Ink Manufacturing and Dispersion of Pigment into Printing Ink

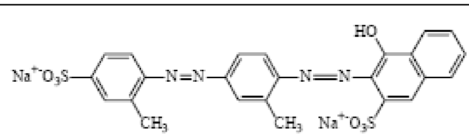
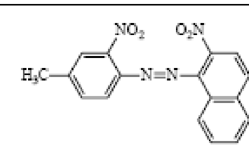
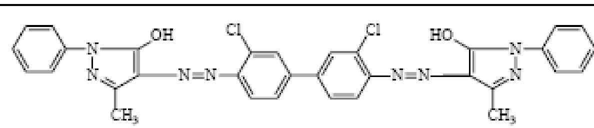
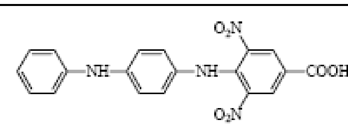
1. Introduction
Printing of one form or another has been with us for centuries and whilst the technologies of both the printing process and the ink formulations have changed considerably the main functions of decoration and information remain.

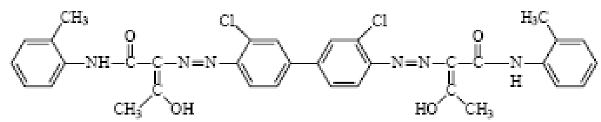
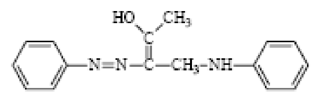
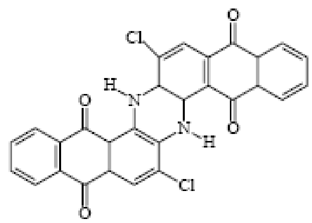
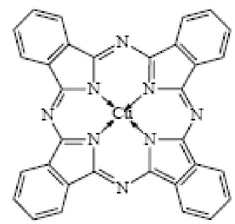
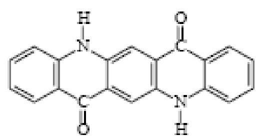
Nowadays, printing inks are composed of a pigment, a binder (an oil, resin or varnish of some kind), a solvent and various additives such as drying and chelating agents.

2. Raw materials
As has already been stated, the raw materials for ink production are pigments, binders, solvents and additives.

2.1 Pigments
The most obvious role of a pigment is to color 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 colors 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**.

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)

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

2.2 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. The most commonly used resins are listed below:

- Acrylics
- Alkyds
- Cellulose derivatives
- Rubber resins
- Ketones
- Maleics
- Formaldehydes
- Phenolics

2.3 Solvents

Solvents are used to keep the ink liquid form 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 gravure5 and flexographic6 processes) require a solvent that evaporates rapidly. These use volatile solvents (i.e. those with boiling points below 120oC) such as those listed in **Table 2**.

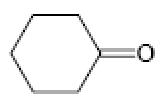
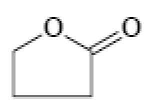
Table 2 - Volatile printing ink solvents

Name	Structure or composition	Boiling point / °C
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 - 320oC) hydrocarbons are chosen as solvents for lithographic inks as the solvent used must be viscous and hydrophobic.

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

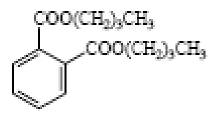
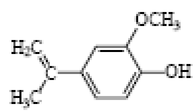
Table 3 - Some solvents used in screenprinting inks

Name	Structure or composition	Boiling point / °C
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		

2.4 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**.

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

3. Manufacture of printing ink

The manufacture of printing ink is a complex process to satisfy requirement of the printing ink. Basically, printing ink manufacturing is the combination of the basic ingredients such as pigments, vehicles and additives.

The physical properties of pigments such as particle size and particle surface are of great influence in the dispersion process. Primary dispersions for ink production demand that the pigment particles are thoroughly wetted by the liquid phase. The pigment particle size strongly affects the color strength since the smaller particle size has the higher surface area and thus the stronger the color. If this dispersion level is not achieved, printing problems will arise. To achieve the optimum benefits of a pigment, it is necessary to obtain as full a reduction as possible to the primary particle size. The primary feature particle sizes is 0.5 micron or specific surface area of 30 to 100 m^2/g.

A number of printing inks are completed in a one or two-step mixing/dispersing process which is usually carried out on a high shear mixer to produce ink with acceptable dispersion.

Generally, the ink manufacture has two stages: first varnish (a mixture of solvent, resins and additives) is made and then pigments are mixed into it.

3.1 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 oil8 such as linseed oil) and non-oleoresinous varnish. Oleoresinous varnish is manufactured at much higher temperatures 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 polymerizing. 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 solvent. Additives such as the chelating agent are added after the batch cools down. Finally, the varnish mixture is reheated to obtain targeted rheological9 properties. The varnish produced is tested before sending to the storage tank.

3.2 Pigment Dispersion

Step 2 - Pigment dispersal

The primary purpose of the dispersion process is to break down pigment aggregates and agglomerates to their optimum pigmentary particulate size and distributes these pigment particles evenly throughout the similar medium i.e. the carrier.

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 by *three roll mills.*

A three roll mill consists of a series of cambered rollers rotating in opposite directions (Fig. 1). The pigment particles are fed into a hopper above the two rear-most rollers and are dispersed by the shear forces between the rollers. A doctor blade is fitted to the front roller to remove the dispersed product.

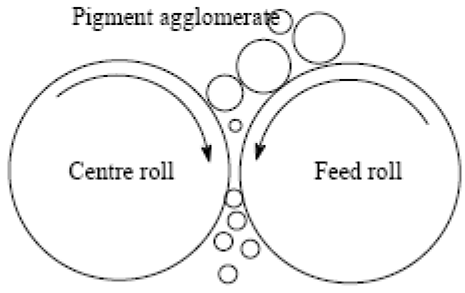


Figure 1 - Pigment Particles enterting a three roll mill

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.

4. Carbon black dispersion

Carbon properties influence ink performance. For example, the smaller particle size increases blackness, tint, UV protection and absorption, electrical conductivity. The higher structure could reduce blackness and tint, improve dispersibility, increases vehicle demand and viscosity, and increases electrical conductivity. The higher porosity could increases vehicle demand and viscosity and electrical conductivity and reduce loadings in conductive applications. High surface activity will improve vehicle wetting, reduce viscosity of liquid system and lower electrical conductivity.

Carbon black dispersion include the follow steps: incorporating the carbon black in the vehicle system, dispersion the air entrained in the carbon black with the vehicle (wetting the pigment), and reducing carbon black macroagglomerates to microagglomerates or aggregates through grinding. Good interaction between the vehicle and carbon black will facilitate wetting and accelerate the dispersion process. In other words, better carbon black/resin interaction means better ink stability. The proper choice of effective wetting and dispersing agents can provide vast improvements in ink performance. In the ink industry, the dispersion is usually characterized by Hegman gages. **The grinding equipments are listed in the Table 5. Among the techniques, the most preferable equipment is three roll mill due to the high shearing action imparted by this milling technique.** Ink makers generally use three-roll mills to handle high viscosity paste ink formulas at relatively low temperatures.

Table 5 Dispersion Techniques for Carbon Blacks In Ink Applications

Dispersion Equipment	Shear force Classification	Premix requirement	Application Type
Three roll mill	High shear	Required	High viscosity paste for heavy offset-litho base inks.
Two roll mill	High shear	Required	• High pigment loading (>20%).

			• High plasticity compound (such as vinyls, nitrocellulose, cellulose acetate, and alcohol soluble resins) dispersion. • High gloss. • Need temperature control the batch stiff. • Better color.
Ball mill	Medium shear	Not needed	• Used in the bead form of carbon black dispersion. • High loading and high output. • Good dispersion obtained only at proper viscosity (between 1600 to 2400 cps at 10-100 sec-1).
Attritor	Medium shear	Not needed	
Rotor stator	Low shear	Not needed	

6. UV ink manufacture

UV curing inks have become one of the fastest growing segments in the graphic industry. UV inks are employed in offset printing and flexo printing as well as in screen printing.

Major benefits offered by UV technology are faster run speeds resulting in improved productivity, quick start-up resulting in less waste, quick turnaround and converting due to instant curing of the ink film, environmentally safe technology without the use of VOCs, and higher print quality (i.e. gloss).

Three roll mills were used for UV inks because bead mills created an uncontrolled thermal reaction which could lead to polymerization.

The composition consists of oligomer, fluorescent dye and photopolymerizable vehicle. Generally, a fluorescent ink concentrate is synthesized first. One example is to combine 38g water with 0.45 g potassium tetraborate, 40.44 g of formaldlehyde, and 104.9 g of toluenesulfonamide. The reaction was heated to 100 C. During the heating process, 26.8 g of Solvent Yellow 85, 3.98 g of Basic Red 1, and 0.7 g of Basci Violet 11 was added and 26.76 g of melamine was added to 85 C. The reaction was held at 100 C, for 5 minutes upon which a solution of 250 g of trimethylolpropane triacrylalte with 0.4 g of hydroquinone was added to the reaction. The mix was heated to 110 C and milled on three roll mill at room temperature, to provide fluorescent orange ink concentrate. The above 7.0 g concentrate was combined with 1.0 g of Ebecryl 3608, a fatty acid modified epoxy acrylate, and 0.3 g of trimethylolpropane triacrylate, to provide a fluorescent ink.

7. Conclusion

In order to make desirable ink, it is widely accepted to employ the three roll mill to process the ink composition by the provided high shear force. Though some other kind of mills are also used, the three roll mill is especially suitable for high viscosity ink like UV ink and high loading carbon black inks.