



Lithographic Paste Ink Vehicle Composition

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What is a lithographic ink vehicle?

The fluid or liquid component of the printing ink

Acts as the carrier & transport system for the
colorants

Binds the colorants to the printed surface

Imparts the necessary drying and film formation
properties

What value does the ink vehicle add?

Dominates the appearance of the printed material

Imparts gloss

Color density and sharpness of the image

Protects the printed film during handling and transportation

Carrier & Transport system for the colorant (pigments, dyes, carbon black)

Wetting & dispersion

Surrounds the pigment particles during flushing,
grinding or ink manufacturing process

Disperses the pigment particles and prevents
flocculation or re-agglomeration

Carrier & Transport system for the colorant
(pigments, dyes, carbon black)

Ink-water balance for lithography

Allows the *miracle* of lithography to occur

Water to clear the non-image areas of the plate

Ink to transfer to the plate/blanket/substrate

Controls Binder & Drying Characteristics

Ink “setting”

Ink drying mechanism

Film properties of the dried ink film

Gloss

Rub

Chemistries

Oil-based (Oleoresinous) - blend of hard resins, petroleum solvents, vegetable oils and additives in free flowing or gel form

Energy Curable (UV, LED, H-UV, EB) - blend of hard resin cuts, acrylated monomers, oligomers and additives in free flowing or gel form

Oleoresinous Resins

Phenolic Modified Rosin Ester - made from a byproduct of paper making process

- Highly compatible with vegetable oils

- Produce high gloss and hard, durable films

- High cost, yellow, water loving and limited compatibility with ink oils

Maleic Modified Rosin Ester - made from a byproduct of paper making process

- Moderate compatibility with vegetable oils and ink oils

- Produce high gloss and hard, durable films with less yellowing

- Higher cost and water loving

Hydrocarbon - DCPD or C9

- High compatibility with ink oils

- Lower cost, improve set speed and hydrophobic

- Low vegetable oil compatibility and regulatory concerns

Hard Resins

Resins are the most viscous and highest molecular weight components of the paste ink vehicle. Therefore they dominate all of the physical properties. Tack, viscosity, solubility, gel character and overall rheology of the vehicle. It also dictates important film characteristics such as gloss, setting & drying rate and rub resistance.

Rosin Based Resins

A group of solid hard resins which are derived from various reactions with rosin.

Rosin:

- Is a natural resinous material extracted from certain pine trees through many processes ranging from mechanical to manual.
- Types of rosin include: Gum, Wood and Tall Oil rosin.
- Each type differs substantially in chemical composition, but all are isomers of Abietic acid.

Rosin Sources

1) Gum Rosin

- China
- South East Asia
- Portugal
- South America (Brazil, Argentina)

2) Wood Rosin

- U.S.A.

3) Tall Oil Rosin

- U.S.A.
- Europe

Maleic Modified Rosin Esters “Maleics”



Adducts of rosin and maleic anhydride or fumaric acid esterified with polyol

- ▶ Typically lower molecular weight vs. phenolics
- ▶ Finds most use as co-resins in letdown vehicles
- ▶ Backbone polymer of overprint varnishes due to lighter color
- ▶ Exhibits good pigment wetting in dispersion vehicles

Phenolic Modified Rosin Esters “Phenolics”



Combines various addition and condensation reactions involving rosin, maleic anhydride/fumaric acid, phenol and formaldehyde esterified with polyol

- ▶ Typically higher molecular weight vs. maleics and hydrocarbons
- ▶ Finds most use as backbone polymer in letdown vehicles
- ▶ Imparts superior chemical and solvent resistance, rub and abrasion resistance, gloss and hold out vs. other resins used for paste ink vehicles

Hydrocarbon Resins

Resins derived from various hydrocarbon feed streams.

- ▶ are by-products of the petrochemical refining process
- ▶ vary in chemical composition and concentration of reactives
- ▶ A consistent feed stream is critical to the manufacturer of these resins.

Hydrocarbon Resins

Aromatic (C-9) based resins:

- ▶ Uses a feed stream high in aromatic fractions (typically styrene derivatives) polymerized by a catalytic process
- ▶ Characterized by very high solubility in hydrocarbon solvents
- ▶ Relatively low viscosity vs. maleics and phenolics
- ▶ Good drying oil compatibility
- ▶ Used in all types of paste ink vehicles, but are most commonly used in news inks and dispersion vehicles

Aliphatic (C-5) based resins:

- ▶ Uses a feed stream with high contents of DCPD (dicyclopentadiene), isoprene, piperylene, and other C-5 fractions
- ▶ Typically produced in an autoclave under high pressure and temperature.
- ▶ Somewhat limited use in paste ink vehicles

Functional Hydrocarbon Resins “Gel Reactive/Hybrid”

Usually made by co-polymerization of C-5 based feed streams with maleic anhydride and tall oil rosin.

- ▶ Complex resins with acid functionality
- ▶ Available in a wide range of molecular weights and solubilities
- ▶ Relatively low viscosity vs. maleics and phenolics
- ▶ Gaining popularity for use as co-resins in paste ink vehicles as molecular weights and viscosities have increased over the years
- ▶ More economical vs. phenolics and maleics

Oleoresinous Diluents



Vegetable oils

Soy bean, linseed and chinawood
dry via oxidation
100% solids and film forming

Petroleum solvents

470, 520, 600
dry via evaporation or absorption
aromatic or aliphatic
VOC; volatile organic compound

Drying Oils

Mixtures of fatty acid triglycerides

Predominant fatty acid components must have at least 2-unsaturated double bonds to readily oxidize. If the double bonds are **conjugated** (located on adjacent carbons), the oxidation reaction will occur more rapidly

Excellent solvents for various hard resins which are not readily soluble in petroleum distillates.

Are a major component of most alkyd resins

Additional Drying Mechanisms

Catalytic polymerization - free-radical cross-linking of the film via energy curable raw materials upon exposure to UV/EB energy source (UV/EB inks, heat catalyzed metal deco)

Resin precipitation - rapid “kick-out” of resin upon exposure to moisture
(moisture set or water washable inks)

Typical Drying Oils

Linseed Oil - drying index of 120(iodine number). The most popular drying oil used in inks and ink vehicles. It is available in many forms depending on end-use application. Main drying component is Linoleic acid. In some inks the polymerized or maleinized oils described below can be used as sole vehicle or litho oil

Alkali Refined Linseed Oil (ARLO) - refined to remove impurities and suspended solids. Gives the oil greater clarity, lighter color and lowers acid value

Blown Oils - made through the oxidation of oil due to the introduction of heat and air. This increases viscosity and pigment wetting

Thermally Polymerized Oils - heated to 575°F - 600°F in an inert atmosphere or vacuum. Allows manipulation of viscosity to any desired level (00 litho body to gum/gel)

Maleinized Oil - oil is reacted with maleic anhydride to make a faster drying product

Typical Drying Oils

Chinawood Oil - drying index of 170. The fastest drying of all the vegetable oils used in ink vehicles. Imparts a very hard film and good lithographic performance to finished inks. The main fatty acid component is eleostearic acid (80%), which has 3-conjugated double bonds

Soybean (Soya) Oil - drying index of 69. Slower drying than linseed. Main fatty acid component is Linoleic acid, Soya is lighter in color and more non-yellowing than linseed or chinawood oil

Oiticia Oil - drying index of 156. Produced primarily in South America. Main fatty acid component is Licanic acid, which also has 3-conjugated double bonds. Dries almost as fast as chinawood, and can be a substitute. However, overprint varnishes formulated with Oiticia tend to have a “greenish” hue

Safflower Oil - drying index of 77. Main component is Linoleic acid (75%). Dries slightly faster than Soya and is lighter in color

Hydrocarbon Solvents & Oils

Derived from highly paraffinic grade crude oil. The predominant hydrocarbon types are the normal paraffins, isoparaffins, and cycloparaffins with small amounts of aromatic compounds also present.

Non-hydrotreated ink oils -(470° -500° F boiling range) contain less n-paraffins/isoparaffins and more aromatic compounds

Hydrotreated ink oils -are aromatic free middle distillates which typically contain 60-65% n-paraffins/isoparaffins, 35-40% cycloparaffins (naphthenics) and less than 1% aromatics compounds

Control of narrow boiling ranges

Start with a constant source of crude oil, which is then processed and fractionated by boiling range into various streams such as naphtha, gasoline, kerosene, fuel oil, lubricating oil, asphalt, and finally wax. Then take the wide kerosene cut and further fractionate it into even narrower boiling ranges.

<u>Boiling Ranges</u>	<u>Typical Application</u>
400 - 460°F	Fast drying/setting vehicle
440 - 490°F	Heatset vehicles & OPV's
465 - 525°F	Primarily used in heatset
570 - 680°F	Primarily used in sheetfed

Oleoresinous Additives



Alkyds

good pigment wetting and set speed

Esters

improve solubility and alternate to ink oils for providing set

Plasticizers

improve solubility without being a VOC

Antioxidants

prevent premature drying

Vegetable Oils Esters

- ▶ There are 2 types of vegetable oil esters used in paste inks
 - ▶ Methyl esters
 - ▶ Can cause blanket swell
 - ▶ Can show some VOC content
 - ▶ Butyl esters
 - ▶ Not as fast for set speed
 - ▶ Has less of the negative attributes
- ▶ There are many different types of source oils used
 - ▶ Tall oil fatty acid
 - ▶ Soybean oil
 - ▶ Fish oil
 - ▶ Mixed food oil – recycled deep fry oil from fast food restaurants

Vegetable Oil Alkyds

Often referred to “liquid resins”

Oil modified polyesters

Dibasic acid + Polyhydric alcohol

Isophthalic acid + Pentaerythritol

Higher in molecular weight compared to solvents
and vegetable oils, but still fluid

Function of Alkyds

Excellent film formers

Impart chemical and heat resistance after oxidation

Drying oil content and polar ester groups wet and disperse pigment

Readily solubilize high molecular weight hard resins

Tool to manipulate the body, flow & transfer properties of paste ink vehicles

Aluminum Gellants

Organo-aluminum compounds which are used to prepare gelled paste ink vehicles for lithographic inks. The role of these compounds in the gelled vehicle is typically that of rheology control; but the addition of gelling agents may also have a significant affect on the viscosity, gloss, hold-out, setting & drying, wetting, and overall lithographic performance of the paste ink vehicle.

Aluminum Octoates & Aluminum Stearates

- ▶ “Soaps” that react to form networks of fibers which entrap resin molecules within this interlacing fiber structure
- ▶ Results in a “mechanical gel”

Alkoxides (and their chelates), Oxyaluminum Acylates

- ▶ React chemically with residual carboxylic acid and hydroxyl groups on the resin molecules to form covalent and hydrogen bonds
- ▶ The $\text{Al-OH}/\text{RCOOH}$ is critical to the degree of gellation
- ▶ Results in a “chemical” gel with stable rheology

Additives

Several additives are used to modify rheology, setting & drying rate, improve adhesion properties, thicken and gel paste ink vehicles. These additives can be specialty solvents, clays, silicas, organo-aluminum compounds and antioxidants.

Solvents

- ▶ Very strong solvents used to maintain or improve resin solubility, control flow and transfer properties (fatty alcohols/TDA & ester solvents/TXIB)
- ▶ Glycol esters and acetates tend to improve paste ink vehicles adhesion to synthetic substrates

Thickeners

- ▶ Used to increase thixotrophy (clays/Bentone, fumed silicas/Cabosil & Rheosil & vegetable oil soluble polyamides)

Anti-Oxidants

- ▶ Inhibits the oxidation polymerization reaction and formation of oxidized “skins” during manufacturing and storage of paste ink vehicles and inks
 - ▶ Volatile type/Oximes (Exkin, Skinno, Cyclohexanone)
 - ▶ Non-volatile type/Phenolic compounds (BHT, Eugenol, Hydroquinone)
 - ▶ Used to formulate “stay-open” inks (dry quickly in thin film, but stay “open” in thick film)

Terms

Setting refers to the time it takes the ink to achieve a **tack free** state

Drying refers to the time it takes to achieve a fully **cross-linked** film

Solubility refers to the balance of compatibility between materials to create a **homogenous mixture**

Drying Mechanisms

Penetration - solvent is absorbed into the substrate via capillary action (news, no-heat web, forms - all very porous substrates)

Evaporation - volatile solvents are driven off via some type of heat source (heatset web)

Oxidation polymerization - drying oils containing unsaturated double bonds cross link upon exposure to oxygen (inks for plastic stock, foil-metal deco, commercial sheetfed)

Quickset mechanism - utilizes penetration and oxidation mechanism as the lower viscosity solvent penetrates into the substrate and then oxidation of drying oil follows (most “sheetfed/quickset” inks)

Energy Curable Monomers



Acrylated diluents for viscosity reduction
of higher viscosity oligomers

Have varying degrees of acrylation which
affect solvency, cure rates and flexibility

Common products; DPGDA, TRPGDA, HDDA,
TMPTA and EOTMPTA

Energy Curable Oligomers



Epoxy Acrylate

General standard base material with good reactivity and high gloss

Low cost

Urethane

Slower reacting material with great flexibility

Good adhesion to flexible materials with good weatherability

Polyester

Fast reacting while maintaining broad flexibility

Good pigment wetting and durability

Yellows

Other Materials

Special resin cuts

Inhibitors

Adhesion promoters

Mist and water control additives

Regulatory Concerns



**Migratory concerns of finished product or materials of concern
for handling in the manufacturing process**

Proposition 65, FDA, Swiss and Nestle Compliant

Oil

Mineral oil

Bisphenol-A (BPA)

Energy Curable

TMPTA

Bisphenol-A (BPA)

Choosing The Right Resin



Resin Type	Phenolic Modified	Maleic Modified	C5, C9 Hydrocarbon
Film Integrity	+++++	+++	++
Heat & Shear Stable	+++++	+++	++
Printability	+++++	+++	++
Gel Reactivity	+++++	+++	+
Viscosity	+++++	++	+
Pigment Wetting	++	+++	+++++
Oxidative Dry	++++	++	+
Non-Yellowing	++	+++++	+
Cost	\$\$\$	\$\$	\$

Typical Vehicle Formulation

Raw Material	Sheetfed	Web Heatset	Coldset /News
Phenolic Modified Resin (Blend of High & Low Molecular Weight)	20 - 30%	0 - 10%	0 - 10%
Maleic Modified Resin (Blend of High & Low Molecular Weight)	0 - 15%	0 - 10%	0 - 10%
Hydrocarbon Resins (Blend of High & Low Molecular Weight)	0 - 10%	15 - 40%	15 - 35%
Drying Oils (Including Alkyds)	5 - 50%	0 - 10%	35 - 55%
Hydrocarbon Solvents (Ink Oil Blend)	0 - 20%	35 - 55%	0 - 10%
Additives (Gellant, Solvents, Anti-Oxidants, etc.)	0 - 4%	0 - 4%	0 - 4%

Thank You !!!