

# Offset Printing Inks

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## Preliminary note

In our technical literature, even at university level, printing inks are underrepresented. On one hand the ink producers give their information quite restrictively to the public. On the other hand detailed textbooks would revert only to a very small community of interested students - and thus very expensive. The world wide only schoolbook with profound and detailed information is the Printing Ink Manual, written by R. H. Leach and R. J. Pierce. The fifth edition of 1993 still is the actual one and costs about 200 €. There is obviously too much work necessary to update it, and too few people and companies would buy it. So with the authors' coming close to retirement, nobody else under the few thinkable experts intends to invest so much work.

The fifth edition is a must for every printing ink chemist and is worthwhile each cent of its price. Even with its age in a rapidly developing matter. It contains the chemical basics for a profound understanding of inks.

Ink formulations are developed and matured in a continuous process. Firstly nearly every day reports comes up about new physiological or environmental risks hitherto harmless substances. This requires immediate work for a possible substitution.

Secondly the fast-paced development in printing techniques and further processing requires continuous adoption, change, and new inspiration in inks. So outside people see that every step of formulation development and understanding of mechanisms is important know how for each ink producer. He must use new experience immediately and upgrade it as soon as possible. His colleagues and competitors are fighting the same problems. So they very scarcely give out patents, because that always comprises the publication of intimate know how.

And in offset inks the binders have mixed compositions of chemically rather similar substances, so that analyses of inks do not give all the detailed information of the composition. And in such a situation it would be hard to prove, that a patent was hurt.

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# 1. Composition and production of offset printing inks

Requirements for offset inks can be divided into two groups. Some are common for all printing techniques like color etc.; some are specifically directed for the use in offset printing like water balance.

General requirements are

- Color, shade, power, printing contrast,
- Gloss, translucency,
- Drying,
- Rub and other resistances, stability against solvent and other chemical attacks,
- Light fastness, and
- Environmental, physiological, and occupational safety requirements.

Used in offset printing an ink must

- Wet the printing areas of the offset plate,
- Take up some dampening solution without catastrophically changing the rheology,
- Accept and expel water as an emulsion dynamically,
- Push a front of surface water while marching through the press,
- Have no problem in emulsification behavior with changing printing materials, press temperatures, speed changes, press types, and properties of the printing job in ink distribution, ink uptake, and all the other manifold parameters.

Three of the four classical printing techniques offset, gravure, and letterpress apply approximately 1  $\mu\text{m}$  of ink film thickness on the material. Material layers can be drafted like in fig. 1. The ink must make an intensive, colorful effect with its tiny film thickness to let us perceive a distinct color impression. To achieve this effect the pigment particles must be very finely distributed in the print layer, much finer than the 1  $\mu\text{m}$  layer thickness. Desired interactions with the printed paper will touch at least the coating film and scarcely reach the fibers. The discussion many years ago about defects in ink drying caused by chlorine free paper fibers was unprofessional nonsense.

A cross section of a printed paper may be as fig. 1 shows. We see the proportions of the different layers.



Fig. 1 Proportions of thicknesses in a coated paper

In the moment of printing offset inks have nearly the composition like after the drying process. Only about 20 % diluents will penetrate into the paper coating and thus leave the ink film. This is a characteristic difference to solvent based inks, because they come with 2/3 of volatile solvents, which evaporate, leaving a dry and hard print film.

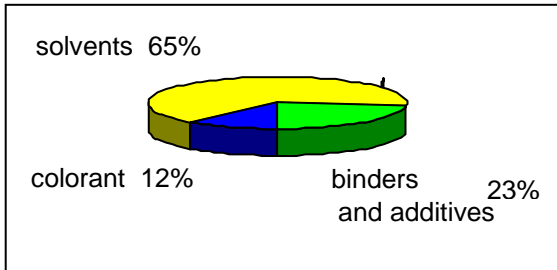
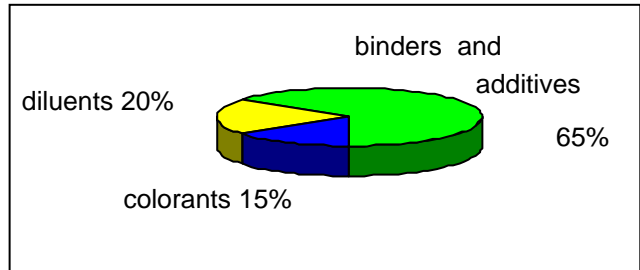


Fig. 2, Solvent based inks



Offset inks

This difference is important in ink transfer in the press. Bulky pigments like platelets or coarse pigments can be transported much more easily with the high volume of solvent inks. Because of the high solvent content it is three times the volume of the final ink film.

Raw materials in an offset ink can be divided into groups:

- 1. pigment 
- 2. varnish
  - resin 
  - alkyd resin 
  - thinner / solvent 
- 3. additives
  - dryers 
  - inhibitors 
  - waxes 
  - others ...

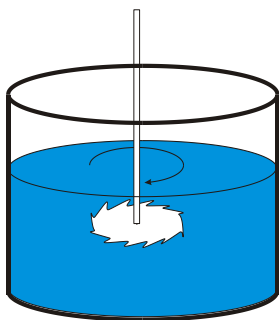
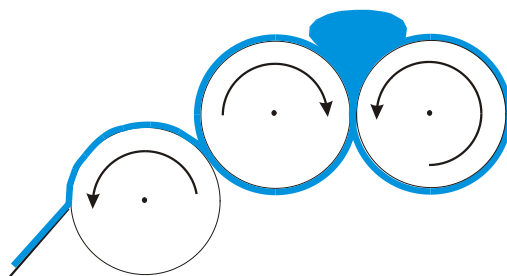
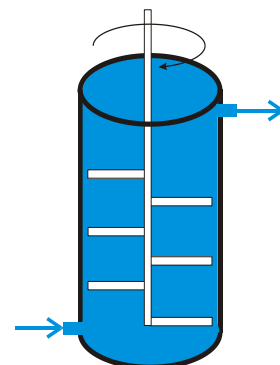


Fig. 3, Dissolver



Three roller mill



Pearl mill,

In a factory for offset inks like in a paint factory no chemical substances are produced. The raw materials are bought from the chemical industry and dispersed (mixed) here thoroughly. The factory technique is mixing, dispersing and filling into tins or containers. Typical equipment is dissolver, three roller mill, and pearl mill.

Dissolvers usually mix the ingredients to a homogenous liquid or paste. This will be dispersed in a roller mill or in a pearl mill to break all coarse agglomerates. All pigment particles are now finely divided and wetted by binders and diluents. The thorough dispersion only brings color strength, translucency and gloss.

We have inks (pigmented), print pastes (uncolored fillers instead of pigments), and varnishes (unpigmented ink, a liquid). As pastes we count transparent white (highly translucent with special fillers like silica) and mixing white (slightly less translucent with more economic fillers like calcium carbonate or dolomite).

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## 2. Colorants

There are two types of colorants. One is soluble in the thinner or solvent of the binder, the other not. Soluble colorants are called dyes and are very rare in printing inks. They are distributed as solvated single molecules in the liquid and combine high color strength, translucency, and purity of color shades with weak stabilities (light fastness etc.). In printing inks we use nearly only pigments - microcrystalline, colored particles. printing layers of 0.3 to 2  $\mu\text{m}$  the classical printing techniques need very, very finely divided pigment particles, grain sizes significantly smaller than layer thicknesses. Substances which are in all aspects like pigments, but do not show colors are called fillers. This in some way deprecatory expression is misleading because such fillers have to fulfill quite complex requirements, e. g. in translucency and rheology.

Up to the 1950s mineral pigments were used in printing inks like lead chromate and cadmium sulfide. But that was abandoned, because they bring high physiological risks (toxicity) directly or by impurities out of the production processes used. With some exclusion we only find organic substances as ink pigments, usually products of the petroleum industry. They are produced in crystalline form, conditioned for the ink type to be used.

Colored pigments are all organic. The black pigment, carbon black, is inorganic, even if it lies rather close to organic chemistry. The uncolored pigments and fillers are inorganic: Titanium dioxide, barium sulfate (covering white), the carbonates of calcium and magnesium, and aluminum hydroxide (transparent and mixing white). Effect pigments usually are also inorganic like metals and alloys of aluminum, copper and brass for metallic inks, coated mica for mother of pearl effects.

The pigments are dispersed finely divided into the binder liquids. By their grain fineness and wettability (more or less polar) they control optical and rheological properties in ink and print.

Among the most important properties of a pigment there are the stabilities (fastnesses), in printing light fastness more than all others. The basic claim for a pigment is to be completely insoluble. This is not always achieved in an ideal way. The stabilities against solvents are called chemical fastnesses, e. g. in alcohol.

If a chemical substance is of interest because of its colorant qualities, in most cases it is soluble in the usual solvents and thinners. Most of these substances are dyes. They have to be chemically fixed to other substances to become solvent resistant. The treatment has not to damage the color effect. Not for all colors we are successful in this aspect. For instance between red and blue there are very intensive and pure pigments like reflex blue or Fanal pigments (brand name of BASF) with weaknesses towards solvents. So often we have problems with varnishing prints containing such pigments. On the other hand sometimes there are only expensive or even no substitutes available with such excellent features.

All powder like raw materials are described by typical properties, which are also important for pigments. The pigment industry continuously improves and develops things like wettability by special media, dispersibility in inks without leftovers of coarse and hard particles. Important are also grain sizes and distributions, and low abrasivity in gravure printing presses (between doctor blade and cylinder). Even the shape of the crystals influences color performance and rheology. For instance some blue shaded pigments form rod shaped crystals. They show a greener shade through their long axis than perpendicular. That means block crystals have a redder shade than needle variations.

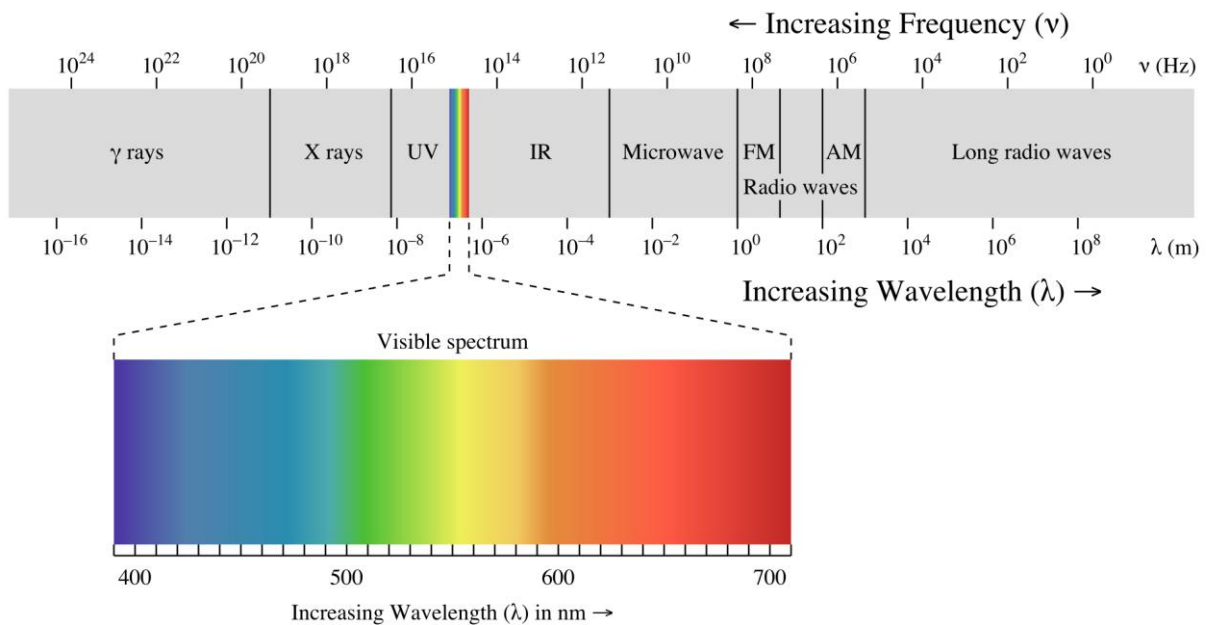


Fig. 4, The electromagnetic spectrum, taken from Wikipedia

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### 2.1. Why does a pigment absorb visible light?

Let's have a look at the ranges in the electromagnetic spectrum, and see which actions are connected to which wavelength. Tab. 1 shows, which event is linked to which wavelength in the world of atomic bonds and orbitals.

	Microwave	Infrared	Visible and UV	X-Ray
$\lambda$ - range	100 $\mu\text{m}$		1 $\mu\text{m}$	10 nm
Effect	Rotation and translation of polar molecules	Vibrations between atoms in molecules	Electron bonds in atoms are excited	Excitation of electrons in inner orbital of atoms
Observation	Increased evaporation of polar molecules	Increased evaporation, start of chemical reactions	Disruption of chemical bonds with consequential chemical reactions	Tissue damage due to ionizing radiation

Tab 1. Effects of wavelength ranges on molecules, taken from The Printing Ink Manual

In the IR we see vibrations of atoms in solid matter and in single molecules, too. Thus we have to accept that pigments will not be transparent in the IR, at most in some parts of the IR. This may be interesting technically, for instance in security printing.

Furthermore there are binding electrons which are excitable with UV and visible light. The electrons are shifted from a basic to a higher energy level. And there they become reactive in chemical sense.

Most of our organic compounds absorb UV light. So called  $\pi$  - electrons (in double and triple bonds) stay already close to wavelengths on the edge to visible light. If several conjugated (1-2-1-2 - sequence) double bonds can communicate (chemically called mesomerism) with each other, the excitation energy becomes lower and broader - until it enters into the visible sector.

The following fig. 5 shows, how the absorption peaks of hydrocarbons come closer and closer to the visible range, as they get more and more conjugated double bonds.

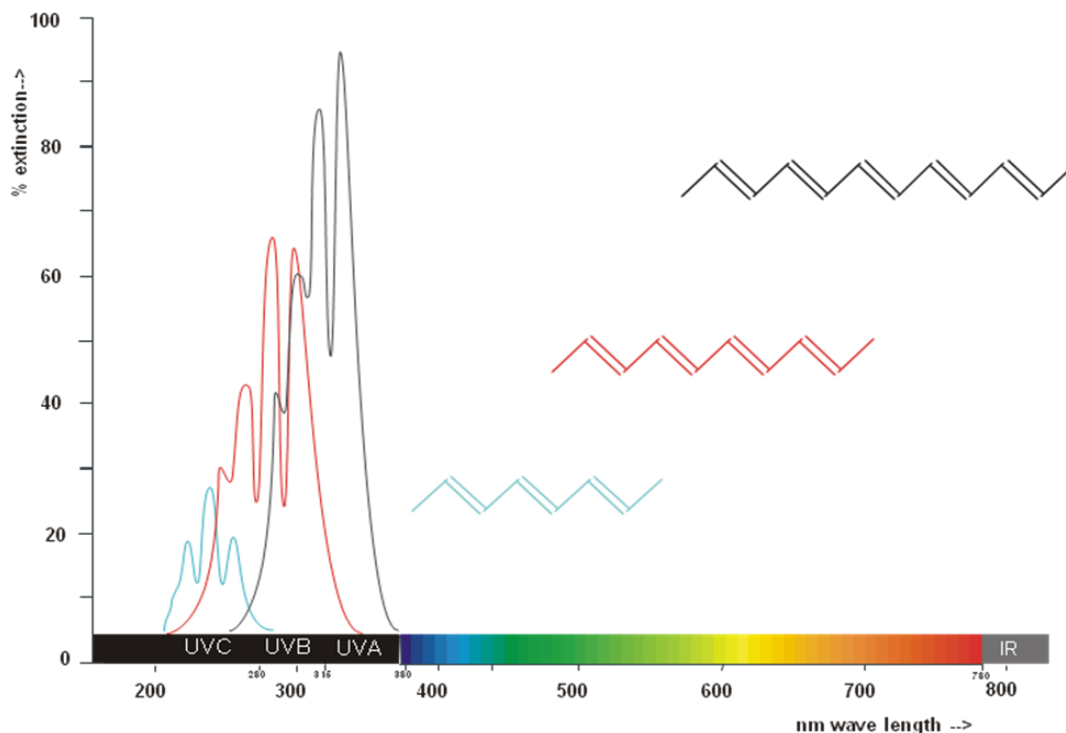
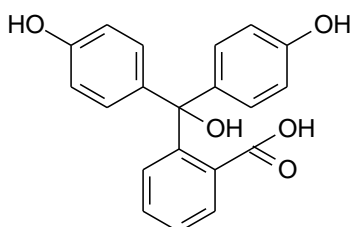


Fig. 5, Some special hydrocarbons and their absorption spectra

Three conjugated double bonds like in benzene obviously are not sufficient enough. Otherwise benzene would be colored. Linking several benzene rings or other  $\pi$  - electron systems with simple bonds for each link (conjugated) lowers the absorption energy - until the substance shows a color.

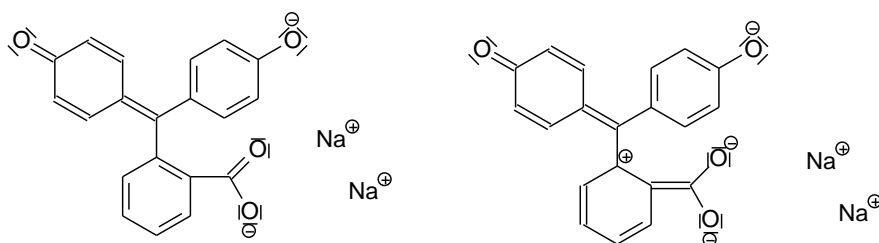


Phenolphthalein, acid-alcohol form

Fig. 6, Molecular structure of the colorless indicator in acid or neutral water

A clear example is the well known pH-indicator phenolphthalein. In acid environment it has its acid like composition. In such a state it has many  $\pi$  - electron systems. But they are separated always by more than one single bond. They are not conjugated and cannot exhibit mesomerism. The solution is clear and colorless.

If we titrate the solution with sodium hydroxide solution, we reduce the concentration of  $H^+$  ions. A nice piece beyond the neutral point, only with pH 10, the indicator changes to intensive red color. Its structure now has the anionic form. How you can see in fig. 7 there are many possible variations of the distribution of the binding electrons. And in chemistry we know that mesomerism makes a mixed form of all these possible extremes.



Phenolphthalein in alkaline environment

Fig. 7, Two out of many extreme structures of the colored indicator

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## 2.2. How do pigment molecules look like?

If we take the phenolphthalein and change some of the substituents, the form in alkaline solution is deeply blue, the substance called thymolphthalein. In similar way we can vary the color effect in many directions. There is an entire group of compounds with chemical relatedness. The group is called "tri-phenyl-methane"-derivates. The well known reflex blue, upgrading pigment for blacks makes part of it as well as the so called Fanal pigments in the color range between violet and blue.



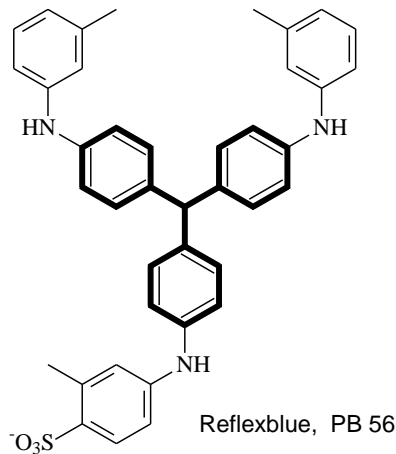


Abb. 8, Reflex blue makes part of the tri-phenyl-methane pigment group.

Yellow and orange pigments make part of the diarylide pigments. Fig. 9 gives an example. Process yellows are of this type.

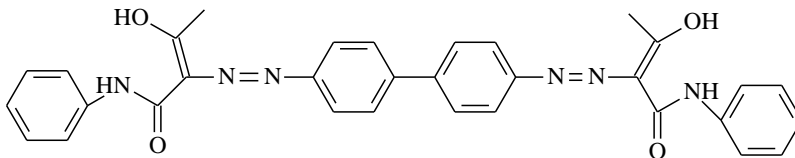


Fig. 9, Basic structure of many yellow and orange pigments

Somewhat more complex, but of immense importance is the group of the phthalocyanines. They have ring shaped structures, which can catch metallic ions as complexes. Slightly simplified these molecules make blues and greens with copper as a central ion. Similar molecules with magnesium make the chlorophyll of our plants and others with iron make the hemoglobin in our blood. We see what variety is possible in one molecule group.

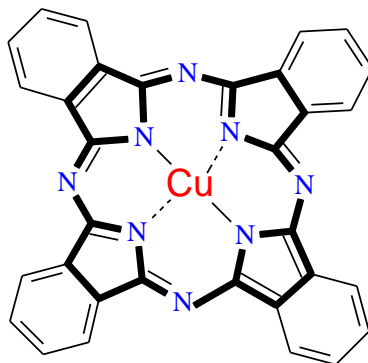


Fig.10, Basic structure of the phthalocyanines, also called phthalo blues

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### 2.3. Pigments in printing inks

The phthalocyanines are among the most useful pigments, because they are completely insoluble in even very effective solvents, light fast and - economic.

The first of these aspects is problematic for many colored substances. Usually they are useful dyes, but many are solved by many and one solvent. They first have to be treated chemically to become insoluble. And only then they are pigments. Chemists usually try to link the molecule to bigger, more inert molecules. This however is only allowed, if it does not damage the color pureness and power. We understand that in the practical technique we find many compromises.

There are many chemical formulas and names. Most of the fabricators are specialists in other areas, not in organic chemistry. Commercial providers often use brand names, which are of no help here. A "Society of Dyers and Colorists" has established a kind of register. This has found worldwide acceptance, because it is an helpful means of communication for all involved. It contains so called color indices for all dyes and pigments. The register gives for every code the pigment name, chemical type, field of application, in a second volume chemical formulas and brand names. The broad usability for everybody made it successful. So a color index is a valid identification for pigments. Process pigments are Pigment black 7, Pigment blue 15, Pigment Red 57, and Pigment yellow 13.

Pigments usually control the price of an ink. In relation to their percentages of 10 - 20 % they are the most expensive components. Exchanging a standard pigment by a more lightfast one will usually increase the inks' material price.

Furthermore pigments have complicated molecular structures. They can perform unexpected catalytical activity and bring surprises. So phthalo blues can work as siccatives. This may cause smell in a food package, even though oxidative drying was excluded in the formulation at first glance. Copper as a metal pigment can cause brittleness in latex products. Nobody should use it for packages of condoms...

Pigments often come out of a chemically complicated multi stage production process. So they are the main suspicious components in an ink for e. g. heavy metal impurities. There have been big efforts to keep down the levels of such toxic heavy metal impurities. From the USA nearly all states have adopted the condition that the sum of the compounds containing lead, cadmium, mercury, and chromium (VI) must not exceed 100 ppm. Such low levels are no problem for analytical techniques. But for the producing industry they can be difficult, because this is partially in the area of the natural concentration of elements in all materials in the world.

Up to now we looked only on the absorption characteristics of pigments. There are other interesting aspects like light scattering (dispersion), reflection and capability to make light rays interfere with others.

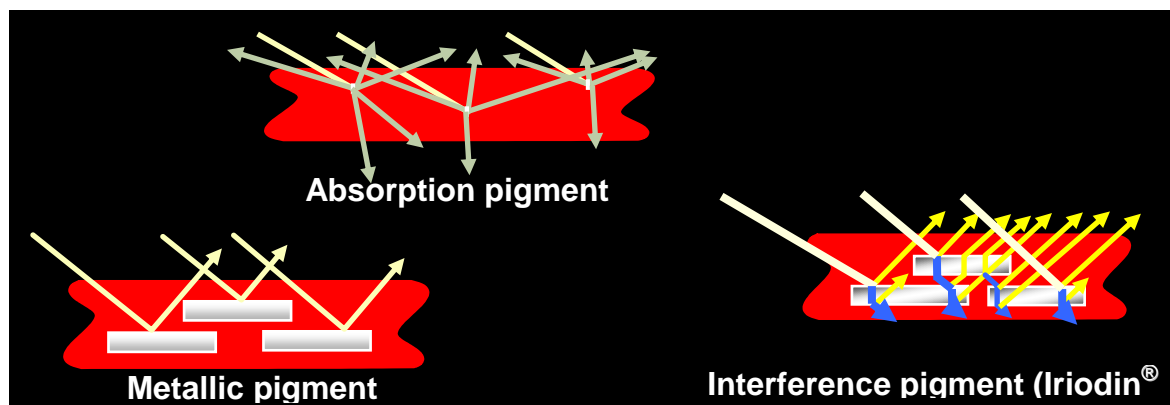


Fig. 11, Pigments with different effects, taken from: Merck Darmstadt

Metallic pigments are produced from grains of aluminum or brass which are ground in special mills to platelets. They have to be treated with care, because under wrong mechanical impact they curl up and lose their reflecting effect. The bigger the plates the better is the metallic reflex. That makes gravure a better transfer technique for such plate shaped pigments than offset.

Interesting are the interference pigments. They are made of mica platelets with very thin layers of titanium dioxide vapor coating. Coming light will be split into two (complementary) rays, according to the impact angle and wavelength. One part is reflected, the other goes through the plate. A surface coated with such pigments shows in one angle one color, in the correspondent angle the complementary color. This effect is known as "color flop" from car bodies.

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#### 2.4. Opacity and translucency

Ink technicians distinguish between transparency and translucency. A 100 % transparent object is like a polished glass pane. As soon as it is colored, but not clouded, it is not 100 % transparent, because some light is absorbed. But it is 100 % translucent, because it has no opacity (covering, scattering power). If we look at a colored and perfectly translucent object, we see - colored - the underground. With a little opacity we find a light shimmer over the look through.

If a pigment is not 100 % translucent, not all light rays pass through it - losing only wavelengths by absorption (becoming colored). The more particles scatter the penetrating light into all directions, the more white light goes back to the observer.

Supposed we have a tin with black interior. We fill it with a usual yellow paint (strongly opaque). Looking from above our eyes see the yellow color, because all the light is scattered, and some blue portion is absorbed. Now we take an ideal ink with 100% translucency. All light except the blue wavelengths falls through the ink and hits the black wall. Here all of it should be absorbed. The ink has to be black seen from above. In practice we will never see this effect clearly, because even highly translucent pigments have a small scattering power, and the thick layer in a tin makes it glaring.

There is a funny misunderstanding in pressroom practice. The printed color shade of two yellows in two different tins may be the same, but in the tin one seems yellow, the other olive-green. The explanation is simple: The greener yellow is more translucent, and the violet color of cobalt driers has more power in the thick layer to show up.

Light scattering may happen with the pigment particles in the print layer. It can be caused by roughness of the print's surface. In densitometry we learn that a dry print brings a lower reading than a fresh one, because its rough surface scatters some measuring light and pretends less color strength. Polarization filters bypass this problem.

The light scattered on the print surface sometimes is colored. That does not mean that the scattering by the rough surface is not any more white. Here we see another effect. If a print with a very finely divided pigment dries, for instance reflex blue, the ink film shrinks. Some pigment particles close to the surface get closer and closer to each other. This can cause a special reflection of wavelengths, which should be absorbed by the pigment. The detailed explanation is quite complex, but logical. So reflex blue gets a dark red luster. The name of this effect is „bronzing“, and only very recent results of research at Wuppertal university help to understand it. Putting a transparent layer on top destroys the bronzing, and the usual color of the print comes up. After varnishing our dark blue print is greener again. Unjustified claims of defect color shades caused by bronzing happen here and there, because not all print experts and buyers understand this.

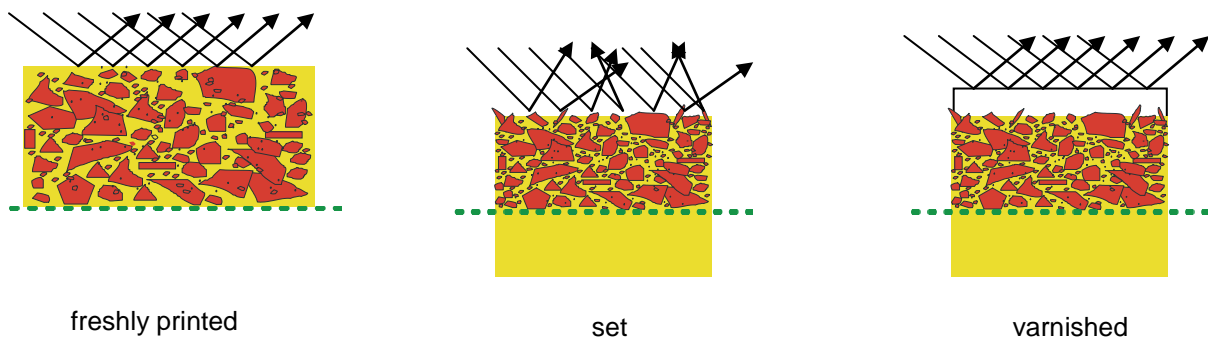


Fig. 12, Print in different moments

Every varnishing deepens the color impression of a print, because it eliminates scattered light. Matt black will for the same reason never be a nice, deep black, always a kind of grey. Spot varnishing with matte and glossy varnishes can produce very nice effects.

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## 2.5. Color and light

If an object is hit by white light, and if it absorbs certain wave lengths, we receive the unused light back, the color that is complementary to the absorbed color. Taken this we must expect that an object may show different colors under different lights. Consciously we recognize that only in drastic examples, e. g. with our pale skin under a yellow street lamp.

How different lights can be show their spectra. Daylight of 5000 °Kelvin (see fig. 13, light standard d 50) has all wavelengths in a hill-like distribution over the visible spectrum. A light bulb however has much in the low energy area of reds and few of violets (see fig. 13, light standard A). Nevertheless we see these lights more or less white. Gas and halogen lamps have completely different spectra. They are not even more continuums, but consist of single peaks.

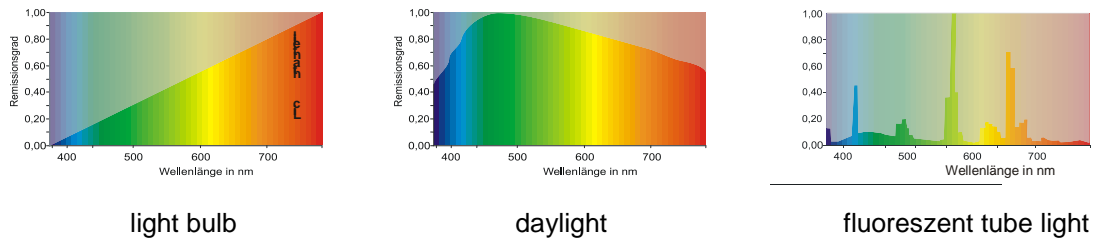


Fig. 13, Three examples of technical light types

Formulating spot colored inks the light type is of utmost importance. I two packages of Kellogg's Corn Flakes look alike under day light, because the same rest of light is sent back to the observer, this is acceptable. But if one package was printed with a mix of different pigments, there is a risk that under supermarket illumination (usually fluorescent bulbs) they have different color shades. For trademarked articles this disturbs the brand image. Let us imagine many Milka chocolate bars, and each shows another violet.

The ink formulator has to get precise information also about the light used. Professionals do so. In physics this limited consistency is called "metamerism". Two objects are metameric to each other, if they seem alike under one light source and different under another. It is understandable that weakly colored prints like gray or beige are sensitive, because few changes can bring easily additional tints. Up to the 80s colorists usually worked visually when mixing spot inks. Only when all was ready they could see under the light cabin, that the chosen pigmentation has brought metamerism. And they had to start from the beginning.

Modern computerized mixing equipment uses spectral photometers. It can compare the spectrum of the original with all spectra of possible mixing components. And it can predict the first results of different starting pigments and estimate the color difference to be expected under 2 given light types. This saves a lot f time.

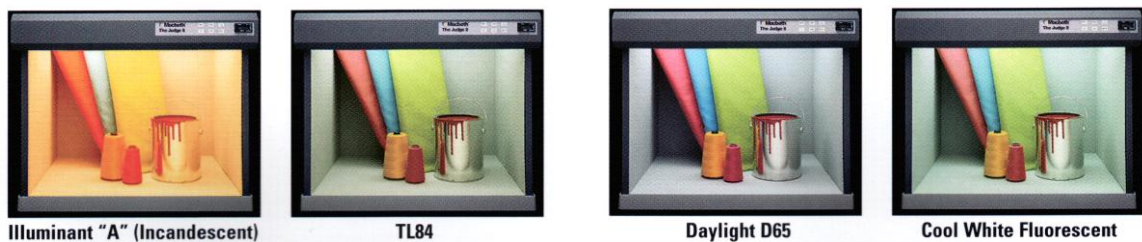


Fig. 14, Diverse light types in a light cabin

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**2.6. Color strength and printability**

We compare two inks with different pigment level, the rest is equal. One will seem more intensively colored, if both are applied in the same film thickness. However the price will be higher in the same ratio, because the pigment drives the price. Printers using the concentrated ink with standard density will consume less ink to the same extent. This raises the question "Why?".

The ink supplier had done better using the same pigment concentration and improving his dispersing and wetting technique instead of adding more pigment. Then he had worked out a better ration of

price to performance. Indeed all involved industries work hard to improve the dispersing conditions of the pigments.

Many people use a kind of yield as a measure for pigment power. A series of differently thick lab prints from one ink and the same set from the other are measured by a densitometer. Put into a simple diagram it shows easily, which ink is stronger, if there is a significant difference. However it does not say that one ink behaves in offset like a more powerful one. For more intensive pictures we need not only more power in solids, but contrasty screens. A simply higher concentrated ink could have emulsification difficulties and therefore bring more dot gain than the standard ink. Thus the advantage may become worthless.

A more refined means of judging the printing power of an ink is the printing contrast. It includes both tinting power and small dot gain. The optical density in a 80 % screen area is measured and compared to full tone density. The difference, divided by the full tone density is defined as printing contrast K.

$$K (\%) = \frac{D_V - D_{80}}{D_V} \cdot 100$$

If we stepwise increase the solids density in offset, it will increase also in the 80 % field. However it grows more rapidly than only caused by higher inking, because simultaneously the dot gain rises. The printing contrast first will rise, then pass through a maximum, and then sink (see fig. 15). This maximum is a very interesting point for the characterization of an ink. The maximal printing contrast is the power peak of an ink paper combination.

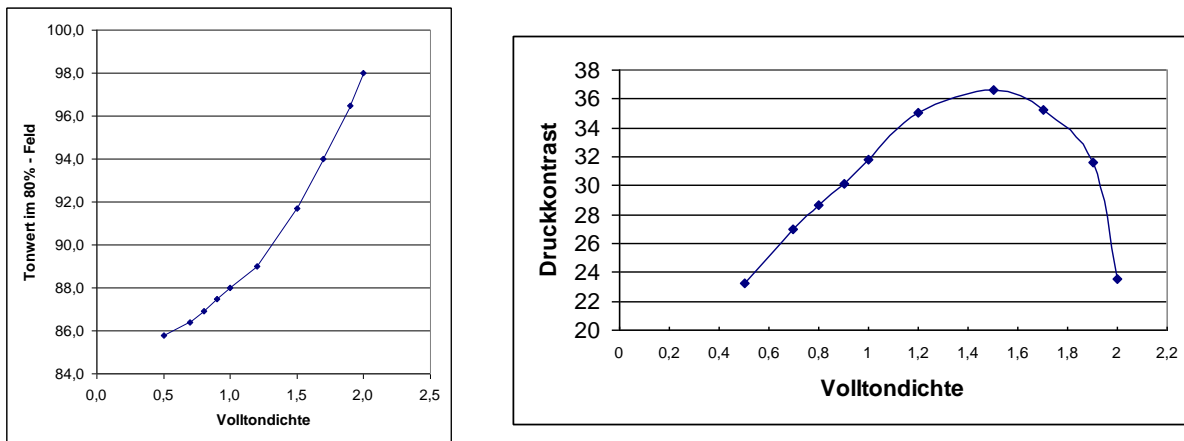


Fig. 15, Printing contrast of an ink paper combination

Some years ago there was a boom of especially intensive process ink series. The idea was to realize an increased color gamut without needing additional press units. Examples are Novaspace by Sun, Aniva by Epple, and hycos by hubergroup.

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### 3. Binders

The binder of an ink tells us if it is printable in offset or in another technique. It regulates nearly all properties of the ink except color.

For offset printing it has to be fatty. Looking closer it needs very decided abilities to emulsify water under various conditions in the form of small droplets. This emulsification must stay within narrow limits to manage that ink is always the continuous phase, and water is the dispersed phase. If with a too strong supply of water the emulsion changes into a water-in-oil-emulsion it behaves like water, not any more as ink. Then we will find it in the fount system and in the non-image-areas of the plate. The offset process then is disturbed.

The water uptake must go quickly in both directions, uptake and ejection. The result must be a dynamic equilibrium under all water conditions.

The binder must carry all demands of litho-behavior, printability, water tolerance, temperature insensitivity, different printing materials and printing speeds. It has to keep all aims in drying like film formation, rub and carbonizing resistance, slip, elasticity, resistances against different attacks, gloss and the bronzing of the prints.

The varnish is the main component of the binder and keeps 50 to 70 % of the formulation. For sheet fed and web offset it classically contains 30 to 40 % resin, 10 to 40 % vegetable oil or alkyd resins, some additives and the rest thinner. In English the thinner is also called solvent. However in offset inks that does not include volatile substances.

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#### 3.1. Hard resins

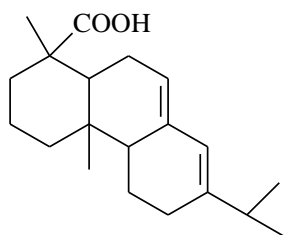


Abb. 16, Abietic acid as chemical structure

As resin, or often called hard resin, we use macromolecular materials, usually based on rosin (colophony, pine resin). It consists mainly of abietic acid, a rather bulky hydrocarbon with two conjugated double bonds and an acid function. The basic body of the molecule is big, fatty and rather inert. The acid function has not at all an effect similar to acetic acid. Because of the big aliphatic lump so close it has no idea to dissociate. This lazy big molecule can be forced into Diels-Alder additions with the double bonds. Or it can be esterified with the acid group. In this way rosin is modified with phenolic, maleic and other resins. The resulting resin gets controlled properties like melting range above 140 °C, a calculated rheology in certain solvents, the limited affinity to mineral oils, acid and bromine number, and all other things the ink formulators want. The starting colophony comes from pine trees in tropic regions, which are grooved to let out the liquid resin.

The pine resin is the reason why binders can be promoted as coming from renewable resources. It makes part of the propaganda that inks may be biologically or environmentally friendly.

Of course the pine resin first of modifying must be purified and brought into a defined state as a valuable technical product. The worldwide applications in the chemical industry cannot work with a seasonal changing summer and winter quality, the brownish color and the characteristic aromatic smell.

The typical melting range of ink resins of 140 °C and higher makes clear that normal offset prints become soft and sticky above this point. Laser printers in business take offset printed forms to apply the powder toner and fix it with a 200 °C roller. Blister packages are sealed by 220 °C hot sealing shoes in some seconds. These are typical sheet fed and even heatset printed pre-products. We see that such processes can work successfully only under well controlled conditions and need printers with specialized skill.

The resin development in the 90s has brought a lot of progress for printability of offset inks, especially by using more elasticity in the rheological behavior.

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### 3.2. Alkyd resins and drying oils

In the past of pasty inks, mainly letterpress inks, linseed oil and other vegetable oils played an important role. They wet (“solvate”) the pigment crystals (in the older years only carbon black) and form a skin at the surface if left some days open to the air. This ability to form films makes them interesting still today for offset inks. So we find linseed oil and some others still in modern offset inks. Nowadays the chemical industry can condition and tailor them quite well to get defined properties. One of the chemically refined forms of vegetable oil is the alkyd resins.

How do we have to imagine vegetable oils and their derivatives?

All vegetable oils in nature are triglycerides. That means a three valid alcohol called glycerin is esterified with three molecules of fatty acids. The here interesting fatty acids are displayed in fig. 17.

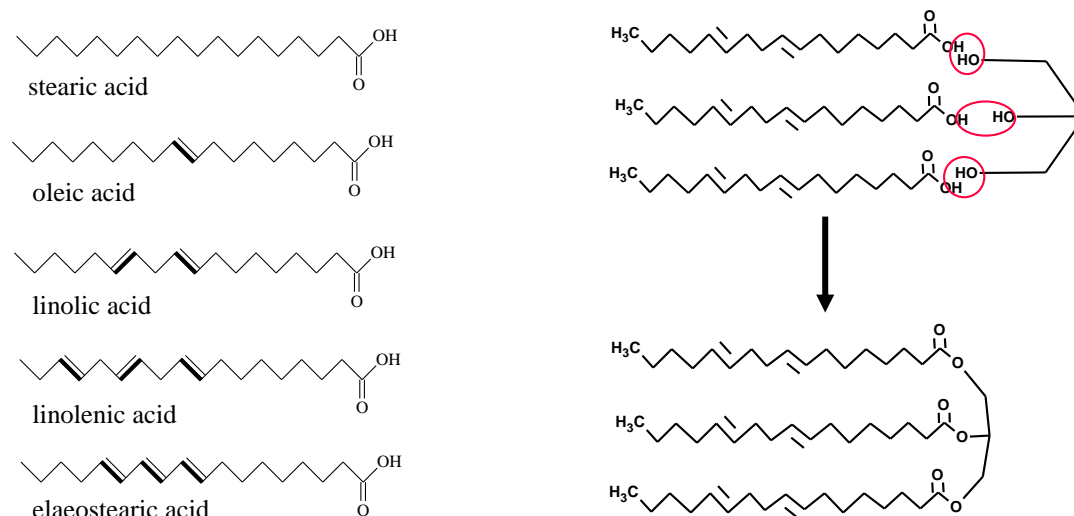


Fig. 17, Fatty acids of plant oils with C<sub>17</sub> - carbon chains and schematic model of the esterification



It is remarkable that these fatty acids all have carbon chains of 17 C-atoms plus the acid group COOH. The acid function is esterified to one of the three alcohol functions of glycerin. For us is interesting only the distribution of double bonds in the chains. We know from food discussion the  $\omega$ -unsaturated fatty acids. These examples clearly make part of them - except the stearic acid. The double bonds grant them a modest reactivity for our digestion and also for oxidative film formation. The more double bonds a molecule has the better it can be linked by oxygen molecules to neighbor carbon chains. And we know already that conjugated double bonds are particularly reactive. If a vegetable oil or a varnish contains some elaeostearic acid in its triglycerides, it will work very well in the oxidative drying. In fact, such vegetable oils (e. g. tung oil, made from special nuts) must be inhibited strongly to only be storable in hobbocks or containers without forming leather like skin. Tab. 2 gives an impression in which quantities the corresponding fatty acids (always as triglycerides) are represented in traditional vegetable oils.

Tung oil	80 %	eleostearic acid
	10 %	linolic acid
	5 %	oleic acid
Linseed oil	50 %	linolenic acid
	25 %	linolic acid
	15 %	oleic acid
Sofflower oil	70 %	linolic acid
	20 %	oleic acid
Soybean oil	55 %	linolic acid
	32 %	oleic acid

Tab. 2, Fatty acids in vegetable oils

The viscosities of vegetable oils are about 1 Pas. This is too high for the use as a thinner / solvent and too low for the use as a binder. For viscosity reasons and to modify many other important properties (drying, wetting of the pigments, ink rheology) the oils are modified into alkyd resins. This is a chemical name for groups of esters, e. g. in the polyester industry. In our case we have esters of a multivalent alcohol (e. g. trivalent like glycerin), a bivalent acid (usually isophthalic acid) and a fatty (mono) acid.

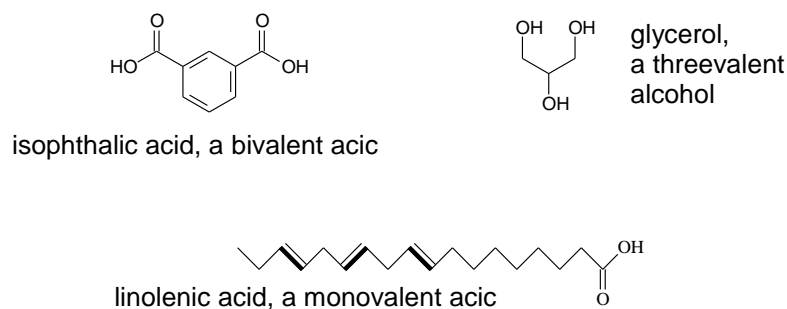


Fig. 18, The construction of alkyd resins for the ink industry

With these three components chemists produce alkyds by esterification of defined viscosity, tack, drying activity, and polarity. There is a huge variety of binder components with much more useful properties than simple vegetable oils could be.

Alkyds and vegetable oils are the carriers of the tack in an ink. They join hard resins with mineral oils and render a binder "compatible" that means stable as a homogenous liquid.

In the commercial propaganda they are "renewable raw materials".

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### **3.3. Thinners and solvents**

The third main component in a varnish is the thinner / solvent. Formerly they were mineral oils, which swelled in big, heated mixing containers (reactors, 180 - 220 °C) hard resins in a way that the total mass became a viscous, sticky material, similar to honey. It is remarkable that these former varnishes were not solutions of resins in oils, but colloidal mixing phased. The hard resin itself absorbs about 2 - 5 % of mineral oil. The mineral oil can solve only very few % of hard resin in the classical sense. The area between, which is used in all varnishes, is describable as an extremely fine dispersion of hard resin in mineral oil called a colloid. Such a colloid coming onto a porous surface like paper lets its liquid component oil unreservedly penetrate into the paper. Here we find ideal conditions for filtering the thinner out of the ink binder and leaving the hard resin as binder component together with the pigment.

Mineral oils are chemically seen alkanes (paraffins). That means saturated hydrocarbons. The alkyl chains usually show 12 - 16 C-atoms, comparable to diesel fuel (Gasoline in comparison 5 - 7 C-atoms). In comparison to fuel ink oils however are much more refined and purified, hydrogenated and fractionated. For example they smell only minimal. Being products of the petrochemistry they come out of fossil recourses. In printing inks fractions are applied with boiling ranges between 210 and 230 °C, between 240 and 270 °C, and between 260 and 290 °C for heatset offset. Sheet fed offset typically applies oil from 290 °C and above. In newspaper inks there are low cost oils of high fractures and even vegetable oils (soybean) directly.

In the 1990s some very interesting derivatives of vegetable oils came to prices and industrial quantities to make them acceptable for offset inks. Today we find them more and more as thinners / solvents in sheet fed inks - and less and less mineral oils.

They are fatty acid esters of the here mentioned oil acids with C<sub>17</sub> chains, mostly without or with rather few double bonds. They became ester interchanged from vegetable oils (triglycerides) to methyl-, isobutyl-, or octyl-esters. That makes them a third of molecule size and the corresponding low viscosity. Now they can carry the penetration drying as well as mineral oils.

They have the advantage to really solve hard resins because of a higher polarity. So no colloid is needed any more with the risk of the separation of the two phases under mechanical stress in the press. The ink binders became more stable in printability by these new thinners.

Furthermore these derivatives from vegetable oils could be presented as renewable materials. This point was used in exaggeration, because the uptake of mineral oil for printing inks is in the general industrial field quite small.

The comparison of the viscosities is interesting:

Mineral oils, Fatty acid esters	0,001	to	0,2 Pas,
Vegetable oils	1	to	3 Pas,
Alkyd resins	5	to	100 Pas.

According to the desired properties a varnish can be made from hard resin and thinner / solvent or from hard resin, alkyd resin and thinner / solvent. The expected drying mechanism influences the decision and general rheology, viscosity, tack, and splitting behavior between the rollers of a press.

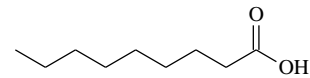
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## 4. Additives

Among the numberless possibilities for additives we will have a look only on the most important groups with certain relevance for printing and printed products. There are the dryers, their opponents called inhibitors, and waxes. They make 0,2 to 1 % of the formulation. Most of them are applied as master batches to make the dosing more easily.

### 4.1. Siccatives = dryers

Dryers are mostly compounds of metals like cobalt, manganese, or iron with organic acids like octanoic acid. Formally they correspond to



the inorganic salts, but because of the fatty influence of the alkyl part in the acid they are not ionized, rather unstable against water and soluble in oils. Coming into contact with water - or even worse with acids or salty solutions in water - they decompose forming cobalt hydroxide and octanoic acid. And with this they lose the catalytic activity as dryers.

We understand that in offset printing with its dampening solution of pH 5 (modest acid) there are risks, which the old letterpress did not know. In fact there is big trouble on the rollers with small quantities of ink and big quantities of dampening solution, which means in jobs with only small ink uptake. Both stay too much time under mechanical sheering, and the water can attack the dryers and destroy them. A special risk is the low pH value, because it means acid attacks. If it comes lower than 4.5, the oxidative drying is surely quenched. Such low pH values are allowed only for inks without oxidative drying, e. g. newspaper printing.

Fortunately since the 1980s paper mills size the paper mass with a nearly neutral resin process. The formerly used potash alum seizing left medium acidic paper surfaces and brought drying risks in offset printing uncoated paper. Coated paper is weakly or medium alkaline - no risk for the siccatives in the oxidative drying.

The oxidative film forming is a so called radical mechanism. Compounds with metal components, which can change the oxidation state, can support the transfer of electrons. Lead octoate up to the 1980s was an important siccative, especially for blacks, which always have some difficulty in film forming. It had to be cancelled from the formulations, because of the toxicity of lead. Nowadays there are four of the most important toxic heavy metals - lead, cadmium, mercury, and chromium VI - limited to a sum of 100 ppm., extremely low even as traces.

Small quantities of siccatives catalyze the drying only a little. Adding more has more effect, until it comes to a maximum, and adding even more then reduces the effect. With a too high dosage the drying runs quickly, but another process, the digestion of the binder molecules with oxygen, comes up. A reasonably formulated ink should already contain the optimal dose. Everything else would be a production defect. So the recommendation is to print inks as they come out of the tin or container. If really the addition of dryer helps more than in psychology, there must be controllable special circumstances. In all other cases it is wrong to add dryer.

Siccatives like cobalt octoate help to bind the oxygen to the double bonds of the fatty acid molecules. As the third necessary component is oxygen = air, we call them surface dryers. If extremely glazed papers are used, and there is very small room for air between the sheets in the pile, it can be helpful to air the pile.

Oxidation is the only drying mechanism for plastic foils in sheet fed offset, because no pores are present to make penetrative drying possible (setting). The sheets often are extremely smooth, and in the pile is deficient air. The printer is in the dilemma that he cannot touch the sheets to air them, because the prints remain fresh, nearly liquid ink. This is one of the special cases in which a dryer helps. Surface dryers are useless. So please leave out everything that is violet (cobalt octoate). Here a dryer is needed with extra oxygen, which can emit it in the right moment. It must be an additive containing peroxide like sodium peroxy borate. As soon as it comes into contact with water, it will decompose and leave the additional oxygen into the printing ink layer - just in statu nascendi, a very aggressive modification. This oxygen can react with the double bond and help the film formation without moving the sheets. It works quickly and lets the sheets solidify over night. We could call these dryers "inner dryers" to make the difference to "surface dryers".

There is one disadvantage in this wonder dryer: It does not need water to decompose. Very slowly it would decompose already in the ink under storage in the tin. So it is impossible to incorporate it in the ink factory. The printer must mix it freshly in the duct. And leftovers of inks with peroxy borate dryers must be thrown away, as they cannot be stored not even for a day.

It also is logical that the inner dryers help only under oxygen deficit. Many trials to intensify oxidative film formation on matte coated paper did not show an acceleration or improvement.

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#### **4.2. Inhibitors = fresh keepers**

A printing ink with siccatives starts film forming as soon as it comes into contact with air. That happens in opened tins: We see skin after some hours. It can also happen in the duct or on the rollers. So we have to wash before rest periods, especially in the evening.

For normal printing jobs, with paper and board, there is a way to organize some comfort and time saving. There are substances, which neutralize or block the dryers. Mixed into the ink it prevents skinning. On the way from the tin to the substrate it has to be removed or destroyed. Such substances are called inhibitors.

Inhibitors have been developed and improved like binders and the other components. In the first years the inhibition could only be used in completely uncritical cases to a higher extent (roller fresh), other with only low dosage (duct fresh), and the rest completely without. In the meantime all inks except those for plastic films are duct fresh.

We should keep in mind that the inhibitors change more than the drying speed. The chemical reaction runs in slightly different ways with some different by products and different risks. There is more smell, and ghosting (gloss-matte-effects and back yellowing) occurs more often. These new risks seem to come much stronger in waterless offset. So obviously even the fount solution does influence this hypersensitive, radical reaction.

Everybody understands that inhibitors as additives are critical. So fresh sprays for sheet fed contain only mineral oil. In heat set and cold set we find inhibitors, because oxidative drying is not used.

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#### 4.3. Waxes

If somebody scratches, even a perfectly filmed print is damageable. There is a very efficient help to improve rub resistance that works in varnishes, inks, paints, and plastic surfaces. Microcrystalline PE powder (polyethylene) is applied. Hardly any liquid will wet it, nearly like with Teflon. If we imagine a 1  $\mu\text{m}$  thick offset print film some PE particles of 5 to 10  $\mu\text{m}$ , they will look out of the film surface (see. fig. 19). In thicker paint films and plastic parts the PE particles swim to the surface - with a similar effect.



Fig. 19, Particles of waxes in and upon the print

If there is now a mechanical attack to the surface, at first the wax particles are hit and smeared over the surface. They give a good slip to the print's surface and protect it.

Of course like all medicines waxes have side-effects. It seems easy to understand that gloss and smoothness of the print will sink. The low wettability of PE waxes tells us that highly rub resistant inks will have risks in subsequent varnishing or laminations. Most of the subsequent contact media like dispersion varnishes or laminating adhesives have difficulties to wet PE. Only the good old oil based offset varnish does not have any problem. And here we see the hint to salvation in difficult cases. A normal offset varnish used as a primer will help, if an expensive job must be rescued.

In sheet fed offset we apply microcrystalline PE that is cooled down deeply and then broken in jet mills. In heat set and cold set, without any subsequent treatment, low priced PE types are acceptable. In sheet fed offset there is a trick for special applications. As usual matte varnishes never will have a good rub resistance (the matting agent is made of small sharply broken stones) we can put rather much wax into a varnish to render it matte. This will have a top rub resistance. At the other hand there is a terrible sensitivity of polishing dashes, again no medicine without side effect.

And waxes have a certain tendency to build up on sensitive surfaces like rollers or rubber blankets...