

# Printing Inks And Their Related Problems In Different Printing Processes For Paper

Ray A.K.

## ABSTRACT

A brief review of the constituents of printing ink for various application on paper substrate is outlined. The optical, physico-chemical, rheological and polymeric properties are highlighted. The working properties of ink is also dealt with. The interaction between ink and paper surface is emphasized. The problems arising due to ink application on paper during different processes are also stressed upon. Some special inks and its applications are also discussed.

## INTRODUCTION

Ink is one of the common areas for all printing methods. The major components of inks in mechanical printing methods are the pigment (solid), binder or dye vehicle (liquid), and the solvent (the carrier phase). Supplementary additives are principally driers, resin, wetting agents, waxes, anti-skinning agents, antioxidants, plasticizers, lubricants and greases etc. Type and quantity of inks varies widely. What combination of pigments, dyes, vehicles, binders, and other ingredients is used depends on the process and drying system employed. Ink film thicknesses can be less than 1  $\mu\text{m}$  and the printed spatial details can be less than 10  $\mu\text{m}$ . The ink per unit area of paper in four-color printing is approximately 1  $\text{gm}^2$ . The mass of ink is less than 5% of the mass of paper. On the paper, an ink film absorbs at

Care should be exercised in mixing and blending different types of inks. From the above table, it can be seen that components of inks designed for different printing processes may not be at all compatible with each other.

The main types of inks are liquid inks, aqueous inks and oil based inks or paste inks. Flexographic and gravure inks are liquid or aqueous inks. Offset inks are paste inks. Aqueous printing inks find use in flexographic printing of newspapers and packaging materials. In rotogravure printing, aqueous printing inks represent a growth area. Within a given type such as inks for a specific printing method, the margins are tighter. The solid toners are used in electrophotography and other particle based processes.

Ink making operations consist primarily of chemical raw material conversion and surface, chemical, and mechanical processing. Ink manufacturing consists of three steps

using dispersion devices or by mixers after dispersion.

An indication of the range of ink systems is the fact that printing ink can be any type of a multicomponent system as shown in Table 1.

## Printing Ink Composition

An acceptable ink must be user and environmentally friendly in the sense that the prints should have sufficient durability and be toxicologically and ecologically acceptable.

## Pigments

Finely divided solids for colour/opacity/ other properties, varying in particle size, refractive index, texture and wettability etc. Each dictates suitability of a pigment, its most compatible vehicle and final product characteristics.

Several factors influence the color of prints starting with the atomic structure of pigments and extending to compatibility of the ink and the

PRINTING PROCESS	DRYING SYSTEM	TYPE OF VEHICLE
Letterpress News	Absorption	Non-drying oil
Letterpress, offset	Oxidation	Drying oil
Letterpress, offset	Quick-setting	Resin oil
Letterpress, letterset	Precipitation	Glycol-resin
Letterpress	Cold-setting	Resin wax
Gravure, Flexographic	Evaporation	Solvent-resin

most more than 99% of the incident light of a given wavelength of a given wavelength band. As these figures suggest, the requirements on inks and their use in printing are very stringent. The printing process and the drying system involved determine the type of vehicle used in the manufacture of printing inks as shown in the following Table.

Department of Paper Technology,  
IIT Roorkee, Saharanpur- 247 001.

with controlling of optimum temperature required.

- Dissolution of the binder in the carrier phase in mixers or dissolvers
- Dispersion of pigment in the vehicle in a sufficiently fine state in the continuous phase with milling or grinding requiring higher shear and impact forces than those for mixers
- Addition of additives in the ink

substrate. The influencing factors are the following:

- Atomic level: Atom groups in pigments resulting in absorption of light
- Molecular level: Molecules containing groups that absorb light
- Pigment crystal level: Crystal structure
- Pigment particle level: Size and shape
- Printing ink: Compatibility of

- pigment and the vehicle dispersion
  - Printed image: Compatibility of printing ink and paper
- The color of organic substances and pigments derives from atom configurations that selectively absorb light.

The organic chromophores (color groups) are:  $-C=C-$ ,  $-C=O$ ,  $-C=N-$ ,  $-N=N-$ ,  $-N=O$ ,  $-CH=CH-$  and the color strengthening auxochromophores are:  $-SO_3$ ,  $-NH_2$ ,  $-OH$ ,  $-NO_2$ ,  $-CH_3$ ,  $-Cl$ ,  $-Br$  etc.

benzidine yellow. Magenta pigments are rubines, naphthols and rodamines. Cyan pigment is phtalocyanine blue, and black pigment is carbon black. Table 3 lists pigments commonly used in process printing inks.

#### Binders

This is used to bind the pigment on the paper substrate. As a general rule, the binder content in inks is approximately the same as the pigment content. High quality inks typically contain more

- Reacting groups occurring in the chain

All the above characteristics influence the glass transition temperature, melting point, solubility, absorption behaviour, and bond strength of the binder. Glass transition temperature and film formation temperature adsorption properties, bond strength and drying potential are functional binder properties.

#### Solvents

**Table 1. States of multi component systems.**

State	Characterization
Solution (Homogeneous)	Consists of molecular particles of the size $<10^{-9}m$ Homogeneous
Hydrosol (solubilized colloid) Homogeneous	Soluble surface-active substance forming an interface between liquid phase Particle size of solid phase $10^{-9} - 10^{-7}m$ Particles visible in electron microscope
Emulsion (colloidal)	Liquid phase surrounded by surface-active substance as small liquid particles in a continuous liquid solid phase Particle size $10^{-7} - 10^{-6}m$ Particles visible in light microscope Interface properties have great importance
Dispersion (colloidal)	Solid phase surrounded by surface active substance in a continuous liquid, heterogeneous For other characteristics, see emulsion
Solid dispersion	As dispersion, but solid phase in another solid phase
Suspension (coarse suspension)	Solid phase in a continuous liquid phase Particle size $> 10^{-6}m$ , surface properties of minor importance Particles visible in light microscope
Aerosols	Liquid in fine form in gas phase Particle size in colloidal range

Inorganic color compounds are the salts of transition metals Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu and compounds that contain an element representing two degrees of oxidation such as Fe(II), Fe(III) cyanides.

Considering molecular structure, pigments can have the following classifications:

- Straight-chain (Yellow, Red, Magenta)
- Polycyclical (Blue, Cyan, Green)
- Open Chain: salts of acid pigments (Red, Magenta, Cyan)
- Open Chain Salts of basic pigments (Red, Magenta)
- Inorganic pigments (White, Yellow, Blue, Cyan, Black)
- Carbon black (Black)

The most common yellow pigment is

binder. Inks can use a wide range of binders obtained from sources such as plants (drying oil), wood processing (pitch, resins), crude oil distillation (hydrocarbon resins) and chemical synthesis.

Printing ink binders are oils or resins. Resins can be natural resins and semisynthetic or synthetic resins. Because binders are polymeric materials, their structure consists of the following characteristics:

- Chain length (molecular weight)
- Chain branching and stiffness
- Double bonds in the chain and secondary forces between molecule groups (ion forces, hydrogen bonds, dipole interaction, and van der Waals' forces)

According to the carrier phase, the inks fall into the following groups.

- Liquid inks (Gravure and Flexo)
- Oil based or paste inks (Offset, Letter Press, Silk screen)
- Aqueous inks (Flexo, Silk Screen)

In offset, the combination of the binder and the oil is a varnish. The general term used to denote the combination is "vehicle". The carrier phase is removed by evaporation (gravure, flexo, heat-set offset), conversion into solid form by oxidation (sheet-fed offset), radiation polymerization (sheet-fed offset), or absorption in to the paper (newspaper offset).

The ability to dissolve binders is the

**Table 2. Printing Ink Composition:**

Component	Function	Description
Pigment 10%-30% Black: Carbon Black Cyan: Phtalocyanines Magenta: Azo Pigments and salts Yellow: Azo Pigments	Light Absorption to give color	Insoluble fine particles dispersed in the continuous phase (=Vehicle) consisting of carrier phase and binder
Binder 10%-30% Pitch (Newspaper printing) Phenolics (all types of ink) Alkyds (Offset) Hydrocarbon resins (News Ink) Drying Oils (Sheet fed offset) Acrylates (UV and Aqueous) Nitrocellulose (Flexo)	Bind the pigment particles to the paper and give gloss	Amorphous polymeric materials called resins or monomers of these or oxidizing vegetable oils
Carrier Phase 0%-70% Mineral Oils (Offset) Vegetable Oils (Offset) Toluene, Xylene (Gravure) Water (Flexo) Alcohols, Esters, Ketones (Flexo)	Provide the necessary fluidity	Solvents (Boiling Point <100°C) And oils (Boiling Point >100°C)

most significant functional property of binders. Solvents used in printing inks are hydrocarbons. High boiling aliphatic hydrocarbons are mineral oils. Fractions reaching the boiling point (230°C-320°C) are used in heat-set printing inks. Fraction with a higher boiling points find use in newsprint and sheet-fed offset printing inks. Liquid toners contain pure aliphatic hydrocarbons.

Aromatic hydrocarbons, like toluene and xylene find use as solvents in rotogravure printing.

Methylated ethyl alcohol finds use in rotogravure and flexo printing of packaging materials. Propanol finds use in aqueous rotogravure and flexo inks because of its complete solubility in water. Cyclohexanol and methyl cyclohexanol are special cases for use in silk screen printing. In the glycol category, ethylene glycol, has application because of its hydrophilic properties. It has use in water-diluted and moisture setting inks. Solvents belonging to the group of glycols are

solvents for various binders such as tall oil-based resins and nitrocellulose. Applications consequently include rotogravure and flexo inks. Examples are ethylene glycol and monomethyl ether.

Kerosene solvents typically have good dissolving capacity. Methyl ethyl ketone (MEK) finds use in rotogravure and flexo printing of packaging materials. In the acetate category, ethyl acetate has use due to its ability to dissolve nitrocellulose.

### Additives

The additives have a profound influence on the functioning of the inks in printing. The additives are typically surface chemically active i.e., they tend to migrate to and accumulate at surfaces such as pigment surfaces (on the micro scale) and on the ink layer surfaces (on the macro scale). Table 4 gives a summary of commonly used additives.

Besides additives that influence drying

from within the ink, the application of additives on top of a printed layer as a separate step can influence the smearing of printed layers in the press. This type of additive includes starch powder used in sheet-fed offset. Its influence is similar to that of waxes in inks. These function by reducing surface energy and by providing a physical barrier. In heat set offset, silicone solution is applied after drying as a thin layer to reduce the surface energy of the printed layer.

### Properties

The properties of inks measured by printer generally are: Color, Viscosity and density. Color belongs to optical properties.

### Optical properties

Four-color printing uses printing inks that are transparent i.e. the inks selectively absorb specific bands of wavelength of light and allow

**Table 3. Typical pigments of four- color inks**

Type	Chemical structure	Color
Azopigments	Monoazo: - N = N- diazo: R - N = N - R' - N = N - R''  For example: Acetoasetarrylamides, arylidic yellow, arylamidic yellows, diaryl yellows = benzidine yellow naphtols	Yellow Magenta Red
Polycyclical pigment	C = N and C = structures composed of aromatic ring units For example: phtalocyanines C <sub>32</sub> H <sub>16</sub> CuN <sub>8</sub>	Blue Green Cyan
Inorganic pigments	Lead chromates: lead yellow Cadmium sulphides: cadmium yellow Iron ferro cyanines Xfe <sup>3+</sup> [Fe <sup>2+</sup> (CN) <sub>6</sub> ] <sub>∞</sub> H <sub>2</sub> O; X: NH <sub>4</sub> , Na, K For example (X = NH <sub>4</sub> ): Milor blue, iron blue, bronze blue, Prussian blue, Chinese blue Treated calcinated kaolins; Ultramarine	Blue
Salts of acid pigments	Salts of azo pigments (rubines) [R - N = N - R' X - ] <sub>2</sub> Y <sup>++</sup> ; X: COO, Cl, SO <sub>3</sub> , OH, Y: Ba, Ca, Na	Magenta
Salts of basic	R - X <sup>+</sup> Y <sup>-</sup> R = X + Y <sup>-</sup> ; X: NH (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> , Y: Cl, Br, CuFe (CN) <sub>6</sub> For example rodamines: PMTA, Victoria blue	Magenta Red Blue
Carbon black (channel and furnace black)	Contains C 90% organic substances 1% - 10% (O, H, S, hydrocarbons)  Manufacture: By burning oil (furnace soot) or natural gas (channel soot)	Black  Blue tone, brown tone
Soot (lamp soot, vegetable soot)	Contains: C 91% -99.7% Moisture 0% - 2.4% Extractives 0.1% - 0.9% Ash 0.01% - 0.3%  Manufacture: By burning tar or crude oil distillation residues	Black  Gray

transmission of unabsorbed light. The selectivity of spectral absorbtion can be measured from prints spectrophotometrically. The results are commonly given as CIE Lab or CIE Lch co-ordinate values. Standards and recommendations are available for the color of ink sets. CIE Lab color values of the European standard inks are given in Table 5. The range of colors obtained on a given paper by using a specific set of inks is called the color range.

### Rheological properties

Rheological properties are fundamental to deformation and flow of materials. They can predict together with surface chemical properties-the transferability of ink in the press and interactions with the paper for ink spreading and penetration. Viscosity is a measure of the resistance ( measured as shear stress, Pa) to flow

under applied forces.

In steady state, Rheological behavior of most fluid can be expressed by generalized form of equation:

$$\tau = -\eta - 0.5 \eta_c \{ \Delta \cdot \Delta \}$$

$$\tau_{yx} = -\eta (dv_x/dy)$$

For Power-Law fluids equation (2.1 and 2.2) can be written as:

$$\tau_{yx} = -m |dv_x/dy|^{n-1} dv_x/dy$$

The Bingham Model

$$\tau_{yx} = -\mu_0 dv_x/dy \pm \tau_0 \text{ if } |\tau_{yx}| > \tau_0$$

$$dv_x/dy = 0 \text{ if } |\tau_{yx}| < \tau_0$$

Printing inks used in different methods that fall in the approximate range as given in Table 6.

The above data are very approximate because the viscous behaviour of offset inks and letterpress inks at the higher end of the scale is shear rate dependent. The ink viscosity decreases with the

rate of shear displaying behavior of shear thinning or pseudoplasticity.

Oil based inks may require a given shear stress before any flow occurs. This is yield value . An ink is plastic when its flow after yielding is Newtonian. Inks that have high real or apparent yield values are difficult to pump. This may impede transfer from ink pans to rollers. A high yield value is advantageous for halftone dot sharpness.

Oil based inks are also thixotropic. Inks are also viscoelastic which means that they have instantaneous deformation component in the flow. Pigment structures may develop elasticity at low speeds, and binder molecules may develop elasticity at high speeds. Elasticity influences halftone dot formation and ink splitting. Moderate elasticity appears to be advantageous. Table 7 summerizes the importance of the rheological behavior of printing inks

**Table 4. Additives in printing inks.**

Additives	Purpose and use
Soluble dyes	<ul style="list-style-type: none"> <li>- Modify the shade provided by the pigments</li> <li>- Used in all types of inks</li> </ul>
Filler pigments: white mineral pigments	<ul style="list-style-type: none"> <li>- Reduce the color strength of the ink</li> <li>- Add "body" in all types of inks</li> </ul>
Wetting, emulsifying, and dispersion agents	<ul style="list-style-type: none"> <li>- Wet and improve dispensability and stability of pigments (and emulsion type binders) in inks</li> <li>- Used in all types of inks</li> </ul>
Gelling agents: Al compounds	<ul style="list-style-type: none"> <li>- Increase the "body" of ink by networking after ink transfer to the paper in an effort to reduce smearing and spreading of ink</li> <li>- Use in oil-based inks</li> </ul>
Waxes: polyethylenes, polytertrafluoroethylenes, paraffine waxes	<ul style="list-style-type: none"> <li>- Reduce surface energy and prevent adhesion of wet print to other surfaces</li> <li>- Prevent physical contact</li> <li>- Reduce ink tack</li> <li>- Used in heat set and sheet fed inks</li> </ul>
Diluents and cosolvents: alcohols	<ul style="list-style-type: none"> <li>- Reduce ink viscosity without influencing the binder</li> <li>- Used in liquid inks</li> </ul>
Defoamers: silicone compounds	<ul style="list-style-type: none"> <li>- Prevent foaming</li> <li>- Used in liquid inks</li> </ul>
Plasticizers: esters with high molecular weight	<ul style="list-style-type: none"> <li>- Improve flexibility of printed ink layers by having a dissolving effect on binders</li> <li>- Used in high quality inks</li> </ul>
Drying catalysts: organic Co and Mn containing compounds in oxidizing inks, aromatic ketones in UV polymerizing inks	<ul style="list-style-type: none"> <li>- Initiate and speed chemical drying</li> <li>- Used in sheet-fed offset inks</li> </ul>
Drying inhibitors: reactive compounds	<ul style="list-style-type: none"> <li>- Prevent chemical drying in can</li> <li>- Used in sheet-fed inks</li> </ul>

**Table 5. Optical Properties**

Colorimetric values of standardized inks (Euro standard)					
Color	L*	a*	b*	c*	h*(°)
Cyan	53.75	-24.05	-48.55	54.15	243.7
Magenta	47.60	76.65	-4.20	76.75	356.9
Yellow	90.00	-12.77	92.56	93.45	97.8

**Table 6. Rheological properties**

The order of magnitude of viscosity in different types of inks	
Ink type	Viscosity (Room Temperature), Pas
Newspaper Offset	2-10
Heat- set offset	5-15
Sheet fed offset	10-50
Gravure	5-50
Flexo	5-50
Letter press	0.1-10

**Table 7. Impact of the rheological behaviour of printing ink for the printing process**

Property	Impact
Viscosity	-Flow of ink in pipes, lifting by rollers from containers, flow through press rolls -Transfer to paper, tackiness, penetration and diffusion on paper
Shear thinning	Fine –tuning of the behaviour of printing ink: transfer vs. set-off, tackiness
Thixotropy Viscoelasticity	As above -Behaviour in connection with rapid change of shear: tackiness, transfer to paper -Behavior at low shearing rate

**Table- Features of different viscosimeters**

Capillary viscosimeter	High-pressure capillary viscosimeters: $D + 10^{-10} s^{-1}$ - Poor suitability for measurement of thixotropic samples (shearing rate in measuring nip not constant) - Suitable for measuring rotogravure, flexo and newspaper offset inks - Correction terms must be marked at high speeds viscoelasticity measurement with die swell and jet thrust methods possible
Rotation viscosimeter conical viscosimeter	Shearing rate range: $10^{-4} s^{-1} - 10^3 s^{-1}$ - Suitable for measuring different types of printing ink because the shearing rate in the nip is constant - Secondary flows and breaking of samples at the free surface restrict the maximum rate - Viscoelasticity measurement as normal force or vibration measurement
Rotational viscosimeter; coaxial cylinder viscosimeters	Shearing rate range: $10^{-4} s^{-1} - 10^3 s^{-1}$ - Suitable for measuring rotogravure and flexo inks; closed measuring space prevents sample from evaporating
Viscosity cups	Shearing rate is determined on the basis of viscosity; not constant in the cup - Suitable for determining the viscosity level of Newtonian liquids (used for controlling the viscosity of rotogravure and flexo inks in the industry)

in the printing processes.

Solvents and oils used in printing inks are liquids with small molecules whose rheological behavior is Newtonian. If the molecular weight of a polymeric binder is small, its content is low, and its solubility into the solvent is good, the rheological behavior of the medium will be Newtonian. Otherwise, the medium will exhibit shear

thinning behavior. Its behavior may also show significant elasticity. If the printing ink contains gels, the flow is typically plastic and thixotropic. Adding a pigment to the medium increases the shear thinning behavior primarily so that the viscosity level measured at low shearing rates increases more than at high shearing rates. Weak floc structures in the

pigment particles increase the thixotropy of the printing ink.

Ink tack is an experimental quantity defined as the resistance of a thin film to splitting. It is relevant to Lithographic inks. The ink films generally split by shear or by tension. Liquid inks split largely controlled by shear. Tension forces are

**Table Methods of Drying Inks Used in Printing Processes.**

Ink-drying method	Letter Press	Flexographic	Lithographic	Gravure	Silk Screen
Oxidation	Yes	No	Yes	No	Yes
Heat set	Yes	No	Yes	No	No
Moisture Set	Yes	No	No	No	No
Polymerization	No	No	yes	No	Yes
Evaporation	No	Yes	No	Yes	Yes
Absorption	Yes	No	No	No	No
Fusion	Yes	No	yes	No	No
Hot Wax	Yes	No	No	No	No
Filtration	Yes	No	Yes	No	No
Radiation	Yes	No	Yes	No	Yes

likely to play a role in oil-based inks due to higher viscosity. Roller devices commonly measure ink tack. The tack reading obtained corresponds to resistance integrated over time, i.e. it is the area of the resistance curves. With an increase in the speed of printing, ink tack usually increases. As a first approximation, tack depends on the product of viscosity and speed. Tack also depends on viscoelasticity- more elastic inks have lower tack values. Because of the shear thinning behavior of inks, measurement of the viscosity should use a shear rate that is representative of the speed conditions in the nip. When a given amount of ink rotates in a roller device, its tack value increases with time due to evaporation of volatile solvents and oils. The slope of the relationship tack vs time can predict the setting and drying behavior of sheet fed and heat-set inks, respectively. At some point the slope tends to become negative, and the tack value reaches its maximum. A high value is disadvantageous because it indicates high stickiness of the drying film.

### **Measuring Rheological properties**

Rotational viscosimeters and rheometers are the common means to determine viscous and viscoelastic ink properties. Capillary rheometers are suitable for measurement of ink-jet inks, and viscosity cups are suitable for routine control. Table 8 compares the features of different viscosimeters.

### **Surface and Colloid chemical properties**

When considering an ink, the phenomena in the form roller and

printing nips primarily have the character of surface phenomena. In these nips the ink transfers to the plate and the paper. In offset printing, the ink also interacts with the dampening water. The interactive behavior of ink in relation to water is called lithographic behavior. Apart from macroscopic surface chemical properties, the surface tension( or energy), interfacial tension( or energy). And ink and water interactions are also influenced by colloidal properties and rheological properties. Colloidal properties predict the surface energy conditions on micro scale, i.e. on the scale of pigment particles. Colloidal properties also influence the stability of inks in the press with changes in temperature and chemical environment. Lack of stability may be manifested as agglomeration of pigment particles in the ink with losses in optical efficiency and accumulation on the press rollers.

The surface tension of liquid inks can be measured directly, even for oil based inks by static contact angle principle. Printing process is however, highly dynamic as surfaces form in milliseconds.

Emulsification tests commonly measure lithographic ink behavior. The test mixes ink and water in given conditions and measures the water up-take of the ink gravimetrically. From the curves of water up-take vs time, one can read the speed and saturation level of emulsification. Mixing of water in ink in printing is necessary to eliminate water from those areas of the plate where it is harmful, i.e. from text areas and from the top of halftone dots. It is necessary between the dots. Fast

emulsification is desirable because the printing conditions after start-up are not stable until the saturation level of water pick-up occurs. The optimum magnitude of emulsification depends on the type of water feeding unit. This is because of differences in the efficiency of water use. A higher efficiency means lower water consumption.

### **Drying characteristics of printing ink**

In the ink drying process, two phases can occur: the ink setting phase and the actual drying phase. As a result of the setting phase, the printing ink forms a touch-proof layer. In drying phase results in a rub-resistant layer. The phases can use the same or different mechanisms. For example, the mechanism is the same when the printing ink contains a solvent that requires evaporation during the drying phase( rotogravure and heat-set inks) or when the printing ink is polymerized after each press unit( UV inks). Conventional sheet-fed offset inks involve two separate mechanisms. The setting uses filtering and evaporation, and the actual drying polymerization by oxidation. Newspaper printing inks donot have any drying stage.

### **Polymerization**

A polymerization reaction occurs in printing inks with UV or IR radiation or due to the oxygen in the atmosphere around a thin ink layer. In the future, electronic radiation will probably also find use as a source of reaction energy. In all these cases, the polymerization is radical polymerization. UV and IR radiation is analogous to the photo-

polymerization used in printing plates.

## Working properties of Ink

The most important properties of ink besides color and color strength are body, length, tack, and drying characteristics.

- **Body**
- **Tack**
- **Ink Length- Long, Short, Thixotropic**
- **Density**
- **pH**
- **Temperature**

### Body.

Body refers to the consistency of the ink, that is, whether the ink is stiff or soft. Ink consistencies vary widely from very stiff inks for collotype to very soft, fluid inks for newsprint, gravure, and flexography. The rheological (flow) properties of the ink determine its working properties on the press and its penetrating qualities on the paper. It is found that the rate of penetration of printing ink into paper is directly proportional to the fluidity of the ink vehicle, but not to the fluidity of the compounded ink. The temperature of the ink is important to the extent that it affects the fluidity of the ink vehicle. Printing inks are non-Newtonian fluids generally exhibiting plastic, pseudo-plastic, dilatant, or thixotropic properties. Inks are, however subject to high rates of shear on the printing press. This tends to overcome any yield value and thixotropy, thus permitting even distribution of ink on the rollers.

### Length

For best results printing ink should have the highest viscosity and yield value consistent with good operation on the press and good printing properties on the paper being used. Inks can be long or short. High-yield value alone results in an ink that is too short; the ink tends to back away from the fountain. Backing away from the fountain caused by too short an ink can be corrected by adding a bodied varnish. Too short an ink results in mottle, a condition of ridges in the ink film. Too long an ink forms filaments which on high-speed presses have an undesirable tendency to fly or mist. This is especially troublesome with news inks. Papers of medium absorbency can be printed with inks of high viscosity and high-yield point, but the flow properties of the ink must be such that the ink distributes well on the

press. For relatively nonabsorbent papers, the inkmaker may add a penetrant, although usually a fairly heavy-bodied varnish with considerable tack will produce good results. When printing nonabsorbent paper, a small amount of light mineral oil may be helpful in reducing the viscosity of the ink, thereby producing more rapid penetration into the paper and reducing offset. Thinner inks are required the faster the speed of the press.

### Tack

In contrast to basic rheological characteristics, tack is not a pure material characteristic though this is closely related to flow. This is commonly visualized as the pull resistance exerted by the ink on the paper surface. The measured tack value depends on the measuring conditions and also on factors related to the design of the measuring device such as bearing friction.

The pull exerted between the printing plate and the paper in letterpress and the blanket and the paper in offset lithography depends on the type of ink, rate of separation of the plate or blanket from the paper surface, area of contact, and film thickness. At the high rates of shear existing on a press, plastic viscosity is the dominant rheological factor affecting tack, yield point being of little influence. The dominant factor in ink tack is not the force but the energy of film separation, which they found to be proportional to the plastic viscosity of the ink raised to the 1.5 power. Film separation is taking place primarily by rupture in a solid pattern resulting from transversal vibrations induced at the paper-ink interface. A certain amount of tack is necessary to cause adherence of the ink paper; if the tack of the ink is not sufficient for the type of paper and press conditions used, the reproduction will be poor. On the other hand, too tacky an ink is likely to rupture or pick the paper surface. In multicolor printing, the various inks must be graded in tack to secure proper trapping, that is, printing the same amount of ink on previously printed ink as on unprinted paper. The first-down ink must be relatively high in tack so that it will lift the second-down ink. The second-down ink should be more tacky than the third-down ink, which in turn should be more tacky than the last-down ink. Inks differ in their rate of increase of tack with increased press speed, and hence it is

possible for two inks to change their relative order of trapping as the speed of the press is increased, with the result that false color values are produced. The tack of ink can be measured by special tack meters, such as the Thwing-Albert-LTF Inkometer and the Tackoscope.

Ink temperature control is common for gravure printing system and also for water-based flexo.

Regular measuring of density allows controlling the ink water ratio and can be used for estimating the addition of water/ amine mixture if required. The measuring of density also allows one to calculate the actual value for residual water left in the printing machine after a wash cycle. The ink density measurement consists of the following steps:

Measure the density of water and density of ink particles before putting it on the machine

Measure ink density when the ink is circulating in the machine or when return from the machine. The following equation allows one to calculate the amount of water to be added to change the viscosity:

$$M_{\text{water}} = m_{\text{ink+water}} * (1 - \rho_{\text{ink+water}} / \rho_{\text{ink}}) / (\rho_{\text{ink+water}} / \rho_{\text{water}} - \rho_{\text{ink+water}} / \rho_{\text{ink}})$$

Where m=weight in kg; v=volume in dm<sup>3</sup>; ρ =density in kg/dm<sup>3</sup>

pH is determined by its formulation. Ink contains amine and /ammonia and ink pH is alkaline roughly between 8 and 10. The pH is probably an indicator of the drying speed of the ink. Rule of thumb is that, for an ink of otherwise similar formulation, the greater the pH the longer the drying time. This does not mean that a fast drying ink has a lower pH than a slow drying ink—that is the prerogative of the way the ink company formulates the ink.

### Letterpress Inks

Letterpress inks are designed for printing form raised surfaces such as type, engravings, and electrotypes. They are usually of moderate tack and viscosity. Most sheet-fed letterpress inks dry by oxidation. These are in paste form and consist of pigments and drier ground in a drying-oil vehicle. They may also contain various resins and special compounds to give functional characteristics such as gloss and scuff resistance. Letterpress inks for web printing can dry by penetration (newsprint ink), by evaporation (heat-set inks), or by precipitation (moisture-



set inks).

Some major types of letterpress inks are: Rotary Ink, Quick set ink, Heat-Set Ink, Quickset Ink, High-gloss Ink, Moisture-set Ink, Water-washable Ink, News Ink, Miscellaneous Job Ink, Non-Scratch Ink etc.

## Lithographic Inks

Lithographic inks are formulated to print from planographic surfaces utilizing the principle that grease and water do not mix. Lithographic inks are generally more highly pigmented and are stronger in color value than letterpress inks to compensate for the thinner films applied. They are the strongest of all inks next to **collotype inks**. The average amount of ink transferred to the paper is about half that of letterpress because of the extra split of the ink film between the plate, and the blanket.

Sheet-fed lithographic inks are similar in formulation to oxidizing letterpress inks. However, they contain water-resistant vehicles and pigments that do not bleed in water or alcohol. Heat-set litho inks are also similar to their letterpress counterparts but use special vehicles and pigments to resist reaction with water and alcohol.

Letterset inks have no restrictions imposed to prevent bleeding into a dampening solution since letterset printing does not use a dampening mechanism. Therefore any pigment used for letterpress may be used for letterset. Letterset inks are stronger in color value than letterpress inks but not as strong as conventional offset inks because they are not diluted or weakened by water emulsified in the ink during running on the press.

The many types and modifications of press equipment, the many different substrates printed and the broad spectrum of applications for lithography require a wide variety of ink formulae to serve the needs of the offset printing industry.

Sheet-fed offset inks are offered in a broad variety of vehicle systems, which, for brevity, can be categorized in five general classes:

- **Oxidative** Containing largely natural or synthetic drying oils
- **Gloss** Drying oils, very hard resins, minimal hydrocarbon solvents
- **Quick Set** Hard soluble resins, hydrocarbon oils and

solvents, minimal drying oils or plasticizers

- **Penetrating** Soluble resins, hydrocarbon oils and solvents, drying and semi-drying oils and varnishes.
- **Radiation curing** Very sophisticated, highly reactive, cross linking proprietary systems, which dry by application of UV, IR or other radiation.

With the exception of the UV-curing type, the four other categories permit much crossing of lines and hybridizing. In addition to the vehicle or combination of vehicles (also called varnish), most formulations also contain compounds, driers, and sometimes extenders to impart desired printing and dry-film performance characteristics.

## Web offset inks are available in the following general types

- **Penetrating** Hydrocarbon oils and solvents, soluble resins.
- **Heat Set** Hydrocarbon solvents, hard soluble resins, drying oil varnishes, and plasticizers.
- **Radiation curing** Very sophisticated, highly reactive, cross-linking proprietary systems, which dry by application of UV, IR or other radiation.
- **Thermal Curing** Sophisticated, reactive, proprietary systems containing little or no solvent which dry by application of heat and use of special cross-linking catalysts.

## Lithographic Problems are:

### Greasing or Scumming, Tinting, Stripping, Printing too sharp, Piling Drying

#### Gravure Inks

Gravure inks are rapid-drying fluid inks with the proper viscosity to be drawn by capillary action from the engraved wells in the cylinder or plate. They dry principally by the evaporation of the solvent in the ink, commonly with the use of heat. Gravure inks must be free of abrasive particles that could scratch the engraved cylinder or plate. A wide variety of solvents are used in gravure inks depending on the substrate.

Most gravure inks are very volatile, and they can cause fires or explosions if not handled properly. Solvent recovery is used in many publication plants to eliminate

pollution from the evaporated solvent. This is practical if only one type of ink and solvent is used. Solvent recovery is not practical for plants that use different substrates requiring different solvents. Water-based inks containing small amounts of alcohol have been developed to eliminate both the fire hazard and solvent pollution. These are reasonably successful for some packaging applications.

## Rotogravure problems

Pinholing, Snow flaking, Skips, Screening, Spilling ( Drag-Out, squeeze - Out ), Fogging ( Scumming ) Volcanoes ( Cratering ), Mottle ( Crawling ), Cylinder Waer, Stripping of Chrome

## Flexographic Inks

Flexographic inks are fast-drying fluid inks similar in viscosity to gravure inks. They are used in printing many kinds of surfaces where the exceptional color effects afforded by flexography are best exploited by using large masses of color. Flexographic inks consist of colorants, which may be either pigment or soluble dyes, mixed with a vehicle or binder and with volatile solvents. The solvent is usually alcohol or water, although other solvents are also used. Alcohol-based inks are the most common and they dry by evaporation. Water-based inks dry by both evaporation and absorption on paper substrates. Flexographic inks with sublimable dyes are used in short- and medium-um heat-transfer printing.

## Flexographic Problems

Adhesion, Blocking, Bleed, Chemical Pinholing, Mechanical Pinholing, Feathering and Fill-In, Souring, Precipitation, Picking etc.

## Screen-Printing Inks

Screen-printing inks are usually of the drying oil type although other types are also used depending on the substrate to be printed. They have the consistency of thick paint. The inks are made in any color with a binder suitable for the material to be printed. The ink must be short and buttery to print sharp and to squeegee with little resistance. To prevent clogging is also used for specialty heat-transfer printing so there are special screen-printing inks with subliming dyes for heat-transfer printing.

## Ink Types

A number of special inks have been

developed for specific types of printing. Some inks have been developed especially to eliminate the need for starch anti-offset spray in sheet-fed printing. Others have been developed to eliminate air pollution from heat-set ink solvents in web printing. Others are used to (1) simulate metallic luster, (2) print on paper images that can be transferred to fabrics, (3) print magnetic characters on checks and other documents to be read on special electronic equipment, (4) impart alcohol and scuff resistance for liquor labels, (5) impart alkali resistance for attractive window or counter displays. Descriptions of special inks follows.

#### **Radiation-Curing Inks.**

These are among the newer types of inks developed to eliminate both the need for spray powder in sheet-fed printing and air pollution from solvents in conventional web heat-set inks. There are two types of these inks; Ultraviolet (UV) and electron beam (EB) curing. Ultraviolet-curing inks consist of essentially solvent-free liquid prepolymers and initiators that on exposure to large doses of UV radiation release free radicals that polymerize the vehicle to a dry, solid, tough thermosetting resin. Because these inks have active ingredients that are more expensive than the solvents they replace in conventional inks, UV inks cost almost twice as much as regular inks. Therefore they are not used much in ordinary web printing except during periods of shortages. They have found some use in luxury packaging such as liquor and cosmetic cartons and are used extensively for metal decorating and screen-printing. The total consumption of UV inks, however, has been limited by economics. An unexpected shortage of gas or oil needed to dry heat-set inks in web-publication printing could trigger a conversion to UV inks for this type printing.

#### **Electron Beam (EB) Curing Inks.**

These make a good alternative to UV inks since expensive initiators are not needed and lower-cost, less reactive prepolymers and other materials can be used. A serious disadvantage of EB curing inks is the high capital cost of the equipment required. Shielding becomes a particularly critical problem because EB radiation produces X-ray when it strikes metal surfaces. There are several successful

commercial installations of EB on a press. EB is very energy efficient since it uses less energy than UV, which in turn uses about half the energy of gas drying.

#### **Quick-Setting Inks.**

These inks have been responsible for phenomenal improvements in printing. They have been particularly successful for printing on enamel and cast-coated papers in both letterpress and lithography. These inks consist of a delicately balanced oil-resin-solvent vehicle system. During printing, on contact of the ink with the paper under the pressure of printing, the paper surface or coating quickly drains some of the solvents from the ink, yielding a film that sets rapidly and permits handling. Quick-set inks usually dry with good gloss.

#### **Super Quick-Set Infrared Inks.**

These inks are a modification of quick-set inks that uses new synthetic resins with controlled solubility properties in combination with specially blended solvent systems and a minimal amount of drying oils. These inks are used extensively in new infrared ink drying systems. The setting of these ink is greatly accelerated by the application of heat energy, and infrared radiation is a convenient way to apply energy on a sheet-fed press. The system is also used for some web presses. Even without heat these inks set almost 10 times faster than conventional quick-set inks, and they are gradually replacing these inks. These inks have caused some problems with "gloss ghosting."

#### **Heat-Set Inks.**

These inks were undoubtedly one of the most important developments in web publication printing. They are quick-drying inks. Heat-set inks are formulated with high-boiling, slow-evaporating petroleum oils and solvents. They provide maximum press stability, yet they dry rapidly with heat application or dryers. The solvents are vaporized as they pass through a heating chamber leaving the pigment and binding resins fixed to the paper in such a manner that there is no chance for spread or excessive penetration into the paper. The printing press must be equipped with a heating unit and with an exhaust system to drive off the solvents and with chill rolls to cool the heated resins.

#### **High-Gloss Inks.**

High-gloss inks contain an additional quantity of varnish that gives them a glossy appearance when dry. For best results, paper stocks specially coated for gloss inks should be used. In general, the more resistance the paper has to penetration of the vehicle, the higher the gloss; this property of the paper is referred to as holdout. When heat is used in drying, it has a tendency to reduce gloss. High-gloss inks are available for both letterpress and offset. These inks are usually tacky, so they can cause problems with picking on weak papers.

#### **Heat-Transfer Inks.**

These inks are formulated with special dyes that sublime under pressure and at temperatures about 260°C. They are used for printing on paper images that are later transferred to other surface, usually textiles. They work best on polyester materials. Gravure is used for long runs; flexography and screen-printing are used for shorter runs on rolls. Lithography is used for sheet printing.

#### **Moisture-Set Inks**

These letterpress inks consist of pigments dispersed in a vehicle composed of a water-insoluble binder dissolved in a water-miscible, or water-receptive solvent, usually a glycol. Upon subjecting the printing to either steam, fine mist, or water, the water-miscible solvent picks up some of the water, which causes the water-insoluble binder to precipitate and to bind the pigment firmly to the paper. Moisture-set inks are relatively free odor making them ideal for food-package printing.

#### **Magnetic Inks.**

These inks were developed to provide a means to increase the speed and efficiency of handling bank checks. The inks are made with pigments that can be magnetized after printing, allowing the printed characters to be later "recognized" by electronic reading equipment. The inks must be formulated to produce high-grade printing that will meet the right requirements of the special electronic reading equipment. Press make-ready, amount of ink, and press conditions must be precisely controlled for consistent results. An illustration magnetic ink printing is shown in Figure 23-8. The 10 number and four symbols each have a distinctive shape which supplies information to a

Table 4. Composition of ink-jet inks

Component	Purpose
Dye or pigment	Coloring material
Binder	Binding the pigment on the paper (not always used)
Liquid phase	Carrier phase for the dye or pigment and binder
Continuous jet: water + alcohol DOD jet: water + glycols	Allows the desired low viscosity of the ink and prevents ink from drying in the nozzle
Charge generation additives (continuous jet) preservatives	Enhances the electrical charging capability of the ink Prevents bacterial decomposition

computer for punching a tape, making calculations, or performing a combination of other functions.

#### Scuff-Resistant Inks.

The inks used for printing on packages and containers must stay bright and appealing despite the shocks and scuffs of shipping and handling. For many years ink manufacturers have been developing new inks that would be sufficiently scuff resistant for the packaging industry. Thanks to continued research, improved scuff-resistant inks of most types are now available.

#### Fluorescent Inks

These inks were formerly limited to screen printing. However, with the development of more finely ground and stronger pigments, fluorescent inks can now be printed in one impression by letterpress, lithography, and gravure. Duotones and even full-color process are now feasible. The naturally bright inks reflect and emit light by absorbing ultraviolet waves and emitting these as visible light, thus increasing the amount of light reflected from the ink. This extra reflectance gives the ink their added brilliance, and the semi transparency of the inks permits overprinting to achieve intermediate color tones.

#### Varnish and Lacquer.

These are used as overprinting for protection as well as for gloss. If the printing is to be lacquered, the inkmaker should be informed so that he can formulate his inks to be lacquer resistant. Otherwise the inks are apt to bleed through the varnish or lacquer, the varnish maker must be informed as to the chemical resistances (soaps, acids, and so forth), scuff resistance, gloss requirements, and other general specifications required of the varnish so that the proper formulation can be selected.

Lacquers are applied off-line on special coating machines. A variety of press-applied varnishes are available. These are used on standard presses without heat, and the drying is by oxidation. Some of the new overcoating system used to eliminate antioffset spray can be formulated to produce high gloss. Special UV cure overprint varnishes can also be used over conventional inks if the press is equipped with UV lamps. e, proprietary systems containing little or no solvent which dry by application of heat and use of special cross-linking catalysts.

#### Drying and Curing

Drying of printing inks is important because a printed piece cannot be handled or used until the ink film has solidified and dried. Printing inks dry in a number of ways; absorption, selective absorption, evaporation, precipitation, oxidation, and polymerization. Most inks dry by combination of two or more of these mechanisms. Exact mechanism widely varies. Absorption is the fastest whereas other is slow.

The first stage in drying is setting, and often this is more important in printing than actual drying.

During drying of the ink on the paper, the ink is transformed from a fluid or semifluid state to a solid state. Drying usually takes place in two ways; by absorption of ink vehicle into the pores of the paper through capillary action; by a hardening of the ink film on the paper. The first is governed by the viscosity of the ink and the porosity of paper and takes place very rapidly. The second, or hardening, stage involves a polymerization and oxidation of the oil vehicle, both of which take place very slowly. During this stage, the drying oil absorbs oxygen from the air, thereby changing from a viscous liquid to a hard, solid film that binds the pigment particles tightly to the paper. During drying, oil-base ink vehicles pass

through a stage where unpleasant odors can be developed. These odors are transient, however, and unless sealed in, as by waxing, will dissipate into the atmosphere.

If the ink dries too fast, the ink becomes tacky on the rollers resulting in picking; if the ink dries too slowly, the print smears on the paper and the ink feels wet. To control the rate of drying with oil-base inks (and some nondrying oil-base inks), it is necessary for the printers to add driers to the ink. Driers are organic salts (e.g., the resonates, linoleates, octoates, and naphthenates of zinc, lead, cobalt, or manganese) that increase the rate of drying of the ink film on the paper by increasing the rate of absorption of oxygen. Cobalt makes the most general, cobalt is classed as a surface drier, lead as an internal drier, and manganese as a combination surface drier, lead as an internal drier, and manganese as a combination surface and internal drier. Driers sometimes lose their effect after the ink has been standing for some time. The loss is greater for inks pigmented with lake colors containing aluminum hydrate and for carbon black, and for this reason, a relatively high percentage of drier is used in inks containing these pigments. The loss in effectiveness of driers in the presence of these pigments can be explained by the fact that the active metal group of the drier becomes absorbed next to the pigment, leaving the inactive organic group projecting into the vehicle. Certain pigments can absorb large quantities of drier, although improved driers have been developed to overcome this difficulty. Too much drier is detrimental to the corking properties of the ink and in some cases may actually retard the drying. Generally speaking, more drier is required during the summer months when the humidity is high and drying is likely to be slower. Inks to be overprinted are sometimes

made slow drying on purpose to prevent them from hardening before the succeeding colors and printed over them. Antiskinning agents, which are in reality antioxidants, may be added to prevent the formation of a skin on the ink, and while these agents offset the effect of the drier to some extent, they are useful in preventing drying or hardening of the ink on the press.

New systems for drying or curing inks have been developed to eliminate pollution caused by the evolution of solvents and other effluents associated with ink drying. New inks that cure by ultraviolet and/or electro beam (EB) radiation are described in the section "Ink Types." New infrared units have been developed for drying low-solvent super quick-setting special inks. Also water-and alcohol-soluble coatings are being used to overcoat wet inks immediately after printing. The coatings dry rapidly, keeping the inks from scuffing, marking, or setting-off while they dry normally. Ultraviolet clear varnishes are also being used for this purpose in sheet-fed printing.

## Conclusions

The constituents of printing ink for various application on paper substrate along with their optical, colloidal, polymeric and rheological properties are found to be important for different

printing processes along with working properties of ink and the design variables of printers. This paper highlights interaction between ink including special inks and paper surface with their respective related problems arising due to ink application on paper during different processes which are very complicated are analysed.

## References

1. Casey, J. P., Pulp and Paper, Chemistry and Chemical Technology, Vol. 4, Wiley Inter Science Publications, John Wiley Sons.
2. Gullichsen, Johan and Hannu Paulapuro, Papermaking Science and Technology, Printing, Book 13, 1999, Finnish Paper Engineer's Association and TAPPI.
3. Bankhead, R., B., Hodgson, K. V., Hamilton, R. T., 1995 Papermakers Conference, TAPPI Proceedings, 373-382.
4. Personal communications with K. T. Hudgson, division of Paper Science and Engineering, College of Forest Resources, University of Washington, Seattle, USA
5. Kokurek M.J. Pulp and Paper Manufacture, Vol.8, Joint Textbook committee of the Paper Industry, 1989
6. Schoelkopf, P.A.C., Gane, C.J., Ridgway, D.C., Spielmann, and G.P. Mathews, Tappi Journal, Vol.2, No.7, July 2003, 19-22
7. William R.L. paper & Ink relationships, Mennonite Press, INC, Newton, Kansas, 1985
8. Wilbert Streefland, International Paper and Board Industry, March, 2006, 1-6
9. Bostrom Bernt, Paper Surface response during printing and surface treatment, Paper test methods-what's new, Fibro System AB, Sweden, 1992 (Nov. 26)
10. Printing Ink Hand Book, 4<sup>th</sup> Edition, Product & Technical Publications committee, National Association of Printing Ink Manufacturers, Inc, USA, 1980
11. Scott W.E. and J.C. Abbott- Properties of Paper An introduction, Tappi Press, 1990
12. Lectures delivered by A.K. Ray at the HRD programme at BILT, Yamunanagar on "Printing", Dec. 2006
13. Lectures delivered by A.K. Ray at the HRD programme at ITC, Bhadrachalam, on "Overview of printing processes", Dec. 2005
14. Lindqvist, Ulf, Jantunen Jaakko, et.al. Paperi ja Puu, No.4 1983, 305-312
15. Cichon Joe, Tappi J., May, 1989, 149-152
16. Sankaranarayanan N., IPPTA, Vol.8, No.2, June, 1996