

How Printing Inks Dry

Content

	page
Preface	2
1. Evaporation	3
2. Penetration	6
3. Oxidative Film Formation	10
4. Precipitation of High Molecular Fatty Acids	13
5. Interdiffusion of Macro Molecules	14
6. Radiation Curing	15
7. Chemical Cross Linking	17
8. Thermally Induced Polymerisation	17
9. Solidification of Fused Binders	18
10. Solidification in Digital Printing	18

Preface

Planning a printing job we decide about the printing technique by the number and quality of desired copies and the intended printing material. The intended use of the printed product, its demands of mechanical robustness, and often the printing material again, decide which drying mechanism or combination will be the best.

A folding box for cigarettes or chocolate will demand quite different properties than one for screws or other small metal pieces. And for a newspaper there is a crucial need to be ready in very short time. We will tolerate even black rub off and fading after five days, if it happens.

So it can help looking more closely at the mechanisms that bring the - usually wet - ink to a defined dry state. Every of them has its typical advantages - and also disadvantages or even risks. In this paper nine mechanisms are chosen. They will describe nearly all actually used ways of solidification for printed inks. Some of them are widespread, some of them rare. For professionals it is useful to know the whole equipment. Only then they can plan specifically and avoid claims.

[↑ content](#)

1 Evaporation of Liquid Components

Boiling temperatures of solvents can be quite high, such as 100 °C with water, and rather modest for example with ether (34 °C). That means, using water will cost more energy to get it off the ink layer than with ether. On the other hand ether will leave the ink film already with room temperature quite quickly. It is possible that the prints dry too quickly and cause problems already in the press. And with ether we have two additional risks: inflammability and narcotic effect on printers. So in every case it is worthwhile to choose the best liquid for each case. And it will save costs and difficulties only to evaporate the liquid at temperatures **much below the real boiling point**. Thus we can save energy and risks for printing material and machinery.

To evaporate a liquid we look for a good relation between vapor pressure and machine temperature.



Fig. 1 Example for evaporation of a liquid significantly below the proper its boiling point

Some classical solvents are used, given by the organic chemistry, which with show considerable volatility already room temperature. There are toluene, alcohols (ethanol, isopropanol), esters (ethylene-acetate), ketones (acetone), or aliphatic hydrocarbons with 6 to 9 carbon atoms (gasoline). It is possible to use water, but then we need higher temperatures and the support of heated air to make it effective (pile temperatures from 30 - 40° C). Even more highly boiling hydrocarbons (mineral oils boiling at 260 - 300 °C) are applied. They need considerably higher temperatures in the equipment, e. g. 120 °C of web temperature, to be expelled.

Evaporation under room or slightly higher temperature

Organic solvents offer interesting properties for technical use. A very volatile solvent will leave the ink film **quickly** and **nearly without residues**. The print will be **immediately dry** and **compact**. An appropriate condensation or absorption equipment can recycle the solvents after the dryer to be reused in the same kind of printing inks. Emissions and expensive material losses can be kept low. However this very consequent solution is cost-effective only for big quantities, as the equipment is rather expensive. The typical example is illustration rotogravure.

On the other hand the volatility of solvents has draw backs: they are easily inflammable. Solvent based printing inks need very special care and precautions. Furthermore many good working solvents cause health problems. For instance the aromatic (not the aliphatic) benzene, C_6H_6 is carcinogenic. Such substances have to be excluded.

There even are non-inflammable solvents with excellent solvent properties, for example halogenated hydrocarbons. These would keep down the explosion and fire hazards. Unfortunately they cause health problems and are ozone killers. So they must not be used. In our industry the risk of inflammability is consciously accepted because we can control it professionally. As people come into close contact to prints and printing ink, no known health hazard can be tolerated.

National legislation regulates the use of solvents, divides them into hazard classes, and prescribes adequate labels.

A furthermore important problem with solvents can be their smell. When a print is dry they evaporate nearly completely - but not really to zero. Some traces will remain. Therefore in packaging printing the residue of some ppm (parts per million) of solvents can be quality-relevant for food or tobacco in printed packages.

Evaporation drying of solvents based inks is typical for illustration and packaging gravure, tampon printing, flexography and screen printing (serigraphy).

In chemistry water is used as a solvent. So it can be in printing inks. However water has several special properties, which make it both, attractive and unfavorable. As it is not inflammable and does not cause emission problems in comparison to organic solvents, it is desirable to use as much water based inks as possible. Unfortunately it is very, very polar and needs completely different binder agents and additives. Some printing materials like plastic films have decisive problems with water based inks, because they are not wetted. And the physical properties of water do not favor low energy treatment: The boiling point is quite high with 100 °C, and the vaporization heat is much higher than with all the traditional organic solvents. However, physiological and environmental motives support the use of water in inks.

Water based inks, using mainly the evaporation of water as a drying mechanism, exist in gravure and flexography. We call them aqueous or dispersion systems. In sheet fed offset most of the presses have a varnishing unit at their end, used for dispersion varnish. Even if this is fixed to an offset press, here we find flexographic printing.

Later in this information the water based printing inks and varnishes will show some additional and very special drying mechanisms. But at the first glance - it is evaporation.

To speed up the evaporation of water with temperatures up to 40 °C we need support. The printed web or sheet is warmed by infrared radiation. It will raise the temperature of the prints effectively to 30

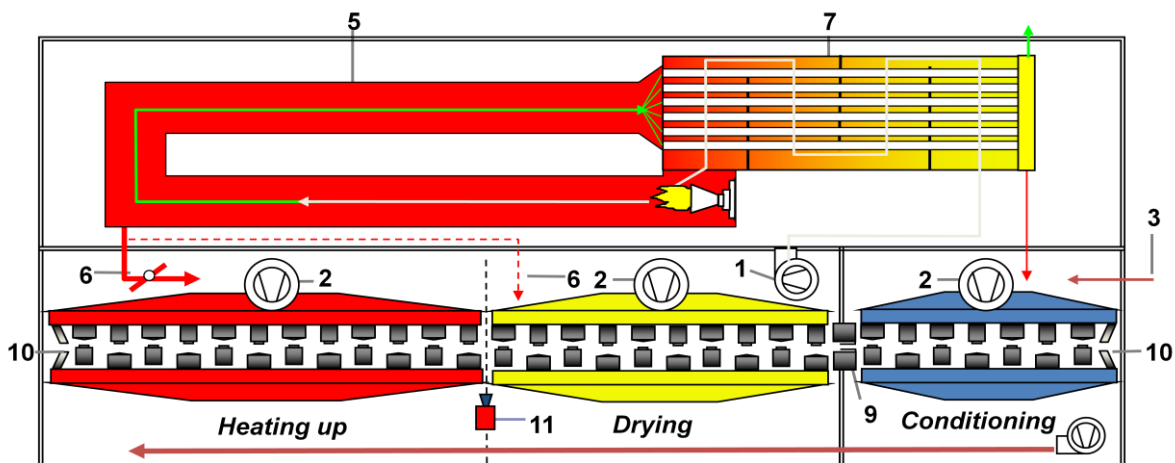
or 40 °C and ease the vapor to be sent out. And as a second help warmed air is applied on top. Warm air eagerly absorbs humidity, and so it carries the vapor away from the print, enabling more vapors to come out.

Evaporation under heat

In weboffset heatset inks there are no classic solvents (volatile) but low viscosity mineral oils with quite high boiling ranges. They **start boiling at 190° C** or more. The freshly printed web runs through ovens, which heat the print surface by heated air or formerly combustion gases. A piece of printed area stays approximately 1 sec in such an oven to lose as much mineral oil as possible.

The necessary heat gas temperatures lie around 240 °C. The web, however, is heated only to 110 - 120 °C. This is already hard for paper, because water is cast out completely, and this over drying weakens the paper (curling alongside the fiber running direction, blistering). On the other hand the mineral oils are not driven out so completely as the solvents in gravure. Moreover the hard resins of heat set inks begin to melt with 140 °C. So immediately after leaving the oven the ink film is soft and sticky. It has to be quenched passing a silicon covered, high gloss polished steel roller. The chill cylinders leave a very glossy, glazed surface on all printed areas, independent of the ink quantity. Consequently a heat set print is identified not only by the curling of the paper edges, but also by a special uniform gloss.

In the past decades the printing speed grew more and more. And with it the requirements for the drying process. Formerly we only had to heat up the prints and to carry away the oil vapors. As air is a rather poor carrier for heat, this costs very much energy. Now a number of clever tricks like recycling of heat and catalytic burning of oil vapors have improved the energy situation decisively. This economic progress considerably improved the position of heatset offset in its competition with illustration gravure.



- | | | |
|---------------|--------------------------|----------------------|
| 1 Exhaust fan | 5 Burning chamber | 9 Air curtain |
| 2 Supply fan | 6 Hot air supply | 10 Heated air-knives |
| 3 Make-up air | 7 Integr. heat exchanger | 11 Web temp. control |

Fig. 2 Example of a modern heatset oven using energy recycling and combustible gases, model Dual-Dry TNV ©, 2010, MEGTEC Systems Inc.

Evaporation drying in general, as a **purely physical process**, has advantages in technical uses. It works **quickly** and with a **well defined result**:

No byproducts nor side reactions.

The state of drying can be measured immediately.

Solvent residues can be measured easily by gas chromatography.

The print is fixed, no change in gloss, color and so on.

Cutting, folding, and creasing are problem-free.

The printed web can be rolled again.

As the printed material does not always have pores, solvent based inks are used on plastic films, aluminum foils and metalized paper. The solvents may even initially etch the plastic surface and allow the print to anchor. This stabilizes the bond between print and substrate.

The evaporation of solvents nearly immediately leaves products ready to further processing or use.

[↑ content](#)

2 Penetration of Liquid Components

With setting or penetration of liquid components we name a drying mechanism, which reminds us of drying ourselves after a shower: The printed substrate must have pores which absorb liquid components of the printing ink. Coated paper and board have such pores in a nearly ideal manner. The coating layer on paper typically consists of a 3 to 15 µm thick layer of coating pigments (tiny platelet shaped particles from china clay or stone - shaped from calcium carbonate), fixed together with low quantities of binder - just enough to stick their contact points together. All the paper coating forms a sponge - like empty structure, highly absorptive for liquids.

The following illustrations show how the setting runs.

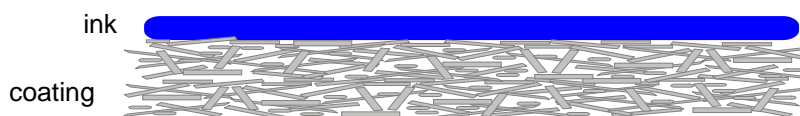


Fig. 3 a freshly printed ink film on paper

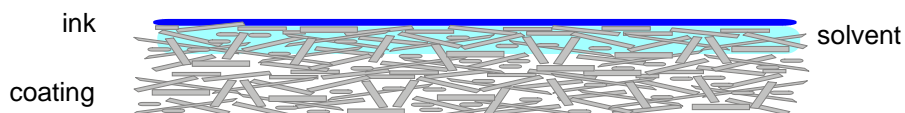


Fig. 3 b ink film after setting

During setting the ink film loses volume, it shrinks. The pigment particles get closer and closer. Some may even come up to the surface of the ink film (see figure 3). This reduces gloss and may bring bronzing effects, a special luster of colored surfaces under reflected light.



Fig. 4 freshly printed ink film ink film after setting

Besides a proper porosity good setting requires an appropriate ink formulation. In offset inks no volatile solvents are used, because they would start volatilize on the rollers. Traditionally we use mineral oils with boiling ranges between 190 and 300 °C. Chemically we have hydrocarbons (alkanes) with chain lengths of C₁₂ to C₁₆. Since the nineties more and more esters of fatty acids are applied, conversion products of plant oils.

Gravure and flexographic inks can use water as a solvent, which is able to penetrate into the paper and also to evaporate with heat. Once there were used special letterpress inks (food packaging) with glycols as penetrating liquids.

The important point for a liquid (solvent or thinner) is a low viscosity to make it penetrate as quickly as possible into the substrate pores. Here laid some of the difficulties of plant oils (linseed, soy bean) in the use as thinners in offset inks, because their viscosity was considerably higher than that of the mineral oils in use.

some physical basics: capillarity

If the liquid component in an ink, the thinner, is expected to penetrate, it must wet well the substrate surface. The Young equation puts the three effective forces as vectors and gives us the conditions:

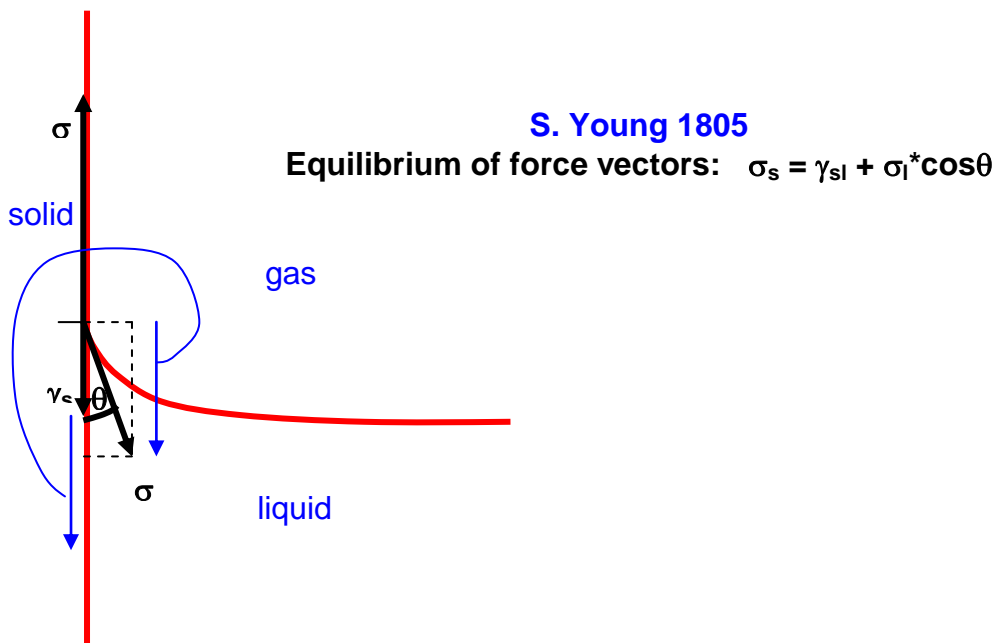


Fig. 5 Scheme of wetting between a liquid and a vertical wall

A small contact angle, good wetting, lets the liquid creep a little piece high on the vertical surface, working against gravity. If we assume not a wall, but a narrow tube, this means the following:

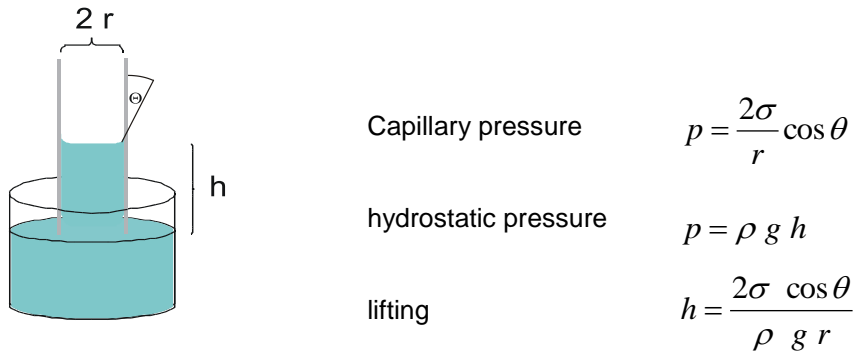


Fig. 6 Calculation of rising height in a capillary tube

In the formula above are used

σ the surface tension of the liquid,

θ the contact angle, and

r the radius of the tube.

As usual ρ stands for density of the liquid and g for the gravitational acceleration.

In the formula above surface tension σ and contact angle $\cos \theta$ are in the numerator. This seems clear for the cosine, because a small angle has a cosine near 1, a steep one however close to zero.

For the first glance it seems strange that also the surface tension is in the numerator. Because in reality a liquid will wet the better, the lower its surface tension lies. This contradiction can be explained with a consideration:

The surface tensions of liquids are found between 30 and 90 mN/m, the cosine of the contact angle uses all its range from 0 to 1. It works like a powerful scaling factor. In fact **not** a rising surface tension will increase the lifting, but only a rising product of surface tension with $\cos \theta$.

In the denominator of the fraction we find the density of the liquid and the gravitational acceleration - and the radius of the tubes. This is an important clue for the setting process: Narrow pores suck much stronger than wide pores. We must not mix this up with small and big pores. A narrow and deep pore strongly sucks much liquid, a wide and flat pore does it slowly and unsatisfactorily. The pore largeness is no good means to characterize absorption power of a paper. More interesting would be the distribution of pore diameters, the pore volume at the utmost additionally.

The equations of fig. 5 show a static state, not a dynamic action. Amongst others the speed of penetration of a liquid into a tube is controlled by its viscosity. So a quickly setting print requires as many narrow pores as possible and a rather thin thinner. An increase of pile temperature brings an increase in setting speed. Infrared radiators (electrically heated ceramic fittings) are a good help for printers.

We can understand that **not the complete ink must be absorbed**. The pores have to be fine enough to absorb selectively the thinner. All binder agents (hard resins and alkyd resins) must be coarse or of high molecule weight to be left like in a filtering process. In mineral oil based inks this is done with hard

resins dispersed as colloid in mineral oil, not solved. In the newer fatty acid ester inks we have real solutions. They have quite different effects as thinners than mineral oils.

A cross section of a printed paper may be as fig. 6 shows. We see the proportions of the different layers.

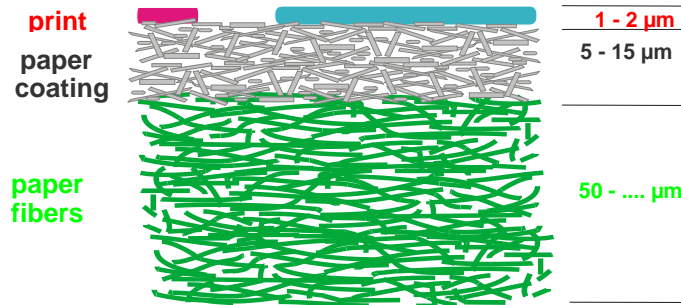


Fig. 7 Proportions of thickness in a coated paper

The coating of an LWC paper, thinly coated paper for web offset and gravure, has about 3 μm of thickness. It does not even hide all fibers on the surface. The better the surface printing quality the thicker is the coating. Art papers have 15 to 18 μm of coating on each side.

On the other hand dry prints have only 1 μm of thickness, which is quite similar in gravure, flexographic and offset printing. That means, for drying and adherence of prints only the coatings count. The prints do not feel anything of the fiber fabrics beneath.

Now, what happens in detail with a fresh offset print?

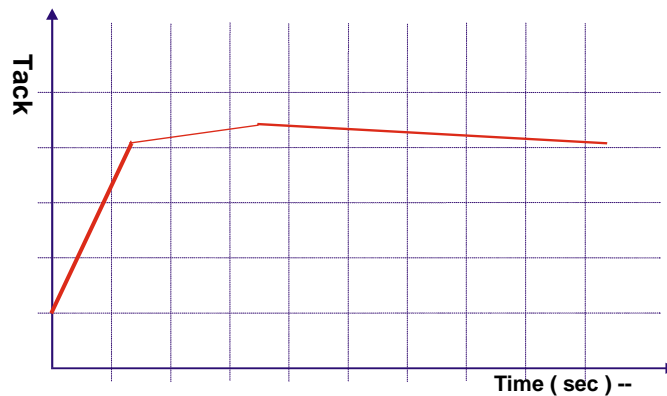


Fig. 8 Trend of the tack in a fresh offset print on coated stock

Conventional offset prints a low tack **emulsion of ink with dampening solution**. In a short instant **the emulsion water** penetrates into the paper surface, because it wets perfectly the surface, and because it has the lowest viscosity of all components. The **print tack jumps up** from emulsion to original ink. In a second phase the thinner of the ink starts to penetrate, and the print starts to get more concentrated. This often makes the tack rise for some extent, but much less than before. Losing more and more thinner the print loses cohesion, because the hard resins begin to coagulate. This now results in tack loss and viscosity boost. When the sheet sets in the pile the third phase must have

made enough progress to leave an only mildly sticky surface, which means with a low tack. All this must happen within some seconds.

Fig. 8 explains why the first phase in setting is a crucial help for ink trapping wet-on-wet in multi color presses. The fresh print has the low tack of the emulsion form. The tack jump from emulsion to original ink in the short moment between two sections makes the first print very tacky, and it can easily trap the emulsion of the next ink layer. Otherwise a following print would never be trapped by the foregoing, but rather stripped back into the machine.

This model clarifies another characteristic of the setting mechanism: If the thinner is sucked out of the print, this will never happen as thoroughly as the evaporation of a volatile solvent. So the print will never have the mechanical robustness of pure resin. It is softer with its thinner leftovers. Especially in box board production, we will need further support in rub resistance, an additional mechanism of solidification. For this reason penetration is usually combined with such a supplemental mechanism. In coldset web offset, newspaper printing, penetration is the only mechanism, due to time and price reasons. So daily newspapers make their compromise in rub resistance.

Like evaporation drying also penetration is a purely physical type. It works within seconds to minutes. So it is quick. Modern mineral oils and fatty acid esters enable us to run presses up to 20 000 sheets per hour, which is profitable in actual equipment. Decades ago inks for letterpress and offset were formulated with vegetable oils as thinners, for example linseed oil. If we shake a bottle of cooking oil we can see, what conditions for the penetration once existed. And furthermore paper surfaces were not so fully developed for absorption of oils as they are now.

In this context we understand that infrared drying is not a real drying mechanism. It accelerates in a mild way physical (penetration) and chemical (oxidation) processes by warming up the prints. But inks with a special quick setting show the most noticeable acceleration under infrared light. For some years they were labeled as special IR inks, a nice promotional trick. But of course we must not mix it up with a proper mechanism like radiation curing (UV, electron beam).

[↑ content](#)

3 Oxidative Film Formation

Very old know how is used as support for the mechanically weak result of the penetration: Some plant oils form a skin on their surface if left in contact with air for some days. The long molecular chains of the oil are cross linked by oxygen leaving bigger molecule structures. This has some affinity to the polymerization in plastic chemistry. If this trick is used for inks (once letterpress, now offset) the resulting print film can be as rub resistant, non carbonizing, as our daily use of brochures, books and boxes requires.

Fig. 9 makes clear how it works.

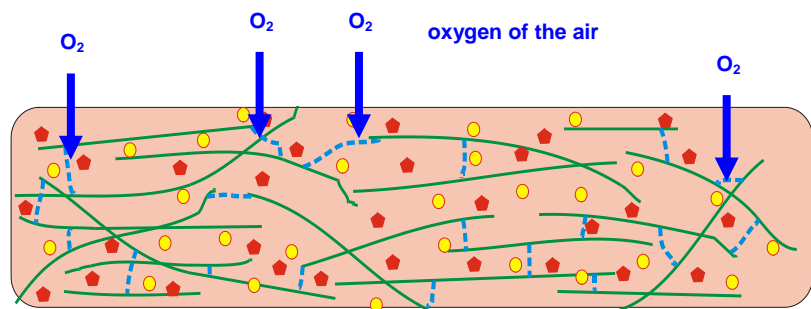


Fig. 9 Oxidative film forming in a print

Green are the chain shaped plant oil molecules in the binder of the ink. They must have double bonds to be cross linkable. There the oxygen molecules can attack, open them and form bridges between two chains, because oxygen is bivalent. Such bridges help to form three-dimensional molecular structures giving good mechanical resistance to the ink film.

Oxidative drying (film forming) is among chemists seen as a radical process. That means numerous possible reactions run their ways over intermediate molecular forms. Accordingly we obtain many byproducts besides the film formation - among them low molecular weight compounds like alcohols and aldehydes, some of them rather volatile. They can migrate within the pile into the sheet above. There they can bring smell (food packages) or react with other substances in the paper surface (optical brighteners, coating binders). They even can condensate on the original sheet surface and reduce gloss in certain areas. This can make a kind of reverse copy of the image on the back of the sheet above.

We see that there are quite a lot of disadvantages in the oxidative film forming. The expert will keep them in mind and avoid or minimize them.

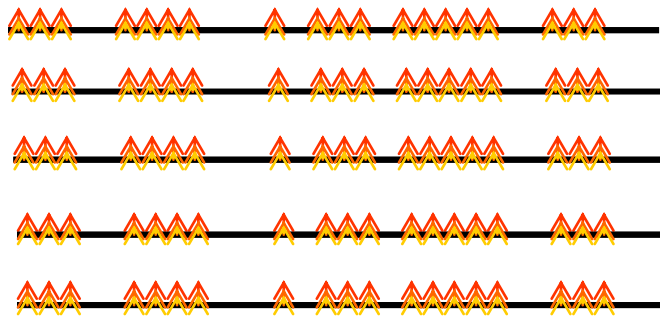


Fig. 10 Prints exude haze during the oxidative film formation

The worst aspect of the oxidation is however its low speed. If we consider the high viscosity of plant oils under room temperature, we see that all here needs time.

Furthermore not only the oxygen molecules have to be excited to react with double bonds in oil. These double bonds then have to be in a fortunate position to each other and to the oxygen, they have to twist and wind. Even with very modern chemically modified plant oils (alkyd resins) oxidation as the only mechanism would take weeks. To have it run at least in hours, we must apply catalysts, so called siccatives. Mostly metal organic compounds like cobalt - octoate are used here. Still we have to accept that such a chemical process takes hours or days. **Within one or two hours the oxidative drying of an offset print has done no measurable progress.** And so it is useless to add drier agents, if we want to print the other side of the sheets after half an hour instead of half a day. The professional solution in this moment would be another ink with a quicker setting.

In these years development of sheet fed offset inks looks for quicker setting - without the sacrifice of weaker rub resistance, even on matt coated paper. So modern inks (and paper qualities!) enable the printer to turn the pile around and go on printing - without waiting for too long. However such jobs cannot show a maximum of gloss or rub resistance.

In some print jobs oxidation is the only way of drying (better: solidification). Plastic films and some synthetic materials give no chance for penetration. Consequently the inks have to dry 100 % by oxidation. But these special cases need time, usually several days. Printing plastic films in offset has another very own handicap: As the surfaces of the sheets are very plain, there is not much place for air in the pile. And this keeps drying speed low, of course.

Experts know a lot of tricks. For this situation we have special dryers. They do not act as catalysts, like the cobalt compounds. These special dryers contain more oxygen in their molecules than normal stoichiometry allows (per-oxo-borates). They decompose with water and release their excessive oxygen. With such compounds very aggressive oxygen (atomic, not as molecules) comes, and the cross linking of the plant oil molecules runs quickly. Unfortunately such "inner" driers (compared to the usual "surface" driers) are not stable enough to be mixed into the ink by the producer. The ink would harden already under storage within some weeks. So such systems have to be used as two-component-systems. The inconvenience can be justified by time gain and production security.

In conventional offset (with dampening solution, in contrast to waterless offset) we have to remember that the normal siccatives (octoates from cobalt and manganese) are **sensitive to water**, even more to salt solutions and most to acids. They react forming octanic acid (oily liquid) and cobalt hydroxide (precipitate) - both not at all active as driers. The dampening solution in classical offset has a pH of $5 \pm 0,3$. So it is a weak acid. And it contains a lot of puffer salts to stabilize the pH.

So the printer has to get **as few dampening solution in contact with the ink as possible**, and in as short contact time as possible. A job with extreme low ink uptake may take some day more to achieve its final rub resistance. Printing on plastic needs extreme awareness of these risks.

The same argumentation explains why the pH of the dampening solution must never be below 4,5, as long as oxidation drying is used. In fact such acid concentrations are known only in cold set offset.

Now it is understandable that elevated salt concentrations in the dampening solution mean dysfunction, if in practice found concentrates are highly overdosed. Only the buffer salts increase the danger of hydrolysis for the dryers. Highly does here mean much more than twice as much as recommended.

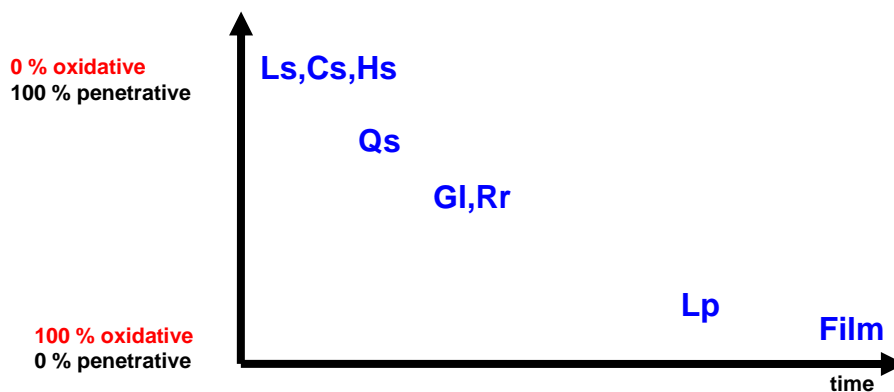


Fig. 11 Time balance of different shares in drying mechanisms

Offset inks can be formulated with different shares of oxidative or penetrative drying components. In food packages (Ls = low smell), cold set (Cs) and heat set (Hs) drying runs exclusively physically. This means quick drying. Stepwise we come from all-round sheet fed inks (Qs = quickset) over more fatty gloss and rub resistant (Gl, Rr) inks and the even more fatty (alkyd resin content) for laser printer forms (Lp) to inks for plastic films in sheet fed offset, which need the longest time for film forming. A further variation of pure oxidative drying is found in tube and can printing. Here we find tung oil (vegetable oil with many double bindings), and drying is done in ovens with 70 °C. At present this rather old technique is being replaced by offset with radiation curing or flexography with solvents or also radiation curing.

[↑ content](#)

4 Precipitation of High Molecular Fatty Acids

In gravure and flexographic printing and the related application of dispersion varnishes in sheet fed offset presses we use water based dispersions. These systems use a very smart drying mechanism. It makes possible that inks and varnishes are diluted and washed away with water. But after drying the prints are water resistant. How does this work?

To understand it we must look into some chemistry of inks. Binders are made of high molecular compounds, in this case polymerized acrylates. In their molecular chains there are a few acid functions. In pH neutral or in acid water these acid functions exist as R-COOH, complete acids. So these binders are kind of very weak organic acids. The main part of the molecules are polymer chains. The poor acid functions are not able to dissociate in water, too weak with all this organic backbone. The entire molecule is not soluble in water. It is an oil or wax. But if such a weak organic acid comes into an alkaline water solution, the H⁺ Ion will be snatched away leaving the salt form of the acid R-COO⁻ and Na⁺ ions. This is soluble or at least dispersible in water. If we however neutralize such an alkaline solution or if we even acidulate it, the insoluble acid form will precipitate again.

Ink chemists use this behavior taking ammonia solution as alkaline component. In the ink or varnish our resin appears in its salt form (R-COO⁻ and NH₄⁺) and has good relations to water. As soon as a print of such water based ink dries, not only the water will volatilize. The ammonia lies in a dynamic equilibrium as NH₃ solved physically in water and chemically dissociated into NH₄⁺ and OH⁻. The more water leaves the ink film the more ammonia will follow and disappear. Thus the pH will sink, and the fatty acids will grab H⁺ ions to precipitate in their acid form, insoluble in water again.

The printed ink film will be waterproof, at least with neutral water or acids. In alkali it is soluble again. And here is the trick, how to clean the press from ink or varnish stains and crusts.

With this background we can explain a rather annoying problem. Varnishing recto verso sometimes the prints block. Even if the first varnished side had been completely dry, the other side will emit a moist and ammoniacal atmosphere in the pile, with danger to attack the formerly dry side again. The result can be a stable block of sheets.

The drying mechanism of precipitating acid forms of resins is only usable as a part of several mechanisms. It can be combined with penetration or evaporation like in dispersion varnishes. It works as quickly as the ammonia volatilizes, which means within a few minutes.

[↑ content](#)

5 Interdiffusion of Macro Molecules, Coalescence

In ink and paint technique we call only water based systems dispersions. Physically seen this is wrong, because in all inks and varnishes, also oil based, we have different phases finely dispersed with each other. But as a technical term this is established, and we are aware of it.

Dispersions are very often met in graphical applications. We find them as paper coating paste, as adhesives for labels or laminating films, or as binders in water based varnishes and inks. They are of importance in gravure and flexography, and in varnishing units of offset presses. In addition to the up to now mentioned drying mechanisms they use a further trick, which again is not a drying in the sense of our everyday language. It works physically and rather quickly. **And it brings extremely important properties to the prints.**

Let us have to closer look into a dispersion binder. It is made of very, very long molecule chains, e. g. poly-styrene-acrylate, better threads than chains. Many of these threads are interlooped with others in every droplet as fig. 12 shows.

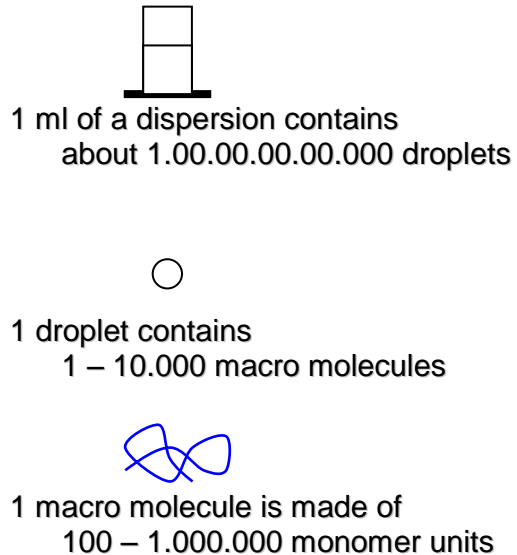
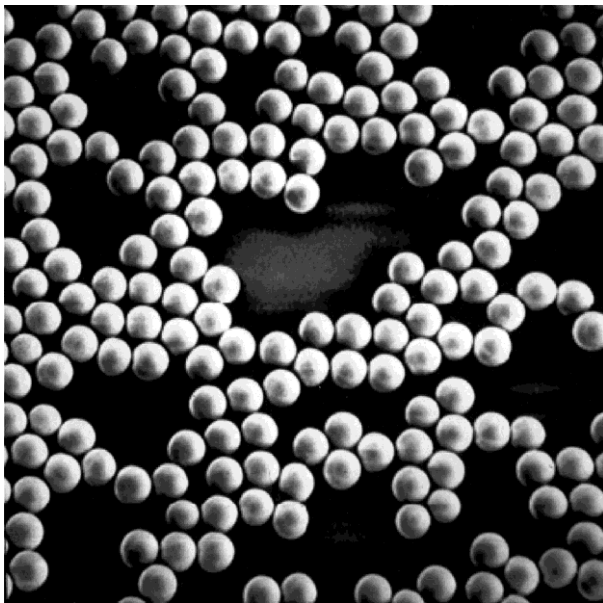


Fig. 12 Construction of dispersion binders, ©: BASF AG, experts seminar

If a dispersion varnish dries the water volatilizes from the varnish film. The latex droplets come closer and closer. As soon as they come into contact with each other, the rest of the water leaves the interspaces between the sphere shaped droplets. A formation like honeycombs results. In every comb we have interlooped macro molecules. With thermal motion the chain ends diffuse into neighbor combs interlooping to further extent. This interlooping is called melting and works physically, because no new chemical bonding is formed. The intimate felting of molecule treads results in sensational strong mechanical properties of this binder film, far better than that by oxidation.

We easily understand that for this coalescence some warmth is helpful to make the molecules move. So every binder has its own minimum temperature to merge. Binders for dispersion varnishes have

merge temperatures below 30 °C. For lamination they can be higher, because then they show better thermal stability.



Fig. 13 Acrylate dispersions form films by interdiffusion. The interfaces between droplets vanish with the evaporation of the water

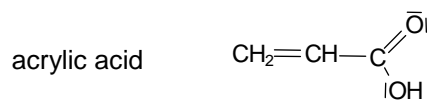
Coalescence runs within minutes to an hour. An offset print, dispersion varnished, is ready for further processing nearly immediately, and some hour later it will have its end stability.

[↑ content](#)

6 Radiation Curing, UV Curing, Electron Beam Curing

The next mechanism goes chemically, but is as fast as lightning. The binders are here again acrylates. However these acrylates are very special: They are monomers and small oligomers full of potential to intense polymerization. In dispersions we applied acrylates, which already were completely polymerized to very long chains. So they could not react any more in polymerizations.

In radiation curing the polymerization is properly used as film forming mechanism. So we need very special chemical substances. The basic unit is acrylic acid, a small molecule with a >C=C< double bonding which can be opened and recombined with neighbor molecules. In this way chains or even close-meshed networks can be made:

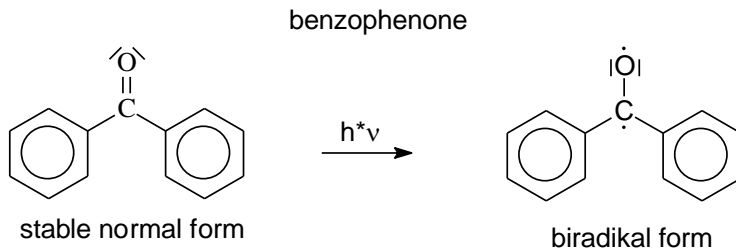


In binders for radiation curing the acrylic molecule is modified to achieve specific properties in the polymerized film. We find HDDA (hexane-diol-di-acrylate), epoxy-, polyurethane-, or polyester-modified acrylates.

The curing reaction is very short and quick, to the most extent done within fractions of seconds. An energy ray (for example electron beam ray from an emitting cathode, a very high energy impulse) starts the polymerization, which proceeds in a radical mechanism (like fire or explosions), until all double bounds are cross linked, which are in sterically favorite positions.

This explains that radiation curing systems typically are 100 % systems - without solvents, diluters etc. And with the dense cross linking we can expect mechanically and chemically extremely stable print layers.

Equipment for electron beams is complex and expensive. Chemists have found a trick with a simpler kit. There are substances which will be excited and split into radicals by cheaper radiation like UV light. And these radicals will attack the acrylates to start the polymerization. Such substances are called photo initiators. For instance benzophenone or similar molecules are useful.



Additionally there are other possible mechanisms of radiation curing, which are not based on a radical, but on a cationic way. For some time it had a certain acceptance in printing industry, but now it was left for some rather sophisticated reason of toxicity in food packaging.

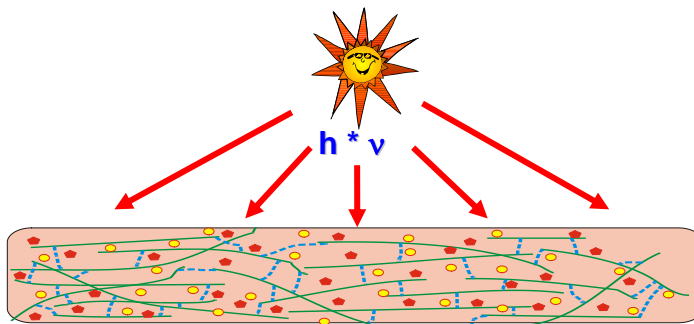


Fig. 14 Cross linking of acrylates hardens the printed ink film

Fig. 14 shows an ink film shortly after being printed. The pigment particles are embedded in a binder matrix of chain like acrylate molecules. The photoinitiator activates them to cross link forming dense, three dimensional structures. Approximately 90 % of the cross linkable bonds react within the first seconds. Then all the ink film is completely stable, and the rest of the reaction may take minutes to hours.

We can easily imagine how the liquid state of the print freezes in an instant. The printed ink film is mechanically completely stable, the print ready for further processing in any technique without any waiting time. This is in many applications a strong reason to use such an expensive way.

Radiation curing inks are formulated for many printing techniques. A recipe for sheet fed offset could be

- 55 % acrylate oligomers (high viscosity)
- 10 % acrylate monomers (low viscosity)
- 10 % photo initiators
- 5 % additives
- 20 % pigments.

If we intend to adjust viscosity, only the ratio monomers / oligomers can be used. But this immediately changes also the reactivity of the mix, possibly even the end hardness. So there is only small space for adjustments in every ink batch, if we needed some for rheological reasons.

The dense cross linking and the superb gloss are the most important reasons to apply such expensive systems: labels, folding box board, and high gloss magazines.

In food packages the typical laundry smell had prevented UV inks for a long time. Now it is used quite often with special photo initiators and prepolymers in offset in line varnishing and in water based flexographic inks. Even electron beam curing was used for some years in soft drinks packaging based on carton board. In these years it seems as if it would revive again.

The main advantage of being mechanically and chemically so stable is also the main disadvantage: Recycling and composting of radiation cured prints is hardly possible.

Working with radiation curing materials is uncomfortable for the involved people. Acrylates need very special hygiene, as they tend to irritate the skin and sensitize it. This is why varnish leftovers and uncured maculature must be combusted in special processes.

However with professional handling and thorough curing they are applied even in food packaging, an extremely sensitive field. Furthermore we find them in big sized ink jet printing as ink film or as thick layer of varnish over prints. A thick UV varnish layer will prevent oxygen from destroying the dye or pigment of big posters, which now can stay for an entire year in outside exposure. Even sun light cannot bleach them anymore, with no oxygen available.

[↑ content](#)

7 Chemical Cross Linking = Two - Component - Systems

In packaging gravure and flexography there is an optional mechanism to strengthen the printed film for solvent and water based inks. We see it as chemical cross linking. If the mechanical (shampoo bottles) or thermal (sterilized medicine packs) resistance of the binder system does not fulfill all requirements, special binder resins are applied, which can be cross linked by additional chemical reactions. One example is polyols. They are cross linkable by isocyanates as hardeners to form polyurethanes.

Cross linking systems are offered as two-component-sets. The cross linking reaction must start really only in the moment desired. The laborious handling is accepted for production safeguarding. The cross linking reaction starts with the warming up of the prints and runs down slowly. Usually one has to wait some hours to achieve the final stability.

[↑ content](#)

8 Thermally Induced Polymerization

Our plastic industry uses prepolymerized epoxy and polyester molding compounds. They are taken as bulk material to fill a press. Then the press is shut and heated to a defined transition temperature. So the polymerization reaction is completed, and car parts like car bumpers are produced.

This trick is sometimes also shared in printing food packages. The binder systems are similar to that of UV inks with epoxy-acrylates. Sometimes special starter compounds decompose under the transition temperature and start the polymerization to solidify the print film. The chemical process is radical - as in UV curing.

[↑ content](#)

9 Solidification of Fused Binders

Inks that are solids with room temperature and melt with elevated temperature are a most interesting target of development. They are filled into a press as pellets and printed as liquids under technically controllable conditions, e. g. 100 °C. Immediately after being printed they freeze by cooling. This trick is not easily put into practice. In industrial printing presses it must work reliably under the actual printing speeds, not an easy task. Once there was such a development project applying it to gravure techniques to substitute the toluene based illustration rotogravure. But it was stopped for technical reasons.

In heatset web offset there are binder resins surface-fused in the heatset oven, and after it solidified with cooling rollers. This could be taken as one mechanism of solidification combined with evaporating mineral oils. It brings the typical uniform gloss over heatset prints.

[↑ content](#)

10 Mechanisms of Solidification in Digital Printing

In the rather young field of digital printing processes we find well known mechanisms of solidification. But we also see newly chosen ways. As here is a lot of dynamics, it is interesting to follow this special matter.

Powder toners contain binders, which work like hot melts. The toner once printed is fixed to the printed material by a heated roller - about 200 °C for a short contact time. Liquid toner in Indigo presses (electro ink) use a similar way, when the last contact, a kind of transfer cylinder, passes the toner to the paper. The liquid is partly left in the press, and partly absorbed by the paper; only the fusible toner is transferred and fixed with modest heat, about 120 °C.

Ink jet prints usually dry by evaporation of solvents or water. But in LFP (large format printing) we also find UV curing. And in some special applications the ink is fed into the press as fusible sticks. It is melted, printed in ink jet technique, and solidifies on the paper.

[↑ content](#)

Bergheim, December 2010