concerned.

Hence the scratch resistance for the water based print is acceptable according to the test results obtained.

The shade of the water based ink was found to be equal to the solvent based ink, as would be expected when the same pigment was used. The pigment used in both formulations was the pthalocyanine blue pigment, Pigment Colour Index number 15:3.

The strength was found to be slightly stronger in the water based ink, as would be expected when only 15% reducer was added, to obtain the appropriate printing viscosity, Compared to the solvent based system, where 20% reducer was used to obtain the appropriate printing viscosity.

The lay of the print or the quality of the print is never as good in the waterbased system as the solvent based system. This was found to be the case in the experimental results, which confirms the thoughts of printers and converters. The lay of the print can, however, be improved by a number of methods. Firstly choosing the appropriate resin, which gives the best print quality, and can only be decided by visual observation. Secondly, additives such as wetting agents, improve the lay of the ink to the substrate, by eliminating any cratering or orange peel type of effects. Finally, the addition of alcohols, such as isobutanol and isopropanol, appears to improve the print quality by having the same effect as the wetting agents. Hence when using waterbased inks for polypropylene printing a slightly inferior print quality/lay may be obtained.

Cost of the formulations used in the experimental study show that the waterbased ink system is higher in cost than the solventbased system. This will obviously be the case in the initial stages of the use of the waterbased system, but as the system improves, that is, the quality of the waterbased system equals the solventbased system, the cost will most certainly decrease. Basically as quality improves, demand increases, the cost of raw materials will decrease, and hence the cost of the ink will decrease to a level equal to that of the solventbased ink system.

Conclusion:

In this experimental study, some of the major properties that a water based ink system will require, if it is to replace the solvent based ink system for printing on flexible substrates, such as polypropylene, were investigated. From the results there are limitations with using a current water based ink system relative to a solvent based ink system. Gloss is not as good, adhesion to the substrate takes at least 24 hours to equal the solvent based system, flexibility of the water based ink system requires at least 7 hours to equal that of the solvent system, print lay/quality of the water based system is not as good as the solvent system and the cost of the water based system is higher than the solvent based system. Hence in order for the water based ink system to be accepted for use in the marketplace these areas need to be improved and, once accepted lowering of the VOC's will be dramatic.

If the printer/converter is prepared to compromise in the early stages of development of water based ink technology, then this technology has a very strong chance of eventually overtaking the traditional solvent based technology. In architectural paints, where traditionally oil/solvent based paints were used, in the last decade great improvements have taken place in water based paint technology. Similarly water based ink technology, given the chance to be improved in the areas mentioned, eventually will become common place technology for the printing of flexible packaging substrates, such as polypropylene.

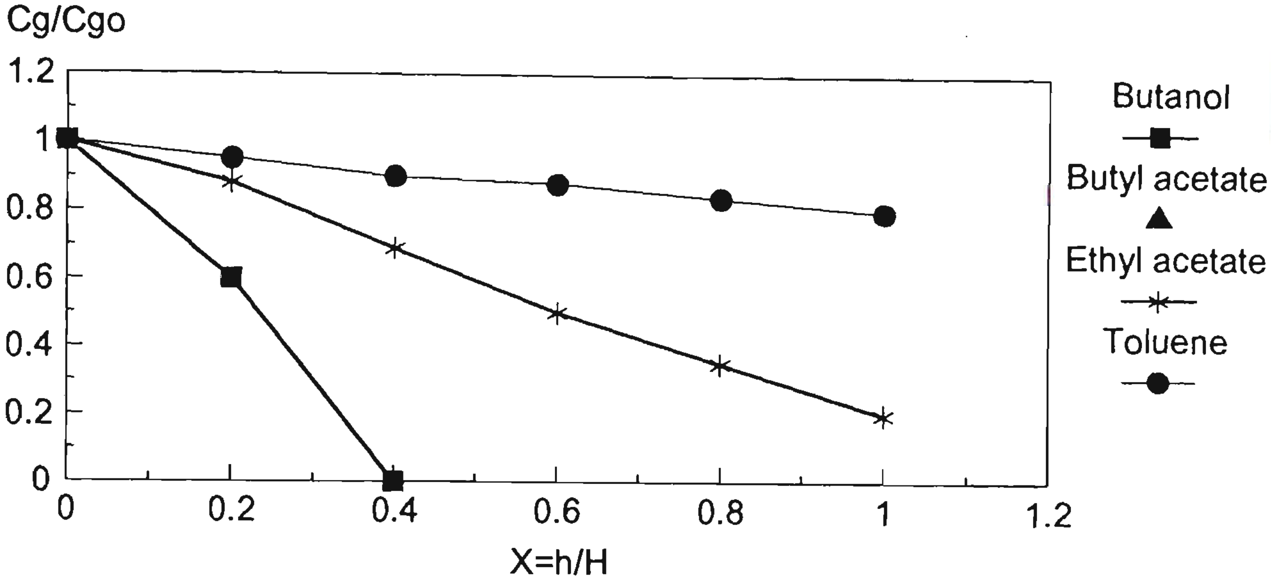
Recommendation:

From this study of the different processes available to reduce solvent emissions in the printing of flexible packaging substrates, the process that is recommended, for the Melbourne Metropolitan Area, under current scales of operation would be the development of waterbased technology. Even as this minor thesis is taking shape the regulations being enforced are now in the process of being relaxed. Compliance target dates are going to be extended to the years 2000/2005 instead of that stated as the 1st July in the EPA Code of Practice 1991 (Verbal information received from Charles Carabutt, EPA, Scientific and Engineering Services Division, September 1993). The reason for the extension of these dates is that less pressure is now being applied by the media and environmental groups. The Code of Practice introduced in 1991 when the government in power was the Labor Party, had a great deal of pressure from particular groups to be environmentally aware. In 1992 the Labor Government was defeated by the Liberal Party and major issues of concern have now shifted from environmental awareness to unemployment and the recession.

Hence, since the time for complying to the regulations is likely to be extended, more time for development of the technologies is available, and therefore water based systems will have the opportunity to be improved.

Due to the large costs and other energy requirements involved in the use of destruction technologies, the only viable alternative to printers/converters in the Melbourne Metropolitan Area is to adopt the prevention of emissions technology. Where UV curing technology has health and safety risks, "waterbased" technology is the most suitable technology available along with cleaner production techniques incorporated at all stages of production

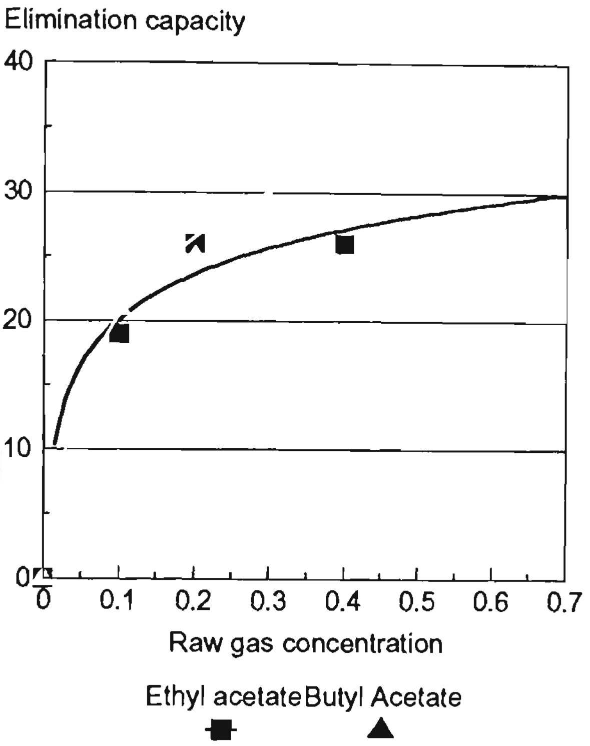
APPENDIX 1.0

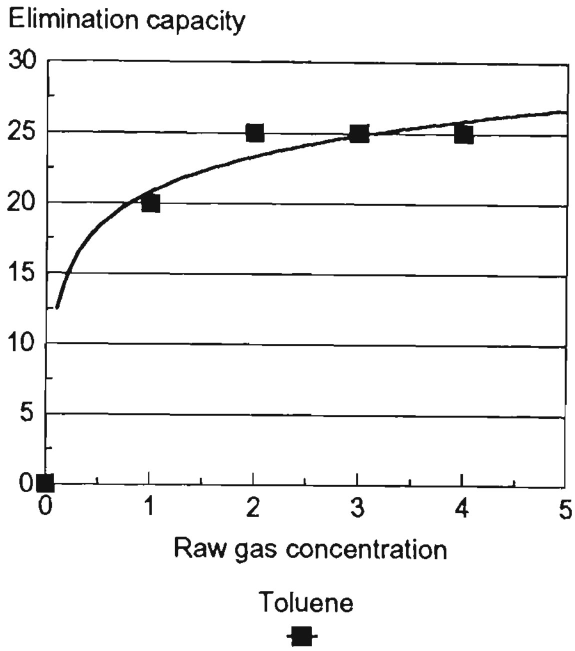


Concentration profiles for several VOC as a function of height in a biofilter.

J. Air.Man.Asoc. Vol41,No.8 Pg1048

APPENDIX 2.0

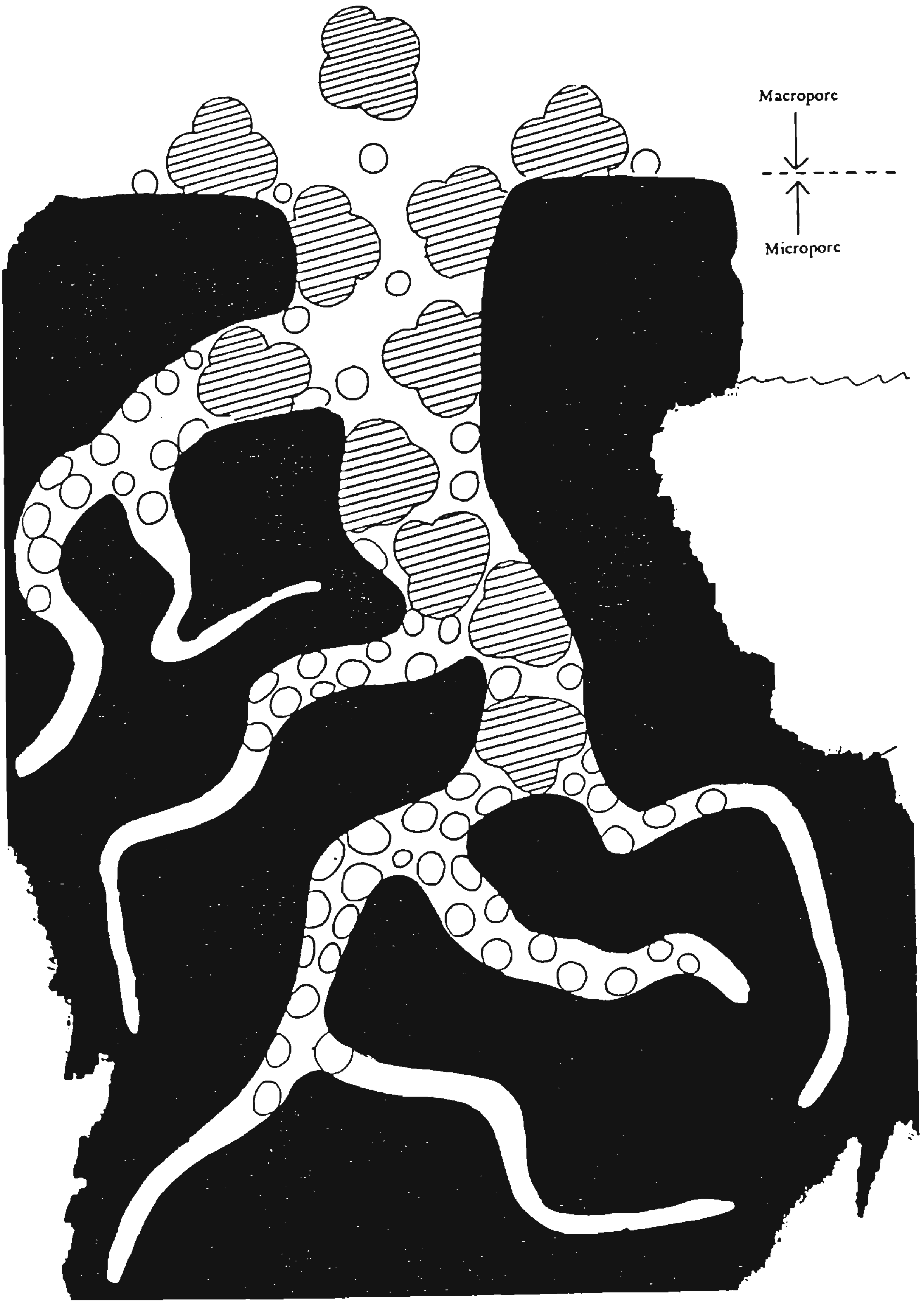




Elimination capacity of a biofilter
for several VOC[ ] .Rate 275m/m/h
J.Air Man.Assoc. Vol41,No.8 Pg1049

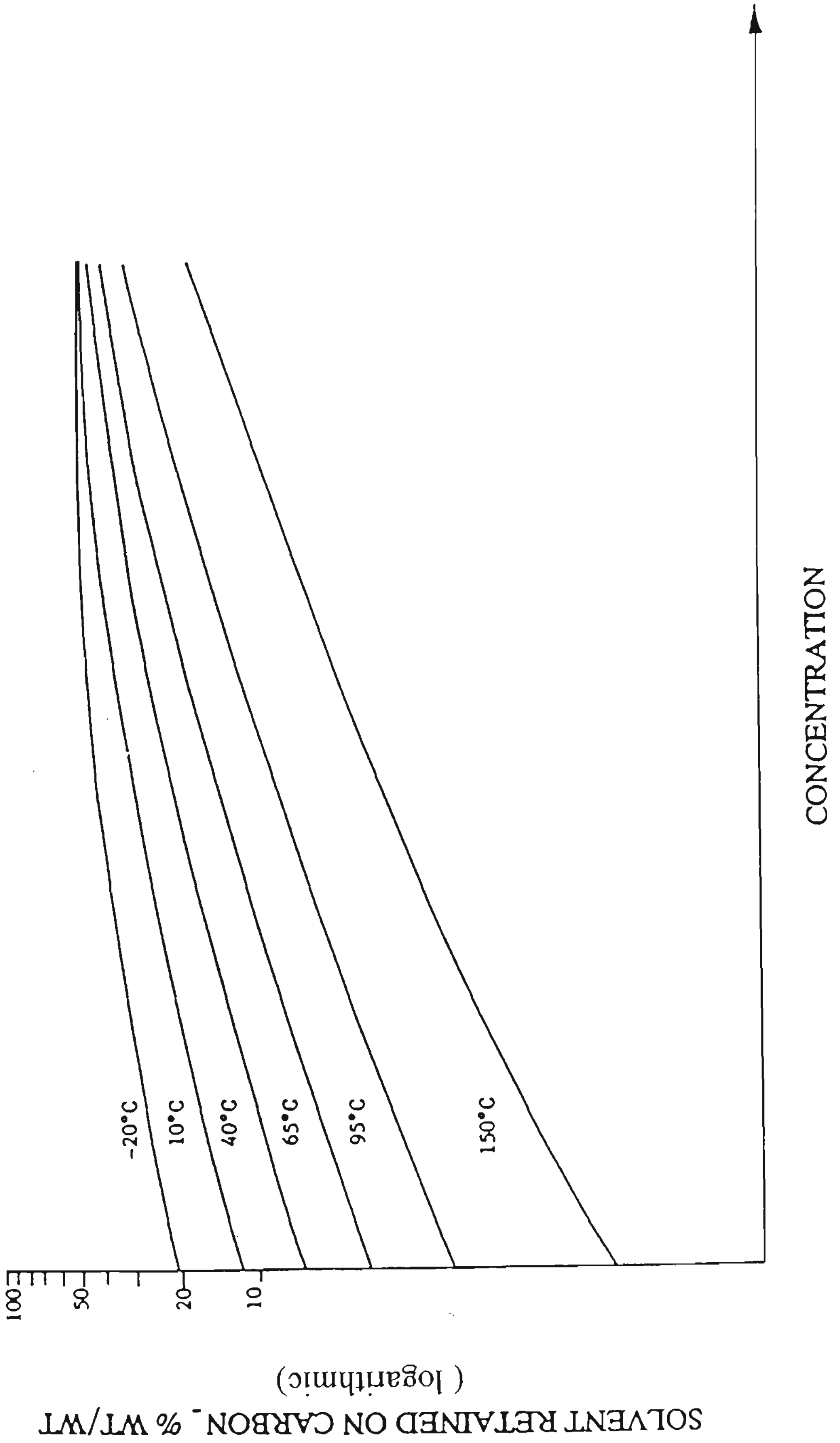
APPENDIX 3.0

An artists impression of activated carbon pore structure.



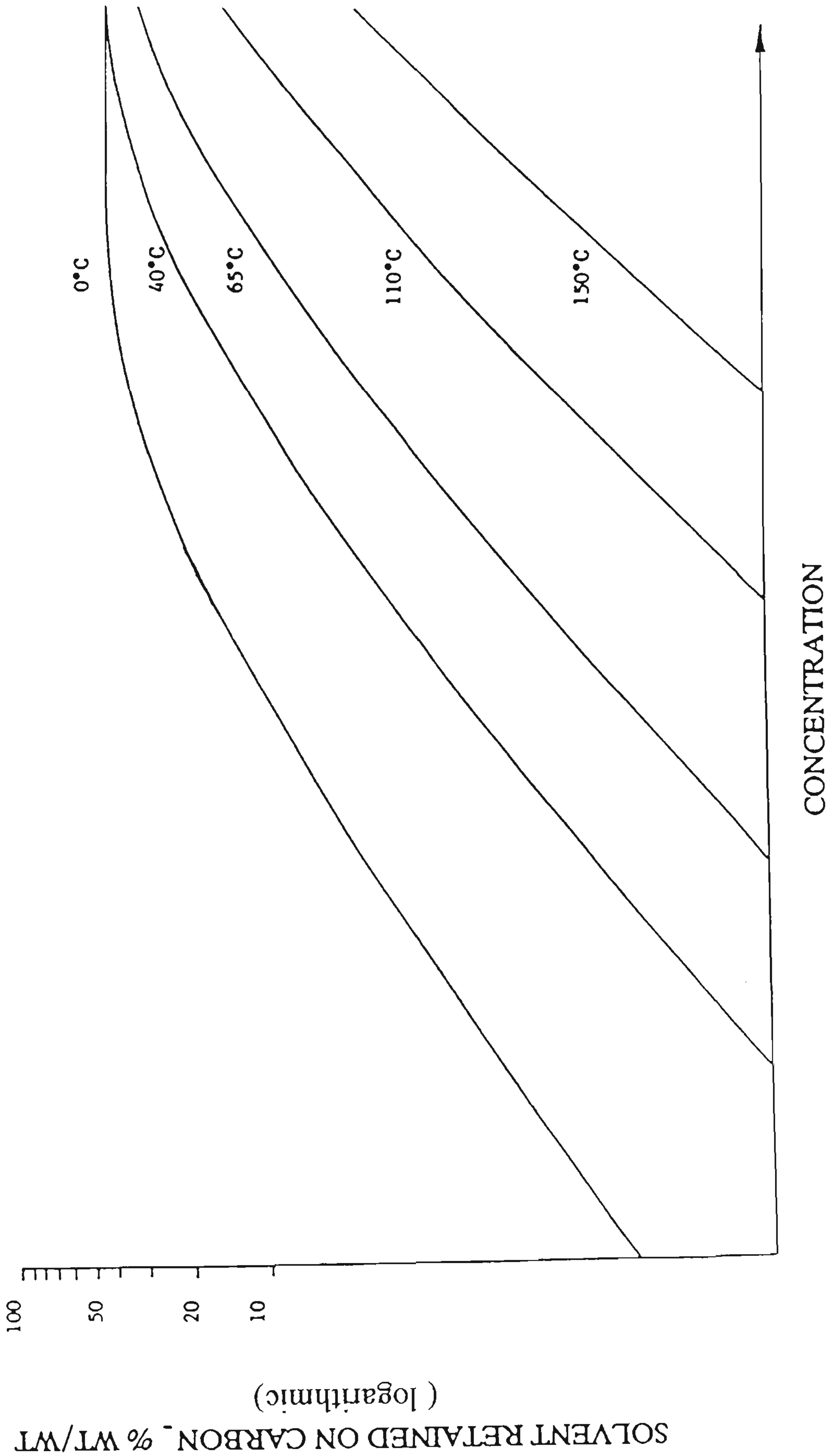
APPENDIX 4.0

Equilibrium isotherms for methyl acrylate on an activated carbon.



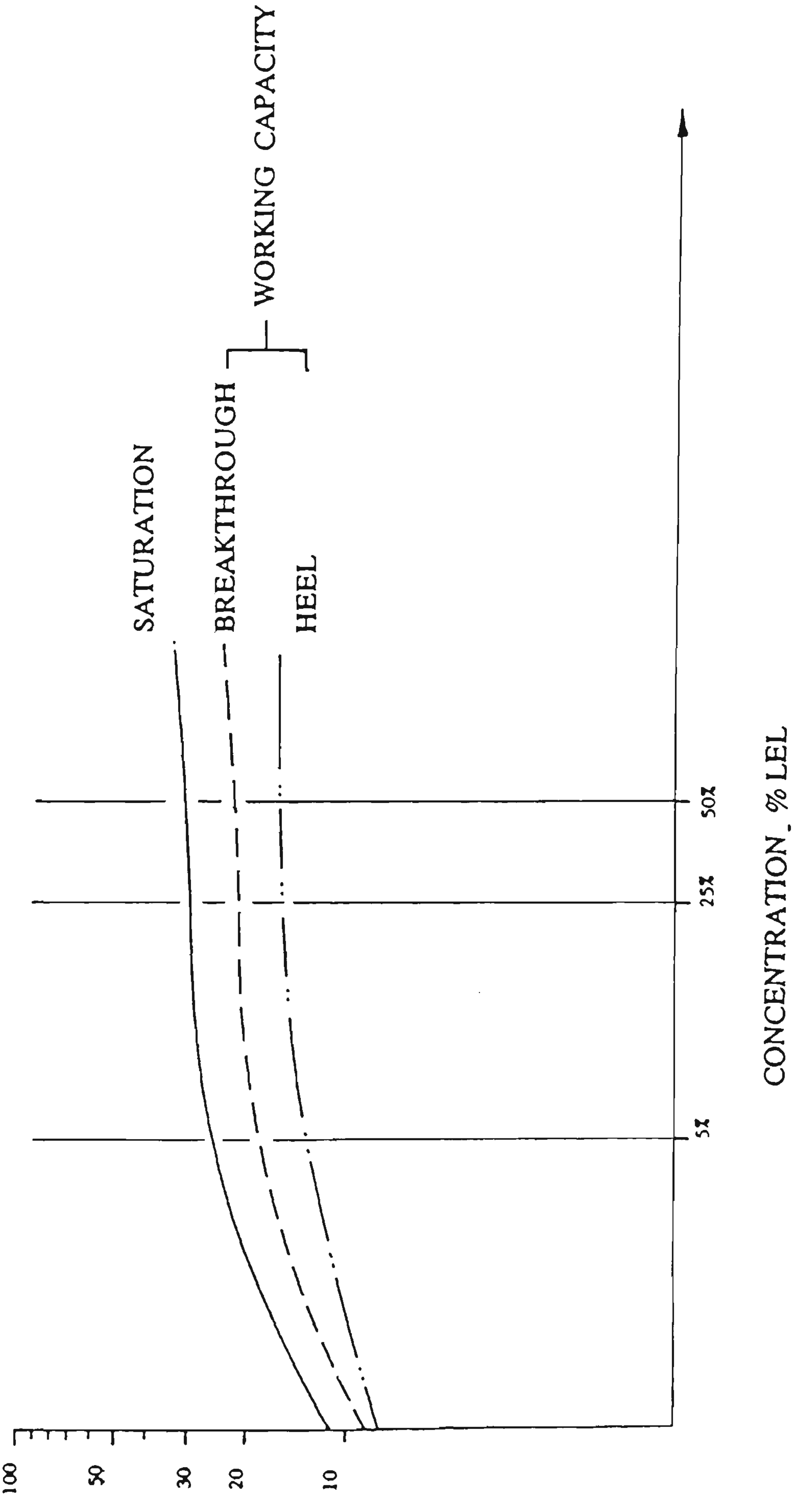
APPENDIX 5.0

Equilibrium isotherm for methanol on an activated carbon.



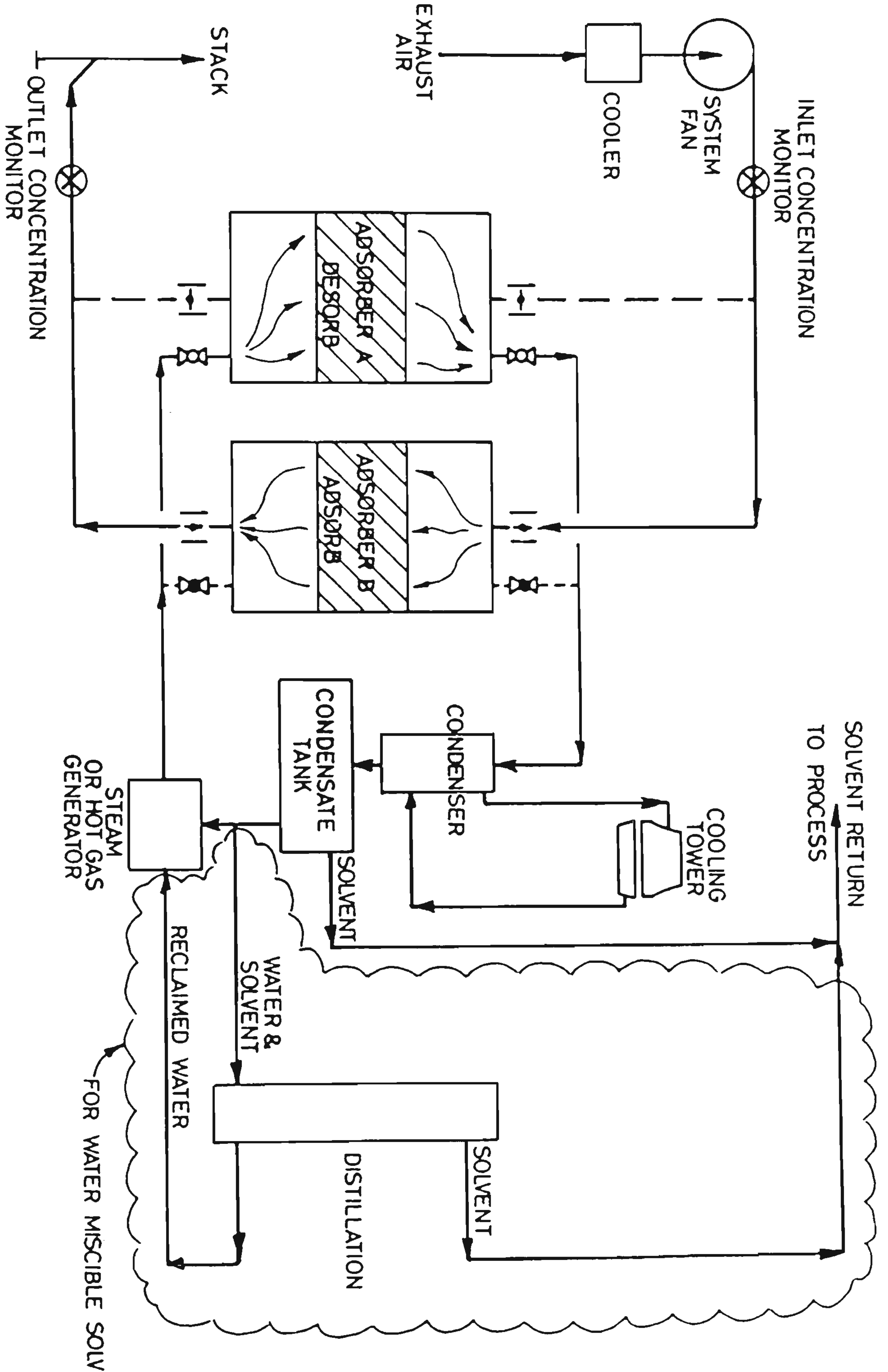
APPENDIX 6.0

Typical hydrocarbon adsorption characteristics on activated carbon.



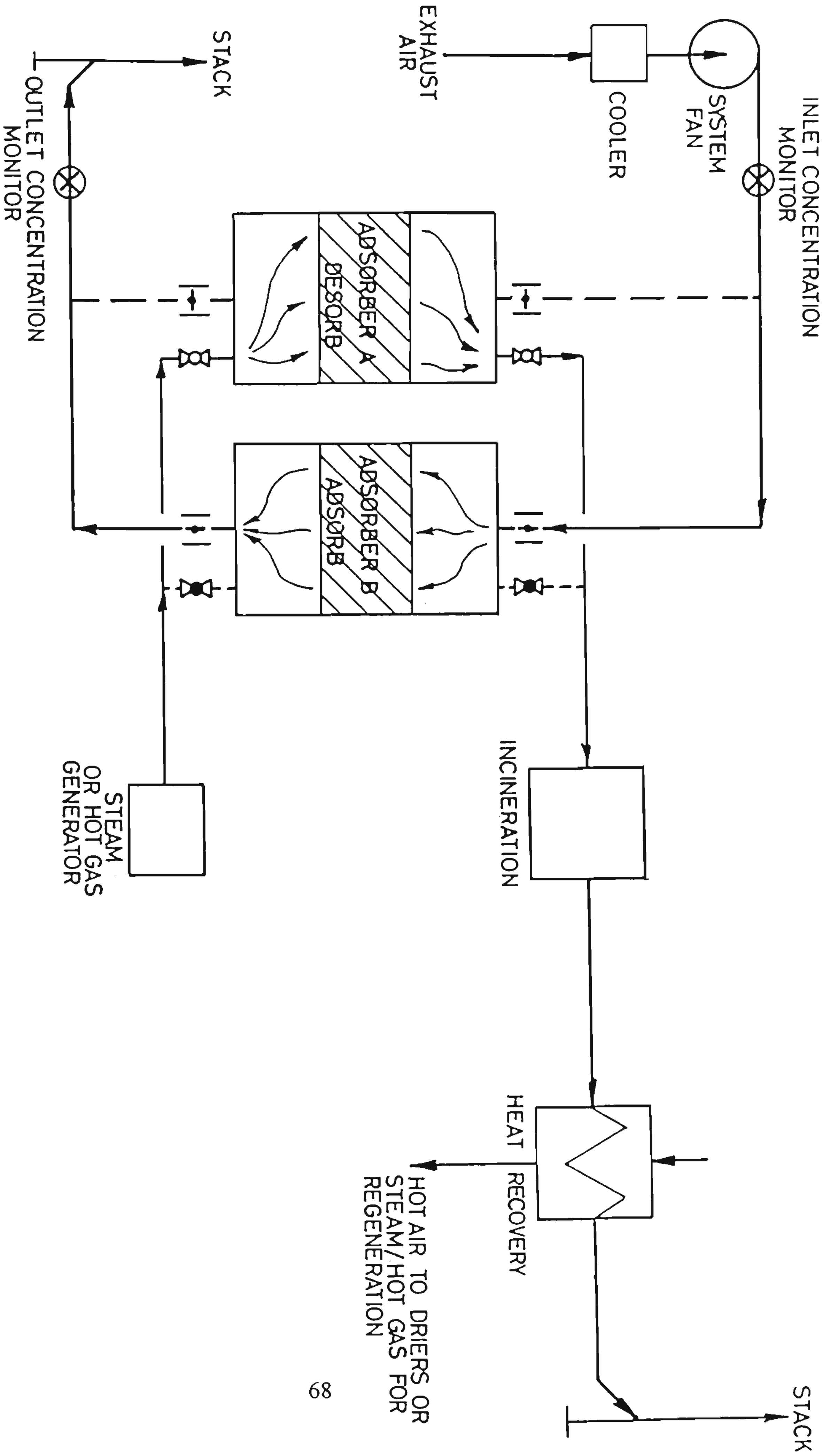
APPENDIX 7.0

Schematic of regenerable activated carbon adsorption system with solvent vapour recovery.



APPENDIX 8.0

Schematic of a regenerable activated carbon adsorption combined with incineration.



APPENDIX 9.0

Standard Test Method; 13-10A (Quality control manual, liquid inks division, Sicpa Australia 1993).
Name; Viscosity measurement test.

Apparatus;
Appropriate Viscosity cup, Constant temperature bath, stop watch.

Method;

Zahn cup method;

Cool or warm the ink sample to a temperature of 25^0 C. Take the appropriate zahn cup and place finger under the base to close the orifice. Fill the cup to the brim with the ink to be tested taking care to reduce the formation of bubbles.

Place a container under the cup, remove the finger from the base and at the same time start timing with the stop clock. Observe the flow of ink from orifice; stop the clock when the flow breaks into droplets, and record the time on the stop clock.

Result;

The result is recorded as time/Zahn cup number at temperature (usually 25^0 C).

APPENDIX 10.0

Standard Test Method; 13-0 (Quality control manual, liquid inks division, Sicpa Australia 1993).
Name; Preparation of proofs.

Apparatus;
Zahn 2 cup, Flexographic hand printer, ink samples, reducer, palette knife.

Method;

Reduce both standard and sample ink with the appropriate reducer to viscosity of 30 seconds on the Zahn number 2 cup at 25^0 C (See appendix 9.0, 13-10A viscosity measurement test).

Lay substrate on a smooth bench surface, and tape down the leading edge.

Take the flexographic hand printer and place approximately 8cm before the leading edge, and using a palette knife deposit ink in the nip of the rollers.

keeping firm pressure on the rollers, pivot handle to an upright position and then roll smoothly down the substrate maintaining a constant speed.

When using a hand printer the ink weight deposited on the substrate may vary. Comparison of the standard and sample must be completed on the same pass.

APPENDIX 11.0

Standard Test Method; 13-15 (Quality control manual, liquid inks division Sicpa Australia 1993).

Name; Volatile Organic Compound (VOC) content.

Apparatus;

Analytical balance, Syringe, Aluminium cups

Method;

Step 1: Weigh empty Aluminium cup
Step 2: Draw sample into syringe
Step 3: Weigh full syringe
Step 4: Inject sample into Aluminium cup
Step 5: Weigh empty syringe
Step 6: Put full cup into oven until sample is dry
Step 7: Weigh full aluminium cup
Step 8: Repeat the above procedure three times.

Calculations;

Before Drying;
(a) Mass of cup empty = g
(b) Mass of syringe full = g
(c) Mass of syringe empty = g
(d) Mass of sample wet = (b) - (c) = g

After drying;
(e) Mass of cup full = g
(f) Mass of sample dry = (e) - (a) = g
(g) % Solids = [(f) - (d)](100) = %
(h) % VOC = 100%- (g) - water content = %

Results;

Results are recorded as a percentage.

APPENDIX 12.0

Standard Test Method; 13-2 (Quality control manual, Liquid inks division, Sicpa Australia 1993)
Name; Visual and Instrumental determination of gloss against a standard.

Apparatus;
Gardner 60^0 glossmeter.

Method;

(A) Visual;

Proof sample against standard on specified substrate, as specified in test method 13-0 (See appendix 10.0).
The gloss is determined by examining the print at various angles, the degree of which can be qualified against the standard.

(B) Instrumental;

Proofs are prepared against standard on specified substrate, as specified in test method 13-0 (See appendix 10.0).
The gloss is recorded for both the standard and sample using the glossmeter, recording 5 readings for each sample, the average of these readings is recorded.

Results;

(A) Visual

Gloss is recorded as either greater/lower than the standard.

(B) Instrumental

Gloss is recorded as a numerical value for both the standard and sample. The highest value has the greatest gloss, the lowest value has the lowest gloss.

APPENDIX 13.0

Standard Test Method; 13-3 (Quality control manual, Liquid inks division, Sicpa Australia 1993)
Name; Adhesion.

Apparatus;
18cm 3M number 600 Scotch tape. Print samples of standard against sample on a specified substrate. Resilient rubber pad.

Method;
Ink must be proofed as per standard method (see appendix 9.0 , test method 13-0). The ink must be dried at the specified keying condition

A strip of tape, approximately 120cm long is smoothed down firmly over the printed area.

With the film held flat, the tape is then pulled back at a little less than 180^0C angle, slowly for the first half length of contact, then rapidly 'snapped' the rest of the way.

Results;

Results are reported as x% tapefast, or % ink retained to the specified substrate.
Test results can be recorded at various time intervals if time allows.

APPENDIX 14.0

Standard Test Method; 13-5 (Quality control manual, Liquid inks division, Sicpa Australia 1993)
Name; Flexibility.

Apparatus;
Print of sample to be tested.

Method;

Ink sample must be proofed according to the standard proofing method (see appendix 10.0) on the specified substrate and dried at the specified keying temperature.

The print is held between the thumb and the forefinger of each hand, leaving approximately 2cm of print between the two thumbs.

Holding both sides of the print securely, both hands are brought together and then quickly rotated ten times, care must be taken not to stretch the print.

Results;

Results are reported in comparative terms as equal/inferior/superior to the standard.
Results can also be reported at different time intervals.

APPENDIX 15.0

Standard Test Method; 13-4 (Quality control manual, Liquid inks division, Sicpa Australia 1993)
Name; Scratch resistance.

Apparatus;
Proof of standard against sample on a specified substrate.
Smooth resilient surface.

Method;

Ink must be proofed according to 13-0 (see appendix 10.0) at the normal dry film weight and dried at the specified keying conditions.

With the proof held on the smooth surface the printed surface is scratched with the back of the nail of the index finger.

Fast 'swipes ' are used at moderate pressure with the nail at an angle to the direction of travel. Be careful to avoid a cutting action with the side of the nail.

Results;

This is a subjective test and should always be performed side by side with the standard. Results are reported as equal/superior/inferior to the standard.

APPENDIX 16.0

Standard Test Method; 13-1 (Quality control manual, Liquid inks division, Sicpa Australia 1993)
Name; Shade/strength, visual appearance.

Apparatus;
Drawdown pad, with a black band.
10cm push knife/blade.

Method;

(a) The sample is reduced to the same viscosity as the standard (see appendix 9.0, test 13-10A).
A small drop of the standard is placed on the left hand side of the drawdown pad and a similar amount of the sample is deposited just to the right of the standard. The push knife is then pulled from top to bottom over the two inks to give them comparable film weights. The ink left on the push knife is deposited onto the pad so that the mass tones may be compared.

The through tone of the inks is observed by viewing the inks with a strong light source in the background, e.g. hold the print up to the light. The mass tone is also inspected for variation.

The inks are also printed on the specified substrate as per standard test method 13-0 (see appendix 10.0). Any variation in strength/colour/print quality to the standard is observed.

Results;

Results are recorded as equal/superior/inferior to the standard.

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