PRINTING INK TECHNOLOGY AND MANUFACTURE

Printing is widely used in our society to pass on information and to decorate objects. This has resulted in printing being used on many different surfaces ranging from aluminium cans and plastic bottles through to paper. Special inks have been developed for use in these different situations.

Printing inks are made of four basic components:

- *Pigments* - to colour the ink and make it opaque
- *Resins* - which bind the ink together into a film and bind it to the printed surface
- *Solvents* - to make the ink flow so that it can be transferred to the printing surface
- *Additives* - which alter the physical properties of the ink to suit different situations

These are formulated into ink in a two step process.

Step 1 - Varnish manufacture
Varnish is the clear liquid that is the base of any ink. Different varnishes are made for different inks, but they are all made by mixing the resins, solvents and additives (often at high temperatures) to form a homogeneous mixture. The resins react together to some extent to make larger molecules, making the varnish more viscous the longer these reactions are allowed to occur.

Step 2 - Pigment dispersal
The pigment is mixed into the varnish and then ground to break up clumps of pigment and to spread the pigment evenly through the ink.

INTRODUCTION

Each time when we pick up a newspaper or packet of biscuits we are looking at examples of printing. Printing of one form or another has been with us for centuries and whilst the technologies of both the printing process and the ink formulations have changed considerably the main functions of decoration and information remain.

The history of ink production

Writing inks were first manufactured in both ancient Egypt and China in about 2500BC. These inks were composed of soot bound together with gums. This paste was formed into rods and dried, then mixed with water immediately before use.

Printing was invented by the Chinese about 3000 years later. They used a mixture of coloured earth, soot and plant matter for pigments, again mixed with gums for a binder. By 1440, when Johannes Guttenberg invented the first printing press with moveable type, ink was made of soot bound with either linseed oil or varnish - similar materials to those used for black inks today. Coloured inks were introduced in 1772 and drying agents were first used in the nineteenth century.

Today's printing inks are composed of a pigment (one of which is carbon black, which is not much different from the soot used in 2500BC), a binder (an oil, resin or varnish of some kind), a solvent and various additives such as drying and chelating agents. The exact recipe for a given ink depends on the type of surface that it will be printing on and the printing method that will be used. Inks have been designed to print on a wide range of surfaces from metals, plastics and fabrics through to papers. The various printing methods are all similar, in that the ink is applied to a plate / cylinder and this is applied to the surface to be printed. However, the plate / cylinder can be made of metal or rubber, and the image can be raised up above the surface of the plate, in the plane of the plate but chemically treated to attract the ink, or etched into the plate and the excess ink scraped off. Different inks are produced to suit these different conditions.

RAW MATERIALS

As has already been stated, the raw materials for ink production are pigments, binders, solvents and additives. In New Zealand, the ink manufacturer buys these materials either locally or overseas, and blends and reacts them to make ink. These materials are discussed below.

Pigments

The most obvious role of a pigment is to colour the ink. However, they can also provide gloss, abrasiveness and resistance to attack by light, heat, solvents etc. Special pigments known as extenders and opacifiers are also used. Extenders are transparent pigments which make the colours of other pigments appear less intense, while opacifiers are white pigments which make the paint opaque so that the surface below the paint cannot be seen. Common pigments used in the manufacture of printing inks are listed in **Table 1**.

Resins

Resins are primarily binders - they bind the other ingredients of the ink together so that it forms a film and they bind the ink to the paper. They also contribute to such properties as gloss and resistance to heat, chemicals and water. Many different resins are used, and typically more than one resin is used in a given ink. Some of these are manufactured in New Zealand (see articles) but most are not. The most commonly used resins are listed below:

- Acrylics
- Alkyds
- Cellulose derivatives
- Rubber resins[1]
- Ketones
- Maleics
- Formaldehydes
- Phenolics[2]

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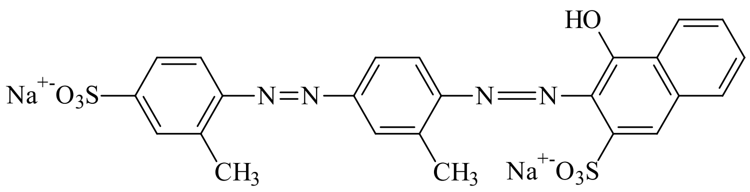
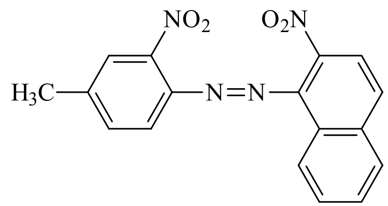
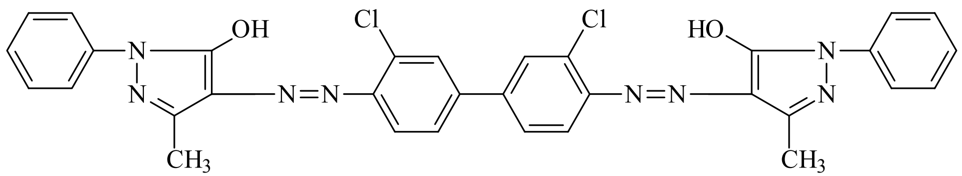
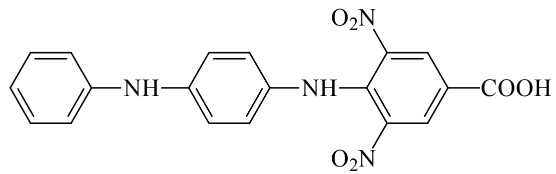
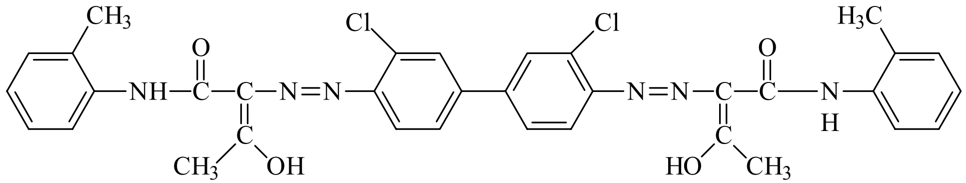
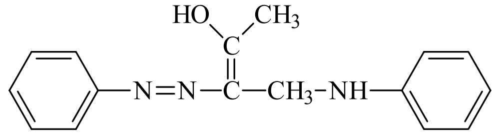
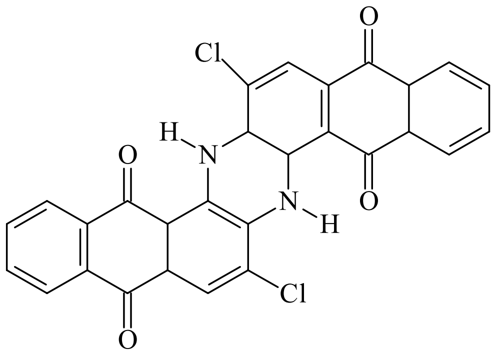
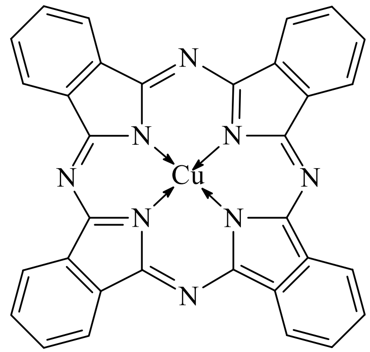
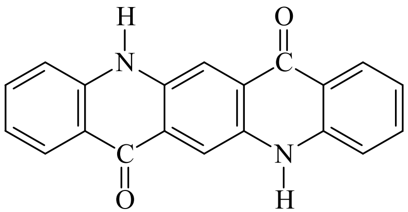
[1]Two types of rubber resin are used in the manufacture of printing inks: chlorinated rubber and cyclised rubber. Chlorinated rubber is produced by chlorinating either a solution or an emulsion of natural rubber. Cyclised rubber is produced by treating natural rubber with an acid catalyst to reduce the degree of saturation.

[2]These are produced by heating a parasubstituted phenol (benzyl alcohol) with aqueous formaldehyde in the presence of an alkaline catalyst. The properties of the final resin depend on the phenol used, the type of catalyst, the molar raio of the components and the reactor conditions.

Table 1 - Common printing ink pigments

Class	Examples	
Inorganic white (opacifiers)	Titanium dioxide (TiO_2) - in either rutile or anatase form	Zinc oxide (ZnO)
Extenders	Calcium carbonate ($CaCO_3$)	Talc - mixed oxides of magnesium, calcium, silica and aluminium
Inorganic black	Carbon black	
Organic red	 Lithol (C.I. 26670[3])	 Toluidine derivative (C.I. 12120)
Organic orange	 Pyrazolone (C.I. 21110)	 Dinitroaniline (C.I. 10390)

[3]Pigments are assigned a five digit number based on structure in the American *Colour Index*.

Organic yellow	 A di azo pigment (C.I. 21095)	 Hansa yellow (C.I. 11660 derivative)
Organic green	Phthalocyanine green	PMTA
Organic blue	 Indanthrene (C.I. 69825)	 Phthalocyanine blue (C.I. 74160)
Organic violet	 $-Quinacridone (C.I. 46500)	Dioxazine or Benzimidazolone

- Epoxides
- Fumarics
- Hydrocarbons
- Isocyanate free polyurethanes
- Poly vinyl butyral
- Polyamides
- Shellac[4]

Solvents
Solvents are used to keep the ink liquid from when it is applied to the printing plate or cylinder until when it has been transferred to the surface to be printed. At this point the solvent must separate from the body of the ink to allow the image to dry and bind to the surface.

Some printing processes (e.g. the gravure[5] and flexographic[6] processes) require a solvent that evaporates rapidly. These use volatile solvents (i.e. those with boiling points below 120^oC) such as those listed in **Table 2**.

Table 2 - Volatile printing ink solvents

Name	Structure or composition	Boiling point / ^oC
methylated spirits		
ethyl acetate	$CH_3COOCH_2CH_3$	77
isopropanol	$CH_3CHOHCH_3$	82.5
n-propyl acetate	$CH_3COOCH_2CH_2CH_3$	101.6

High-boiling point (T_b = 240 - 320^oC) hydrocarbons are chosen as solvents for lithographic inks as the solvent used must be viscous and hydrophobic.

Screenprinting inks need to have solvents with moderately high boiling points. Some commonly used solvents are listed in **Table 3**.

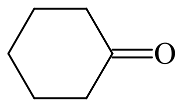
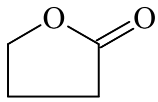
Additives
Many different types of additives are used to alter the final properties of the paint. The most common types of additives (with typical examples) are listed in **Table 4**.

[4]Shellac is derived from the secretion of the insect *Laccifer lacca kerr*.

[5]A process in which the image is engraved into a cylinder, ink applied and the excess ink removed with a 'doctor blade'.

[6]A process in which the image is in relief above a printing plate, and ink applied to the plate.

Table 3 - Some solvents used in screenprinting inks

Name	Structure or composition	Boiling point / ^oC
Cyclohexanone		155.6
Butoxyethanol	$HOCH_2CH_2O(CH_2)_3CH_3$	171 - 172
Aromatic distillates	mixture of compounds chosen by boiling point	240 - 290
Butyrolactone		b.p.$_{12}$[7] = 89
Methoxypropanol acetate		

THE MANUFACTURING PROCESS

Ink is manufactured in two stages: first varnish (a mixture of solvent, resins and additives) is made and then pigments are mixed into it.

Step 1 - Varnish manufacture

Varnish is a clear liquid that solidifies as a thin film. It binds the pigment to the printed surface, provides the printability of the ink and wets the pigment particles. There are two main sorts of varnish: oleoresinous varnish (which incorporates a drying oil[8] such as linseed oil) and non-oleoresinous varnish. Oleoresinous varnish is manufactured at much higher tempeartures and in much more rigorous conditions than non-oleoresinous varnish. The two manufacturing processes are discussed below.

Oleoresinous varnish manufacture

These varnishes are typically manufactured in closed kettles where the oil and solvent are heated to allow for rapid solutioning or transesterification. The temperatures involved in the process will vary but may range from 120°C to 260°C. Cooking times may range from a few minutes to several hours. Temperature control is critical in the process. Rate of temperature change, maximum temperature attained and cooking duration are closely monitored. A condenser is usually used to prevent solvent loss.

Since these varnishes include a drying oil, atmospheric oxygen must be excluded to prevent this from polymerising. For this reason cooks are often done using a nitrogen blanket.

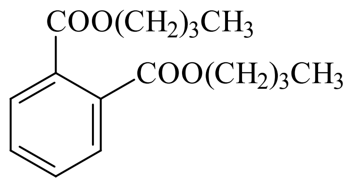
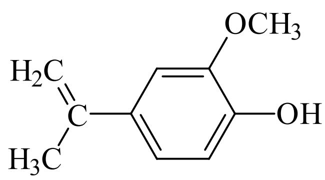
In the production of a typical oleoresinous ink varnish, drying oil, alkyd and other solvents are added to the vessel under nitrogen prior to cooking. Hard resins are then added when the correct temperature is attained. The cooking process continues until the reactants are either totally consumed in the transesterification process or achieve adequate solubility in the

[7] Boiling point at 12 torr (i.e. 1.6 kPa)

[8] See paint article, X-D

solvent. Additives such as the chelating agent are added after the batch cools down. Finally, the varnish mixture is reheated to obtain targeted rheological[9] properties. The varnish produced is tested before sending to the storage tank.

Table 4 - Common classes of printing ink additives

Type	**Function**	**Typical example**
Plasticiser	Enhances the flexibility of the printed film	 dibutyl phthalate
Wax	Promotes rub resistance	Carnauba - an exudate from the leaves of *Copernicia prunifera*. Consists of esters of hydroxylated unsaturated fatty acids with at least twelve carbon atoms in the acid chain.
Drier	Catalyses the oxidation reaction of inks which dry by oxidation	salts or soaps of cobalt, manganese or zirconium
Chelating agent	Increases the viscosity of the ink (aluminium chelate) and promotes adhesion (titanium chelate)	
Antioxidant	Delays the onset of oxidation polymerisation by reacting with free radicals formed during the autooxidation thus preventing them from reacting further	 eugenol
Surfactants[10]	Improves wetting of either the pigment or the substrate	
Alkali	Controls the viscosity / solubility of acrylic resins in water based inks	$HOCH_2CH_2NH_2$ monoethanolamine
Defoamer	Reduces the surface tension in water based inks, meaning that stable bubbles cannot exist	hydrocarbon emulsions

[9] Rheology is the study of how particular fluids flow.

[10] See soap article, XI-A

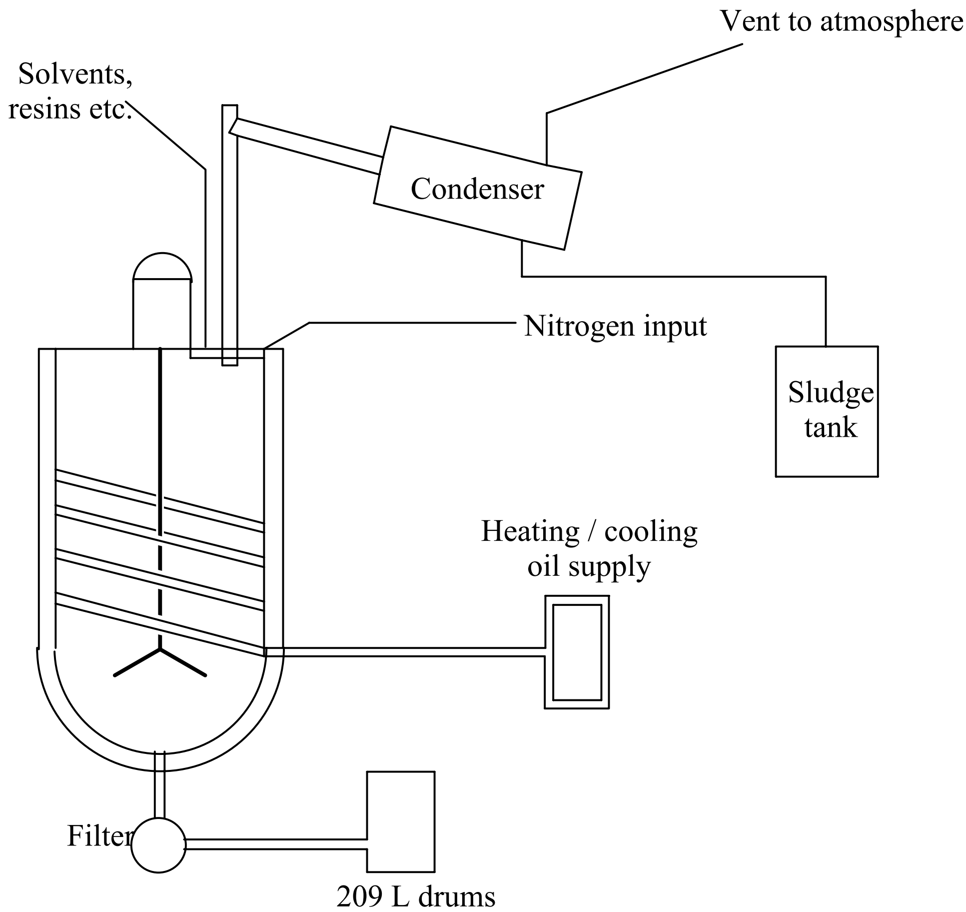


Figure 1 - Typical kettle set-up for an oleoresinous varnish

Non-oleoresinous varnish manufacture
Varnishes of this type are usually simple resin solutions that do not require high temperatures to effect a reaction. They are manufactured by breaking up the resin particles and dissolving them in a solvent in either a cavitation or a rotor / stator mixer. Cavitation mixers contain a saw tooth disc on a driven shaft and are used to produce high viscosity resin solutions. They can operate at variable speeds. Rotor / stator mixers operate at a fixed speed. Varnishes produced in these mixers must be of lower viscosity than those produced in cavitation mixers because the agitation in the mixer is much less. Heat sensitive resins cannot be used in a rotor / stator mixer because the high friction within the mixer produces high temperatures.

Step 2 - Pigment dispersal
Once the varnish (containing the solvent, resin and additives) has been produced the pigment is mixed into it. At this point the pigment particles clump together. These clumps must be broken up and the pigment dispersed evenly through the resin. There are three main types of equipment used to do this, and which is chosen depends on the tack (stickiness) and rheology of the ink. The three equipment types are discussed below.

Three roll mills
A three roll mill consists of a series of cambered rollers rotating in opposite directions. The pigment particles are fed into a hopper above the two rear-most rollers and is dispersed by the shear forces between the rollers. A doctor blade is fitted to the front roller to remove the dispersed product.

Roll pressure, speed ratios and temperature must be carefully controlled to allow reproducible dispersion. Each of the rolls is water cooled to reduce the build up of frictional heat.

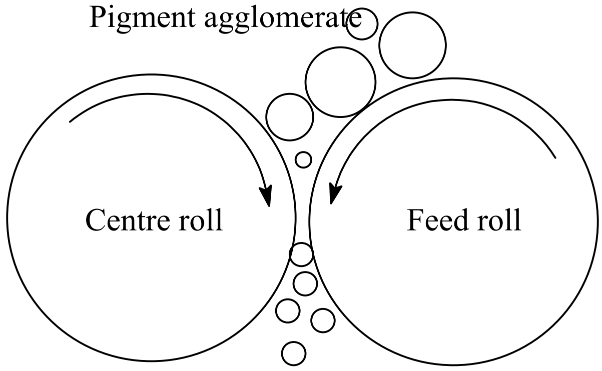


Figure 2 - Pigment Particles enterting a three roll mill

Bead Mills

A bead mill consists of a cylindrical chamber filled with beads and surrounded by a water jacket for cooling. Ink is pumped into the chamber and the beads (known as the 'charge') set in motion by a series of spinning discs or pins. The charge grinds the ink, breaking up the pigment clumps and evenly dispersing the ink. The ink then flows out of the chamber through a sieve and the charge remains behind to be re-used.

The bead size depends on the viscosity and rheology of the ink. Typical bead sizes range from 1-2 mm for a high quality low viscosity product such as a gravure ink up to 4 mm for a medium viscosity paste or screen ink. The beads can be made of zirconium oxide, glass or stainless steel. Certain beads discolour certain inks, so it is important that each ink is tested with the different beads before grinding to ensure that appropriate beads are used.

Cavitation Mixers

The use of cavitation mixers for the production of resin solutions has already been discussed. However, mixers of this type are also very efficient at dispersing certain pigments, notably titanium dioxide, and allowing predispersion of a number of others. In a highly viscous ink system a cavitation mixer may be insufficient to ensure even dispersal and as a consequence an additional sweeper blade may be added.

COMPOSITION OF INKS

The compositions of inks used in different situation are shown in **Tables 5-9**.

Table 5 - Letterpress ink for newspaper

Ingredient	Function	Amount / % w/w
carbon black	black pigment	13.00
9 poise mineral oil	used instead of varnish as a wetting agent	68.00
0.5 poise mineral oil	used instead of varnish as a wetting agent	10.00
asphaltum solution		5.00
280 - 320^{o}C petroleum distillate	solvent	2.00

Table 6 - Lithographic ink for paper

Ingredient	**Function**	**Amount / % w/w**
organic pigment	coloured pigment	18.00
quickset varnish		40.00
gloss varnish		15.00
fast setting varnish		15.00
polyethylene wax paste	prevents damage to the ink film from rubbing	5.00
anti set-off paste		3.00
cobalt / manganese driers	catalyses drying oil oxidation	1.00
280 - 320^{o}C petroleum distillate	high boiling point solvent	3.00

Table 7 - U.V. curing lithographic ink for paper

Ingredient	**Function**	**Amount / % w/w**
C.I. pigment blue 15:3	blue pigment	16.00
C.I. pigment black 7	black pigment	4.00
epoxy acrylate resin	binder	30.00
fatty acid modified epoxy acrylate	binder	25.00
tripropylene glycol diacrylate	binder	8.00
benzophenone	photosensitiser	8.00
2-chlorothioxanthen-9-one	photosensitiser	3.00
aromatic amine	alkali - controls the viscosity and solubility of the resin	4.00
additives	waxes, antioxidants etc.	2.00

Table 8 - Flexographic ink for polyethylene film

Ingredient	Function	Amount / %w/w
titanium dioxide	white pigment and opacifier	35.00
alcohol soluble nitrocellulose	resin	5.00
alcohol soluble polyamide	resin	15.00
dibutyl phthalate	plasticiser	1.00
polyethylene wax	prevents damage to the ink film from rubbing	1.00
amide wax	prevents damage to the ink film from rubbing	1.00
ethanol	low boiling point solvent	30.00
n-propyl acetate	low boiling point solvent	8.00
n-propanol	low boiling point solvent	4.00

Table 9 - Gravure ink for paper

Ingredient	Function	Amount / %w/w
C.I. pigment red 57:1	red pigment	10.00
alcohol soluble nitrocellulose	resin	20.00
ketone resin	resin	10.00
dioctyl phthlalate	plasticiser	2.00
polyethylene wax	prevents damage to the ink film from rubbing	1.00
ethanol	low boiling point solvent	30.00
n-propyl acetate	low boiling point solvent	20.00
ethoxy propanol	low boiling point solvent	7.00

THE CHEMISTRY AND PHYSICS OF INK FUNCTION

The science of colour

Modern colour printing technologies are based on the Young-Helmholtz theory of three colour vision. Young and Helmholtz observed that although white light is composed of light from a continuous spectrum of wavelengths, humans only perceive three broad bands of this light. These bands are seen as blue, green and red light. Any other colour of light can be created from an appropriate mixture of these three. In particular, red and blue light together produce magenta, blue and green produce cyan and red and green produce yellow. These colours are known as subtractive colours because they are produced by 'subtracting' one of the three primary colours from white light.

When white light hits an object, some of the light is absorbed and the remainder reflected. The colour of the reflected light is the colour that we perceive as the colour of the object, thus a leaf appears green because it absorbs all colours except green.

Printing is usually done using four different colours of ink: cyan, magenta, yellow and black. The subtractive colours are chosen because by 'overprinting' these inks, all other colours can be formed. For example, red is produced by overprinting yellow and magenta, as the yellow absorbs the blue light (because yellow is the emission of red and green light) and magenta absorbs the green light, leaving behind pure red light. Black ink is used because although in theory cyan, magenta and yellow should add together to give black, in practise they usually give brown.

Conjugated systems
In organic pigments the colour is due to light energy absorbed by the delocalised B electrons of a conjugated system. A conjugated system is one consisting of alternating single and double bonds in which the B electrons are delocalised, i.e. the electrons of the second electron pair of the double bond (the B electrons) are free to move between all the conjugated atoms. This phenomenem is discussed in more detail in article X-D.

Ink drying and curing
After the ink has been applied to the surface to be printed it must bind there to ensure it stays. This can happen simply as a result of the ink drying, or can take place in a series of cross-linking and polymerisation reactions that form a film and to bind it to the printed surface. These reactions are known as curing reactions. Ink drying and curing can happen *via.* any one (or a combination) of the following processes:

- *Oxidation*. If drying oil is present in the solvent, it will react with oxygen in the atmosphere and undergo curing reactions. Drying oils are discussed in more detail in the article X-D.

- *Evaporation*. Some inks, usually those used in applications where speed is important, are designed to dry and cure as the solvent evaporates off. Volatile solvents such as methylated spirits are usually used, but solvents with boiling points above 120^{o}C are used for screen-printing inks to prevent the ink from drying during application.

- *Penetration*. Inks that are printing on porous surfaces are sometimes designed so that the solvent penetrates into the bulk of the printing surface, leaving dry ink on the surface.

- *Radiation curing*. Radiation (usually U.V.) is fired at the ink, instigating a series of polymerisation reactions. Most of the inks that cure this way are water-based.

- *Precipitation*. Excess water (usually in the form of steam) is added to an ink system that is only sparingly miscible in water. The sudden increase in diluent concentration causes the solubility of the resin to decrease sharply and the resin precipitates onto the printed surface. The excess water evaporates off.

THE ROLE OF THE LABORATORY

The laboratory is primarily involved in quality control, although in some larger companies it is also involved in designing special ink formulations for unusual printing situations. Inks are tested for a variety of properties during and after manufacture process. Most of the tests are dictated by their end use. Typical tests include:

- Non volatile content
- Viscosity
- Dispersion
- Shade
- Adhesion
- Slip
- Scratch resistance
- Gloss
- Flexibility
- Water resistance
- Heat Resistance
- Opacity

Article written by Heather Wansbrough from information supplied by Derek Taylor (Coates New Zealand. Extra information supplied by David Yuen with reference to:

- Kirk-Othmer, *Encyclopedia of Chemical Technology (3rd Edition)*, V.13 (374-397) & V. 19 (110-175), Wiley & Sons, New York, 1981.

- *Color Index (3rd Edition)*, American Association of Textile Chemists and Colorists, London, 1971.