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# The use of barium sulfate in printing inks as filler material

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<p>Blanc fixe is a transparent pigment made from barium sulfate. It is used in inks as a filler pigment and its main function in inks is to replace partly the need of the most expensive part of ink, coloured pigment, and hence reduce the cost of the ink.</p> <p>The purpose of the study was to produce knowledge for the client about inks in general and their properties in printing technology. Also, it was to untangle how the properties of sheet-fed offset inks change when pigment is replaced by Banc fixe filler. Pigment material was replaced in such a manner that the filler content in ink was 4, 8 and 12 weight percent. The pigments studied were two different grades of Blanc fixe and a competitive filler. Also, ink without any additive filler was tested to produce the reference values.</p> <p>Inks were tested by printing strips on an IGT-printability tester after which the ink amount on the paper was calculated. From the printed strips, densities of un-touched, set-off and print through areas as well as gloss and colour-values were measured. Results of measurements were tabulated and trend curves for different determinations were constructed from them. Following, ink requirement, set-off, print through, gloss, colour-values and colour differences were calculated in the target density.</p> <p>The most essential conclusion was that against the results of this study, the Blanc Fixe filler pigments of the client's repertoire are possible to use in sheet-fed offset inks so that the total cost of the ink can be reduced without affecting crucially to the properties of an ink film. Some declination was perceived in commensurate to the increase in filler content. However, for example decrease in absolute values of gloss and increase in colour differences were tolerable. All things considered, the best performers were the competitive filler and the Blanc Fixe product with smaller particle size. Results of this study are intended to be suggestive and as a result the client had a positive indicator for the continuance on the study on Blanc fixe products used as ink fillers.</p>	
Keywords	Blanc fixe, filler, extender, pigment, printing ink

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<p>Blanc fixe on bariumsulfaatista valmistettava pigmentti, jonka pääasiallinen tehtävä painoväreissä on toimia täyteaineena korvaten painovärin kalleimman komponentin, värillisen pigmentin, tarvetta, jolloin painovärin kustannuksia pystytään alentamaan.</p> <p>Insinööriyön tarkoituksena oli tuottaa asiakkaalle tietoa painoväreistä ja niiden painoteknisistä ominaisuuksista sekä tutkia miten arkkioffset-painoväreissä ominaisuudet muuttuvat, kun pigmenttiä korvataan Blanc Fixe täyteaineella. Pigmenttiä korvattiin täyteaineella siten, että täyteainepitoisuus painovärissä oli 4, 8 ja 12 painoprosenttia. Blanc fixe tuotesarjasta valittiin kaksi eri pigmenttilaatumia ja lisäksi testattiin kilpaileva täyteainepigmentti sekä referenssiarvot tuottanut painoväri ilman lisättyä täyteainetta.</p> <p>Työssä testattavat painovärit koestettiin IGT-koepainolaitteella, jonka yhteydessä laskettiin testipaperille siirtynyt värimäärä. Painojäljistä mitattiin sekä koskemattoman painojäljen ja sen aiheuttaman läpipainatuksen että erilliselle set-off-paperille syntyneen painojäljen densiteetit. Lisäksi mitattiin väri- ja kiiltoarvot. Mittaustulokset taulukoitiin ja niistä muodostettiin trendikäyrät eri määrityksille koskemattoman painojäljen densiteetin funktiona. Trendikäyrien avulla laskettiin testipaperin värintarve, set-off, läpipainatus, kiilto- ja väriarvot sekä värierot tavoitedensiteetissä.</p> <p>Keskeisin johtopäätös oli, että tutkimuksen tulosten valossa Blanc fixe täyteainepigmenttejä voidaan käyttää arkkioffset-painoväreissä siten, että niiden avulla pystytään laskemaan painovärin kokonaiskustannuksia vaikuttamatta kuitenkaan merkityksellisesti painojäljen laadullisiin ominaisuuksiin. Joitakin laadullisia heikkenemisiä havaittiin täyteainepitoisuuden kasvaessa, mutta esimerkiksi kiiltoarvon absoluuttinen vähentyminen sekä värieron kasvaminen oli siedettävissä rajoissa. Kokonaisvaltaisesti katsottuna parhaita suoriutujia olivat kilpaileva täyteaine sekä partikkelikooltaan pienempi Blanc fixe tuote. Työn tulokset ovat tarkoitettu suuntaa-antaviksi, ja niiden perusteella yritys sai positiivisen indikaattorin jatkaa tutkimuksia Blanc fixe tuotteiden käyttämiseksi painovärien täyteaineena.</p>	
Keywords	Blanc fixe, täyteaine, pigmentti, painoväri

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# I LITERATURE PART

## 1 Introduction

The development of offset inks is currently not a topic of significant research mainly because this well known printing process was established such a long time ago. Just like in any mature market the primary pressure is on cost. Indeed, it is a common view that the supply of offset inks is a commodity market with price being the determining factor in the choice of an ink. To cut down the cost of ink it is essential to be able to compensate some of the need of the coloured pigment; it is the foremost factor influencing the ink cost.

This is where extenders, or filler pigments, are open to question. Indeed, many manufacturers of chemical industry have their own products entered into this market. Fillers like calcium carbonate and kaolin are already used in inks, just like in many other applications like paints and polymers. The orderer of this thesis work was Sachtleben Pigments Oy, a leading manufacturer of top-quality chemical products with a unique range of white pigments and extenders. Their functional extenders are based on barium sulfate which is still rather uncommon material in the means of ink filler. The product range of Blanc fixe, produced from barium sulfate, is a commodity in paints, and now there is a growing inclination to be entering the printing ink market as well.

Hence, concluding all of the above, the primary motive behind this study was to find out whether the Blanc fixe product range of Sachtleben can be used to compensate some of the high-priced pigment concentration in ink formulations in such a manner that the print quality is not compromised to excess. The aim of this study was to get indicative results to either encourage further studies, or failing that, to reveal reasons for it coming to grief.

In addition to conduct the test series it was also essential to produce theory and information about inks in general, and the ways they are tested and analysed. This segment is fulfilled in the literature part of this study.

## 2 The offset lithographic printing technology

Lithography, on which the offset printing is based on, is a planographic process, where the image and non-image areas are in the same plane. Lithography was introduced by the playwright Alois Senefelder and dates back from the 1790s. It was originally called chemical printing as the theory behind it was that the water protected the non-image area of the printing plate and the ink adhered only to the hydrophobic areas. This continues to be the basic concept of lithographic process, however, it is only a vast oversimplification of the situation, and from the early days of lithographic printing process, the component responsible for the chemical distinction between the image and non-image areas has progressed from water to a finely tuned multi-component solution, fortunately for pressroom chemists. (Dyster 1993:86; Leach & Pierce 2007: 15.)

By the chemical treatments, areas of different surface energy on the plate are created. As illustrated in Figure 1, water repellent, ink-accepting image areas and water accepting, ink repellent non-image areas are ensued. Thus, with the exception of waterless plate printing, all types of offset printing plates require application of dampening solution to active and maintain the distinction between ink-accepting image areas and ink-repelling non-image areas. (Dyster 1993: 86; Leach & Pierce 2007: 15 & 343.)

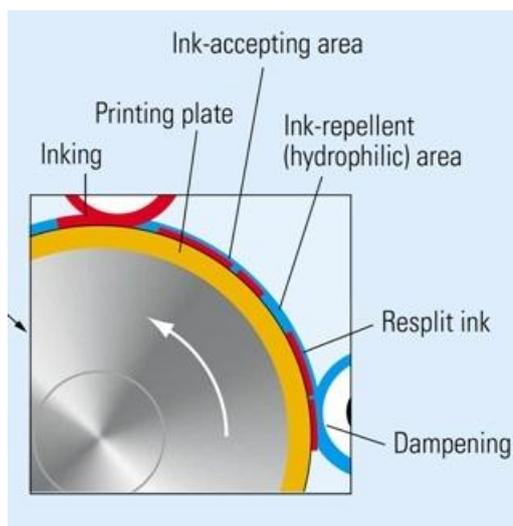


Figure 1: Lithographic offset printing: Basic principle (Kipphan 2001: 207).

## 2.1 Offset printing process

The lithographic process is now days called offset lithography (later referred also only as offset) for it being an indirect printing process where the inked image on the plate does not print directly on to the plate, but is first ‘offset’ onto a rubber blanket cylinder, and thence transferred to the printing substrate. The principle and components of offset printing is shown in Figure 2. Dampening rollers apply a thin layer of dampening solution (aka fountain solution) onto the printing plate where it will only adhere to the hydrophilic non-image areas. This is followed by several inking rollers transferring a thin ink film onto the plate where it will only adhere to the hydrophobic image areas of the plate. This principle of inking is shown in Figure 3. The ink layer is then transferred onto the blanket cylinder before being transferred to the paper as it passes through a nip between the blanket cylinder and impression cylinder. (Oittinen & Saarelma 2009: 55.)

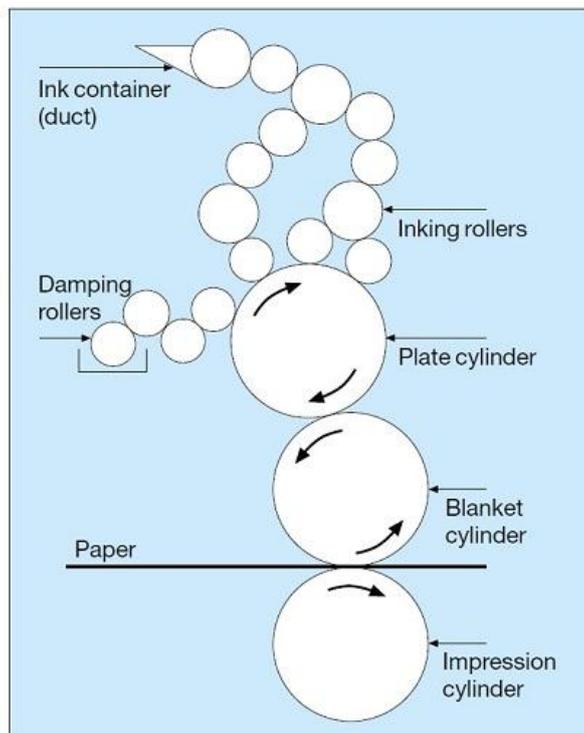
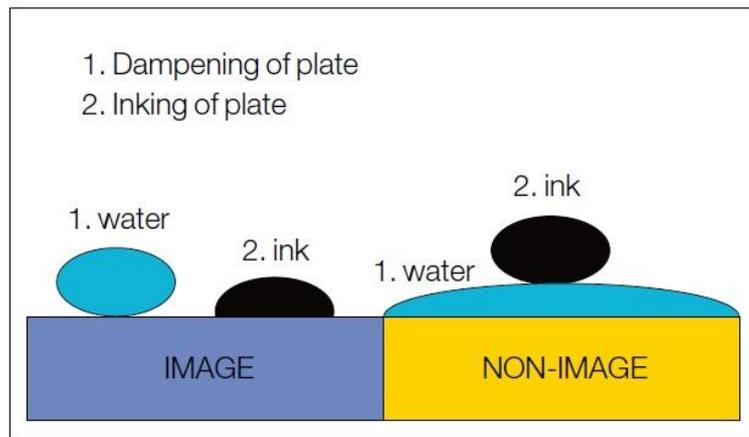


Figure 2: Principle of offset printing (The Printing Process 2003: 3).



**Figure 3: Inking of the printing plate (The Printing Process 2003: 3).**

Offset printing is a wet-on-wet printing method which means that the process colours are overprinted successively without drying. This causes some ink transfer onto the blanket cylinder of the subsequent printing unit. After the last printing unit, the ink film may be dried by a number of processes including absorption, polymerization, oxidation and evaporation. The drying mechanisms of inks are explained further on in chapter 3.3. (Oittinen & Saarelma 2009: 55-56.)

Offset printing can be divided into two different methods; sheet-fed and web-offset. These methods differ in their ink drying mechanism, ink composition, press design, substrate form and product applications. Web-offset is furthermore divided into heat-set and cold-set offset. Within this study, focusing only to the sheet-fed offset is essential and web-offset related matter is out of the scope. However, to provide an overview on different offset printing methods, they are listed with their application areas below in Table 1. (Oittinen & Saarelma 2009: 56.)

**Table 1: Offset printing methods and their application areas (Oittinen &Saarelma 2009: 56).**

	Sheet-fed	Heat-set	Cold-set
Application	<u>High quality print jobs</u> Direct mail Magazines Brochures Packing materials Books	<u>Large and fast print jobs</u> Magazines Directories Catalogues	<u>Tight schedule, fast</u> Newspapers Catalogues Phone books Books
Run length	1 000 – 100 000 copies	50 000 – 1 000 000 copies	50 000-1 000 000 copies
Printing speed	1-4 m/s (5 000 – 18 000 sheets/h)	Max. 15-16 m/s	Max. 15-16 m/s
Papers	<u>Sheets</u> High-quality coated papers (>80 g/m <sup>2</sup> )	<u>Web</u> Coated papers Uncoated papers Boards (<200 g/m <sup>2</sup> )	<u>Sheets</u> Uncoated fine papers (high porosity and roughness Newsprint Slightly pigment-ed/coated papers

## 2.2 Printing unit

To describe the structure and action of an offset printing unit, an example of a typical sheet-fed printing press is illustrated in Figure 4. Referring to the figure, a printing unit consists of inking and dampening units, the plate cylinder with the printing plate, the blanket cylinder with the blanket connected to it, and the impression cylinder. The blanket cylinder is inked when the plate cylinder with the inked printing plate rolls over its circumference. In turn, the blanket cylinder rolls over the impression cylinder. The contact line between the blanket cylinder and the impression cylinder is called the printing nip. The paper sheet is attached by grippers on the impression cylinder. Figure 5 is also provided to illustrate the printing unit of offset printing from another view angle. (Kipphan 2001: 221; Leach & Pierce 2007: 15.)

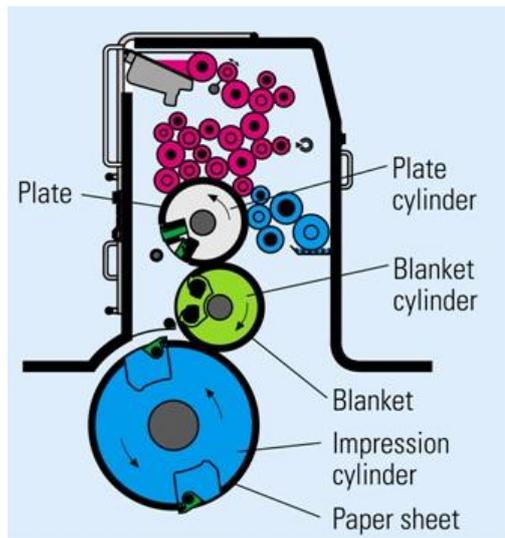


Figure 4: Offset printing unit, cylinder configuration (Kipphan 2001: 222).

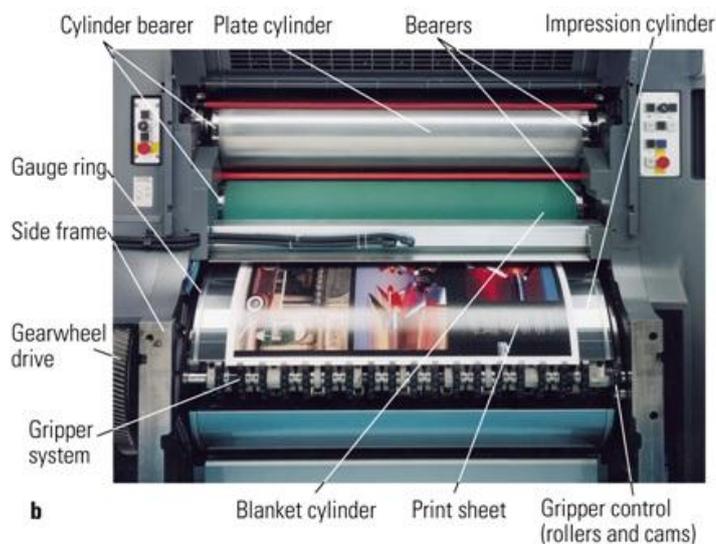


Figure 5: Offset printing unit, bearers, gearwheel and gripper control in Heidelberg's sheet-fed offset press (Kipphan 2001: 222).

### The offset blanket

The offset blanket is responsible for transferring the ink to the substrate, and consequently much of the resulted printed image is governed by the properties of the blanket. Offset blankets consist of multiple layers that conform under nip pressure. The backing fabric that is made of several cotton plies or manmade fibres reinforces the blanket and provides stiffness. The compliant layers adjust the conformability of the blanket and the printing layer accepts ink and is typically made of elastic rubber. The total thickness of

the blanket is usually between 1,7 and 2,0 mm. (Leach & Pierce 2007: 22; Oittinen & Saarelma 2009: 60.)

Blankets come in many varieties to suit different print materials or inks, e.g. conventional inks, UV-cured inks, heat-set inks, varnishes and lacquers. The surface roughness and hardness impact the ink release, and for different materials and presses there are different hardness recommendations. Optimum roughness to give desired ink release properties varies between 0,4 and 0,6  $\mu\text{m}$ . In general, soft blankets transfer ink more effectively and uniformly and produce smaller dot gain due to the more intimate ink-substrate contact. Hard blankets, however, are durable and give up ink easily. (Leach & Pierce 2007: 22; Oittinen & Saarelma 2009: 60.)

### **The inking system**

The inking system consists of several inking rollers and an ink fountain (container/duct) that is a reservoir for the ink supply. Both are illustrated in Figure 2. This inking mechanism deposit ink on the printing image but in case of essentially plastic, relatively high in their viscosity, offset ink, it also has to work the ink to a semi liquid. It must deposit a uniform, thin and smooth ink film on the image. (Destree 1994: 15:17; Oittinen & Saarelma 2009: 56.)

The ink fountain consists of a steel roller, called the fountain roller, and a doctor blade. One edge of the blade is set very close to the fountain roller, and the space is adjustable. The amount of ink fed on the inking rollers is controlled by the size of this gap between the roller and the blade. Many of the ink fountains has ink fountain key that can be adjusted so that it moves the doctor blade either toward or away from the ink fountain roller so that it thereby decreases or increases the amount of ink on the roller. (Adams & Co. 1996: 355; Destree 1994: 15:17.)

The roller train, i.e. the consecutive inking rollers, usually consists of metal oscillating rollers and a series of resilient rollers. Some smaller presses may also use hard rubber rollers. The roller train must be long enough to work the paste ink properly. Each time the ink film is transferred from one roller to another, it is split in the roller nips. The ink

film thickness  $h_n$  on the plate after  $n$  roller nips can be determined from the following equation:

$$h_n = \frac{h_0}{n+1},$$

where the  $h_0$  is the thickness of the ink film fed on the roller train. During the transportation in the ink rollers, ink film thickness decreases, and when the ink reach the form rollers that ink the plate, it is almost uniformly thick. (Destree 1994: 15:17-15:18; Oittinen & Saarelma 2009: 56.)

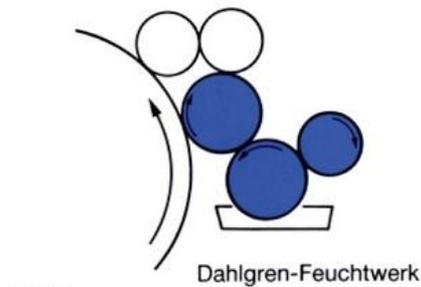
### **The dampening system**

As already stated before, offset printing technology relies on a chemical distinction between the image and non-image areas situated in the same plane of the image carrier. Thus, with the exception of waterless plate printing, all types of offset printing plates require application of dampening solution to active and maintain the distinction between ink-accepting image areas and ink-repelling non-image areas. (Destree 1994: 15:20; Dyster 1993: 86; Leach & Pierce 2007: 343.)

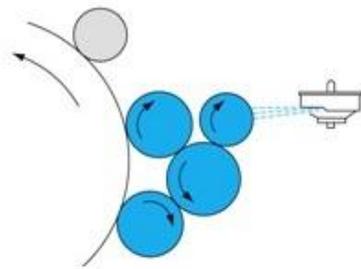
The dampening system supplies a carefully controlled amount of dampening solution to non-printing elements of the printing plate. This layer of dampening solution prevents ink from spreading, cools down the printing press and keeps the non-image areas clean. How the dampening solution actually gets to the printing plate is governed by the type of dampening system on the press. (Dyster 1993: 87; Kipphan 2001: 217; Leach & Pierce 2007: 193.)

The dampening units are often similar to inking units with the difference of fewer rollers. These conventional systems are direct methods and have the disadvantage that ink and paper dust can easily contaminate the dampening solution pan. Figure 6 is to illustrate conventional Dahlgren dampening system. Indirect dampening systems, however, have no physical contact between the dampening pan and the rollers, hence eliminating any contamination problems. In these systems dampening solution is for example sprayed onto the rollers as a continuous stream of droplets. Brush-type

dampening system is illustrated in Figure 7. (Kipphan 2001: 217; Leach & Pierce 2007: 19; Oittinen & Saarelma 2009: 57.)



**Figure 6: Conventional dampening system (Viluksela 2005: 17).**



**Figure 7: Brush-type dampening system (Kipphan 2001: 220).**

### *Dampening solution*

From the early days of lithographic printing process, the dampening solution has progressed from water to a finely tuned multi-component solution. This is due to the fact that it must perform a number of roles on the press. These include for example the following:

- prevent the transfer of ink onto non-image areas of the printing plate;
- rapid optimization of the ink/dampening solution balance to facilitate fast press startups and reduce press downtime;
- maintenance of pH;
- prevent/reduce corrosion; and
- cool the ink in order to keep its viscosity constant.

As this list of only a couple of examples suggests, something a little more complex than water is necessary. The dampening solution consists still mainly of water, but for better performance additives are also used. In addition to water it usually contains plate preservative agents, wetting agents and isopropyl alcohol (IPA) to reduce surface tension and to induce an increased evaporation rate, buffer substance and antimicrobial additives to prevent the growth of algae. (Dyster 1993: 86-87; Kipphan 2001: 211; Leach & Pierce 2007:21 & 343.)

What comes to the use of IPA, there is a growing demand for more environmentally friendly methods to produce the dampening solution and, therefore, the reduction of use of IPA is a current topic for many offset presses. The benefits of reducing or eliminating IPA use includes reduced cost, improved working environment and reduced fire risk, among other things. Dampening solutions can in fact also be alcohol-free. This technique is called alcohol replacement when alternative chemicals such as glycols or glycol ethers are added into the solution. (Kipphan 2001: 21; Reducing IPA Use 2004: 8 & 10.)

Many printing problems in offset printing process are associated with the pH of the dampening solution. The dampening solution should have a pH value between 4,8 and 5,5. May the pH value be too high, excessive ink/water emulsification problems may occur, while too low pH values can cause ink drying difficulties, loss or sharpening of image on the plate, or poor definition of dots. Experience has also shown that the water used in the dampening solution should have hardness level of between 8 and 12° dH. (Kipphan 2001: 211; Leach & Pierce 2007: 21.)

Some dampening solution is always absorbed by the printing ink; this is referred as an emulsification. In physical/chemical terms this is ink/water dispersion. In the ink the dampening solution is entered in the form of droplets and some of it sets on top of the ink film. May the dampening solution droplets fall below a certain size the separation of the printing and non-printing plate elements is no longer possible and the transfer of ink onto the plate is no longer even or in accordance with the image. This results as scumming where the non-printing areas on the plate also print. This course of events

results the immediate break on the printing process. Thus, the water/ink balance should always be under a careful control. (Kipphan 2001: 221.)

### **3 Printing Inks**

Printing inks are formulated to impart image to a printing substrate. The image may be simple text, large solid areas of single colours, or full-colour produced by printing a number of different coloured inks as half-tone dots in superposition. Printing inks are used on a wide range of different substrates, such as papers, boards, plastic, glass and textiles. Ink film thicknesses in printing can be less than 1  $\mu\text{m}$  and the ink per unit area in substrate in four colour printing is approximately 1  $\text{gm}^2$ . As all of the above suggest, the requirements laid on printing inks are very stringent and desired properties manifold. (Leach & Pierce 2007:5; Oittinen & Saarelma 1998: 257; Thompson 2004: 325.)

This chapter is to cover printing inks, the emphasis being on offset inks. The chapter will be divided into 4 sections and the first subchapters are to give an overview of ink composition and the raw materials of inks, the emphasis being on pigments. The following sections discuss drying mechanisms of inks, ink properties, the emphasis being in optical properties, and the characteristics of offset inks.

#### **3.1 Ink composition and raw materials**

In general, all printing inks are composed out of colourant, binder, carrier substance (vehicle) and additives. The most important tasks of components of ink are as follows:

- colourants (pigments & dyes)
  - gives ink their colour and determine the colour intensity
- binders
  - anchoring of the colorant on the print carrier
  - drying of the ink
  - binding colorant into a printable form
  - contribute to the gloss of printed ink film

- carrier substances
  - transport of the colorant and absorption or evaporation afterwards
- additives
  - influence of the ink behavior (e.g. drying, flow behavior, abrasion resistance etc.). (Kipphan 2001: 130-132.)

Table 2 is provided as an example of ink composition; it compiles types of materials used in offset inks with their proportions and functions, excluding additives.

**Table 2: Offset ink composition (Oittinen & Saarelma 2009: 265).**

<b>Component</b>	<b>Function</b>	<b>Description</b>
<b>Pigment 15-30%</b> Black: carbon black Cyan: phtalocyanines Magenta: azo pigments and salts Yellow: azo pigments	Light absorption to give colour	Insoluble fine particles dispersed in the continuous phase (= vehicle) consisting of carrier phase and binder
<b>Binder 10-30%</b> Pitch (newspaper printing) Phenolics Alkyds Hydrocarbon resins (news ink) Drying oils (sheet fed offset)	Bind the pigment particles to the paper and give gloss	Amorphous polymeric materials called resins or monomers of these or oxidizing vegetable oils
<b>Carrier phase 0-70%</b> Mineral oil Vegetable oils	Provide the necessary fluidity	Oils (boiling point > 100°C)

Before discussing the different components any further, it must be noted that the classification of these components can be somewhat confusing. Some parties divide the components of ink into two categories; a colourant and a vehicle system, where the vehicle system itself includes all the other ingredients but the colourant. Some call the

mixture of the carrier substance (vehicle) and binder a varnish, whereas others say that vehicle and varnish is the same thing. In the context of this study all the components of an ink are discussed separately under the main classification of vehicle system and colourants. (Eldred 2001b: 175; Faigle 2010: 49; Thompson 2004: 327.)

### ***3.1.1 Colourants***

Colourants can be divided into two groups: pigments and dyestuffs. In printing inks, pigments are used almost exclusively, while the most important exception is in ink jet technology, though the trend there is also towards pigments. Hence, the dyestuff is out of the scope of this study. (Faigle 2010: 29; Kipphan 2001:130-132.)

Dyestuff are rather uncommon components in printing inks, and their importance lies mainly on ink jet and flexographic inks and in some special applications, such as heat transfer printing, invisible (i.e. fluorescent) inks, and cheque security inks. For being usually soluble in water, the dyestuffs are a bit more common in water-based inks than elsewhere. (Faigle 2010: 30; Kipphan 2001:130-132.)

Pigments, as they and their properties are rather relevant and in importance of this study, are discussed in a broader scale in their own subchapter, 3.2 Pigments.

### ***3.1.2 The vehicle system***

The vehicle system is a liquid in which the pigment is dispersed to transport it onto the substrate. It also has the role of binding the pigment particles together and the ink onto the substrate. In addition it will be the source of imparting gloss to the finished ink film. The vehicle system consists mainly on the binder and the carrier substance, which together are called the varnish. In addition to the varnish, the vehicle system includes waxes, driers, wetting agents, and other additives. (Eldred 2001b: 175; Oittinen &Saarelma 1998: 270; Thompson 2004: 327.)

The vehicle system is the backbone of any kind of ink and especially in sheet-fed inks it is the component which has the greatest effect on the physical properties of the ink. It

carries the pigment, controls the flow and, after drying, binds the pigment onto the substrate. Thus, the vehicle system has a major influence for example on the setting speed, transference, gloss, drying speed and stability, tack and flow. Correct vehicle formulation is necessary to achieve desired properties in an ink, and therefore it is the single most important aspect of the ink formulation. Figure 8 shows three examples of the components of a vehicle system for printing inks. (Eldred 2001b: 175; Leach & Pierce 2007: 369 & 400.)

<b>Type of ink</b>	Sheetfed offset	Heatset weboffset	Flexo
<b>Binder</b>	Rosin modified phenolic Linseed alkyd	Phenolic resin Hydrocarbon resin	Maleic resin Nitrocellulose Plasticizer
<b>Additive</b>	PTFE wax	PTFE wax	PE wax
<b>Diluent or solvent</b>	Hydrocarbon oil 510-600°F BP	Hydrocarbon oil 460-520°F BP	Ethanol Ethyl acetate

Figure 8: Components of a vehicle system for printing inks (Eldred 2001b: 180-181).

### Binders

Binder is the part of the vehicle system that solidifies and holds the pigment particles in a dried ink film. In general, the binder content in printing ink is approximately the same as the pigment content. Binders in printing inks are oils or resins. If oil is used in binder, it typically dries through oxidation in air, in contrast to non-drying oils that are used as a carrier phase. Resins used in binders can be either natural resins, semi synthetic resins or synthetic resins. Chemically resins are polymers, solids or rather viscous liquids, and most of them are of a non-crystalline structure. (Faigle 2010: 60; Oittinen & Saarelma 1998: 269; Thompson 2004: 327.)

### The carrier substance – solvents

The carrier substance, aka solvent, in printing ink vehicle system is used to dissolve the binders and convey the colourant to the printing substrate. Solvents impart mobility to

the vehicle system, and are only needed until the ink film is formed. Therefore, removability from the printed substrate or conversion into solid form are equally important process requirements. In addition, solvents are also used to adjust the viscosity of the ink. The most important examples of the raw materials of carrier substances include:

- toluene, xylene;
- mineral oil;
- mineral spirits;
- ethyl acetate, isopropyl acetate;
- methanol, ethanol, isopropanol, n-propanol; and
- water. (Faigle 2010: 63; Oittinen & Saarelma 1998: 269; Thompson 2004: 327.)

### **Additives**

Besides the main components, vehicle system contains various additives added to give the ink special characteristics. It is particularly the additives that mark out different inks from each other as they may have a profound influence on the functioning of the ink in printing, on the price of the ink and on its desired properties. Filler pigments fall down also to this category of additives. However, as they are the one most important part of this study, they will be discussed in their own chapter: 4 Extender pigments. Some of the other additives of importance to sheet-fed inks are introduced under chapter 3.5 Off-set inks – characteristics. (Adams & Co. 1996: 498; Oittinen & Saarelma 1998: 270.)

Typically additives are surface chemically active. This means that they tend to migrate to and accumulate at surfaces such as pigment surfaces on the micro scale, and on ink film surfaces on the macro scale. This denotes that even as small as a few percent of additives have an effect to the ink. Table 3 lists some of the commonly used additives. (Adams & Co. 1996: 498; Oittinen & Saarelma 1998: 270.)

**Table 3: Additives in printing inks (Oittinen & Saarelma 1998: 271; Wansbrough 2002: 7).**

<b>Additive</b>	<b>Purpose and use</b>	<b>Typical example</b>
Soluble dyes	Modify the shade provided by the pigment <i>Used in all kind of inks</i>	
Filler pigments	Reduce the colour strength of the ink Add “body” in all types of inks Reduce the price of ink by reducing the need of coloured pigment	Calcium carbonate, kaolin
Gelling agents	Increase the “body” of ink <i>Use in oil-based inks</i>	
Waxes	Reduce surface energy and prevent adhesion of wet print to other surfaces Prevent physical contact Reduce ink tack <i>Used in heat-set and sheet-fed inks</i>	Polyethylenes, polytetrafluoroethylenes, paraffine waxes
Plasticifiers	Improve flexibility of printed ink film by having a dissolving effect on binders <i>Used in high quality inks</i>	Esters with high molecular weights
Drying catalysts	Initiate and speed chemical drying <i>Used in sheet-fed offset inks</i>	Organic Co and Mn containing compounds in oxydizing inks, aromatic ketones in UV polymerizing inks
Drying inhibitors	Prevent chemical drying in can <i>Used in sheet-fed offset inks</i>	Reactive compounds
Antioxidant	Delays the onset of oxidation polymerization by reacting with free radicals formed during the auto-oxidation and thus preventing them from reacting further <i>Used in inks that dry by oxidation/polymerization</i>	Eugenol

## 3.2 Pigments

Pigments are finely ground solid materials that provide the colour and contrast necessary to impart information by printing. Thus, it is reasonable to say that pigments, with dyestuff, are probably the most important ingredients in printing ink formulation. A pigment functions by scattering and absorbing wavelengths of light, the relative amount of which determine the opacity and observed colour of printed pigmented ink films. These in turn are largely influenced by the particle size of the pigments and the nature of the printing substrate. (Eldred 2001b: 125; Leach & Pierce 2007: 141; Thompson 2004: 325.)

Pigments function by selectively absorbing and reflecting specific wavelength of light; some of the multiple wavelengths are absorbed by the chemical bonds of the pigment and others are reflected and the colour sensation created (see Figure 9). (Horiba Scientific 2008.)

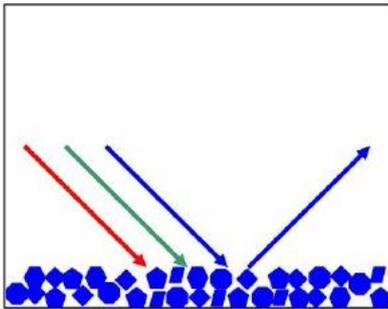


Figure 9: Pigments create a new spectrum of light which creates the appearance of a colour (Horiba Scientific 2008).

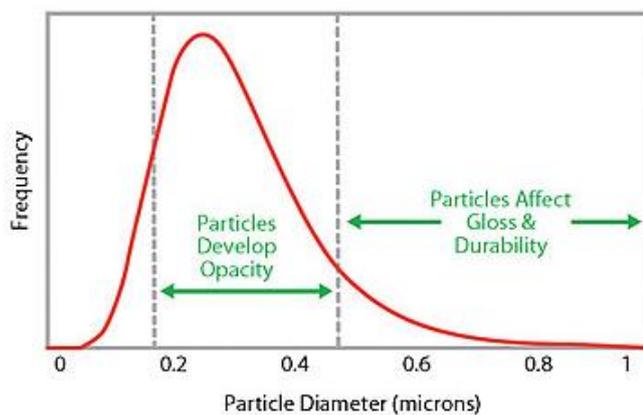
### 3.2.1 Pigment properties

Before discussing the pigments any further, it is useful to examine their required properties for use in printing inks, and the different factors impacting those properties. A pigment may have many good properties and yet it may not be suitable for use in the printing ink. For instance, phloxine is a relatively inexpensive magenta pigment which has an excellent shade, but because it contains lead, bleeds in alcohol, the colour fades rapidly and therefore is not suitable for printing inks. Important properties for pigments

in printing inks include tinctorial (colour) strength, transparency/opacity, gloss, durability, particle size, specific gravity, refractive index, wettability, dispersibility, and light, heat, and chemical resistance. And as the pigments vary very much in these properties, each pigment requires individual consideration in ink formulation. (Eldred 2001b: 125 & 128; Thompson 2004: 325.)

### Particle size

The particle size of pigments is important factor when defining the functionality of the printing ink. Particle size influences both the optical and bulk properties of pigment dispersions and thus must be carefully controlled in order to deliver products that meet the desired requirements of the printing ink. Particle size is related directly to the efficiency with which a pigments scatters light, which in turn affects the opacity, tinting strength and the undertone associated with a given pigment. It can also be related for to the properties of gloss and weather resistance; durability. These occurrences are illustrated in Figure 10. In addition, many of the bulk properties of pigments, which determine the stability and handling qualities, can also be understood trough particle sizing. These include dispersion/flocculation, viscosity and rheology. (Kippax 2005:1; Kippax 2006; Thompson 2004: 325.)



**Figure 10: relationship between particle size and opacity and durability for a typical titanium dioxide size distribution (Kippax 2006).**

### *Particle size distribution*

Particle size distribution denotes the range that the particle size may vary over. Particles of a suspension produced in grinding operation will always vary by some factor. To

describe such situations the range is braked up into a number of classes and try to find out how many particles are in each size range. For a good performance a narrow particle size distribution is preferred. Too many large particles, for example, may affect negatively so that the benefits of the small mean particle size are lost. Figure 11 shows the particle size distribution of a typical titanium dioxide; each bar represents the percentage that fall within a narrow range size. (MacEvoy 2005; Particle Size Distribution 1999.)

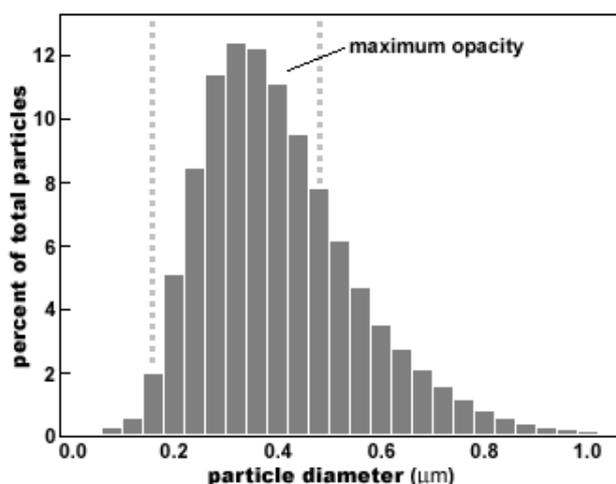


Figure 11: Particle size distribution for typical titanium dioxide (MacEvoy 2005).

#### *Particle size & optical properties*

The particle size of an ink pigment range from about 0,01 to 0,5  $\mu\text{m}$ . A fine particle size is required to give the correct optical and colour properties to the final ink film. As an example, Figure 12 illustrates the impact of the particle size to the shade of the ink. Carbon blacks have the smallest particle size, hence the excellent flow properties they exhibit. Coarse pigments, such as titanium dioxide, generally produce opaque inks. They also sometimes collect or “pile” on the ink rollers, offset plates, and blankets and special formulations are often needed to make such inks transfer properly. (Eldred 2001b:127; Thompson 2004: 325.)

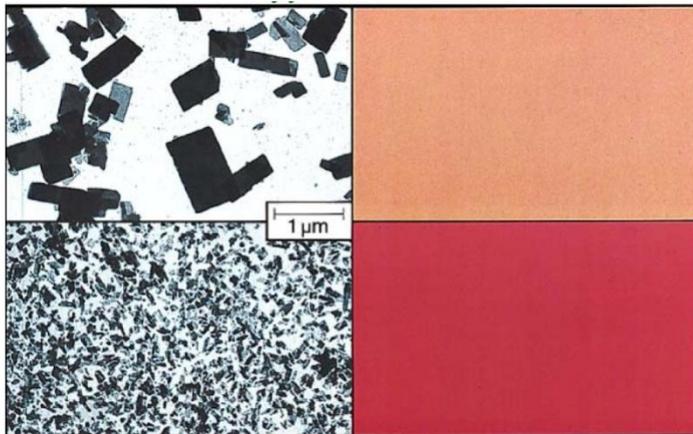


Figure 12: The effect of pigment particle size on the shade of the colour (Viluksela 2004a: 2).

In offset printing the ink film is very thin, of the order of 1,2-2  $\mu\text{m}$  and high colour intensities are required for pigments in order to maximize the colour gamut available. In addition, in multicolour printing where cyan, magenta and yellow ink films are overprinted, pigments must have high transparency (low opacity) for the light must pass through all the three ink layers and then reflect back through them to the eye, with absorption only of their complementary colours. Both of these properties, colour strength and opacity, are determined by particle size. (Thompson 2004: 377.)

Opacity is a function of scattering and if the scattering is so intense that no light passes through the material, it is said to be opaque. Very small particles scatter very little light and accordingly scattering increases with increasing particle size until these reach a size which is in the order of the wavelength of light, where after, scattering again decreases. This also means that the opacity of an ink pigment is maximum at around half the wavelength of light (200-400 nm), falling off on either side of the particle size spectrum. In addition, colour strength (absorption coefficient) increases with decreasing particle size having a dramatic asymptotic rise at around 0,1  $\mu\text{m}$ . Figure 13 provides illustration of the effects of pigment particle size on its properties. (Thompson 2004: 377.)

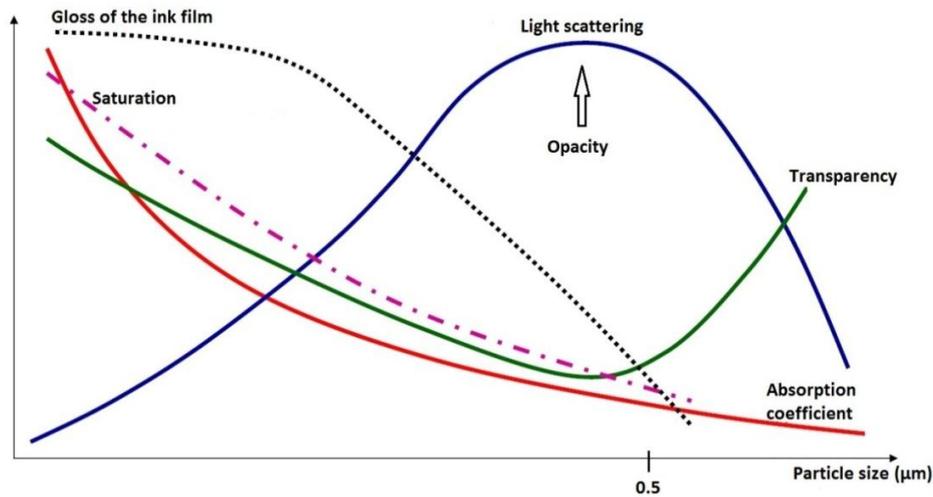


Figure 13: Effect of the particle size of a pigment on its properties (Viluksela 2004b: 25; Thompson 2004: 377).

#### *Particle size & rheological properties*

The particle size of the pigments affect not only the optical properties of ink, but it is also one factor that influences the rheological properties of a given pigment dispersion. Decreasing the size of the pigments will lead to an increase in the strength of any particle-particle interactions. This will increase the likelihood of agglomeration, and furthermore it will lead to an increase in the viscosity of the system as illustrated in Figure 14. In addition, increased particle size will also make the change in viscosity with increasing pigment volume concentration become more pronounced. (Kippax 2005: 3.)

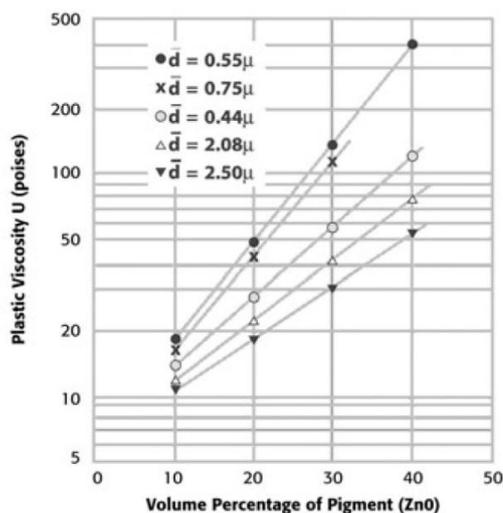


Figure 14: Viscosity as a function of pigment size and concentration (Kippax 2005: 3).

### Refractive index

The refractive index measures the bending (or refraction) of rays of light entering the pigment. It is an expression of the ratio of the velocity of light in vacuum to the velocity of light in another substance, in this case pigment. For example, the refractive index of rutile titanium dioxide is 2,76, which means that light travels 2,76 times faster in vacuum than it does in rutile. By definition the refractive index of a vacuum is 1, but in practice, air makes little difference to the refraction of light and has an absolute refractive index of 1,0008, so the value of the absolute refractive index can be used assuming the incident light is in air. Since light slows down when it enters a substance, the refractive index of a substance will always be greater than 1. (Natural pigments 2004.)

The refractive indexes affect directly to the opacity of a substance; this is explained in the section of transparency & opacity. The refractive indexes of pigments vary much more than the refractive indexes of vehicles. Inorganic pigments, such as titanium dioxide, have higher refractive indexes than organic pigments. Consequently, organic pigments are more transparent than inorganic. Some examples of the refractive indexes of printing ink components are given in Table 4. The notation air<sup>n</sup> medium denotes a ray passing from air into a medium of different optical density, such as glass or water. (Eldred 2001b: 127; Thompson 2004: 143.)

**Table 4: Refractive indices of materials used in printing inks (Thompson 2004: 143).**

Substance	air <sup>n</sup> medium	Function
Titanium dioxide	2,70	white pigment
Calcined china clay	1,60	extender (filler pigment)
Alumina hydrate	1,50	extender (filler pigment)
Linseed stand oil	1,50	ink vehicle
Maleic resin	1,51	binder

### **Transparency & Opacity**

Opacity or hiding power, of a given pigmented system is a measure of its ability to completely mask the underlying substrate. It is determined by how an object reflects or scatters light. Transparency in a contrast means, that pigments selectively absorbs specific bands of wavelength of light and allow transmission of unabsorbed light. Lack of transparency is called opaqueness, i.e. opacity is pure. (Faigle 2010:33; Oittinen & Saarelma 1998: 272.)

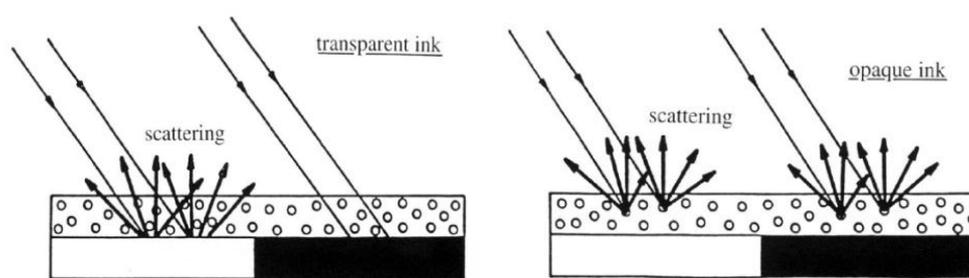
Scatter is primarily dependent upon the refractive indexes of the pigment and the medium in which it is dispersed. Light scatter within any medium is as function of the difference in the refractive indices between the pigment and the medium; if the ratio is close to 1, in the vehicle in which it is suspended, the light of rays pass through the ink without being bent and consequently the whole system appears transparent. If the ratio is significantly greater than 1, the rays of light will be bent and scattered as they pass through the pigment, and thus the ink film will be more or less opaque. The greater the difference in refractive indexes, the more opaque the ink film is. However, opacity is a complex phenomenon that is also affected by the particle size and shape, degree of aggregation and the wavelength of the light. For maximum opacity a particle size 0,2-0,4  $\mu$ , or about half the wavelength of light, is necessary as Figure 14 shows. (Eldred 2001b: 127; Kippax 2005: 2; Leach & Pierce 2007: 102.)

Particle size plays also an important role on transparency and opacity; an enormous number of individual reflecting surfaces are necessary for total diffuse scatter of light. If the particle size is too small, however, the rays of light pass by without being scattered. Every pigment has a particle size at which scattering power reaches maximum, and it can be calculated from the following equation, which is fairly correct for the visible light:

$$D = \frac{\lambda}{2,1} (n_1 - n_2),$$

where  $D$  is the optimum particle diameter,  $\lambda$  the wavelength of irradiation and  $n_2$  the refractive index of the pigment and  $n_1$  the refractive index of the medium. (Hocken 2000: 5.)

Since the average particle size of a pigment is close to wavelengths of visible light, i.e. 0,4-0,7  $\mu\text{m}$ , the ordinary laws of optics cannot be applied, and radiation is scattered by the small particles. This is illustrated in Figure 15; with opaque inks, the pigments scatter the light, and with transparent inks, the substrate is involved as well. (Eldred 2001b: 127; Faigle 2010: 33.)



**Figure 15: Formation of transparent and opaque inks (Faigle 2010: 33).**

As explained above, opacity of a pigment is closely related to its ability to scatter incident light, but absorption also plays part, and so the overall opacity depends upon both of these properties. In the case of a high opacity white pigment, little or no absorption occurs and the opacity is due almost entirely to scatter. On the other hand, very fine pigments, such as carbon black, are opaque due to their high light absorption. (Eldred 2001: 127; Leach & Pierce 2007: 102.)

### **Tinctorial strength**

Tinctorial strength, also known as colour strength, of a pigment is a measure of its ability to impart colour in a system; to absorb incident light and colour a medium. The initial tinctorial strength of a pigment is related to its chemical composition, particle size and distribution. Figure 16 shows the relation between the pigment particle size and the ability of a pigment-vehicle system to absorb visible electromagnetic radiation, which has a large contribution to the tinctorial strength of a pigment in its application medium. The ability of a pigment to absorb light, and therefore the tinctorial strength, increases

with decreasing particle diameter and accordingly increased surface area, until it approaches the point at which the particle is entirely translucent to light. Beyond this point, the particle size does not improve the tinctorial strength. However, unusual optical characteristics may be found in transparent systems that for instance printed layers are. These characteristics may change the relation between tinctorial strength and particle size. (Field 1999: 139; Herbst & Hunger 2004: 118-119; Leach & Pierce: 102; Wet-ting and dispersing additives 2007: 2.)

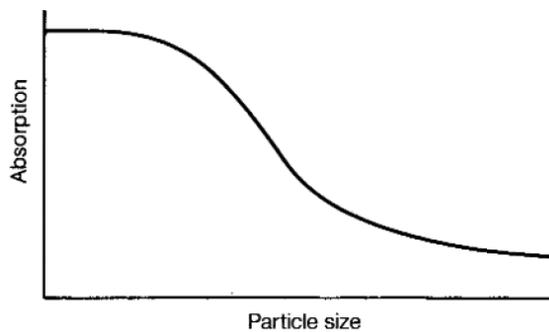


Figure 16: The relation between the particle size and absorption ability of a pigment (Herbst & Hunger 2004: 119).

In practise, however, tinctorial strength is commonly used as a measure of the amount of ink per unit area required to produce a given strength of colour. Hence, the actual value defined this way also depends upon the film thickness and the concentration of pigment in the ink. With high-tinctorial-strength inks thin ink films may be run, thus minimizing dot gain and maximizing resolution. In addition, trapping and drying problems are probably decreased and less ink will be consumed. Possible weaknesses with high-tinctorial-strength inks include higher cost, lower gloss, higher viscosity, and the increased forces required to split ink films. Moreover, consistent colour strength is more important than the absolute level. (Field 1999: 139; Pierce & Leach 1993:102.)

### Specific gravity

The specific gravity of a pigment describes the ratio of the weight of a given volume of the pigment to the weight of the equivalent volume of water. Simply said, it is the weight of the pigment to the weight of the water it displaces in solution (ink). The specific gravity of water is 1 whereas all pigments have it greater than 1. This means that they weight more than the volume of water they displace, and therefore sink in

solution. Inorganic pigments have higher specific gravity than that of organic pigments. (Eldred 2001b: 127; MacEvoy 2005.)

### Specific surface area

Specific surface area of a pigment is measured in squared units ( $m^2$ ) and is usually defined for 1 gram of pigment. Typical values for example for organic pigments are between 10 and  $130m^2$ . The surface area of pigment is fundamentally affected by the particle size; with a fixed quantity or weight of pigment the smaller particle sizes create a larger total surface area, as illustrated in Figure 17 with a single cubic crystal of pigment. (MacEvoy 2005; Surface area & Oil absorption 2011.)

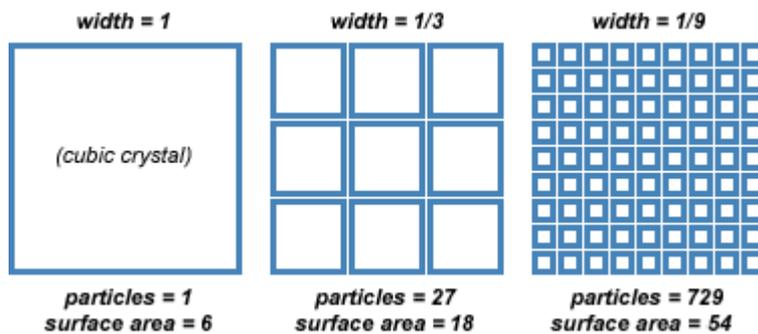


Figure 17: Effect of particle size on pigment surface area (MacEvoy 2005).

The surface area is closely linked to the pigment's demand for vehicle. As the size of particle of pigment is small, the area of surface becomes large and more vehicle is required to wet each of pigment particles. Larger particles have a smaller surface area and therefore a lower demand for vehicle. Large surface area is also related to the tinctorial strength of pigments; the greater is their effective surface area, the higher their absorbing power and consequently the higher the tinctorial strength. (MacEvoy 2005; Surface area & Oil absorption 2011; Wetting and dispersing additives 2007: 2.)

### Wettability

Wettability of a pigment tells how easy the pigment is to wet by the ink vehicle. With offset inks complete pigment wetting is required to prevent breakdown and emulsification in dampening solutions. The wettability can be increased by surface treatment of pigments with low-surface-energy materials. (Eldred 2001b: 127.)

## Dispersibility

In addition to wettability, pigment particles must also be dispersible. The incorporation of the pigment agglomerates into the medium of application is known as pigment dispersion. It refers to the distribution throughout the application material, accompanied by a reduction of the agglomerates; agglomerates (Figure 18a) are broken down into primary particles (Figure 18b) and smaller aggregates by the dispersion process. Unsuccessful dispersion may lead to flocculation (Figure 18c). (Kippax 2005: 3; Wetting and dispersing additives 2007: 6.)



**Figure 18:** Schematic diagram of (a) agglomerated, (b) dispersed, and (c) flocculated pigments (Wetting and dispersing additives 2007: 6).

A pigment is more or less easily dispersible depending on the mechanical forces that have to be applied in order to develop the required application properties in a given pigment or pigment-vehicle system. This performance is largely controlled by the pigment particle size distribution; as shown in Figure 19 a dramatic change in the dispersibility will be observed as the pigment particle size decreases. For large particles the adhesion force between particles is small and therefore dispersion is more easily achieved, whereas for particles below 20 $\mu\text{m}$  in diameter, colloidal forces become dominant and the adhesion forces increase rapidly. To overcome this diminished dispersibility it is necessary to control the surface chemistry, either by surface coating of pigment or by changing the properties of the vehicle system. (Herbst & Hunger 2004: 72; Kippax 2005: 3.)

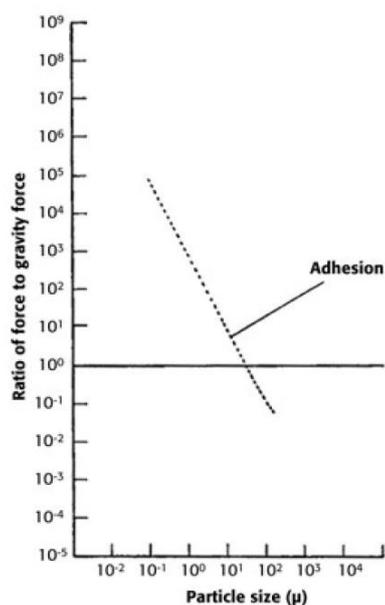


Figure 19: Force of adhesion between particles as a function of particle size (Kippax 2005: 3).

Dispersibility of pigment particles enables the vehicle to surround and separate the particles. Dispersibility also depends on the wettability, and the surface energy of the pigment should be compatible with the solvent and oils used in inks. In addition the strength of the pigment granules, among other things affects the dispersibility. The dispersion has effect on the behaviour of a pigment vehicle system; the better the dispersion of pigmented system the more the pigmented system will:

- exhibit increased tinctorial strength, particularly in white reductions;
- undergo a change in shade;
- be more transparent/less opaque;
- provide enhanced gloss; and
- increase in viscosity. (Eldred 2001b: 128; Herbst & Hunger 2004: 72; Thompson 2004: 326.)

### Texture

Texture describes the hardness or the softness of a pigment in its dry form. The pigment is soft if it rubs out easily to a smooth and soft powder, and if it feels gritty between fingers it is hard. (Eldred 2001b: 128.)

### Lightfastness

Lightfastness describes how fast a pigment fades when it is exposed to light. Many pigments, especially from the organic classes, have a tendency to fade in the presence of ultraviolet light, i.e. when the pigment lacks lightfastness. This must be minimized and good lightfastness is required where the printed end product is likely to expose to UV. Lightfastness is specified in a scale of eight steps, ranging from 8 (excellent) to 1 (very poor). For the scale being logarithmic, “good” is achieved already in level 5. The following Table 5 gives approximate indications on how long a certain degree of lightfastness stands up to the influence of daylight whereby the season and geographical position etc. play a decisive role. Pigments with high lightfastness are generally quite expensive. (Eldred 2001b: 128; Faigle 2010: 41; Lightfastness 2002: 1-2; Thompson 2004: 325.)

**Table 5: Lightfastness degrees. (Lightfastness 2002: 2).**

Degree of lightfastness	Summer	Winter
3	4 – 8 days	2 – 4 weeks
4	2 – 3 weeks	2 – 3 months
5	3 – 5 weeks	4 – 5 months
6	6 – 8 weeks	5 – 6 months
7	3 – 4 months	7 – 9 months
8	over 18 months	

Lightfastness of the final ink film depends on the chemical nature of the pigment and the thickness of the printed ink film. The alternation of lightfastness is influenced by many of the pigment properties; the chemical constitution, the concentration, particle size and distribution and crystal modification, among other things. Also the vehicle with its protective properties enveloping the pigment is an influencing agent. Inorganic pigments are more stable than organic ones. In general, black is the most lightfast of all the common inks. Blue and green organic pigments are more stable than red and yellow ones. (Eldred 2001b: 128; Faigle 2010: 41; Lightfastness 2002: 2; Thompson 2004: 325.)

### 3.2.2 *Types of pigments*

There are hundreds of different types of pigments produced. While some are formed by nature in mineral or vegetable forms, most of them are synthetic material produced from variety of chemicals. A simplified, though not ideal, classification is to divide the pigments into the two categories: organic and inorganic pigments. Of the large number of different types of pigments produced, only a few find their way into ink manufacture with its delicate needs and special demands. Many are uneconomical to produce while others do not meet the demands of tinctorial strength, particle size or other specific combinations of properties required for successful ink formulation. (Leach & Pierce 1993: 141; Thompson 2004: 326.)

This section is to introduce the most commonly used pigments throughout the ink manufacturing industry. As a head note Table 6 introduces shortly the features of organic and inorganic pigments. For their importance to this study, belonging in the class of inorganic pigments, white pigments and filler pigments are discussed in their own chapter: 4 Filler pigments.

**Table 6: Features of organic and inorganic pigments (Christensen 2003: 6).**

Organic	Inorganic
<ul style="list-style-type: none"> <li>• Wide range of heat and light stability performances</li> <li>• Generally bright, intense colours</li> <li>• High colour strength (colour effect per kilo)</li> <li>• Generally high ‘per kilo’ cost</li> <li>• Mostly translucent (few transparent, few opaque)</li> <li>• Generally difficult to disperse</li> </ul>	<ul style="list-style-type: none"> <li>• Most have very high heat stability</li> <li>• High lightfastness (resistance to fading)“</li> <li>• Many have relatively dull shades</li> <li>• Generally low ‘per kilo’ cost</li> <li>• Most have high opacity</li> <li>• Generally easy to disperse</li> <li>• Some contain heavy metals</li> </ul>

### Organic pigments

As the term organic refers, organic material are derived from “living organisms”. In practice, most of the organic materials are made from petroleum and a lesser amount is made from coal, trees, and animal or vegetable fats and oils. Synthetic organic chemicals are made by processing these materials. Organic pigments are the major source of industrial colorants, based on benzene, toluene, naphthalene and anthracene compounds. Typical classes include for instance the azo dyes and pigments that give the hansa yellow, benzidine yellows, permanent reds, lithol rubines and lake red C. In addition, the phthalocyanines give a variety of blue to green pigments including that what is used to formulate the cyan process ink. (Eldred 2001b: 135; Thompson 2004: 327.)

In general, the properties of organic relative to inorganic pigments are as follows:

- superior colour strength;
- brighter shades ;
- lower relative densities (less tendency to settle in the tin);
- soft texture (less plate wear); and
- high transparency (required for overprinting).

The disadvantages with organic pigments include the following:

- a large variation in stability to heat, light and chemicals;
- a tendency towards poor soap and oil resistance (vehicle components);
- a tendency to bleed in solvents; and
- some might be carcinogenic. (Thompson 2004: 327.)

The colour of organic substances and pigments is founded on atom configurations called chromophones that selectively absorb light. Examples of these are:  $-C=C$  (ethene),  $-C=O$  (ketone),  $-C=N$  (coal-nitrogen) and  $-N=N$  (azo) and their colour strengthening auxochromophores such as  $-SO_3$ ,  $-NH_2$  and  $-OH$ . For these organic colour compounds there is a connection between the structure of the molecule containing chromophores and auxochromophores and the wavelength of light absorption. Molecules with a great mass and close structure absorb long wavelength radiation (red),

and in contrary, straight-chain molecules with a small mass absorb a short wavelength irradiation. Figure 20 illustrates the relation between colour and structure of organic pigments. (Oittinen & Saarelma: 1998: 265-266; Viluksela 2004b: 18.)

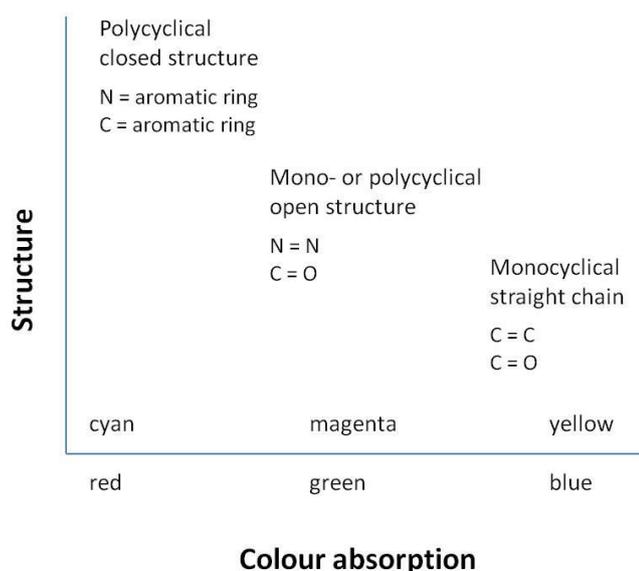


Figure 20: The relation between colour and structure of organic pigments (Oittinen & Saarelma 1998: 266).

### *Coloured organic pigments*

The pigment is the key colouring compound in an ink. Three very important pigments are those used in process colour printing inks: cyan, magenta and yellow. The most common yellow pigment is bezidine yellow and cyan pigment is phtalocyanine blue. Magenta pigments are rubines, naptols and rodamines. However, the selection of process colour pigments is based upon a number of considerations including for example lightfastness and spectral absorption. (Oittinen & Saarelma 1998; 266; Thompson 2004: 371; Viluksela 2004b: 20.)

Important property of process ink pigments is their well defined absorption peak, thus cyan absorbs strongly in the red part of the spectrum (reflecting blue and green light), the magenta absorbs in the green (reflecting blue and red) and the yellow absorbs in the blue (reflecting green and red). Thus, the criteria necessary for process colour printing is that the inks control the red, green and blue reflectance in a way that reproduces the redness, greenness and blueness of the original, as closely as possible. Ideal process ink

pigments absorb one third of the visible spectrum and transmit the other two thirds. (Field 1999: 124; Thompson 2004: 371-372.)

### *Organic black pigments*

Black pigments are very important, and not only because of the greater use of black ink compared to others, but also because black pigments are the most permanent. Black pigments are chemically inert, extreme fast to heat, light, acids, alkali, solvents and soaps. The most important black pigments are under the classification of carbon blacks which accounts for over 95% black ink usage. Carbon blacks are the most important pigment at all for they are the only pigments used in the manufacture of the most important printing ink, the black one. (Eldred 2001b: 130-131; Faigle 2010: 35.)

Carbon blacks are extremely fine in their particle size and with colour varying from a grey masstone (the undiluted colour) with blue undertone to a dense jet black masstone with brown undertone, dependent on the method of manufacture. In addition, the oldest pigment known, vegetable blacks are used as matt blacks, although they have been almost entirely replaced by furnace blacks, unless cost is a factor. (Eldred 2001b: 130-131; Leach & Pierce 2007: 187.)

Carbon blacks differ from each other in particle size, pH value and volatile matter content. In Figure 21 particle sizes of some carbon black pigments are shown. Structure, particle size and surface chemistry are all significant in the means of determining the behaviour of carbon black pigments in ink. The finer the particle size, the higher the viscosity. And the higher the tack of the ink vehicle, the more work is required to wet the carbon in order to produce eligible carbon dispersion. And as the particle size and other properties vary with different methods of producing the carbon blacks, ink properties depend upon the carbon black that is used. (Eldred 2001b: 131.)

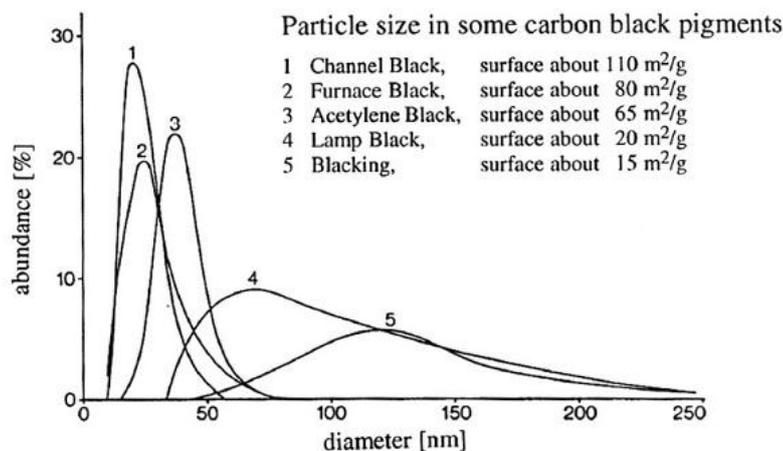


Figure 21: Particle size in some carbon black pigments (Faigle 2010: 35.)

### Inorganic pigments

The class of inorganic pigments is the earliest known to man. Although the use of inorganic pigments is declining, some of them still have a big role to play, especially in the packaging industry. Coloured inorganic pigments are not used in great extends anymore these days, but the most important classes of inorganic pigments, white pigments and extenders, are of great importance. For their significance in this study, they are contributed by their own chapter: 3 Filler pigments. (Thompson 2004: 326.)

Many of the inorganic pigments are formed by precipitation, by mixing chemical solutions that react to form the insoluble pigment, which further on precipitates, or settles out. First, the pigment is separated by filtration, washed to remove soluble salts, and finally either flushed into a varnish or dried. In general, inorganic pigments are not pure chemical compounds but complex mixtures which formulation conditions such as proportions, concentration, temperature and pH value, must be carefully adjusted and controlled to get the desired properties like colour and strength. (Eldred 2001b: 135; Thompson 2004: 326.)

Inorganic pigments are very hard and consequently they cause wearing of plate surfaces and doctor blades. In addition, they are typically difficult to grind and may have poor working properties. Nevertheless, the advantages are that they are opaque and therefore very useful when hiding power is required, lightfast, chemical resistant and cheap. (Thompson 2004: 326-327.)

### *Coloured inorganic pigments*

The main advantage in using inorganic coloured inorganic pigments is that they are relatively inexpensive. In addition, they have good opacity and lightfastness but can exhibit poor working characteristics and poor texture if not formulated properly. Coloured inorganic pigments containing chrome or lead, for example chrome yellow and orange, and cadmium yellow and red, have variety of desirable properties that made them useful in certain inks. However, the metals contained in these pigments have made their use very limited by various environmental and health regulations. Another common inorganic coloured pigments include iron blue, ultramarine blue and magnetic black. (Eldred 2001b: 136-137.)

The colour of inorganic pigments is also a function of chemical composition, but it is strongly influenced by the crystal form of the substance. Inorganic coloured compounds are the salts of transition elements Sc (Scandium), Ti (Titanium), V (Vanadium), Cr (Chromium), Mn (Manganese), Fe (Iron), Co (Cobalt), Ni (Nickel) and Cu (Copper) and compounds that contain an element representing two degrees of oxidation such as Fe (II) Fe (III) cyanides. Subsequently, the most important coloured inorganic pigments are introduced. (Mäkelä & Co. 2005: 186-187; Oittinen & Saarelma 1998: 266.)

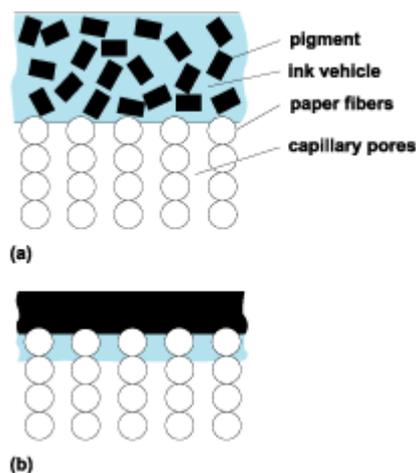
### **3.3 Drying mechanisms of inks**

After the ink film has been printed onto a substrate, it must be able to dry, as quickly as possible. If the ink doesn't dry, it is useless. In the drying process, two phases can occur: the ink setting phase and the actual drying phase. After the setting phase has occurred, the ink is touch-proof whereas the drying phase results in a rub-resistant layer. The two phases can use either the same or different mechanisms. For example, the conventional sheet-fed offset inks involve two different mechanisms; in the setting phase filtering and evaporation is used whereas the actual drying uses polymerization by oxidation. (Oittinen & Saarelma 1998: 282; Thompson 2004: 344.)

All together, there are at least eight different methods by which printing inks can dry: absorption, evaporation, oxidation/polymerization, radiation polymerization, catalytic polymerization, gellation, infrared radiation, and precipitation. Lithographic inks set and dry by all of these methods except precipitation. In fact, several methods may occur with one type of ink. In the case of web inks used in offset, flexographic, and gravure printing processes, setting and drying usually happens by heating the ink to evaporate the solvent. Newspaper printing inks do not have any true drying stage, as the ink is simply absorbed into the paper. (Eldred 2001b: 207.)

### Absorption

Absorption represents actually no true drying; it is basically just penetration of the ink into the printing substrate as illustrated in Figure 22. For example, most news inks dry primarily by absorption, and for no true drying, the black pigment in the news ink comes off on the reader's fingers the next morning, or even weeks later. Absorption occurs also in many other printing methods, actually it runs through whenever ink is printed on porous material, such as paper and board; the solvents in gravure, flexo, heat-set, and even sheet-fed offset inks penetrate to some extent, and the viscosity of the ink remaining on the surface of the paper increases. (Destree 1994: 13:12; Eldred 2001b: 210; Thompson 2004: 344.)



**Figure 22: Ink drying by absorption setting. (a) Ink film on uncoated paper immediately after printing. (b) Ink film after absorption of the vehicle by the paper (Bassemir 2008).**

## Evaporation

Evaporation of the solvent is an important mechanism of ink setting and drying; the ink is dry when the solvent is evaporated. The binder left behind bonds the pigment to the printing substrate. Evaporation occurs in webs printed by any process. For example in heat-set web offset printing, the absorption assists in the setting of the ink, but evaporation of solvent is the primary method of drying. (Destree 1994: 13:13; Eldred 2001b: 210.)

Evaporation is simple in its concept; in the process molecules escape from the surface of the liquid into the air and away from the mother liquid (Figure 23). As evaporation occurs very rapidly the control of this drying method is crucially important if the print is to be delivered dry without overheating it. This to be said, the evaporation is in practice assisted by supplying heat energy to the printed ink film. (Eldred 1994: 211; Thompson 2004: 345-346.)

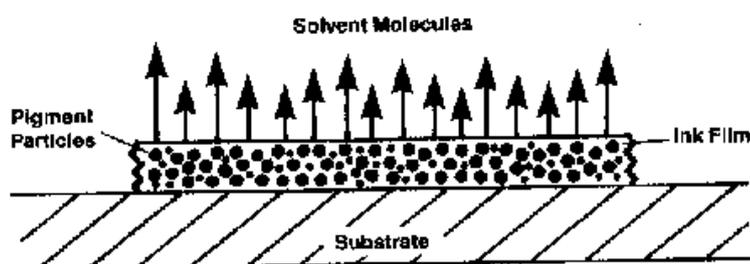


Figure 23: Schematic diagram of ink drying by evaporation. The solvent evaporate, leaving a dry ink film on (Casama & Schall 2002).

## Oxidation/polymerization

Oxidation is the classical drying mechanism for lithographic inks and it involves the oxygen-induced free radical polymerization of unsaturated (drying) vegetable oils such as linseed and tung. It is a chemical process, where these oils react with oxygen in the air to form a chemical called a hydroperoxide. This process can be catalyzed further or accelerated by a small amount of appropriate metal, usually transition-metal such as cobalt or manganese salt. As a result, the hydroperoxide forms a free radical, which reacts with another oil molecule, forming a molecular chain that continues to grow. Meanwhile the chain gets longer and longer, the ink flows less and less readily until,

after 2-24 hours, there are enough chains formed so that the ink flows no longer, i.e. it is dry. (Destree 1994: 13:12-13:13; Leach & Pierce 2007: 346-347.)

The oxidation/polymerization drying method is affected by many different factors including the following: the kind of pigment, the kind and amount of drier, the type of varnish in the ink, pH of the paper, and the pH of the dampening solution, among others. Consequently, if drying problems occur, it can be very seldom blamed on one factor only. (Leach & Pierce 2007: 346-347.)

### **Radiation polymerization**

Inks containing acrylates, especially reactive monomers, react very quickly under the influence of ultraviolet radiation or electron beam radiation. Unlike oxidation/polymerization, which requires several hours, radiation polymerization is complete in a fraction of just a second. Although these inks cost more than conventional sheet-fed or web inks, their use means increased production, the benefits of no spray powder is required to prevent set-off, and for applications with varnished prints the result has a smoothness that cannot be achieved by conventional sheet-fed inks. (Eldred 2001b: 213-214.)

### **Catalytic polymerization**

If the printing substrate, such as metal cans or glass, can withstand the heat, a slow-reacting polymerization can be used to cure the ink. For example in the case of beverage cans and bottles, melamine formaldehyde polymers can give a hard, resistant print or varnish on them. To achieve this hard coating, melamine formaldehyde prepolymer is mixed with a catalyst that initiate the polymerization on baking. (Eldred 2001b: 214.)

### **Gellation**

Gellation is the method for quickset inks to dry. In the mechanism of gellation ink's viscosity is increased so that it will set to form a gel. These inks contain a gel varnish that has been cut to desirable body with a relatively small amount of solvent. When the solvent is absorbed by the printing substrate, the gel varnish gets back to its original high body and the ink has set. (Destree 1994: 13:14; Eldred 2001b: 210.)

### **Infrared radiation**

Infrared radiation (IR) is a not mechanism of drying but a method of speeding the process and it can be used to accelerate both the setting and drying of inks. It aids both these steps by warming the printed ink. As a result, the drying time required for sheet-fed inks can be reduced by 76 %, and prints are often ready for cutting in less than an hour. (Destree 1994: 13:14; Eldred 2001b: 214.)

## **3.4 Printing ink properties**

### ***3.4.1 Optical properties***

The most important optical properties of an ink film, gloss and colour, will be discussed as a part of the print quality, in chapter 5. In addition, the transparency and opacity have already been explained in the context of pigments under the section pigment properties. Hence, chapter 3.4 is only to cover some of the most important rheological properties of ink.

### ***3.4.2 Rheological properties***

Rheology studies the flow and deformation of matter. The aim of rheological science is to define and evaluate such terms as consistency, viscosity, tack, flow, stiffness and body, in terms of the physical properties of the materials. Related to the printing industry the main areas of interest are the flow of liquids (inks and varnishes) and the control of viscosity, body and tack. This chapter studies the main rheological properties that are relevant to lithographic, and therefore to offset, inks. These include viscosity, yield value, thixotropy, flow and tack. (Leach & Pierce 2007: 345 & 766.)

### **Viscosity**

Viscosity is a measure of the resistance of a fluid to flow; the greater the resistance to flow, with a given applied force, the greater the viscosity. Scientifically viscosity was first considered by Sir Isaac Newton who reasoned that if a certain amount of force would turn a stirrer in a liquid, then doubling the force would double the speed the

velocity of flow. In ideal liquids, called Newtonian liquids, the shearing force is directly proportional to the amount of shear. If no stress is applied, no strain is produced and the liquid does not flow. As a resultant the graph relating shear stress to shear strain is a straight line passing through the origin. The higher the viscosity, the higher the slope in the rheogram as Figure 24 shows. Table 7 provides information for the magnitude of viscosity for different types of inks. (Leach & Pierce 2007: 767; Thompson 2004: 358-359.)

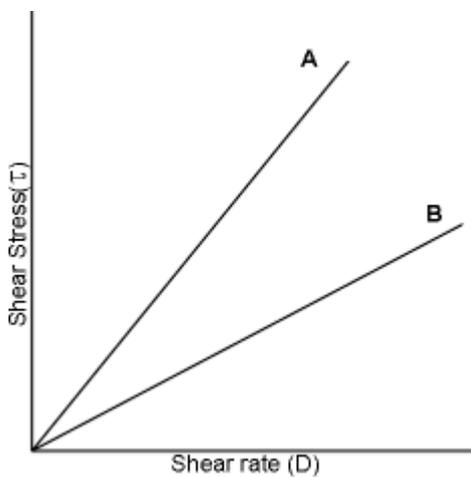


Figure 24: Rheogram for Newtonian liquids. A - high viscosity, B - low viscosity (Dittmer & Mayer 1997).

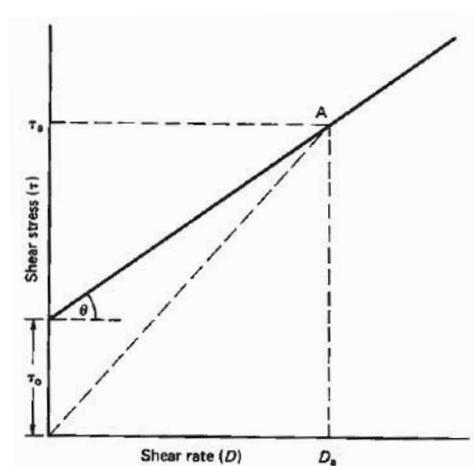
Table 7: The order of magnitude of viscosity in different types of inks. (Oittinen & Saarelma 1998: 275.)

Ink type	Viscosity, Pas (room temperature)
Sheet-fed offset	10-50
Heat-set offset	5-15
Newspaper offset	2-10
Flexo	5-50
Gravure	5-50
Letterpress	0,1-10

### *Deviations from non-Newtonian behaviour*

Many liquids, however, do not respond to the shear as the Newtonian liquid and have ratios of shear stress to shear strain that are not constant. In the case of inks, the introduction of pigments, resins, dryers and so on creates liquids or semiliquids (pastes) that have complex interactive structures that produce considerable deviations from Newtonian behaviour are produced. This phenomenon is due to particle association, by chemical bonding and physical interaction during flow and they are unable to flow at very low applied shear stress because they have to overcome a number of mutually attractive forces, and entanglements, before they are able to move. These liquids are called shear-dependent or non-Newtonian. (Eldred 2001b: 160; Leach & Pierce 2007: 768; Thompson 2004: 362.)

Rheogram in Figure 25 illustrates the ideal behaviour of plastic viscosity; the flow commences only when the shear stress reaches a specific value, in this case  $\tau_0$ . This finite amount of force is also known as the yield value. During the period from a value of zero to the yield value, the system is absorbing the applied stress and using it to break down the attractive forces holding it together in a pseudosolid state. When the shear stress is great enough, at the point  $\tau_0$ , it overcomes the internal forces in the ink and begins to flow. Once flow starts it is exhibited in a Newtonian manner, and plastic viscosity is also known as the apparent Newtonian viscosity. (Leach & Pierce 2007: 769; Thompson 2004: 363.)

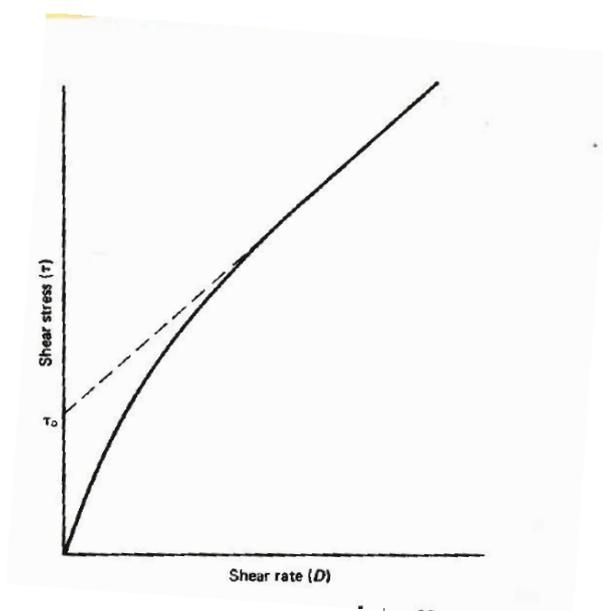


**Figure 25: Ideal plastic substance (Leach & Pierce 2007: 769).**

Plastic viscosity occur mainly with very crowded disperse substances such as heavily pigmented inks. These inks also tend to be thixotropic which is discussed hereafter. (Thompson 2004: 363.)

### *Pseudo-plastic flow*

In the case of pseudo-plastic substances the flow curve is non-linear, indicating that the apparent viscosity decreases with increasing shear stress. These pseudo-plastic substances are said to be shear thinning. However, at the higher shear rates the curve becomes approximately linear and in the ink industry this portion of the curve is extrapolated to the stress axis, as shown in Figure 26. (Leach & Pierce 2007: 770; Thompson 2004: 370.)



**Figure 26: Pseudo-plastic substance (Leach & Pierce 2007: 780).**

Pseudo-plastic flow occurs with long-chain molecules and can be imported into inks where long-chain solvents and oils are used in the formulation. (Thompson 2004: 364.)

### *Dilatant flow*

Dilatant substances become more solid rather than more fluid, under the increasing shear stress; the apparent viscosity increases with increasing shear stress (Figure 27) Dilatancy occurs when particles in the fluid pack and form rigid structures and hence it is associated with inks that have a high proportion of pigment or extender. Dilatant

substances would be useless as lithographic or letterpress inks as they cannot be used for fast running presses since the ink would fail to distribute properly on the inking system, retard the movement of inking rollers and could damage the press. Dilatancy may sometimes be found in stiff pastes of very high pigment concentration that are designed to function as the base of inks to which varnishes are added in preparing an ink for printing. (Leach & Pierce 2007: 771; Thompson 2004: 364.)

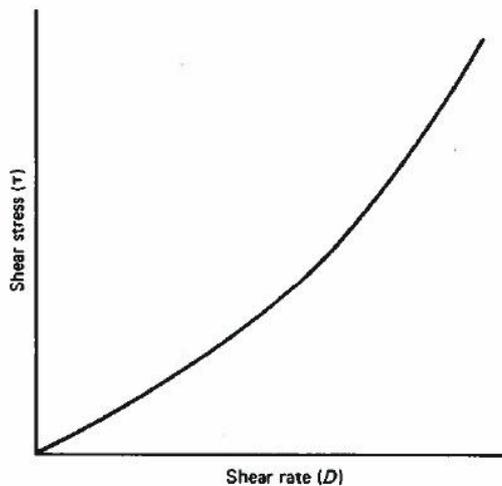


Figure 27: Dilatant substance (Leach & Pierce 2007: 772).

### *Thixotropy*

Thixotropy refers to time-dependent breakdown in viscosity. It is assumed in flow curves, such as those for plastic, pseudo-plastic and dilatant flow in Figures 25-27, that the breakdown of structure and its restoration are instantaneous. This is true for some materials, but in the case of most printing inks among many other substances, the process of breakdown and especially restoration of structures can take a measurable amount of time, leading to a condition of hysteresis in the ink. Hysteresis refers to the dependence of a system not just on its current environment but also on its past. (Leach & Pierce 2007: 772; Sethna 1994; Thompson 2004, s. 365.)

Thixotropy occurs when the viscosity of a substance decreases with time when a shearing stress is applied at a constant rate. On the other way around, the viscosity then increases when the shearing action is removed. Inks that have been worked on the press rollers have a lower viscosity than inks that are allowed to stand on paper. Hence, thixotropy has an effect on setting of paste inks after they have been printed. Thixotropy

also contributes to the problems encountered if additives are failed to mix thoroughly; without working, the ink is too stiff and the additives are not uniformly distributed. (Eldred 2001b: 164; Thompson 2004: 365.)

#### *Visco-elasticity*

Whereas a purely viscous liquid will move on application of a minimal stress and the deformation remains on removal of the stress, an elastic solid will recover its original form immediately on removal of the stress. Most materials contain both of these characteristics and are called visco-elastic. Most inks come within this classification; they have an instantaneous deformation component in the flow. At low speed elasticity may be developed by pigments structures, and at high speed this may be developed by binder molecules. Elasticity influences dot formation and ink splitting, and moderate elasticity appears to be advantageous. (Leach & Pierce 2007: 774; Oittinen & Saarelma 1998: 276.)

#### *Temperature coefficient of viscosity*

Flow behaviour is strongly dependent on temperature and hence the viscosities of all liquids change rapidly with the temperature. The viscosity of liquid is always reduced when the temperature is increased. The change of viscosity per degree Celsius change in temperature is called temperature coefficient of viscosity, and is characteristic of a particular liquid. For inks this coefficient is about -10 % per degree Celsius. This means that for example increase of 8 °C will reduce the viscosity of the ink by about 50 %. The indication of this example is obvious; the control of temperature in the printing presses is critical. (Eldred 2001b: 162; Thompson 2004: 363.)

In the case of lithographic inks, the temperature coefficient of viscosity helps the ink to set. When the ink passes from warm ink rollers onto cool plates and blankets, the occurring cooling of the ink greatly increases its viscosity. Most of the energy fed into offset printing press is converted into heat on the ink rollers as they distribute and split the ink. This heat helps then to make the ink adequately fluid to flow readily, and this is a weighty reason for the relatively complicated inking system found on offset printing presses. Furthermore, when the ink cools in going from roller to plate to blanket to

printing substrate its viscosity increases rapidly, contributing to the goal of printing dry with wet ink. (Eldred 2001b: 163-164.)

### **Tack**

Ink tack defines the stickiness of an ink and is an experimental quantity as the resistance of a thin ink film to splitting. The tack of an ink is a major factor influencing its transfer to the printing substrate and it is relevant particularly in the case of lithographic inks. With fast running printing presses the tack must be below the critical point where the ink will pick the paper at the required printing speed. However, it should also be as great as possible, as high-tack ink results in less increase in tonal values (dot gain), better water stability in the ink, thus cleaner prints, and higher ink transfer in offset printing. A tacky ink has less tendency to waterlog or break down and emulsify in the dampening solution, but the tack is always altered by emulsification with water or moisture picked up during printing. (Eldred 2001b: 167-168; Nießner 2000: 8; Pierce & Leach 1993: 786; Oittinen & Saarelma 1998: 277; Thompson 2004: 366-367.)

In multicolour printing where one ink film is trapped on top of another which is still wet, the degree of this acceptance will depend on the relative tacks of the inks. The simplified general principle suggests that it is desirable that once the first ink down is successfully trapped onto the paper, subsequent colours must have progressively lower tack values so that they are pulled from their printing surface onto the substrate rather than reverse – back-trapping. If back-trapping occurs, ink is pulled back of the print, removing some of the previous layers with a consequent loss of colour balance and printing control. (Pierce & Leach 1993: 797; Thompson 2004: 367.)

Ink tack is not understood as well as viscosity, and there is not necessarily a direct and simple relationship between them two. A very rough general relationship between tack and plastic viscosity suggests that extremes of high and low plastic viscosity are usually related to high and low tack values respectively. (Pierce & Leach 1993: 787; Thompson 2004: 363-367.)

### **3.5 Offset inks – characteristics**

The theory of the lithographic offset printing process has been dealt with in chapter 2 of this study, and the general aspects of printing inks in previous sub-chapters under chapter 3. In this sub-chapter the characteristics of offset printing inks together with their properties and the raw materials used, will be examined. Furthermore, as sheet-fed offset inks are of the greatest importance within this study, more stress is laid on discussing them.

#### **3.5.1 *General characteristics***

As lithography offset printing relies in a chemical distinction between the image and non-image, it requires application of an aqueous fountain, dampening solution, to active and to maintain the distinction between ink-accepting image areas and ink-repelling non-image areas. The image and non-image areas are differentiated by the differences in surface energies and surface tensions. For the ink succeed in wetting the image areas, the surface energy of the plate coating must be greater than the surface tension of the ink. Also, when the ink and dampening solution have widely different surface tension values, they will be immiscible as liquids and the ink will effectively be rejected from the dampened, non-image areas. (Leach & Pierce 2007: 343-344; Thompson 2004: 332.)

In practice, however, the relationships between ink and dampening solution are more complex than what was explained above because under the high shearing action in the roller nips, the two are milled together and some emulsification of water into ink takes place. Indeed, to perform well, an offset ink must emulsify water to some extent. If it does not, the ink will not transfer properly on the ink rollers, and they become stripped of ink. On the contrary, if an ink emulsifies too much water, or too large droplets, it becomes short and again fails to transfer well; the ink is waterlogged. The tendency of the ink to emulsify water is determined by all of its compounds, but predominately by those in the varnish. (Eldred 2001a: 30; Leach & Pierce 2007: 344; Thompson 2004: 333-334.)

In order to achieve the required ink/water balance, the degree of emulsification must be carefully controlled. Achieving this and at the same time retaining all the other necessary properties of the ink are the essence of offset ink formulation. Overall, the demands for offset inks are greater than for other processes due to the presence of the dampening solution; their water emulsification should be within well defined limits. (Leach & Pierce 2007: 344; Thompson 2004: 333-334.)

### **Drying mechanisms**

Offset inks dry by the methods of penetration, oxidation/polymerization, evaporation and chemical reaction. However, for the ink films being relatively thin and considerable amounts of fount are present in the ink film, it is a troubled thing to define the exact method of how each type of ink dries. This is especially the case for sheet-fed offset inks. Whereas the web-offset cold-set inks “dry” solely by penetration and heat-set inks by evaporation of the solvent phase, sheet-fed offset inks dry by a mixture of processes which may be categorized as penetration, quick-setting/phase separation and oxidation/polymerization. (Leach & Pierce 2007: 346 & 390.)

Most offset ink vehicle systems consist of film-forming resin components like drying vegetable oils, and distillates such as mineral oils. Mineral oils do not polymerise as drying oils do, and for these components the drying occurs via penetration into absorbent substrate separating them from the ink constituents. Also, in general, for uncoated papers and boards penetration is the first phase of the drying cycle. After the distillate contained in the ink is drawn into the paper leaving the resin and higher viscosity materials, such as alkyds, on the surface of the paper, it rapidly rises in viscosity to the point where the printed ink film becomes immobile. However, final drying to a hard, rub resistant film then proceeds via the mechanisms of oxidation/polymerization, which is relatively slow process, but can be accelerated by adding catalysts. On coated papers, for example, this chemical drying should be largely complete after about 6 hours. (Leach & Pierce 2007: 391; Nießner 2000: 2-3.)

In general, offset inks represent a major compromise between the conflicting requirements of press stability and drying. Whereas the former demands that thin ink films must retain fluidity throughout the distribution and transference process, the latter

requires rapid formation of hard, solid ink film at only slightly lower ink film thicknesses. Hence, setting and drying properties may be jeopardized and among the specific difficulties encountered are set-off, carry-over piling, slow drying and poor rub resistance. (Leach & Pierce 2007: 426.)

### ***3.5.2 Required properties***

The expected properties of conventional offset inks have not changed substantially over the years although the achieved levels have increased. The properties of offset inks that are under greatest concern are as follows:

- stability on the rollers of the press at high press speeds;
- transference and trapping on print;
- speed of setting;
- rapid drying to a rub-proof surface;
- good colour strength;
- good print gloss;
- sharp reproduction of the image with minimum dot gain; and
- reduced press downtime and paper wastage.

Each of the inks has their own kind of balance between these properties as none can provide the best performance in all areas. It is in these properties that ink manufacturers products differentiates from each other, and one suppliers products may suit better an individual printer's particular needs. The grades of raw material used and the proportions will determine the performance of the ink. (Williams 200: 1.)

The nature of offset printing process requires certain properties of an offset printing ink. To achieve these requirements the raw material selection and formulation principles has to be specifically considered. These formulation principles are dealt later on within sub-chapter 3.5.3: Formulation principles. (Leach & Pierce 2007: 400.)

## **Rheological properties**

Sub-chapter 3.4.2 covers in detail the theory of ink rheology and consequently these topics are only outlined in this section concerning the offset inks particularly.

### *Viscosity*

Offset inks are non-Newtonian substances primarily due to the high pigment content present; un-pigmented offset varnishes frequently approach Newtonian behaviour. One very important feature of the non-Newtonian behaviour of offset inks is that they usually have a finite yield value; a distinct shear stress must be applied before any flow or deformation takes place. Those to be said, offset inks are paste inks with relatively high viscosities that are changed into the proper viscosity as it is worked in the inking system. Offset inks are generally also thixotropic; their viscosity depends not only on the shear rate but also on the previous shearing history of the sample under investigation. This means that offset inks thicken on standing, and this structure can be broken down by stirring. (Destree 1994: 13:2; Leach & Pierce 2007: 348-349.)

High viscosity, substantial thixotropy and high yield value, that are at stake with offset inks, can all produce problems in transferring the ink from the container to the duct of the press. The correct rheological properties are also critical for the long ink distribution train employed to roll out relatively viscous offset inks to an even film for application to the offset plate. Too high viscosity and poor flow may hamper distribution, particularly where the image demands rapid ink replenishment in certain areas. Generally, low viscosity and yield value will advance transference but these factors will however result in a greater physical dot gain in halftone printing. Rheology is also involved in many other complex ways in offset printing and if not carefully adjusted, may produce problems such as scumming and piling. (Leach & Pierce 2007: 349-351 & 425.)

### *Tack*

Tack is relevant in all stages where ink distribution or transference occurs. Too high tack may cause some form of rupture in the printing substrate since this may require less work than what splitting the ink film does. Consequently, it is clearly advantageous to use inks with low tacks especially with weak papers. However, very low tacks may

produce a variety of problems from the ink roller train right through to final print quality. Some examples are as follows:

- Insufficient cohesion to transmit the frictional forces across the printing nips, resulting in inadequate ink feed and distribution.
- Unsuccessful multicolour (wet-on-wet) printing if the initial colours printed are very low in tack – back-trapping.
- Dot gain. (Leach & Pierce 2007: 352-353.)

### ***3.5.3 Formulating principles***

The nature of offset printing process imposes certain fundamental requirements on the chemical, physical and strength characteristics of an offset printing ink. To achieve these requirements the raw material selection and formulation principles have to be specifically considered. This section is to concentrate on sheet-fed offset printing inks and their formulation contents; vehicle systems, solvents/diluents, and additives. (Leach & Pierce 2007: 400.)

A typical offset ink could be expected to contain:

- pigment that provides the colour (organic as well as certain inorganic pigments);
- filler pigments, such as calcium carbonate;
- vehicle system, like a combination of varnishes, resins and drying oils, driers and petroleum distillate solvents to adjust the viscosity and aid transfer; and
- additives such as waxes to improve rub resistance, and tack modifiers to grade tacks for multicolour printing. (Nießner 2000: 2; Thompson 2004: 334.)

One example of a typical quick-set sheet-fed offset ink formulation is provided in Table 8.

**Table 8: Example of quickset sheet-fed offset ink formulation (Eldred 2001b: 15 & 176.)**

Parts	Component
20	Phthalo blue
24	Rosin phenolic ester
24	Linseed oil
24	Petroleum distillate
6	Long-oil linseed varnish
2	Paste drier

### Pigments

Printing with offset process the thickness of an ink film is lower than with any other conventional printing process. Hence, it is essential that offset inks are produced at the highest colour strengths (tinctorial strength) possible. This requires careful selection of pigments that must be inherently strong and able to develop their strength when dispersed in offset ink vehicles. (Leach & Pierce 2007: 408.)

Dispersibility to fine particle size is essential not only for colour strength development but also to ensure that the presence of particles substantially bigger than ink film thickness is limited. In addition the pigments chosen must not produce unacceptable rheology in terms of too high viscosity, yield value or excess thixotropy. However, overriding all these requirements it is necessary that the pigments selected are fundamentally insoluble in, and un-reactive with, the aqueous/alcohol dampening solution employed within the ink. (Leach & Pierce 2007: 408.)

Some of the major pigment types which have the right performance to satisfy the fundamental demands of the offset printing process and which have established bulk use in offset ink formulations are:

- The process colour pigments for four-colour halftone printing:
  - Diarylanilide yellow (CI Pigment Yellow 12 ) and Benzinidine yellow (CI Pigment Yellow 13).

- Lithol rubine B (CI Pigment Red 57:1).
- Phthalocyanine blue BGS (CI Pigment Blue 15:3).
- Carbon black (CI Pigment Black 7).

The Hansa yellows, for example, are restricted in use because of their poor strength, rheology and transparency. However, for their soap resistance and good lightfastness they are used in some relevant applications.

- White:
  - Titanium dioxide (CI Pigment White 6), rutile grades.
- Extenders (filler pigments):
  - Calcium carbonate (CI Pigment White 18). (Leach & Pierce 2007: 408; Chemical Land21.)

### **The vehicle system**

As already discussed in in the section of vehicle system (2.1), the vehicle system is the component which has the most greatest effect on the physical properties of the sheet-fed offset ink, such as setting speed, gloss, viscosity, yield value, flow, tack, hardness of drying and emulsion formation. It will govern whether the ink will perform satisfactorily or not, and is therefore the single most important aspect of the ink formulation. In addition to resins and solvents vehicle systems for offset inks contain a number of additives to control the rheology and to promote drying to hard glossy finish. (Leach & Pierce 2007: 400; Thompson 2004: 338.)

Vehicles used in offset inks can be divided into two major classes; the oleoresinous (hard resin and drying oil alkyd) systems used to produce quick-set, heat-set and oxidation drying inks and the acrylate systems used in radiation curing inks. The latter is out of scope and this sub-section is restricted to a consideration of oleoresinous vehicles, whether drying exclusively by oxidation or by the quickset mechanism. However, it is worth noting here that while the pigments remain similar to those used in conventional inks, the other parts of the formulation differ significantly chemically. The solvents are low-viscosity monomers, capable of reacting in their own right and the vehicle is composed of oligomers, usually acrylates. Also the additives used in these

inks are special, including a large amount of photo-initiators. (Leach & Pierce 2007: 400 & 641.)

Quick-set vehicles are useful in sheet-fed printing where high production speed require rapid setting. These vehicle systems are composed of two liquids marginally soluble in each other, for instance high viscosity oil and a solvent. This is described in Table 9. When the ink is printed on a coated substrate, the low viscosity solvent is quickly absorbed by the coating and the high viscosity oils are left on the surface. (Leach & Pierce 2007: 400.)

**Table 9: Oxidation drying vehicle vs. quick-set vehicle (Leach & Pierce 2007: 400).**

Oxidation drying vehicle	Quick-set mechanism vehicle
Hard resin(s)	Hard resin(s)
Drying oil/alkyd	Drying oil/alkyd
	Petroleum distillate

### *Oils & Resins*

The resin chemistry used in offset inks must meet a number of fundamental requirements, such as:

- solubility in weak solvents;
- controlled water tolerance; neither fully miscible nor totally water repellent;
- cohesive; and
- low surface energy.

The range of resins which match with this demanding set of requirements is very limited. The vast majority of these hard resins used in oleoresinous systems fall into two categories; the modified rosin ester and modified hydrocarbon groups of resins. (Leach & Pierce 2007: 401.)

The varnish in offset inks may be a modified drying oil (with driers), a solution of a resin in a solvent, or it may be a combination of these. Sheet-fed inks contain varnishes made from linseed oil and alkyds or other resins that dry by oxidation/polymerization. Commonly used materials in offset ink varnishes are linseed oil, dehydrated castor, tung, or soya oils reacted with an alkyd or other synthetic resin. The majority of alkyds are long oil modified isophthalic esters of either glycerol or pentaerythritol. (Destree 1994: 13:7-13:8; Leach & Pierce 2007: 401.)

Vehicle components may be manipulated in order to achieve the optimum balance for the particular offset printing performance required. Within the limited range of chemistry available, combinations of materials are also executed sometimes to enable improved compromises to be achieved. One of the classic examples of this is the combination of modified rosin ester and modified hydrocarbon resins to achieve water tolerance properties. (Leach & Pierce 2007: 405.)

### *Additives*

In common with all other inks, offset inks are also usually modified with small percentages of various additives to improve the printability or the final properties of the ink film. The main classes of additives used in sheet-fed inks are:

- driers;
- anti-oxidants;
- waxes;
- anti-set-off compounds;
- lithographic additives;
- rheology modifiers; and
- extenders/fillers.

Only a few of the most important additives are shortly introduced here. However, for their importance, a separate chapter: 4 Filler pigments, is dedicated to discussing extenders and white pigments. (Leach & Pierce 2007: 409.)

Driers are used to accelerate the oxidation/polymerization of drying oils and drying –oil modified alkyds. Various types of driers, having different reactions or reaction rates, are used in sheet-fed offset inks. Normally all these driers are all based on transition metals for their ability to exist in stable forms in more than one oxidation state. (Leach, s. 410; Destree 13:8)

Anti-oxidants are used to control the oxidation drying potential to prevent skin formation in the ink in containers or ducts. They function by reacting with the free radicals formed during oxidation, thereby preventing polymerization occurring. Hence, their use is always a compromise between drying speed and the length of the time which the ink remains skin free. The main types used in sheet-fed inks are oximens, e.g. methyl ethyl ketoxine, substituted phenols, e.g. butylated hydroxyl toluene and quinines like hydroquinone. (Leach & Pierce 2007: 411.)

The use of anti-set-off compounds can prevent set-off either by protecting the ink surface or shortening the ink. For instance, compounds that contain wax or grease shorten the ink and thereby decrease gelling time and speed up its setting. The use of spray powder (starch) to prevent set-off is very common. It works by reducing contact between adjacent sheets as the grains of starch are large enough to separate the sheets from the ink film. The disadvantage is that the particles sticking to an ink film roughness the surface reducing gloss. (Destree 1994: 13:9-13:10; Leach & Pierce 2007: 412; Thompson 2004: 266 & 333.)

Additives used exclusively in lithographic offset inks are to control undesirable reactions between fount and ink that might jeopardize otherwise good machine performance of a basically good formulation. These additives will either increase or decrease the emulsification tendencies of an ink and there are a number of proprietary products available. For example oleates or amine derivates such as oleomides increase the water pick.-up and are effective emulsifying agents can improve lithographic performance. (Leach & Pierce 2007: 413.)

### Typical formulations for sheet-fed offset inks

The formulations of offset inks and vehicles vary depending on the intended use of the end-product and the exact method of printing, such as sheet-fed offset, and even then a variety of approaches may be applied. Hence, no right formula can be given to any application but all inks intended for that specific application will share a number of key characteristics such as viscosity, yield value and rub resistance. This section is to give some examples of the formulations of inks and varnishes for sheet-fed offset inks. (Leach & Pierce 2007: 413.)

Inks manufactured for printing on paper substrates use the quick-set mechanism followed by oxidation as the standard drying process. An example of a general-purpose quick-setting vehicle system is provided in Table 10 and a general purpose gloss vehicle system in Table 11. (Leach & Pierce 2007: 413-414.)

**Table 10: General purpose quick-setting vehicle system (Leach & Pierce 2007: 414).**

Component	Parts (total 100)
Insoluble rosin-modified phenolic resin	30
Hydrocarbon resin	5
High viscosity linseed alkyd	25
280-320 °C aromatic free distillate	20
260-290 °C regular distillate	19,5
Aluminum-based gelling agent	0,5

**Table 11: General purpose gloss vehicle system (Leach & Pierce 2007: 414).**

Component	Parts (total 100)
Soluble rosin-modified phenolic resin	42
Low viscosity linseed alkyd	22
280-320 °C regular distillate	35,25
Aluminum-based gelling agent	0,75

The exact proportions of these vehicles can be alternated to optimize the balance between gloss and setting speed as desired. In Table 12, an example of a complete ink formulation (sheet-fed offset) with the above vehicles is provided.

**Table 12: Sheet-fed ink formulation example (Leach & Pierce 2007: 414).**

Component	Parts (total 100)
Organic pigment	18
Gloss vehicle and/or Quick-set vehicle	67
Polyethene wax compound	5
Anti-set-off compound	3
Cobalt driers	0,5
Manganese driers	1
Anti-oxidant compound	0,5
280-310 °C distillate	5

One of the advantages of using two different vehicles in an ink formulation is that within a four-colour set individual inks can be optimized in terms of performance. For example to avoid carry-over piling, the first one or two colours are normally made to set slower than the subsequent colours. Depending on the desired properties the last colour can be made either very fast setting to prevent set-off or glossier to enhance the gloss of the final ink film. (Leach & Pierce 2007: 413-414.)

## 4 Filler pigments

Filler pigments, extenders and white pigments, are the single most important pigment classes in inorganic pigments. Dividing the line between these two is anything but precisely defined and therefore this chapter is to discuss them both. A guideline could be given that whereas the white pigments are white and opaque, extenders are transparent. But at the same time even pigments usually considered to be opaque are actually transparent in a highly refractive medium. Using a medium of high refractive index it can be shown that the most opaque colours, even lead white, appear transparent.

However, in the context of this study, the emphasis is on the pigments used as additives in inks playing the role of a filler (or extender). As this study is to examine the effects of filler pigments on offset inks, it is crucial to discuss them in detail and understand how they function in the ink. (Thompson 2004: 326.)

## **4.1 White pigments**

In general extenders are considered to be transparent or translucent rather than opaque, whereas white pigments are opaque pigments that reflect light from their surfaces and cover or hide the background on which they are printed. The most widely used white pigments in printing inks are based on Titanium dioxide. Other white pigments used less extensively include Zinc sulphide, Lithopone and Zinc oxides, among others. Different white pigments vary greatly in their cost, specific gravity, particle size and opacity when ground in ink vehicles. These pigments can be used either alone or in a combination with other pigments to add opacity or lighten the colour. In addition, as a precursor printed on transparent stocks, white pigments increase the brilliance of subsequent coloured ink films. (Charvat 2005: 146-147; Eldred 2001b: 136; Gooch 1997: 215.)

### **Titanium dioxide**

Titanium dioxide ( $\text{TiO}_2$ ), a brilliant white, opaque pigment, is by far the most important white pigment currently in use; it accounts for over 80% of all whites used. The most important attribute of titanium dioxide is its remarkably high refractive index, which enables it to produce opacity or hiding power far greater than any other white pigment. Table 13 is to introduce the refractive index of titanium dioxide compared to some other white pigments and extenders. In addition titanium dioxide is inert material that is resistant to everything, very lightfast and heat resistant. Thus, it has mainly replaced nearly all other whites. Titanium dioxide has also a high specific gravity and a particle size of about 0,2-0,3  $\mu\text{m}$ . For these qualities it has earned the status of one of the most widely used of all ink pigments as the advantages of its use are myriad. (Charvat 2005: 146; Eldred 2001b: 136; Leach & Pierce 2007: 190; Titanium dioxide pigments 2001: 12.)

**Table 13: Refractive indices of some white pigments and extenders (Titanium dioxide pigments 2001: 12).**

Pigment	Refractive index
Rutile TiO <sub>2</sub>	2,70
Anatase TiO <sub>2</sub>	2,55
Zinc sulphide	2,37
Lithopone 30%	1,84
Zinc oxide	2,02
Kaolin (China clay)	1,57

Titanium dioxide is available in various grades with coatings of zinc, aluminium, zirconium, or silica oxides to optimize opacity and to aid dispersion and durability. Two different crystal forms are available; rutile and anatase. Rutile form of titanium dioxide is the most widely used white pigment; it has the highest refraction index (2,7) of any material that can be manufactured in pigment form at a reasonable cost, making it the most efficient white pigment available. Rutile form is also harder, more abrasive, and durable than anatase. For its compact structure it also possess some important characteristics compared to anatase; higher refraction index, higher specific gravity and greater chemical stability makes it more abundant than anatase. Softer and less durable anatase has a refractive index of 2,55 making it less opaque than rutile. Figure 28 is to show the refractive scattering power of these two forms of titanium dioxide, and in addition some other white pigments and extenders are illustrated. (Charvat 2005: 146; Eldred s. 136; Leach & Pierce 2007: 190; Titanium dioxide pigments 2001: 12.)

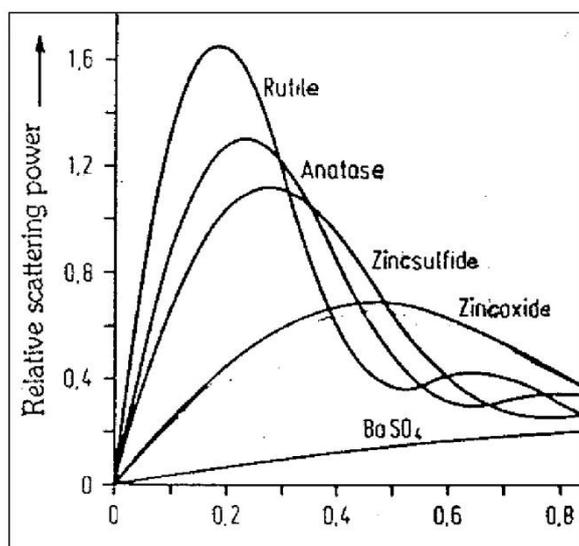


Figure 28: Scattering powers of some white pigments and extenders (Hocken 1997: 6).

#### *Composition and manufacture*

Table 14 shows composition of titanium dioxide. The production of titanium dioxide is carried out either by the sulfate or chloride processes. In the sulfate process, titaniferous feedstocks are roasted and ground and digested in sulfuric acid. Impurities are removed, and the resulting titanyl sulfate is hydrolyzed to form a feedstock that is subsequently calcinated and then subjected to downstream finishing. (Charvat 2005: 147; Leach & Pierce 2007: 191.)

Table 14: Composition of titanium dioxide (Leach & Pierce 2007: 191).

Component	%
TiO <sub>2</sub>	80-99.9
(Al, Si, Zr or Zn)O	0-20 + organic coating

In the chlorine process, titaniferous feedstocks are reacted with chlorine at high temperature and in the presence of a carbon source, to produce TiCl<sub>4</sub>, titanium tetrachlorine, and other metal chlorides. TiCl<sub>4</sub> is then purified and subsequently burned in high-temperature oxygen to produce TiO<sub>2</sub>. There is some reluctance to use chloride process because of abrasivity. (Charvat 2005: 148; Leach & Pierce 2007: 191.)

### Zinc sulphide

Zinc sulphide is opaque white pigment that is resistant to everything but acid. It has a good heat resistance and it is stable in its colour. Zinc sulphide is not as opaque as titanium dioxide but it is excellent for abrasion resistance and its UV reflectance is greater than what titanium dioxide has. Zinc sulphide is used in printing inks of all systems except acid vehicles and it has gained favour as an extender for titanium dioxide for its cost. In Table 15 composition of zinc sulphide is introduced. (Leach & Pierce 2007: 191).

**Table 15: Composition of zinc sulphide (Leach p.191)**

Component	%
ZnS	97
ZnO	<0.3
Solubles	<0.4
Moisture	<0.2
Residue	3

### Lithopone

Lithopone is chemically inert, highly efficient, brilliant white and opaque pigment. It is insoluble mixture of barium sulfate and zinc sulfate that precipitates upon mixing solutions of barium sulfate and zinc sulfate. Lithopone is available in easily dispersible micronized forms, decomposed by acids. Even though it today is replaced in many applications by titanium dioxide, it is still widely used in a number of products such as water paints. Composition of lithopone is introduced in Table 16. (Leach & Pierce 2007: 109; Lithopone 2011.)

**Table 16: Composition of lithopone (Leach & Pierce 2007: 190).**

Component	%
BaSO <sub>4</sub>	60-72
ZnS	28-40

## 4.2 Extenders

Extender pigments are transparent or whitish pigment particles that are added to ink formulations in order to improve the consistency and general working properties of the ink. All extenders have refractive indexes that vary from 1,45 and 1,65. As these values do not markedly differ from the values found in most vehicles, extenders give neither opacity nor much colour when they are added into ink formulation. This is the reason for they appear as transparent. (Beck & Hare 2001:7; Thompson 2004: 326-327; Todd 1994: 385.)

Extenders are used in such manners as rheology modifiers, impacting the viscosity and flow properties of the ink and to reduce the colour strength without introducing unwanted whiteness and opacity. They are also used as fillers to lessen the need for a high cost coloured pigments and thereby to reduce the final cost of the ink. This section is to cover the typical extenders used in printing inks, but more stress is laid on the barium sulfate (Blanc fixe), and its use as a filler pigment, as it is the one under the examination in this study. As a headnote Table 17 compiles the main roles of extenders. (Thompson s. 326-327; Todd 1994, s. 385.)

**Table 17: Role of extenders; they may be used to provide or enhance the following properties (Beck & Hare 2001: 3).**

Aesthetic properties	Processing properties	Physical properties	Performance and resistance properties	Other
Gloss control	Viscosity	Hardness	Abrasion and scrub resistance	Cost control
Opacity	Flow and leveling	Porosity	Permeability	
Brightness	Ease of dispersion	Resistance to applied stress	Chemical resistance	
Texture and smoothness	Sedimentation and settling	Film reinforcement		

As mentioned, since extenders are relatively cheap compared to the most expensive part of the ink which is usually pigment, one of the purposes of extenders is to work as a filler and reduce the cost of the ink. Pigments can often contribute even a greater cost to the ink than all the other ingredients together, thus by bulking up the ink with fillers without affecting the printing properties is a significant factor behind the use of fillers. The use of filler pigments reduce the need off the coloured pigment and therefore reduce the total cost of the ink. In point of fact, this is the single most important motive behind this study. Thousands of tons of fillers are used every year in the manufacture of printing inks, and to get piece of this market share, also the Blanc fixe products by Sachtleben are aimed to enter. Table 18 is provided to give indicative information about the relative cost of different fillers. (Rothon 2001: 4; Thompson 2004: 327.)

**Table 18: Approximate relative volume costs of some common extenders (Rothon 2001: 4).**

Extender/filler	Approximate relative volume cost
Ground calcium carbonates (GCC)	0,15-0,30
Coated GCC	0,25-0,50
General purpose clays	0,25-0,50
Calcined clays	1,2-1,6
Coated calcined clays	2,2-2,6
Precipitated calcium carbonates	1,7-2,0
Precipitated silicas	2,0-3,0

#### ***4.2.1 Theory of spacing***

This section introduces the theory behind the filling effect of extender materials in superseding the need of full amount of coloured pigment in inks.

The extender materials are used for pigment stabilization as a spacer and with the spacers the pigment concentration can be reduced according to the increased efficiency. The concept of spacing is rather simple: If two or more pigment particles are not

completely dispersed but still have contacts to each other, it can be calculated, that the theoretical maximum of pigment efficiency is not reached. Because the scattering volumes are larger, more than doubled, compared to the particles themselves, the volumes will overlap, influence each other and are all together decreased therefore. (Hocken 1997: 9; Barium sulfate 2009: 9.)

However, if it is possible to place an inert filler particle just between these agglomerated pigment particles, they are pushed apart letting the scattering volume be free again. This situation is illustrated in Figure 29. In order to achieve highest efficiency, it is necessary for each adjacent pigment particle to intercept the light wavelength at the same point in the wave pattern. This means for instance in the case of titanium dioxide (Figure 30), that as the wavelength of light is on average somewhat longer (0,4-0,7  $\mu\text{m}$ ) than what is the particle size of an optimally dispersed  $\text{TiO}_2$  (0,25  $\mu\text{m}$ ), it is necessary use spacers to boost the centre to centre spacing between the two adjacent particles of  $\text{TiO}_2$  so that it equals one full wavelength. Scattering power recovers to 100% of the theoretical maximum value and due to the increased efficiency of the pigments the pigment loading can be reduced respectively. (Beck & Hare 2001: 7; Hocken 1997: 9.)

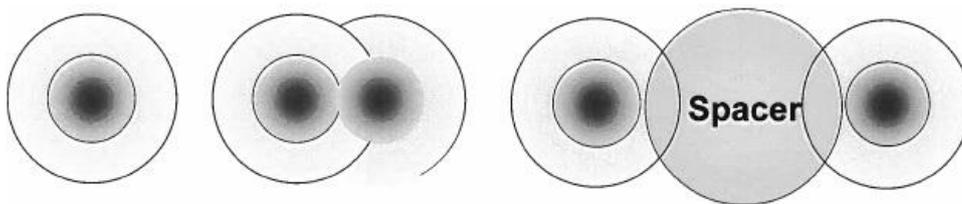


Figure 29: The pigment concentration can be reduced according to the increased efficiency (Blanc fixe additives 2009: 5).

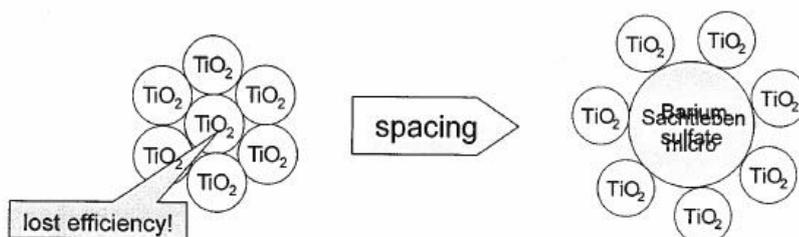


Figure 30: A spacer recovers the whole potential of a white pigment (Barium sulfate 2009: 8).

Although the concept of spacing is simple by its basics, there are some important necessities which have to be fulfilled all for achieving a successful filling. These include the following:

- The surface chemistry of pigment and spacer has to be compatible in such a matter that the spacer “wants” to be located between the pigments.
- The spacer should not be too small for that the scattering volumes of the pigments are kept apart completely. For instance, the spacer for titanium dioxide (particle size around  $0,3\mu\text{m}$ ) should roughly be around  $0,6\mu\text{m} - 0,8\mu\text{m}$ .
- However, the spacer should be as small as possible, so that enough particles are available to space as many pigment particles as possible. Figure 31 illustrates the volume relation between different barium sulfate particles and titanium dioxide as unit volume.
- Excess deterioration of properties such as gloss or dispersion is not acceptable.
- If, by chance, there are no aggregates of pigments in the formulation, the effectiveness is already 100 % and the concept of spacing fails. (Hocken 2000: 10.)

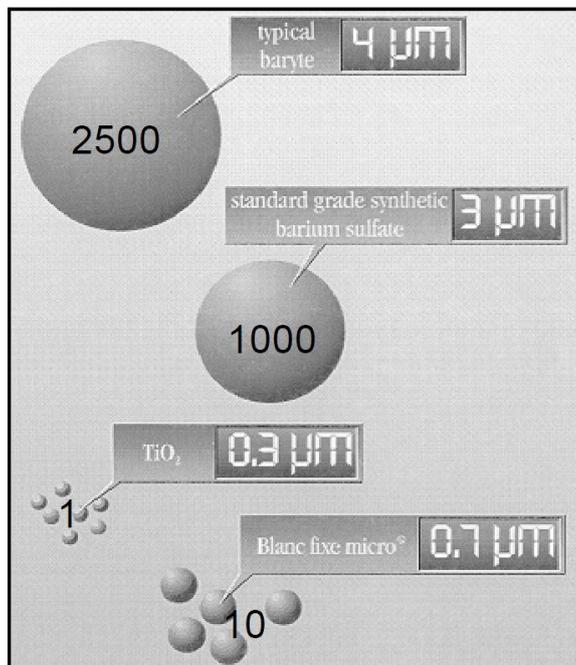


Figure 31: Number of titanium dioxide particles which are necessary to fill up one spacer particle (Hocken 1997: 10).

The stabilization should be done due to electrostatic effects and the spacer used should have minimum effect on product properties such as gloss or viscosity or on the colour metric. (Blanc fixe additives 2009: 9.)

Using the extenders is always balancing between the print properties and should be done without crucially affecting the print quality. In order to maintain the print quality the extender/spacer has several requirements:

- Extremely fine particle size (0,2-0,5 micron) to minimize abrasion and degradation of gloss.
- Low refractive index for allowing a high transparency in the bonding agent.
- High light transmission for that it has no influence on the colour metric.
- No unsatisfactory effects on product properties such as gloss or viscosity.

Extender content in lithographic inks seldom tops more than 2-4%, but in gravure or flexo inks it may be as high as 15-20%. (Blanc fixe additives 2009: 9; Eldred 2001b: 137; Gooch 1997: 130; Todd 1994: 74.)

#### **4.2.2 *Blanc fixe***

Blanc fixe is a clean, white extender produced from synthetic barium sulfate. Its basic composition is introduced in Table 19. Originally it was designed as an extender for rather cheap and mostly flat coatings and for a long time it was only known as an extender for coatings and plastics. However, today it is gaining more and more significance as an indispensable additive. In ink formulations Blanc fixe is used as an extender mainly in paste inks, although recent innovations in particle size are beginning to make available grades eligible for liquid ink application. Its tendency to matt down can be prevented by the resin solids of the ink system. (Blanc fixe additives 2009: 5; Hocken 1997: 1-2; Leach & Pierce 2007: 159 & 193.)

**Table 19: Composition of Blanc fixe (Leach & Pierce 2007: 193).**

Component	%
BaSO <sub>4</sub>	97-99
SiO <sub>2</sub>	0-2
Residues	0-1

There are several different grades of Blanc fixe with varying particle sizes suitable for different applications and inks. The particle sizes can vary approximately from 0,002 to 10 µm. The grades relevant to this study are introduced in the materials chapter in the experimental part of this study. (Hocken 1997: 2; Leach & Pierce 2007: 159 & 193.)

### **Production**

Blanc fixe is produced from natural barium sulfate ores (barytes) which, similar to any other naturally-occurring and mined material, contains impurities such as crystalline silica, various silicates and other contaminants. Iron compounds reduce the natural colour of it and create a yellow to dark, grey tint. In the production process of Blanc fixe the aim is to remove all of these impurities so that as narrow as possible particle size distribution is obtained. (Hocken 1997: 2.)

To achieve top final qualities, a rather extensive chemical route is required. The production process of Blanc fixe is illustrated in Figure 32 on the next page. In the production process the raw material is finely ground, mixed with coal, and heated in a continuous rotary kiln. In the ongoing reaction the coal reduces the sulfate into a sulfide ion, yielding barium sulfide. As a result of this processing state, the barium sulfate has become a water soluble compound, where all the impurities remain insoluble. (Hocken 1997: 2.)

The process produces exhaust gases, but in means of recycling and reuse, the gases can be desulfurized. This recovery process creates no waste but promotes recycling and is therefore not only economical but environmentally friendly. The described method is in use at Sachtleben Chemie. In the process the absorbed sulfur dioxide is desorbed again and pumped to a sulfuric acid plant where this “waste” is used as a raw material for the

production of sulfuric acids which again is a raw material for the production of titanium dioxide. (Hocken 1997: 2.)

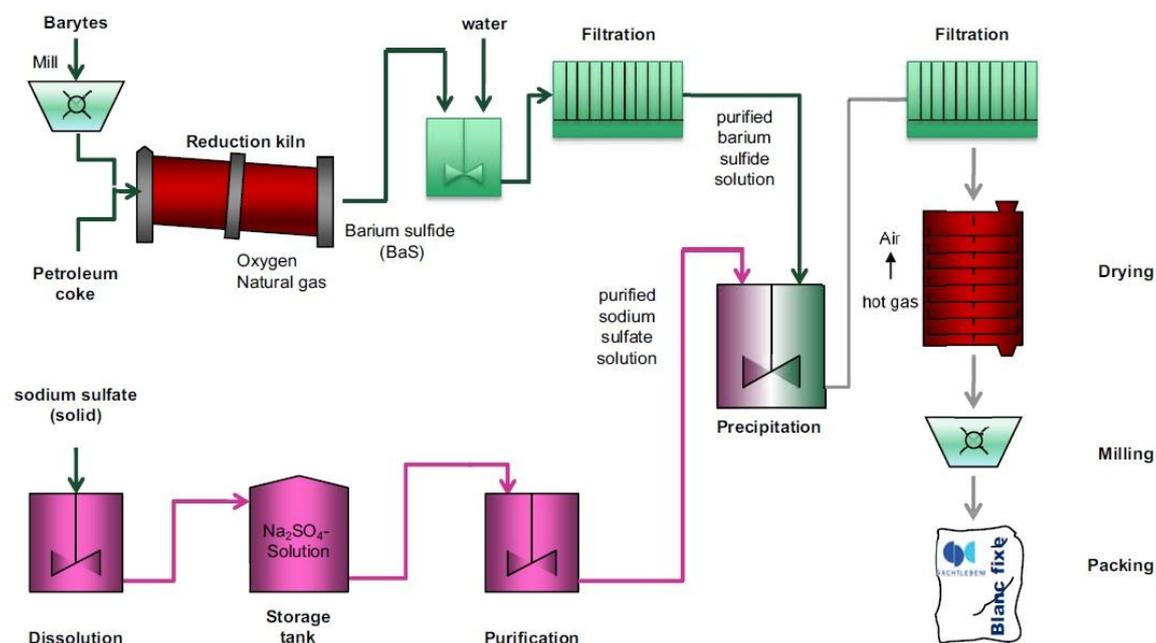


Figure 32: Blanc fixe production (Sachtleben – worldwide 2011: 8).

By combining precipitated barium sulfate with another sulfate solution, pure white Blanc fixe with defined narrow, particle size, is accomplished. To create different soluble Barium compounds, the basic production, described above, is modified by using further steps. The raw material gained can be further refined by milling steps such as micronizing or inorganic and organic treatment. (Hocken 1997: 3.)

### General properties

Blanc fixe is a totally inert substance and thus exhibits very high resistance properties to weathering and chemicals; good lightfastness and heat stability. It is also a very safe and inert substance from a toxicological point of view; it is even used as an X-ray contrast drink. In addition, Blanc fixe has very high brightness and absence of any catalytic elements. This is due to the chemical synthesis of Blanc fixe, which make the material very pure. (Hocken 1997: 3-4.)

Blanc fixe has the highest density of any extender and therefore considerable amounts by weight can be added to an ink without loss of printing strength. It also exhibits a high diffuse continuous reflectance of light providing a pure white, which essentially helps to retain the original brilliance and tone of colours mixed with it. What more, synthetic barium sulfate has a very low grit content because the crystals are grown from solution in controlled conditions, as a contrast for just “milled down”. Due to this same reason, the amount of extremely small particles, which could potentially create viscosity problems, is also low. The quality of the extender depends on the purity of material that is used for production and the method of processing. (Hocken 1997: 2 & 4; Leach & Pierce 2007: 159 & 193; Wypych 2000: 37.)

Table 20 is provided to sum up the technical information about barium sulfate, the source of Blanc fixe.

**Table 20: Barium sulfate, technical information (Wypych 2000: 36.)**

<b>Property</b>	<b>Value</b>
Density, g/cm <sup>3</sup>	4,0-4,9
Chemical resistance	resistant to acids and alkalis
Moisture content, %	0,1-0,3
Colour	White
Reflectance, %	90
Whiteness	95-96
Brightness	65-99
Particle shape	depends on grade
Particle size, μm	3-30 (barites and some synthetic grades), 0,7 (Blanc fixe), <0,1 (special grades)
Oil absorption, g/100 g	8-28

### 4.2.3 Other extenders

This section introduces some of the other common extender (filler) pigments used in inks.

#### **Kaolin (China clay)**

Kaolin, also known as china clay, is hydrated aluminium silicate,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , that occurs in many parts of the world. It contains impurities of calcium, magnesium, iron, quartz and mica. Kaolin is cleaned and segregated into grades by levitation in settling tanks. Its compositions are tabulated below in Table 21. (Leach & Pierce 2007: 193.)

**Table 21: Compositions of kaolin (Leach & Pierce 2007: 193.)**

<b>Component</b>	<b>Hydrous (%)</b>	<b>Calcined (%)</b>
$\text{Al}_2\text{O}_3$	37-45	42-45
$\text{SiO}_2$	44-53	51-53
(Fe, Ca, Mg)O	12-14	1

Kaolin is chemically inert and inexpensive filler pigment and therefore very useful in a wide range of applications. Kaolin has higher oil absorption than most of the other extenders (except alumina) and hence it can be used as a thickener. Kaolin is typically extremely fine material. Table 22 is to introduce the main properties of kaolin. (Eldred 2001b: 138; Leach & Pierce 2007: 159; Wypych 2000: 100-101.)

**Table 22: The main properties of kaolin (Wypych 2000: 99).**

Property	Value
Density, g/cm <sup>3</sup>	2,58-2,62, 2,5-2,63 (calcinated)
Moisture content, %	1-2 (up to 7%), slurry 20-30%
Colour	white, cream
Refractive index	1,56-1,62
Whiteness	88-91
Brightness	69-90 (classified) 85-91 (beneficiated), 84-95(calcinated)
Particle shape	Platy
Particle size, $\mu\text{m}$	0,2-7,3
Oil absorption, g/100 g	27-48 (classified) 50-60 (beneficiated), 45-120(calcinated)

## Talc

Talc, also known as French chalk, is hydrated magnesium silicate, locally produced from talc, soapstone or stealite. Talc's compositions, which are tabulated below (Table 23), can vary in makeup. (Leach & Pierce 2007: 194.)

**Table 23: Compositions of talc (Leach & Pierce 2007: 194).**

Component	Pure (%)	Average (%)	Bad (%)
MgO	31-32	25-30	20-70
SiO <sub>2</sub>	60-64	52-56	15-40
CaO	1	2-5	2
Fe <sub>2</sub> O <sub>3</sub>	1	1-3	1
Al <sub>2</sub> O <sub>3</sub>	1-2	1-2	5
Residues	4-5	4-10	

Talc is chemically inert, lightfast and heat stable up to 850C. It is also cheap and useful ingredient. However, many of talc versions can reduce gloss unless the binder is adequate to compensate. To turn this characteristic in advantage, talc is also used to reduce the gloss of the ink giving a matting effect and a satin finish. Talc is mainly used in quality lithographic inks, giving a good removal for excess tack, improving rub resistance and to reduce setoff and/or blocking. Table 24 compiles the main properties of talc. (Eldred 2001b: 138; Leach & Pierce 2007: 194; Wypych 2000: 153.)

**Table 24: The main properties of talc (Wypych 2000: 150).**

<b>Property</b>	<b>Value</b>
Density, g/cm <sup>3</sup>	2,7-2,85
Moisture content, %	0,1-0,6
Colour	White
Refractive index	1,57-1,59
Whiteness	70-94
Brightness	78-93
Particle shape	Platy
Particle size, µm	1,4-19
Oil absorption, g/100 g	22-57

### **Silica**

Silica is transparent white light flurry matt pigment with a high oil absorption property. It is completely inert and therefore un-affecting the resistance properties of inks. Only the synthetic version of silica is used for inks. It can be used as a flattening, anti-settle, and bodying agent for any kind of ink system. It is perfect for reducing tack, but the flip side is that this is done at the cost of a lower gloss level. Silica's composition is introduced in Table 25. (Leach & Pierce 2007: 194.)

**Table 25: The composition of silica (Leach & Pierce 2007: 195).**

<b>Component</b>	<b>%</b>
SiO <sub>2</sub>	98
Other oxides	0,1
Ignition loss	2,0

### **Calcium carbonate (chalk)**

Calcium carbonate, also known as chalk, is the cheapest and most widely used extender. It occurs widely in nature as chalk or limestone. It is also produced synthetically by slaking quicklime and exposing the slurry to carbon dioxide. In addition, it is obtained in water purification. As an extender, it comes in a variety of particle sizes and surface

treatments, coated and uncoated. Calcium carbonates basic compositions are tabulated in Table 26 below. (Eldred 2001b: 138; Leach & Pierce 2007: 158 & 192.)

**Table 26: The basic compositions of Calcium carbonate (Leach & Pierce 2007: 192).**

Component	Natural (%)	Synthetic (%)
CaCO <sub>3</sub>	95-98	98-99
MgCO <sub>3</sub>	<1-3	<1-1,5
SiO <sub>2</sub>	<0,5	<0,1
(Al, Fe) 0	<0,5	<0,3
H <sub>2</sub> O	<0,2	<0,2

Calcium carbonate is mainly used to reduce the cost of inks without affecting printing quality. It is white by nature, but dull. It is extensively used as filler for its many good properties and relatively low price. Table 27 is to introduce the main properties of Calcium carbonate. (Gooch 1997: 130; Rothon 2001: 10.)

**Table 27: Properties of Calcium carbonate (Wypych 2000: 48.)**

Property	Value
Density, g/cm <sup>3</sup>	2,7-2,9
Chemical resistance	reacts with acids
Moisture content, %	0,01-0,5
Colour	White to gray
Reflectance, %	86-94
Whiteness	80-98
Brightness	82-94
Particle shape	irregular
Particle size, μm	0,2-30, 0,02-0,4 (precipitated)
Oil absorption, g/100 g	13-21

**Alumina hydrate (aluminium hydroxide)**

Alumina hydrate is white, soft-textured and quite transparent extender. It is resistant to everything except diluted HCl (hydrochloric acid) and is heat stable and lightfast. Alumina hydrate is used to improve the gloss and flow properties of lithographic inks. It is easy to disperse, but is rather priced as an extender. The empirical formulae of Alumina hydrate is:  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ . (Leach & Pierce 2007: 193; Thompson 2004: 327.)

## 5 Print quality and control

Printing is a duplication process where the copies should be similar to the original; thus the evaluation of print quality for assessing whether the print reproduces the original and meets the standards well enough. Print quality measurements are needed to give print quality a numeric value which then can be assessed and used to control print production. For instance, print density is a conventional way to control consistency of the printing process; monitored off line or on line. Objective instrumental measurements attempt to estimate the perception of an average observer. As visual evaluation is the main criterion in assessing print quality, the measurements are mainly optical measurements. (Oittinen & Saarelma 2009: 318.)

Print quality and its measurements are one of the most extensively studied topics in the printing industry and hence this chapter aims to give an overview at a general level. The emphasis is on the quality parameters that are used in print evaluating and was in the scope of this study.

### 5.1 Gloss

Gloss of the ink film is a much desired property for high quality print; it is often considered to be eye-catching and therefore particularly demanded where it is needed to make a marketing impact. Print gloss is a measure of the surface reflection of light from a printed surface and it quantifies the amount of light reflected at a specular angle from the printed surface. Gloss is dependent on the formation of a smooth, continuous ink film and hence strongly influenced by the absorptive and surface smoothness of the

substrate and the chemical and physical properties of the ink. (Leach & Pierce 2007: 430; Oittinen & Saarelma 2009: 325; Todd 1994: 310.)

Gloss of the printed surface is determined by the surface roughness and the refractive index of the printed surface. As for the ideal case for the ink film, if the surface is absolutely smooth, it reflects light only in one direction and is called regular or specular reflection. Such a surface exhibits gloss, and in most cases high gloss. If the surface is not smooth, the incident light will be reflected or scattered in all directions. This is called diffuse reflection and such a surface is matt, or at best, semi-glossy. The mechanisms of reflection and scattering are illustrated in Figure 33. To achieve high print gloss it is required that the paper is smooth or that the ink layer can fill rough profile of the paper; this is possible if the roughness depth is smaller than the ink film thickness. In the case of offset printing, relations between ink and paper, like ink setting speed and changes in ink leveling due to this, may also affect print gloss. (Oittinen & Saarelma 2009: 325; Oittinen & Saarelma 1998: 234; Oyarzún 2000: 50.)

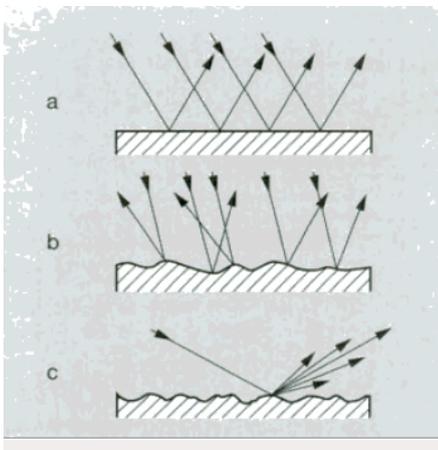


Figure 33: Types of reflection on surfaces: a= specular ref on a smooth surface b=diffuse ref on a rough surface, c= scatter ref caused by microscopic surface irregularities (Oyarzún 2000: 50).

### 5.1.1 Ink gloss

Poor ink gloss may be a result of poor pigment wetting, poor transference and flow, or the presence of a material with too large particle size. The perceived gloss of the ink layer is also affected by the degree of pigment dispersion and the particle size distribution of the pigments. Well dispersed small particles with a narrow particle size

distribution pack well at the ink film surface and produce a uniform surface finish. This surface uniformity combined with the high scattering power of smaller particles, results in a higher degree of gloss. This is common phenomenon especially in very thin applications such as in offset printing, which produces ink films less than 1µm thick. Large particles in offset ink film are detrimental to gloss, thus the coarse tail of the size distribution of pigments can significantly impact gloss performance. In addition, in those cases where the reflecting ink film shows a strong absorption, its absorption coefficient also has an influence on the gloss. (Kippax 2005: 2; Oyarzún 2000: 50.)

### ***5.1.2 Improving the ink film gloss***

A number of options exist to improve gloss by ink modification. For instance, increasing the oil or alkyd content of the ink is beneficial in various ways; it improves pigment wetting and boosts compatibility. Also, use of a lower viscosity resin in the ink vehicle makes the increase of solids possible and thus promotes hold-out of a smooth ink film on then substrate surface. This will give a superior gloss compared with an ink film that has penetrated extensively into the paper and therefore allowed light to be scattered from protruding paper fibres and coating particles. (Leach & Pierce 2007: 383 & 431.)

The use of flushed pigments and readily wetted wax grades, which break down to fine particle sizes in the ink manufacturing stages, have a particular advantageous impact on gloss levels because of their excellent dispersion and wetting. However, if dry pigments have to be used, the pigments chosen should be of an easily wetted nature and easily dispersed on manufacturing equipments such as three-roll mills or shot mills. Incomplete wetting of the pigment particles by the ink vehicle will cause light scattering within the ink film which reduces the gloss. In addition, it may also promote over-emulsification of ink with fount which will inhibit the transference and flow properties that are very important to ensure the formation of a smooth ink film on print, and hence contribute the gloss. Especially material protruding through the thin ink film will act as light scattering sites and thus impair the gloss. (Leach & Pierce 2007: 383 & 430-431.)

Within appropriate limits, a reduction in the pigment content, and hence in tinctorial strength, of the ink can be used to increase gloss. This is due to the heavier ink film thickness which will be necessary to achieve the required density; it boosts hold-out and flow. The disadvantage of this, and the use of more compatible vehicles, is that set-off becomes more problematic. In this respect, the only techniques that can improve gloss without detriment to setting are in the areas of pigment choice and manufacturing method for improving wetting and reducing presence of over-sized particles. (Leach & Pierce 2007: 383 & 431.)

### ***5.1.3 Gloss measurement***

Gloss is measured by gloss meters which normally allow measurements of specular gloss at more than one angle. A high angle of 75° is recommended for low-gloss samples whereas low angle of 20° is better for high-gloss surfaces. Angles of 60° and 85° are also used, but they are originally defined for the paint industry. As the angle affects the measurement value it should always be given together with the results. (Oittinen & Saarelma 2009: 325; Oittinen & Saarelma 1998: 235.)

## **5.2 Colour**

Colour science is a wide subject that involves both physics and psychology, thus a comprehensive discussion of colour is beyond the scope of this study. Nonetheless, as colour measurements are perhaps the most important and at the same time the most delicate measurements of print quality, this chapter is to introduce the basics of colour and methods for measuring and controlling it. For that human colour perception varies somewhat from person to person and people have poor colour memory, numerical values are necessary to control the colour of the ink film on the print. That to be said, measurements are the key to total production control and to ensure that all manufactured items are within the quality tolerances defined. (Eldred 2001b: 138 & 145, Oittinen & Saarelma, s. 321; The Color Guide and Glossary 2004: 3.)

Today the most known and widely used standards for printing are determined in the ISO standard 12647-1-6 series. The part that covers the sheet-fed-offset printing is ISO 12647-2. The primary parameters for printing quality specified in the ISO 12647-2 include the colours of solids and the print substrate, among others. (ISO 12647-2 2004: V; Vesalainen 2009: 16-17.)

The colorimetric values of process inks are specified under the ISO 2846-1, a standard to determine colour and transparent conformity of four-colour offset printing inks. The colorimetric specification of inks was developed in order to attain an agreement on the colour of the inks for CMYK printing among printers and ink manufactures. The correct control of the raw material before printing reduces the colour variation of press runs and will result in consistent end product in their colour. The first parameter for determine the colorimetric values was the range of ink film thickness (density) for printing and consequently for measuring of process inks. Colorimetric values have indeed been the one to supersede the use of density values in ISO standards. The relation between density and colorimetric values is discussed in more detail in the subchapter 5.4.2, as it affects in the hue and chroma of inks. (Beattie 2006: 2; Uribe 2006: 61.)

### ***5.2.1 Attributes of colour***

Colour is an optical phenomenon that is produced as an irradiation in our eyes by light. Accordingly, it is not a physical variable and therefore has no physical unit. When sunlight radiates onto an object it is partially reflected; the sensation of the colour we perceive in our eyes is depending open the area of visible spectrum the object reflects. An object reflecting completely the entire visual spectrum appears to be white, and in the contrary, a completely absorbent body appears to be black. (Colour & Quality 1999: 10-11.)

Each colour has its own distinct appearance that is based on three elements: hue, chroma and lightness. Hue can be described as the element of how we perceive colour of an object, whether it is red, green, blue etc. Figure 34 illustrates the continuum of colour from one hue to another. Chroma, also known as saturation, describes the vividness or dullness of a colour; how close the colour is to either gray or the pure hue. This ap-

pearance is illustrated in Figure 35. In addition, the degree of lightness is called the luminous intensity of a colour, illustrated in Figure 36. (Color Communication 2007: 7-8.)

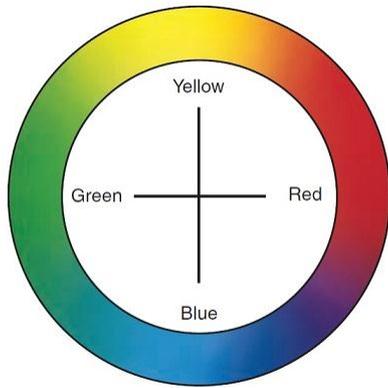


Figure 34: The continuum of colour from one hue to another (Color Communication 2007: 7).

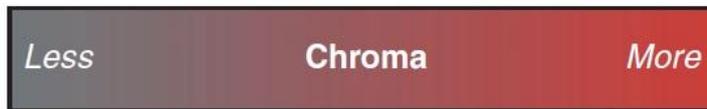


Figure 35: Chroma of colour (Color Communication 2007: 7).

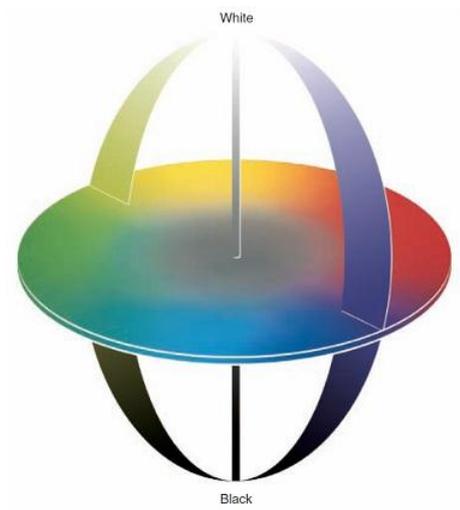


Figure 36: Lightness of colour (Color Communication 2007: 7).

### 5.2.2 Colour space and systems

In order to be able to measure and understand the results of colour measurements, one should be familiar with certain concepts and terms. Perhaps the most essential is the concept of colour space; a geometric representation of colours in a space, commonly of three dimensions. There are number of colour spaces used, but the principle for all is the same. Colour can be described by its three attributes, or “dimensions”, introduced in the previous subchapter; hue as its basic colour (i.e. blue etc.), saturation as the vividness or dullness of a colour, and lightness as its brightness or darkness. These three attributes offer three coordinates to map a colour in a colour space; hue varies as a circular movement, lightness is the centre vertical axis and saturation is the horizontal axis that extends from the lightness axis. Example of a colour space is illustrated in Figure 37. (Oittinen & Saarelma 2009, s. 322; The Color Guide and Glossary 2004: 11 – 12.)

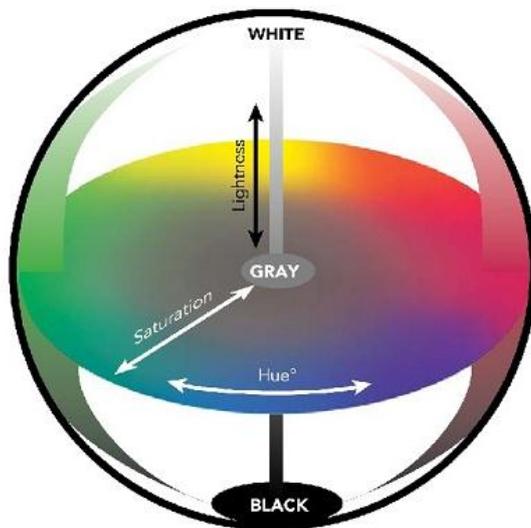


Figure 37: Colour space (The Color Guide and Glossary 2004: 12.)

In 1931, the CIE – the Commission Internationale d’Eclairage (the International Commission on Illumination), standardized a series of colour spaces representing the visible spectrum. The CIE spaces include three device independent colour spaces: CIE XYZ, CIE  $L^*a^*b^*$  and CIE  $L^*u^*v^*$  w. (The Color Guide and Glossary 2004: 14.)

### CIE XYZ

The basic CIE colour space is CIE XYZ which is based on the visual capabilities of a standard observer; a hypothetical viewer which was derived from the CIE's extensive research of human vision. The CIE performed colour-matching experiments and then used the results to create colour-matching functions (Figure 38) which are the values of each light primary, red, green and blue that must be present in order for an average human visual system to perceive all the colours of the visible spectrum. These RGB (red, green and blue) values were translated into a different set of all positive tristimulus values, called XYZ, which formed the first CIE colour model. Onwards, from these XYZ coordinates, the CIE constructed the xyY Chromaticity Diagram (Figure 39) which defines the visible spectrum as a three-dimensional colour space. (Color Models 2000; The Color Guide and Glossary 2004: 14.)

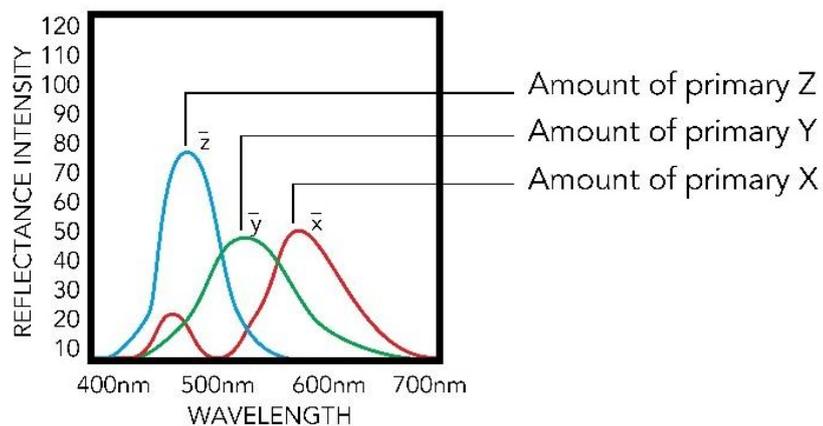


Figure 38: The CIE standard observer colour matching functions (The Color Guide and Glossary 2004: 14).

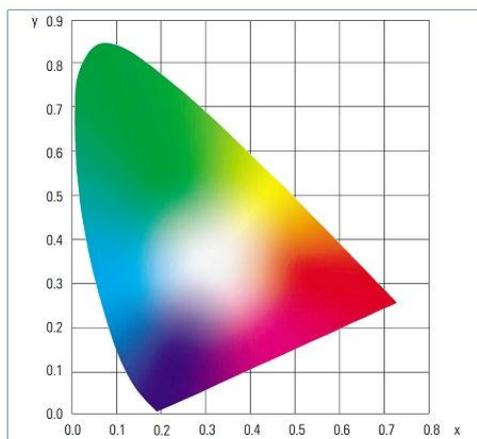


Figure 39: CIE XYZ chromaticity diagram (Kipphan 2001: 72.)

## **CIELAB**

The ultimate target of CIE was to develop a system of colour communication standards for manufactures of paint, inks, dyes and other colorants. The most important function of these standards was to be repeatable and to provide a universal framework for colour matching. The XYZ colour space and standard observer were the foundations of this framework, but the unbalanced nature of the XTYZ space made these standards difficult to clearly address. As a result, the CIE introduced more uniformed colour spaces; CIELAB and CIELUV. Of these two, CIELAB is the most widely used. (Field 1999: 89-90; The Color Guide and Glossary 2004: 16.)

The CIELUV colour space is recommended by the CIE to be used only in applications that used additive colour mixing (printing uses the contrary; subtractive method), for example television and computer monitors, thus this colour space is not integral part of this study and therefore not discussed more extensively. In contrary, the CIELAB colour space has been widely adopted for surface colour measurement applications and what comes to the printing industry, the colour measurements are usually based on the CIELAB colour system. It has achieved almost de-facto standard status in the printing industry and in the ink manufacturing; it is used for instance in preparing ink formulae or for quality control in printing. (Field 1999: 89-90; Oittinen & Saarelma 2009: 322; The Color Guide and Glossary 2004: 16.)

The CIELAB colour system is based on the theory that a colour cannot be both green and red, nor blue and yellow at the same time. As a result a colour is defined using a three-dimensional coordinate system where single values can be used to describe the lightness, the red/green and the yellow/blue attributes. L-value represents the lightness with a maximum value of 100, representing a perfect reflecting diffuser, while the minimum value 0 represents black. A-value represents the redness (+) or greenness (-), and b represents yellowness (+) or blueness (-). None of these axes have limited numerical values. Figure 40 is to illustrate the CIELAB colour space. (Colour & Quality 1999: 79; Field 1999: 90; Oittinen & Saarelma 2009: 322.)

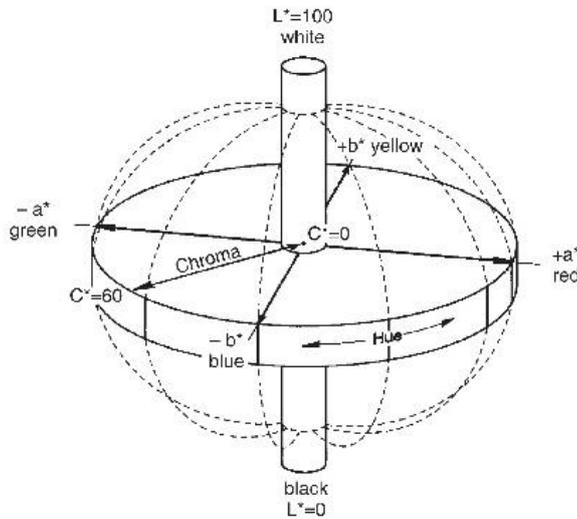


Figure 40: CIELAB colour space; The L value is represented on the center axis. The a and b axes appear on the horizontal plane (Color Communication 2007: 13.)

### 5.2.3 Colour measurement

In the printing industry, colour measurements from printed samples are done for various purposes, for instance to specify the colour gamut (i.e. that portion of the colour space that can be reproduced) for a certain printing process with certain consumables. Colour measurements are also needed for defining the colour differences between samples or a sample and reference values. From these purposes the determination of the colour difference, delta E, was essential to this study and therefore discussed more exact within this chapter. (Oittinen & Saarelma 2009: 322-323.)

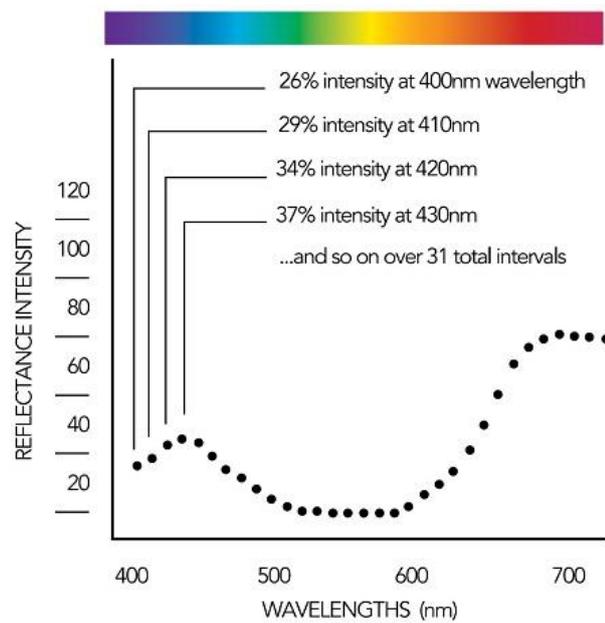
Colour can be measured and specified using either a colorimeter or a spectrophotometer. Both types of instruments apply the principles laid down by the CIE and provide data obtained over the same range of visible wavelengths. They also follow the principle of the visual stimulation of colour in the human eye and brain. The difference however lay in the means of how these instruments treat the data. The colorimeters measure colorimetric quantities directly, whereas the spectrophotometers calculate colorimetric quantities from spectral data. (Oittinen & Saarelma 2009: 322; Thompson 2004: 421.)

### **Colorimeters**

Unlike the spectrophotometer, which can analyse the colour of a surface in small increments of wavelength, the relatively cheap tristimulus colorimeter has only three measuring values derived from three coloured filters: red, green and blue. It breaks the measured light down into its RGB components in a manner similar to the human eye, and measures the amount of red, green and blue collected from the object. The numeric value for the colour is then converted using the CIE XYZ colour space or its derivatives, such as CIELAB. These measurements are then visually interpreted in a colour space graph. (Oittinen & Saarelma 2009: 322; The Color Guide and Glossary 2004: 24; Thompson 2004: 421.)

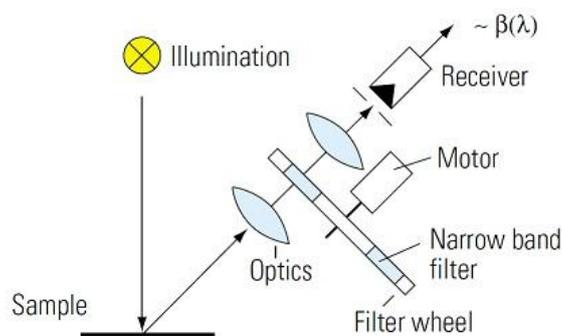
### **Spectrophotometers**

Spectrophotometers are the most accurate and versatile instruments for measuring colour. Hence, the status for being the most widely used instrument for the purpose. It is also the method of colour measurement within this study. Spectrophotometric measurements are based on the principle that any colour can be described as an additive mixture of spectral colours and therefore it measures spectral data – the amount of light energy reflected from an object. The visible spectrum to be recorded is broken into small intervals and the light intensity in each wavelength interval is measured individually, as Figure 41 illustrates. (Eldred 2001b: 150; Kipphan 2001: 77; Oittinen & Saarelma 2009: 32; The Color Guide and Glossary 2004: 25.)



**Figure 41: Spectrophotometers build a spectral “fingerprint” by examining how a measured surface affects light at different wavelengths (The Color Guide and Glossary 2004: 25).**

A spectrophotometer consists of an illuminating source, an optical system for defining the geometric conditions of measurement and dispersing light, and a detector and signal processing system (Figure 42). A modern spectrophotometer is a versatile instrument that can be used for several purposes, in addition to colour coordinates and gamut, all density values and derived quantities such as area coverage, dot gain, contrast and so forth can be determined from the spectral values. Measurements and their comparison between measured and reference values indicate colour location deviations which need to be calculated to adjust the inking units for changing the ink film thickness for the process colours in the press. (Kipphan 2001: 107; Oittinen & Saarelma 2009, s. 323.)



**Figure 42: Spectrophotometer (Filter wheel) principle (Kipphan 2001: 107).**

### 5.2.4 Colour difference and tolerance methods

The difference between two colours can be represented in a numerical value by their distance apart in colour space (Figure 43). This is known as delta E ( $\Delta E$ ), and is measured to indicate how much a colour deviates from an accepted standard. The higher the  $\Delta E$ , the more inaccurate the colour is. The human eye is only capable of detecting colour difference at certain thresholds, hence the fact that it is not needed to achieve a delta E of zero. In principle, the value of 1,0 should correspond to the smallest colour difference that the human eye can detect. In practice, however, this correspondence varies from position to position in the colour space and therefore some colour shifts bigger than 1,0 are acceptable. Delta E between 2 and 6 is typically considered an acceptable match in the graphic arts industry. Tolerances of less than 2 units are normally unachievable when taking the normal process variation into account. In Table 28 meanings for different delta E values are given. (Delta E, delta H, delta T 2007: 2; ISO 12647-2 2004: 8; Leach & Pierce 2007: 114; The Color Guide and Glossary 2004: 39.)

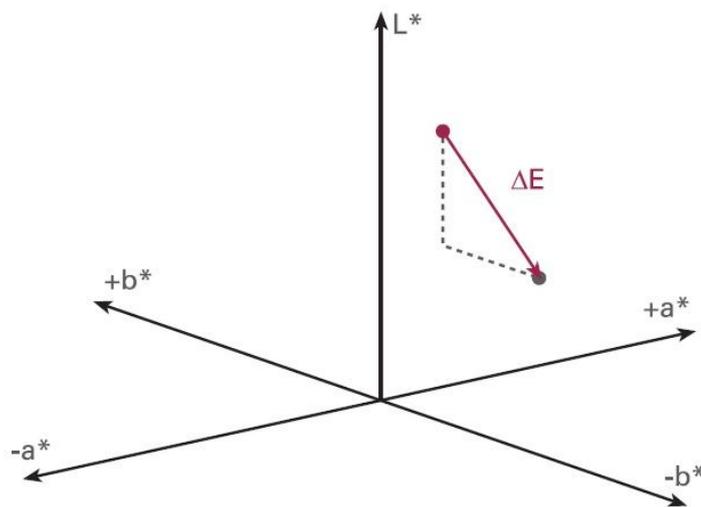


Figure 43: Colour difference, delta E (Delta E, delta H, delta T 2007: 1).

**Table 28: Different delta E values (Delta E, delta H, delta T 2007: 2).**

Delta E value	Meaning
0-1	A normally invisible difference
1-2	Very small difference, only obvious to a trained eye
2-3,5	Medium difference, also obvious to an untrained eye
3,5-5	An obvious difference
> 6	A very obvious difference

When we are dealing with process colours, for instance in the means of ink testing, that will be overprinted and the final imprint is produced by half-tone dots producing secondary colours (red, green, blue), different thresholds are used. ISO 12647-2 determines the delta E tolerances for the solids of the process colours in the CIELAB colour space which are given in Table 29. The delta E values of overprint (secondary) colours red, green and blue are given only as “informative”. (ISO 12374-2, s. 6-8.)

**Table 29: CIELAB  $\Delta E$  tolerances for the solids of the process colours (ISO 12647-2 2004: 8).**

Parameter/Colour	Black	Cyan <sup>a</sup>	Magenta <sup>a</sup>	Yellow <sup>a</sup>
Deviation tolerance	5	5	5	5
Variation tolerance	4	4	4	5

<sup>a</sup>The contribution of the hue difference shall not exceed 2,5

When calculating and interpreting the delta E values it has to be considered that it is only a single value which takes into account the differences between the L, a, and b of the sample and standard. If delta E is out of tolerance it does not indicate which parameter(s), L, a, and/or b, are out of tolerances. In addition, the value of delta E may be misleading in some cases where delta L, delta a, or delta b is out of tolerance, but delta E is still within tolerance. (CIE Lab Color Scale 2008: 2.)

### Calculating delta E

There are several methods to calculate delta E values, the most common being delta E 1976. This is the standard CIE colour difference method and according to the ISO

standard the one to be used. Delta E 1976 calculates the Euclidean distance between two colours in three-dimensional Lab-colour space. The colour difference between two colours in Lab-colour space is calculated as follows in equation below. In addition, Figure 44 is to illustrate the use of the formula.

$$\Delta E = \sqrt{(L1 - L2)^2 + (a1 - a2)^2 + (b1 - b2)^2},$$

where  $\Delta E$  is the colour difference,  $L1$ ,  $a1$  and  $b1$  the Lab-values of the reference colour and  $L2$ ,  $a2$  and  $b3$  the Lab-values of the colour under investigation. (Lindbloom 2003; CMYK Guide 2010: 2.)

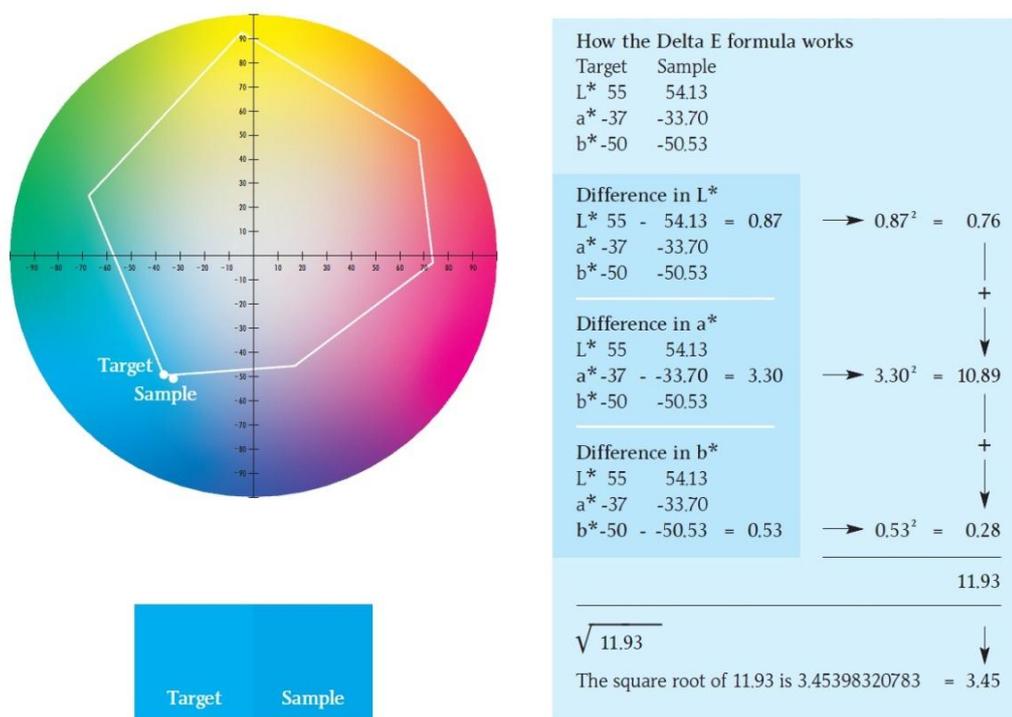


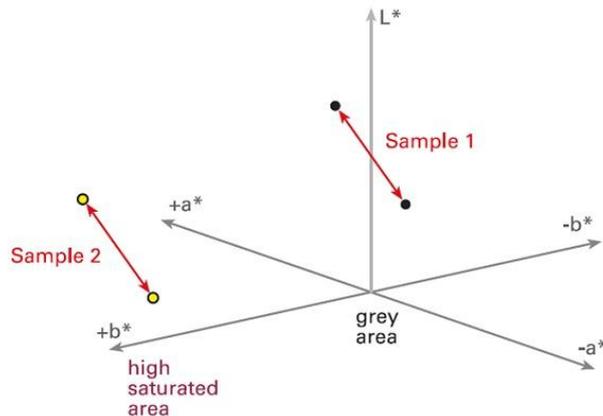
Figure 44: Calculating delta E (Triangle Colorscale 2010: 2.)

This formula calculates purely the distance between two points in a three-dimensional colour space and ignores the actual position of the points themselves. However, as the human eye is more sensitive to some areas of colour and less sensitive to others the actual positions are also noteworthy. This fact is not taken into account in the CIE1976

colour difference formula. For instance, comparing samples between two oranges or two blues the noticeable difference varies; in blue the small difference can be seen easily, while in orange delta E value can be more bigger and samples still looks visually equal. (Delta E, delta H, delta T 2007: 1.)

To compensate the inadequacies of the human eye, further formulas for colour difference have been developed. These formulas do not create new colour spaces but are merely new tolerance systems that are based on the Lab-colour space to calculate the amount of “closeness” between two colours using a variety of colour tolerance methods. For instance colours in highly saturated area can be assigned less importance than colours along the gray axis, which is where the human eye is most sensitive. (Delta E, delta H, delta T 2007: 1; Lindbloom 2003; Millward 2009: 23-24; The Color Guide and Glossary 2004: 38-39.)

Still no tolerance system is perfect, but improvements have been made all the time. For example in 1994 the CIE made an attempt to correct for the visually non-uniformity of Lab by weighting lightness, chroma, and hue in different proportions. As a result CIE94 was introduced; a formula that was not overly complicated but correlated better with visual difference. Furthermore, CIE2000 was an improvement to the CIE94 equation by adding more weighting factors depending on the hue angle of the colour. This is the most complicated equation mathematically but it tends to correlate better to the visual agreement. In addition, CMC equation was created by the Color Measurement Committee and is used primarily in the textile industry. The weighting in CMC is placed on the lightness, chroma, and hue of the colours. An example between the tolerance methods CMC and CIE76 is provided below in Figure 44. (Delta E, delta H, delta T 2007: 1; Millward 2009: 23-24; Color Communication 2007: 18.)



Sample 1		Sample 2	
CIE $L^*a^*b^*$	6.78	CIE $L^*a^*b^*$	16.78
CMC	9.95	CMC	5.63

**Figure 45: Colour samples in different areas of the Lab-colour space, that are evaluated using CIE76 and CMC –colour formulations, show very different results in their delta E-values. (Delta E, delta H, delta T 2007: 2.)**

Even though delta E 2000 is considered to be the most accurate formulation to use for small delta E calculations (<5), delta E 1976 is still the one to be used according to the ISO standards. This is also the formula that will be used within this study. However, whatever the formula to be used, it is important that the type of the formula is taken into account when comparing results. Results calculated with different formulas, i.e. different tolerance methods, are not comparable with each other.

### **Hue difference, delta H**

Delta E is only partly suitable for evaluating the colour difference, and for instance the grey balance. Therefore, as an addition, the current ISO 12647-7 standard includes the hue difference delta H for primary colours and gray scales. Hue difference is the absolute colour difference between two samples; differences in lightness and saturation are ignored. Figure 46 illustrates delta H; the close up shows constructed samples in a circular (red line) around the colour circle (hue). In delta H only changes within this line govern it. In the example of Figure 46 the sample number 6 has delta H of zero. According to ISO, a maximum tolerance of 1,5 is permitted in gray areas and 2,5 in the primary colours. (CMYK Guide 2010: 7; Delta E, delta H, delta T 2007: 3.)

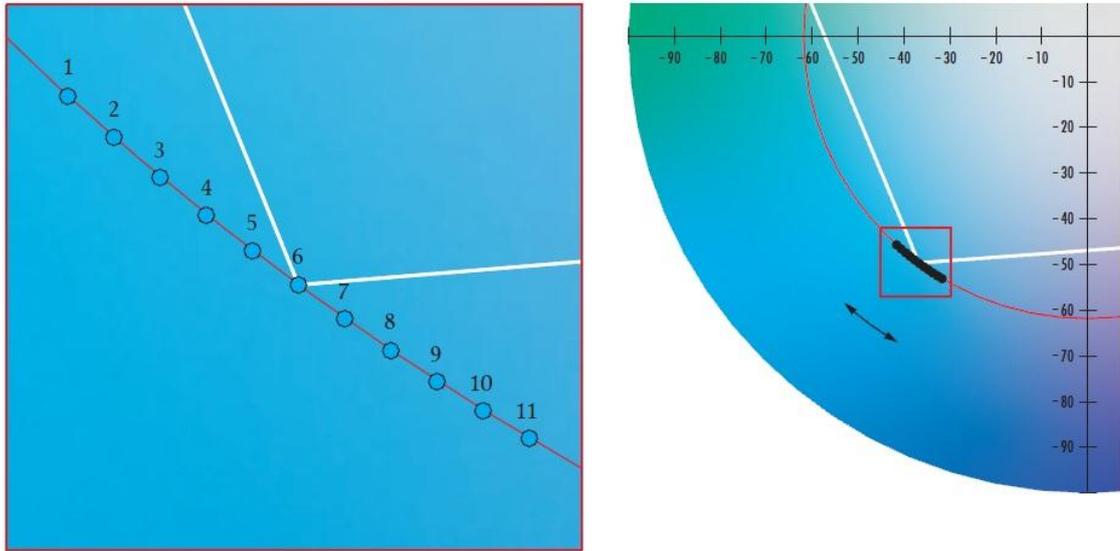


Figure 46: Delta H (CMYK Guide 2010: 7).

### 5.3 Densitometry

Although colour measurements have partly displaced density measurements, densitometers are still widely used in the printing industry. Regardless the fact that densitometry is essentially colour-blind method and strictly speaking cannot be used to measure colour, it is still widely used as the “colour” measuring instrument. For long it has been used for monitoring ink film thicknesses and associated printing variables such as dot gain, trapping and print contrast. Indeed, this continues to be a common way in process colour printing as the densitometric measurements are comparatively fast, easy and therefore cheap way to measure and control the printing variables for both on- and off-press monitoring. And even with the newest technology with presses integrated with spectrophotometers, the values are still widely interpreted as densities. (Field 1999: 93; Nikkari 2011; Oittinen & Saarelma 2009: 323; Thompson 2004: 410.)

The importance of densitometric values shifts in the contexts of the processes delivered in the printing presses. This means for example that if the printing press functions in accordance with ISO standards it is compulsory for them to follow the exact colour-values (Lab) produced by a spectrophotometer. But for instance in Finland this is not the case for a majority of the offset presses. A high number of the presses are relatively small, operate with limited resources and follow no strict standards. Further-

more, in many of these places the press operators have no sufficient knowledge about the Lab-values and they continue to work with much better understood density values. (Komulainen 2011; Nikkari 2011.)

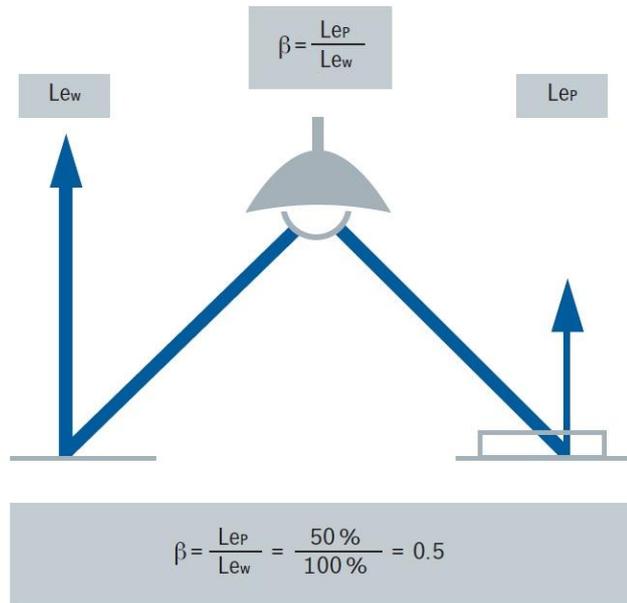
In the pressroom for the solid patches of each ink printed, the density is measured. The density values indicate to the press operator whether the amount of ink (ink film thickness) should possibly be increased or decreased. As a colour control method, it is especially important that the densities of the different process colours are in balance, as the hue of the red, green and blue overprints will shift along the density. (Densitometry 2003: 5.)

### ***5.3.1 Density by its definition***

Print density, in principle, is a measure of the contrast between the printing ink and the substrate. It is the light-absorbing strength of a printed ink layer, abbreviated “D”, that is measured by comparison of the intensity of light falling onto a surface with that absorbed or reflected by it. Reflection density is defined in the form of a logarithmic ratio between the incoming light intensity and reflected light intensity (equation below).

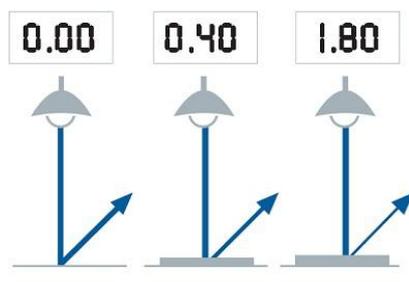
$$D = \log I / \beta = \log I_0 / I,$$

where  $\beta$  is the reflectance factor, the ratio of the light intensity  $I$  of the light remitted by the ink film in relation to the intensity of light  $I_0$  remitted by the blank paper. The reflectance factor  $\beta$  is calculated as illustrated in Figure 47; the  $L_{ep}$  is the light reflected by the measured ink and  $L_{ew}$  the light reflected by the reference white. The reflectance factor  $\beta$  indicates the ratio between the light reflected by a sample, the printed ink, and a “white”, a reference value where the densitometer is zeroed to. (Colour & Quality 1999: 48 & 53; Eldred 2001a: 116; Oittinen & Saarelma 2009: 324; Thompson 2004: 411.)



**Figure 47: The reflectance factor (Expert Guide 2008: 29.)**

A logarithmic scale is used because it provides a better representation of human visual perception than a linear scale does. In addition to reflection densitometers, the density can also be measured by transmission densitometers, which measure the optical density of a transmitting material and is used for instance to measure film blackening. Hence, the transmission densitometry is out of the scope of this study. Figures 48 and 49 illustrate both of these methods of densitometry. (Colour & Quality 1999: 48; Eldred 2001a: 116; Oittinen & Saarelma 2009: 324; Thompson 2004: 411.)



**Figure 48: Reflection densitometry (Heidelberg expert guide, s. 26)**

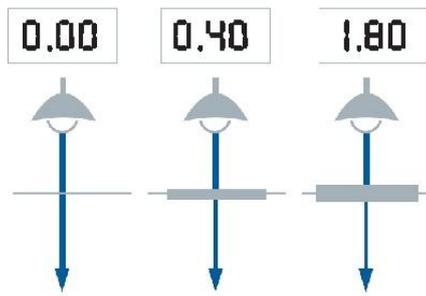


Figure 49: Transmission densitometry (Heidelberg expert guide, s. 26)

Figure 50 below illustrates how reflection densitometry works, taking a coloured ink as an example. Ideally, the incident white light consists of equal components of red, green and blue. The printed ink in this example contains pigments that absorb the red and reflect green and blue, which is why we call it cyan. Densitometers are intended to measure the absorption range of each colour, where density and ink film thickness closely correlate. The example therefore uses a red filter, which blocks blue and green and only allows red to pass. (Colour & Quality 1999: 49.)

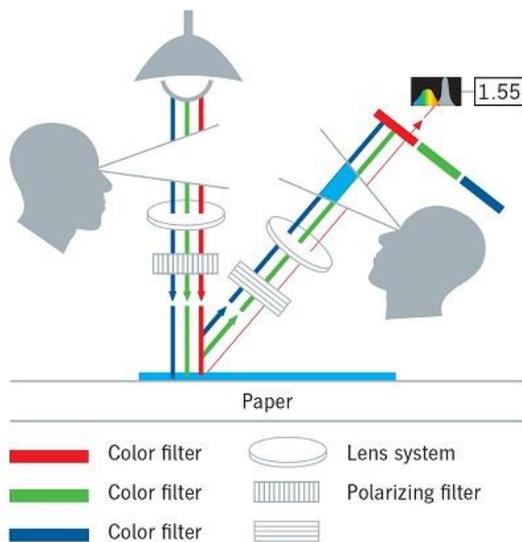
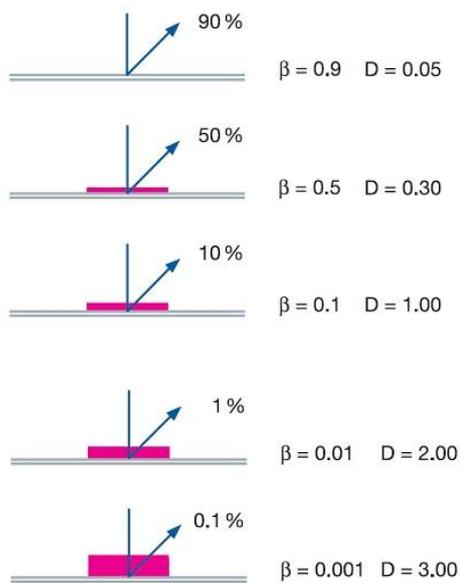


Figure 50: Reflection densitometry principle (Expert Guide 2008: 48).

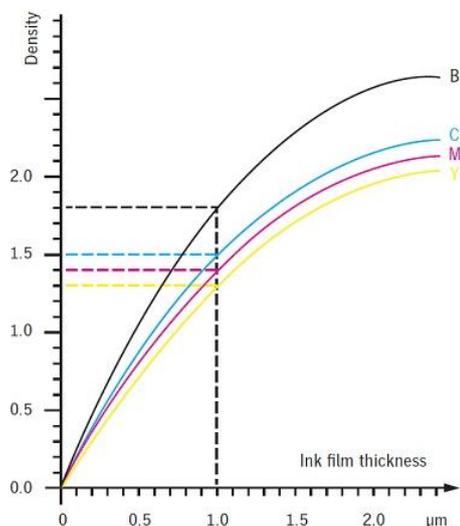
### 5.3.2 The significance of print density

Print density refers to the thickness of the ink film; there is a close correlation between ink film thickness and ink density which is shown in Figure 51. When the ink film thickness increases, light reflectance decreases and therefore the ink density value increases. (Expert Guide 2008: 30.)



**Figure 51: Print density and ink film thickness (Expert Guide 2008: 30).**

The relation between ink film thickness and density can be described in the form of a density curve. Figure 52 illustrates the correlation between ink film thickness and ink density for the four process colours in offset printing. The dotted vertical line indicates the usual ink film thickness, approximately one micrometer, used in offset printing. (Heideberg 1999: 54-55; Oittinen & Saarelma 2009: 280 & 324.)



**Figure 52: The variation of density with ink film thickness for a typical set of process colours (Expert Guide 2008: 30).**

This known model shown in Figure 52 predicts that density increases proportionally to the ink film thickness, which can be interpreted as an increase of the concentration of ink pigments over the same area on the paper. This linear relation is true at the low and medium levels of the ink film thickness scale; indeed in the non-saturated area density and ink film thickness have almost linear association. However, after a certain point it plateaus and a further increase in the ink amount no longer produces increased print density. This is consistent with the fact that the opacity of an ink film will reach a limit where, no matter the amount of ink added, the reflectance will not decrease since the darkest limit has been achieved for this colour. This level of density, typically values of 1,8 or so, is hardly achieved in printing, because other parameters like detail rendering start to decrease when the ink amount is increased over this certain amount. (Color measurement in offset printing 2005: 5; Colour & Quality 1999: 54-55; Oittinen & Saarelma 2009, s. 280 & 324, Thompson 2004: 415; Uribe 2006: 60.)

### ***5.3.3 The need for density control***

Proper control of the amount of ink applied to the printing substrate, i.e. ink film thickness, is one of the most important factors for succession in multicolour printing process. Since in multicolour printing is several colours have to be printed together to gain the eventual colour desired, the inks used must be transparent or translucent. If the

ink films vary in thickness they also vary in their light-absorbing efficiency. Consequently, their lightness and darkness, as well as colour, may vary. Increasing the ink film thickness naturally produces a darker colour, but in addition the other dimensions of colour, hue and saturation, may also shift. The saturation increases with the increase of ink film thickness until it reaches a certain point and it starts to decrease. This is when the masstone effect becomes dominant. For example, too high cyan ink film thickness may cause the colour to become greyer. The hue of the ink film will shift towards the colour with greatest transmission; magenta shifts towards red, cyan shifts towards blue and yellow shifts very slightly towards red. (Field 1999: 153-154 & 190; Kipphan 2001: 100; Measuring Ink Density 2005: 1.)

In addition, the ink film thickness influences a number of print factors other than the colour properties. For instance, higher ink film thicknesses produce higher gloss. Also, when the ink film thickness is increased, the print contrast and hence the image sharpness is increased. This happens until a certain point is achieved after which the contrast and sharpness is reducing due to dot gain. Overly thick ink films however cause for example drying and set-off problems, whereas too thin ink film thickness may cause picking problems (offset and letterpress). Thin ink film can also result in mottled or uneven solids. There is no simple specification of ink film thickness that will produce the optimal result for all situations, but target density values, defined by experience and colour standards, are offered by various actors in the printing industry trying to fulfil this task. (Field 1999: 153-154 & 190; Measuring Ink Density 2005: 2; Nieppola 2011.)

### **5.3.4 Density vs. CIELAB**

As more sophisticated colour determinations has been introduced and the spectrophotometric measurements have become more general, the density values are not part of the international standard; the ISO 12647-2 only determines Lab-values irrespective of the required density. This is due to the fact that offset inks are produced in compliance with ISO 2846-1 (standard for Colour and transparency of ink sets for four-colour-printing) and most of the parameters specified therein cannot be applied in practise. For instance, the specifications for transparency figures and colour co-ordinates of a defined ink film

thickness can only be determined in a laboratory. Also, as a known fact, various inks produced in accordance with ISO 2846-1 have different Lab-values even if the density values are the same. (Seidel 2010: 1; ISO 2846-1:1997 2011.)

But as already discussed, for printing presses to keep it more simple and easier to control the on-going printing processes, in some printing presses the target densities are still generally preferred over the Lab-values. This approach to colour control requires that the eligible Lab-values have to be translated to match target density values. Thus, printing services providers, material vendors, and for instance research institutes, give recommendations for the observance of density values on different types of paper. For example The Finnish association of Graphic Industry (Graafinen teollisuus ry.) with the help of The Technical Research Centre of Finland (VTT) has published a guide called Technical quality recommendations for printing, where target densities are given. This guide is based mainly on ISO 12647 -2:2004 and ISO 12647-3 standards and on hands-on experienced measurements, and the results can be considered as recommendations or target values. Within this study the recommendation target values of this guide are used. In Table 30 are these target density recommendations for sheet-fed offset. (Tekniset laatusuosituksset 2005: 1-2; Nikkari 2011.)

**Table 30: Target densities for sheet-fed offset by VTT (Tekniset laatusuosituksset 2005: 2).**

<b>Target density</b>	<b>Uncoated paper</b>	<b>Light weight coated</b>	<b>Heavy weight coated</b>
Cyan	1,20 +/-0,05	1,45 +/-0,05	1,55 +/-0,05
Magenta	1,10 +/-0,05	1,40 +/-0,05	1,50 +/-0,05
Yellow	1,10 +/-0,05	1,25 +/-0,05	1,45 +/-0,05
Black	1,40 +/-0,05	1,75 +/-0,05	1,85 +/-0,05

Not many studies have been conducted on the relationship between densitometry and colorimetry, i.e. density vs. CIELAB. However, large variations of pigment concentration on an ink are studied to generate undesirable shifts in chroma and hue, though under a narrow density range the behaviour of process inks have roughly no perceivable variation in hue and are almost linear in lightness and chroma. A tolerance

of 5 units in chroma difference is shown to be equivalent to the densitometric tolerances of  $\pm 0,10$  solid ink density. This chapter will examine these existing assumptions of the relationship between ink density (ink film thickness) and colour appearance. (Uribe 2006: 57 & 60.)

An increase in the pigment concentration of an ink will result as an increase in ink density. A study of Modified Colorimetric Methods for Graphic Arts, conducted By Roy Hensel in 1989, examined the relationship between pigment concentration and CIELAB colour space. The CMY inks were printed using pigment concentrations ranging from 4% to 200%, 100% being equivalent to the standard density achieved for printing. Figure 53 shows the results of this study in the CIELAB colour space. (Uribe 2006: 60-61.)

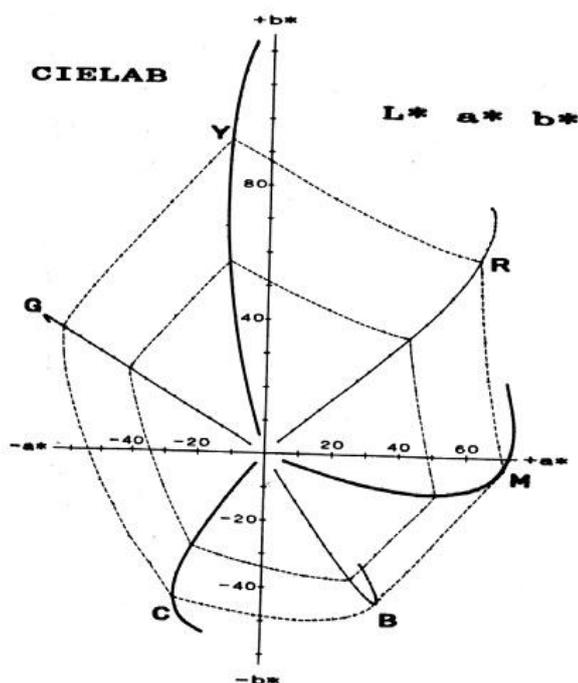


Figure 53: CIELAB vs. pigment concentration (Uribe 2006: 61.)

Figure 52 presents the behaviour of the colour in a relation to the pigment concentration. The CMY curves are conducted from the actual measurements, while the RGB curves are derived from calculations. The outer dotted line represents the 100% pigment concentration and the inner line is for 48% concentration; these can be interpreted as a corresponding change in density. As the curves of process colours indicate, the chroma

and hue angles of inks may change substantially at different levels of ink film thickness; especially magenta has a clear non-linear behaviour with a dramatic 90° hook close the higher concentrations. (Uribe 2006: 60-61.)

Lightness was not part of the results, but as it is commonly known and studied by, for example, the National Printing Ink Research Industry (NPIRI), it was expected to correlate inversely with density. Indeed, the L value correlates with density in almost linear manner for the specified ink film thickness range. The same linear correlation, as the literature expects, was perceived in the measurement data gained at the experimental part of this study. As an example, Figure 54 illustrates the correlation between density and L-value measured of the reference ink. (Uribe 2006: 61-62.)

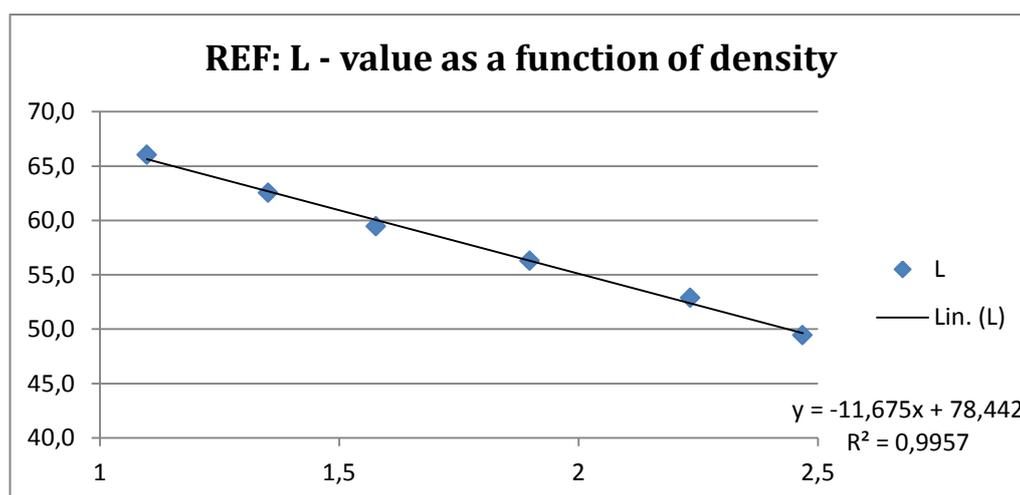


Figure 54: Reference inks L- value as a function of density.

As an example of the behaviour of a- and b-, which explains the chroma and hue aspects, in relation to the density, cyan ink, as it was the colour used in the experimental part, is reviewed.

The behaviour of a-value (redness/greenness) of cyan ink has been studied to show a negative slope at the lower levels of ink film thickness and then for higher ink film thickness it shows a tendency to increase gradually. This assumption was reproduced also in the experimental part of this study, as Figure 55 illustrates. The shape of the curve b-value (yellow/blueness) is almost linear in the significant density range; this was also true in the case of the experimental part and is illustrated in Figure 56. As a

resultant of the shape of the a-curve in relation to the almost linear b-curve, a hue shift at different ink film thickness is perceived. (Uribe 2006: 62-64.)

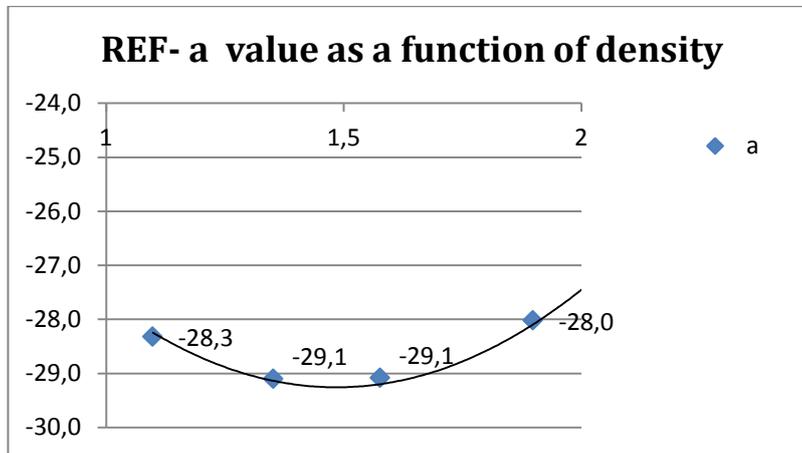


Figure 55: Reference inks a-value as a function of density.

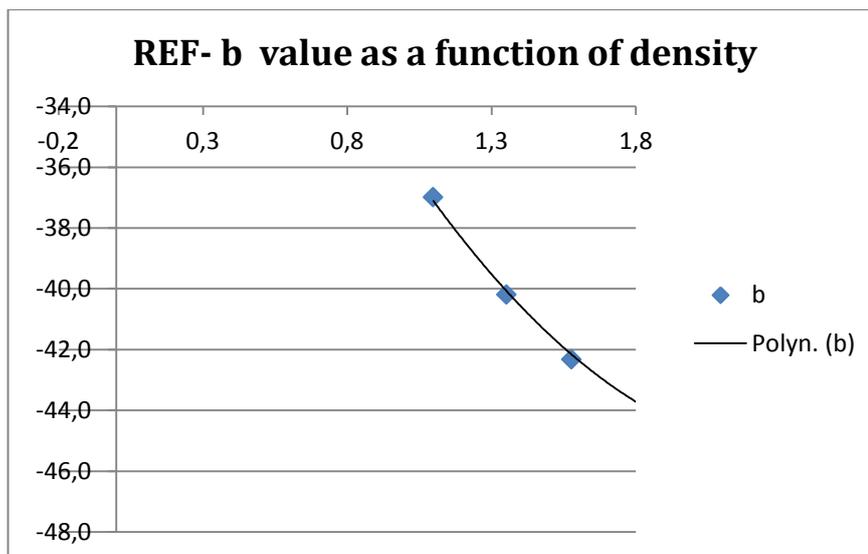


Figure 56: Reference inks b-value as a function of density.

In spite of the variation in the a-value, it is important to notice that as the variation is very minor, the hue shift might not be perceivable. However, this variation still accentuates the importance of the density and/or colour measurements during the printing process as if the density levels vary too much, the most likely output is an undesirable hue shift. (Uribe 2006: 64.)

## II EXPERIMENTAL PART

The purpose of this study was to examine the effects of Blanc fixe filler materials – products of Sachtleben – on properties of a printed ink film.

This experimental part of the study includes 5 chapters, from 6 to 10, that will introduce the materials and equipment used within the experimental part, discuss the determinations and work process behind the results, and finally resolve the results and their meaning for the continuance of this study.

## 6 Materials and equipment

This chapter is to introduce the materials and equipments used in the experimental part of this study. These include filler materials, ink, paper, and testing equipment; IGT-printability tester and measurement devices.

### 6.1 Filler materials

In the light of the preliminary tests performed at Sachtleben Pori mill, two grades of Blanc Fixe products were chosen to this study. In addition, competitive filler was also tested. This section is to introduce these three filler materials.

As already discussed in the chapter of extenders, Blanc fixe is synthetic barium sulfate ( $\text{BaSO}_4$ ) produced from highly purified solutions in a defined growth process. Blanc fixe 1 is a product typically used as an extender in plastics, paper, powder-coating systems, paints, and coatings, whereas Blanc fixe 2 has application areas including printing inks, PCB (Printed Circuit Board) inks, high solid coatings, and powder coatings among others. (Fritzen 2011: 3; Sachtleben 2009.)

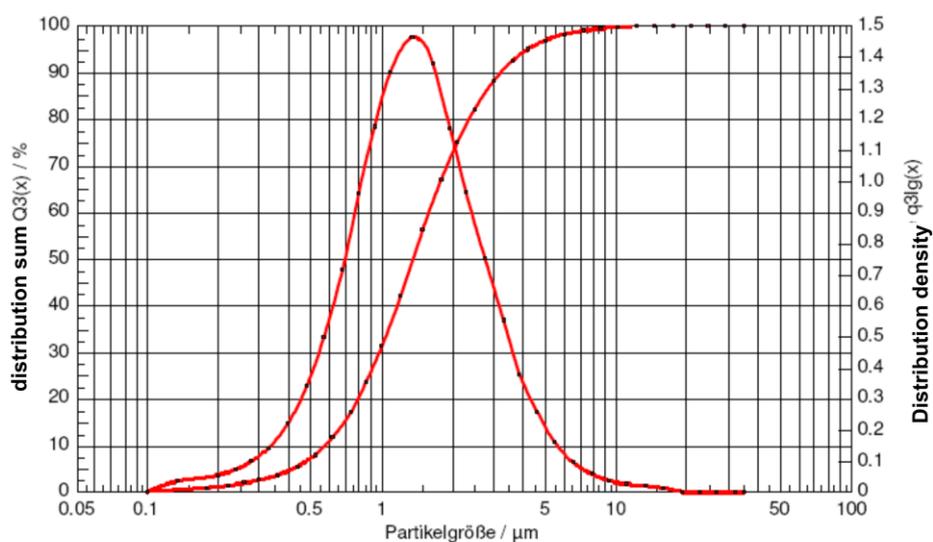
The competitive filler is treated kaolin with an organic surfactant, produced from hydrous aluminum silicate. It is used in industrial adhesives and sealants, and for example in offset inks to improve rheology as a viscosity builder and act as filler pigment. (Lithospense 7005 CS 2009; Lithospense 7005 CS 2011.)

The foremost difference and the single biggest factor that can be assumed to influence the test results are the differences in particle sizes of the pigments. The particle size of the Blanc fixe 1 is 1,0  $\mu\text{m}$ . and of the Blanc fixe 2 is 0,7  $\mu\text{m}$ . The competitive filler, kaolin, has a particle size of 0,4. It is expected that the smaller particle size results better performance in general. Table 31 concludes the most essential parameters of these different particles. Blanc fixe has highest density of all extenders which means it increases the weight of the ink which is sold on weigh. (Fritzen 2011: 3; Sachtleben 2009.)

Table 31: Particle parameters for different filler materials (Fritzen 2011: 3; Leach & Pierce 2007: 193; Sachtleben 2009).

Parameter	Blanc fixe 1	Blanc fixe 2	Kaolin
<b>Base material</b>	Barium sulfate	Barium sulfate	Hydrated aluminium silicate
<b>Particle size, median value <math>d_{50}</math> [<math>\mu\text{m}</math>]</b>	Approx. 1	Approx. 0,7	Approx. 0,4
<b>Organ treatment</b>	Yes	None	Yes
<b>Specific surface area [<math>\text{m}^2/\text{g}</math>]</b>	Approx. 4	Approx. 3	Approx. 15
<b>Sieve residue [%]</b>	<0,004	<0,01	Not measured
<b>Mohs' hardness</b>	3	3	2-2,5
<b>Refractive index</b>	1,64	1,64	1,56
<b>Density [<math>\text{g}/\text{cm}^3</math>]</b>	4,4	4,4	2,6

Also the particle size distribution is of essence; narrow particle size distribution exclude better too large particles which can be detrimental to the properties of ink, for example gloss. Figures 57 and 58 illustrate the particle size distributions of Blanc fixe 1 and 2.



$X_{10} = 0,57 \mu\text{m}$  (10 % of the particles are smaller than 0,57  $\mu\text{m}$ )

$X_{50} = 1,37 \mu\text{m}$  (50 % of the particles are smaller than 1,37  $\mu\text{m}$ )

$X_{90} = 3,27 \mu\text{m}$  (90 % of the particles are smaller than 3,27  $\mu\text{m}$ )

Figure 57: Particle size distribution of Blanc fixe 1 (Fritzen 2011).

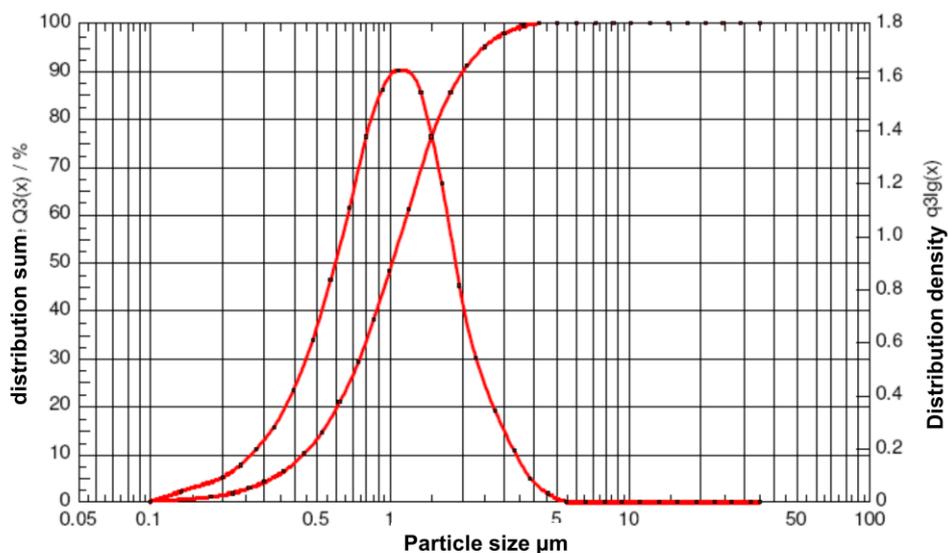


Figure 58: Particle size distribution of Blanc fixe 2 (Fritzen 2011).

## 6.2 Ink

Ink chosen to be tested was SunLit Diamond produced by SunChemical, the world's largest producer of printing inks and pigments. SunLit Diamond is a conventional ink series for 4-colour process printing, and it is formulated for use on all commercial sheet-fed offset presses allowing printing on wide range of paper and board. It is suitable for publication and commercial printing as well as for packaging and wet glue labels. (SunLit Diamond 2010: 1.)

SunLit Diamond is based on an innovative resin/oil combination that provides strong stability and optimum press performance for lithographic printing process. Its compounds are bio-based materials, such as vegetable oils, vegetable oil derivatives and alkyd and rosin based resins. SunLit Diamond is very lightfast (8) and offers low misting. In addition, it is fast setting and dries rapidly allowing quick work and turn or further processing of the print work. In addition, SunLit Diamond promotes the realization of ISO 12647-2 in offset pressrooms and complies with industrial standards as ISO 2846-1 (colour). (SunLit Diamond 2010: 1-2; SunLit Diamond 2009.)

For its technical aspects SunLit Diamond process colours are compatible with an extensive range of dampening solutions, and the reduction or elimination of IPA is supported. SunLit Diamond can be used with all types of offset printing plates. It dries by absorption and oxidation/polymerization. It is ready to use, and no additives are required. (SunLit Diamond 2010: 2.)

### **Filler in the ink**

What should be acknowledged is that the ink, SunLit Diamond, used in the test series was ready made ink. For this being the case, it already contained 4 % of filler material; ASP 101 kaolin. This specific grade of kaolin, ASP 101, is hydrous aluminium silicate treated with magnesium stearate. ASP 101 is typically used as filler for example in offset inks, paints and coating applications where ease of dispersion, hydrophobicity and resistance to abrasion are needed. Most essential properties of ASP 101 can be found in Table 32. (Ash 2007: 20; ASP 101 2011.)

**Table 32: Properties of ASP 101 (Ash 2007: 20).**

<b>Particle size</b>	0,4 $\mu\text{m}$
<b>Brightness (GE)</b>	87
<b>Refractive index</b>	1,56
<b>Density</b>	2,6 $\text{g/cm}^3$

## **6.3 Paper**

As the printing results are governed by the printing substrate, in this case paper, it had to be carefully chosen. As it was desirable to measure the gloss of the ink, a coated paper was to be used. To measure the print through, it was also important not to choose paper with too high grammage or too thick coating. On the strength of these requirements, light coated paper, EuroBulk,  $90\text{g/m}^2$  was chosen as a print substrate for the tests.

EuroBulk, a product of M-real, Europe's leading primary fibre paperboard producer and a major paper supplier, is a white, matt-coated fine paper for sheet-fed and heat-set web offset printing. With a voluminous surface and a bulk of 1.1, it allows for the use of lower basis weight (cost savings) and has an uncoated feel. EuroBulk is ideal especially for books, brochures and magazines, among others. Table 33 compiles the basic technical information about EuroBulk in basis weight of 90 g/m<sup>2</sup>. (EuroBulk datasheet 2004; EuroBulk Paper Profile 2008: 2; M-real 2011.)

**Table 33: Technical values of EuroBulk 90g/m<sup>2</sup> (Antalis Oy 2004.)**

Caliper	Brightness	CIE Whiteness	Opacity	Gloss	Smoothness
0,091 mm.	94 %	113 %	91,0 %	11 %	4,8 µm.
Test methods: Caliper ISO 534, Brightness ISO (R45/D65), CIE Whiteness ISO 11475, Opacity ISO 2471, Gloss TAPPI T 480 (75°), Smoothness PPS ISO 8791-4.					

## 6.4 Equipment

### IGT-printability tester

The test strips for the experimental part of this study were printed on IGT AIC2-5 printability tester. This section is to shortly introduce this equipment. In addition, appendix 1 is to illustrate the part list of IGT and appendix 2 demonstrates the operation principle of IGT printability tester so that the subsequent tests for this study can be repeated comparable.

IGT AIC2-5 –printability tester is a well-known product of IGT Testing Systems. For many decades it has been used by the printing industry for numerous types of tests on different substrates and inks in quality control and research. It can be used for both ink and paper testing and it is possible to print a wide variety of materials, such as board, plastic film, cellophane, laminate and metal. Possible tests include determination of ink requirement, ink transfer, lightfastness, set-off and mottle, among many others. Besides printing ink, it can be used to test resins, lacquers, coatings, and raw materials. (IGT AIC2-5 2002: 1-3; Leach & Pierce 2007: 838.)

IGT-printability tester is composed of an ink distribution system, aka inking unit, and a print unit. The inking unit used at Metropolia printing laboratory is AE inking Unit (Figure 59); a slow running inking unit which can be used to ink maximum of 4 printing discs simultaneously. (Inking Unit AE; Leach & Pierce 2007: 838.)



**Figure 59: Inking Unit AE (Inking Unit AE).**

IGT AIC2-5 print unit, illustrated in Figure 60 on next the page, consists of an impression cylinder of a 150° sector, on which 25-mm wide strip of printing substrate is placed, and a choice of one or two printing forms (printing discs). One of the principal properties of the AIC2-5 tester is that there are two speed types to be chosen from; a constant speed of 0,2-5 m/s, and an increasing speed of 0,5-7 m/s. Both of the speed types are adjustable continuously. The printing force is also continuously adjustable from 50 to 1000 N. (IGT AIC2-5 2002: 2; Leach & Pierce 2007: 838.)

IGT AIC2-5 of Metropolia comes without the possibility to use dampening solution, and therefore no tests can be made to study the ink/water emulsification. This is one aspect that has to be considered when interpreting the result part of this study.



Figure 60: Print unit of IGT AIC2-5 at Metropolia Printing laboratory.

### Densitometer

GretagMacbeth's Gretag D19C Reflection Densitometer (Figure 60) was used for the measurements of density. Besides measuring the density, it can also be used to calculate the halftone dot gain. Before the measurements are started, the densitometer must be calibrated to zero against the paper white (reference white) of the same paper that is used in the test prints. This is done in order to eliminate the influences of paper colouring and surface characteristics. The colour selection for the measurement can be done either manually or automatically. Density value is showed in the display in Figure 61. (D19C Densitometer 1998: 2.)



Figure 61: Gretag D19C Reflection Densitometer.

## Spectrophotometer

For the measurement of the colour-values (Lab), Hunterlab UltraScan XE was used. The UltraScan XE is a spectrophotometer with a dual beam xenon and a wavelength range from 360 to 750 nm. It is illustrated in Figure 62. (UltraScan XE 2008: 1.)

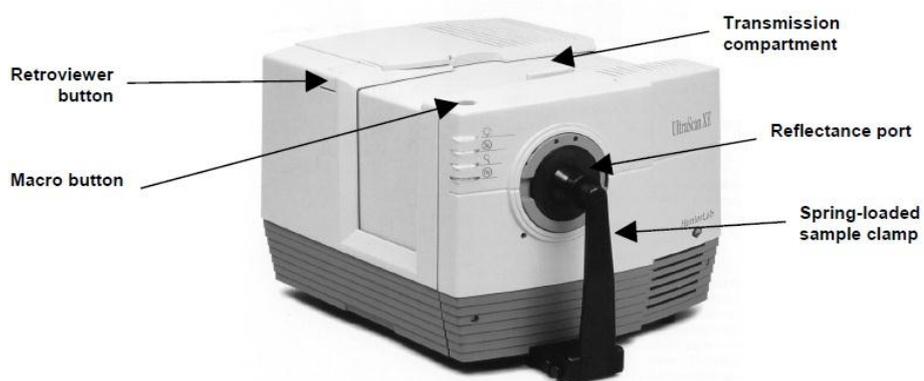


Figure 62: UltraScan XE (UltraScan XE 2008: 1).

## Gloss meter

As a gloss meter, Picogloss 503, a gloss measurement tool by Erichsen (Figure 63) was used. Picogloss 503 is a portable three-angle gloss meter with measurement geometries of 20°, 60° and 85° allowing the use for all three gloss ranges “high gloss”, “medium gloss”, and “low gloss”. In addition, it can be used in compliance with standardized measurement for instance with DIN & ISO. (Gloss Meter PICOGLOSS 503 2009.)



Figure 63: Picogloss 503 (Gloss Meter PICOGLOSS 503 2009).

## 7 Determinations

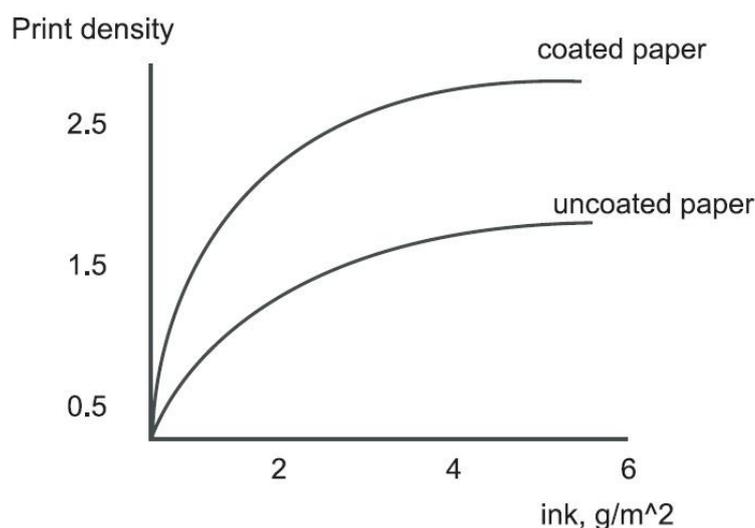
To study the characteristics and behaviour of ink printed on paper, a variety of measurements are needed. However, the results gained from these measurements may not reveal any significant information alone and therefore they are typically used only as a data for different kinds of determinations. For example density value itself does not always tell enough unless the ink amount used for gaining the corresponding density value can be determined. For the purpose of that, this chapter is to examine the different determinations made from the printed samples; what are they, why they are important and what their significance for this study is. It is also delineated how these determinations are defined; what are the measurements required and calculations needed.

### 7.1 Ink requirement

Ink requirement, or mileage, is defined as the quantity of ink required for reaching a given level of optical density on the print. A small number is advantageous as the less the ink is needed to produce the required density and/or colour, the better. Controlling the ink requirement means also controlling the density and colour of the print and the thickness of the ink film, and thus it is the most basic and generally speaking the most important printability factor. (Oittinen & Saarelma 2009: 233; Seidel 2010: 1.)

As the density increase can be interpreted as an increase of the concentration of ink pigments over the same area on the paper, it can be concluded that the ink requirement is in a substantial relation to the pigment concentration of an ink. Ink requirement is also affected by penetration of ink into the paper and variation in the ink film thickness. The influence of penetration is caused by the fact that, in essence, the part of the ink penetrated into the paper becomes part of the light scattering paper. Light scattering directs light intensity away from the ink, thus reducing the light absorption. That to be said, uncoated paper that allows more penetration compared to the coated paper, is more likely to result in higher ink requirement than the coated; see Figure 64 with a typical curve on print density as a function of ink requirement. The variation of ink film thickness occurs in consequence of uneven contact between the ink film and the paper surface.

The variation acts by reducing density, due to the exponential relationship between reflection and ink film thickness. (Håkans 2002: 7; Oittinen & Saarelma 2009: 233; Uribe: 60.)



**Figure 64: Print density as a function of ink requirement. A coated paper typically gives a higher print density than a paper with less, or no coating. (Håkans 2002: 7.)**

### **Why do we need to determinate ink requirement?**

For a printer, a target density is the simplest and easiest way to control the print quality. Therefore, the target of determination the ink requirement is done to find out exactly how much ink is needed to produce the target density, or ink film thickness, desired. Furthermore, the target density values can be used to produce the desired colour (CIELAB) values, for instance in accordance to ISO 12647, and are therefore the base for determining the optimum inking – ink requirement - to produce these values. (Oittinen & Saarelma 2009: 233; Seidel 2010: 1.)

As described in chapter 5.2, densitometry is still the most extensively used method for controlling the colour and thickness of an ink film. Thus the density values representing the ink film thickness are very important for the printing press operator for inking metering. Target densities are used as a fixed point of reference that will produce the smallest possible colour difference compared to standard values and the most suitable ink film thickness. (Seidel 2010: 1.)

### Determination of ink requirement

To calculate the ink requirement for a specific target density (ink film thickness) the amount of ink transferred to the paper is determined from the test print. First the test print is done with IGT printability tester and the amount of ink transferred to the paper is calculated via weighing the printing roller before and after the printing. Then the corresponding print density is measured from the test strip. As there will be approximately 5 test strips produced with decreasing amount of ink, this method will give us corresponding amount of data points. Print density and the corresponding amount of ink on the paper are plotted against each other in a graph from which the ink requirement at any given point can be determined. (Nieppola, 2010: 3.)

This plotted graph represents the ink requirement ( $\text{g/m}^2$ ) as a function of a density. As described in chapter 5.2, it behaves as a logarithmic curve and thus a logarithmic trend curve can be constructed. Furthermore, from the equation of this trend curve the values for the target density can be calculated. As the ink requirement behaviour changes with the ink and paper used, this trend curve has to be constructed for each test series separately. (Nieppola 2010: 3.)

To clarify the determination of the ink requirement, an example is provided. Following example is the ink requirement calculation for the reference ink tested in this study. The quantity of ink applied (in  $\text{g/m}^2$ ) is calculated from the following formula:

$$F_p = \frac{(G_1 - G_2) \times 10\,000}{a}$$

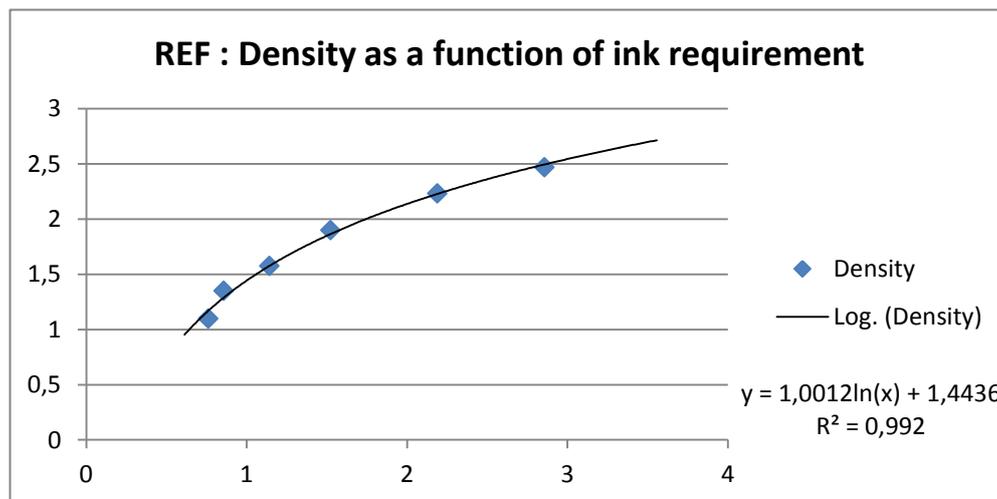
where

- $F_p$  = Quantity of ink ( $\text{g/m}^2$ )
- $a$  = inked area ( $\text{cm}^2$ )
- $G_1$  = weight of the printing disc after inking, before printing (g)
- $G_2$  = weight of the printing disc after printing (g) (Nieppola 2010: 3; Nießner 2000: 13.)

From the equation above, we need the  $F_p$  - the ink amount transferred per square meter - value with a corresponding density value, for plotting the ink requirement graph; density as a function of ink requirement. This is illustrated in Table 34 and in Figure 65.

**Table 34: The ink amount transferred ( $\text{g}/\text{m}^2$ ) and the corresponding density value.**

$F_p$	Density
2,86	2,47
2,19	2,23
1,52	1,90
1,14	1,58
0,86	1,35
0,76	1,10



**Figure 65: Trend curve for density as a function of ink requirement.**

After the trend curve is constructed, the ink requirement value in the target density can be calculated from the formula. In this example case from the following equation:

$$y = 1,0021 \ln(x) + 1,4436$$

$$\rightarrow x = e^{-1,4336/1,0012}$$

where  $y$  is the density and  $x$  is ink requirement ( $\text{g}/\text{m}^2$ ). As our target density value, according to the recommendations by VTT, is 1,45, the result from this equation is

$\approx 1,06 \text{ g/m}^2$ . In other words,  $1,06 \text{ g/m}^2$  reference ink is needed to produce the density of 1,45.

#### *Ink film thickness*

The determination of ink film thickness can be easily calculated after the density with the corresponding quantity of ink is known; dividing the quantity of ink in grammage per square meter by the density yields the ink film thickness as follows:

$$S = \frac{F_p}{\delta}$$

where S is the ink film thickness ( $\mu\text{m}$ ),  $F_p$  is the quantity of ink and  $\delta$  is the corresponding density value. (Nießner 2000: 13.)

#### **Coloric determination of ink requirement**

Alternatively, or additionally, it is possible to determinate the ink film thickness range in which a colour match to the reference is achieved (within a permitted tolerance). This is done by plotting the calculated colour differences against the corresponding ink quantity. The position of the minimum then indicates the optimum approximation to the ideal colour. Figure 66 illustrate situation where ink 1 has the ideal value at  $1,1 \text{ g/m}^2$ , ink 2 at  $1,4 \text{ g/m}^2$ , and ink 3 at  $1,2 \text{ g/m}^2$ . These can also be converted into percentages which show the difference very clearly:

- Ink 1 = 100 %; it exhibits a very good approximation to the ideal.
- Ink 2 = ca. 42 % weaker in colour; it is well outside the tolerance limit.
- Ink 3 = ca. 17 % weaker in colour; it is just within the tolerance limit. (Nießner 2000: 15-16.)

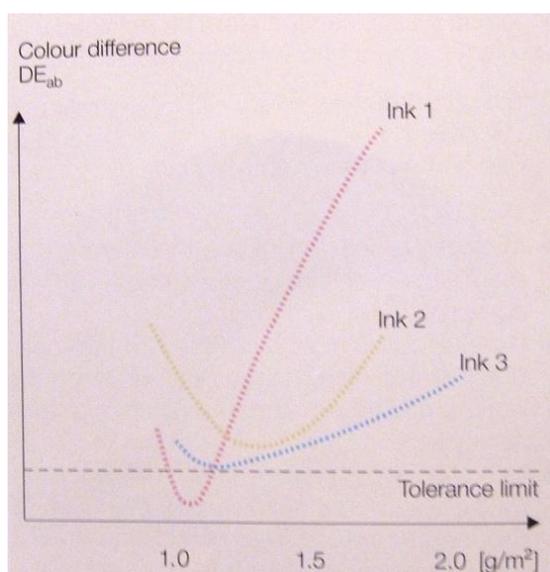


Figure 66: Colorimetric determination of mileage (Nießner 2000: 16.)

## 7.2 Print through

Even with no ink penetrated into the paper, the print would, to some degree, be visible from the reverse side of the paper. This is if the paper opacity is not 100%. Print through is defined as the magnitude of visibility in density unit on print in the reverse side of the paper. Values above 0.1 density units are unacceptable from a subjective viewpoint. (Nieppola 2010: 3; Oittinen & Saarelma 1998: 234.)

The contribution of the transparency of the paper to print trough is called show trough. Print through is also affected by the ink consists; pigment penetration of the ink acts by reducing the effective thickness of paper and inks oil penetration by reducing the light scattering of the paper. (Nieppola 2010: 3; Oittinen & Saarelma 1998: 234.)

As mentioned above, print trough is measured as a density on the reverse side of the paper. To study its affect, it will be defined as a function of the density and calculated in the value of the target density. (Nieppola 2010: 3.)

### 7.3 Set-off

An ink film is reputed to be set when it is touch-proof. Set-off occurs when the ink does not set properly and it causes the wet ink to transfer to the next sheet in the delivery pile. Set-off is largely contributed by an excessive ink film thickness and is a particularly problem with low absorbency coated papers. It can be prevented by using of UV curing inks or anti-set-off compounds discussed in chapter 3. (Destree 1994: 14:24 & 15:31; Thompson 2004: 266 & 333.)

Set-off is tested where another surface (paper) is pressed against a print with a controlled pressure. The set-off determination is typically produced both during initial setting, immediately after the printing, and during the subsequent drying stages. To get the value for set-off, the optical density transferred to the counter surface is measured. It is represented as a function of the density of the untouched print. The curve is exponential and a trend line is constructed for getting the set-off value in the target density of a printed impression. In Figure 67 a set-off data points and curve are represented as a graph for reference ink used in the experimental part of this study. (Leach & Pierce 2007: 399; Nieppola 2010: 3; Oittinen & Saarelma 1995: 200.)

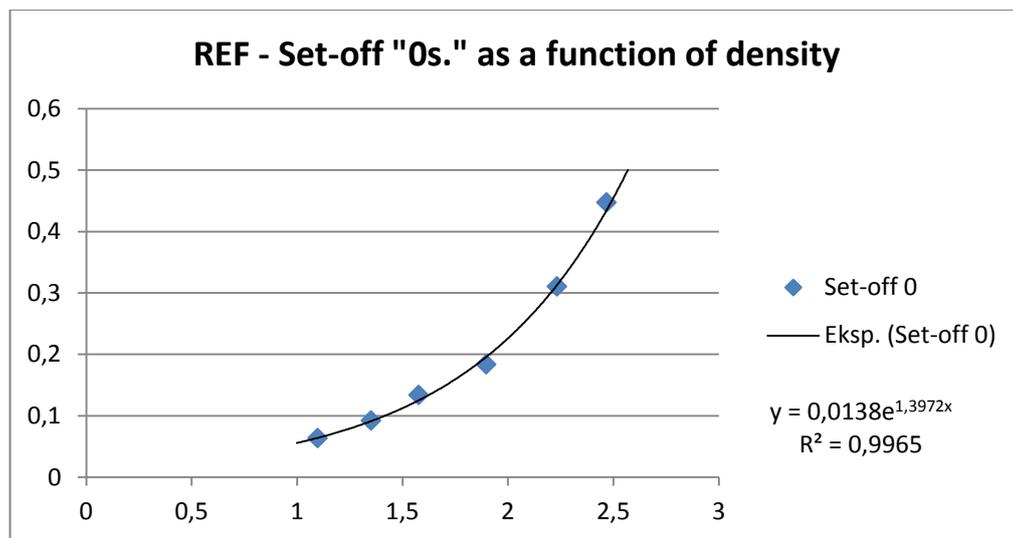


Figure 67: Set-off as a function of density

The equation in the reference ink graph in Figure 65 is as follows:

$$y = 0,0138e^{1,3972x}$$

where  $y$  is set-off as a density value and  $x$  is the corresponding density value of an untouched print. Using the target density value of 1,45, the result from this equation is  $\approx D0,105$ .

As mentioned, set-off is largely contributed by ink film thickness which presumably will vary between different inks in their target density. For example if one ink requires notably more ink than another to produce the same density value, it is inevitable that the set-off will vary also. For this being the case, the set-off was also determined independent from the density, as a function of the ink quantity (Figure 68.) This would tell if the filler concentration would affect the set-off.

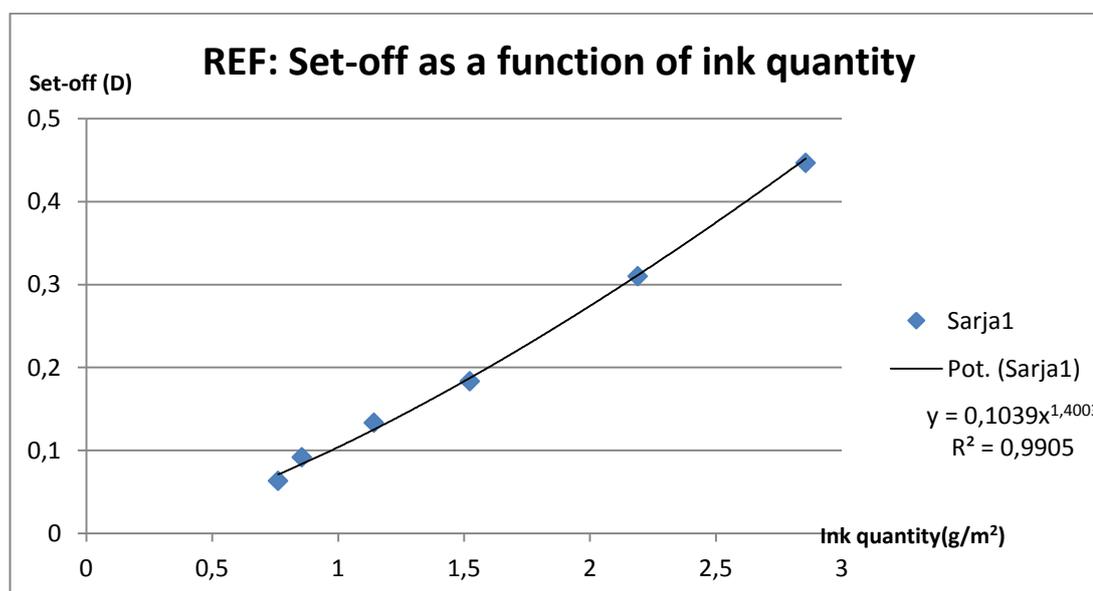


Figure 68: Set-off of reference ink as a function of ink quantity.

## 7.4 Gloss

The gloss of the ink is discussed in more detail in chapter 5.1. The gloss values for the corresponding density values are gained directly from the gloss measurements with gloss meter. But as we need a fixed point of reference for comparing the results of different inks, we need to solve the gloss in the target density we have used in all other determinations as well. This is done similarly to any other determinations; a graph is constructed from the data points of density and corresponding gloss values. There is no

known function for this relation, as far as I have discovered any information, so a well behaving curve has to be found. From the experience in this study, third-degree equation is needed for fitting the data points in a curve.

## 7.5 Colour

Lab-values for offset print are defined in the ISO standard. Whether printing strictly in accordance with any standard or not, controlling the colour is essential for printing presses. After the Lab-values were measured with a spectrophotometer, the measured values were plotted with corresponding density values and a fitted curve of Lab-values as a function of density was created. Again, it is important to fix the values to some point of reference (target density) and for that the function was needed.

As an example, Figure 69 and 70 illustrate the Lab-values of the reference ink as a function of density. The plotted points are the measured data points and L is the trend curve for these data points against the density values on x-axis. From this information the equations can be constructed to calculate the Lab- values in target density.

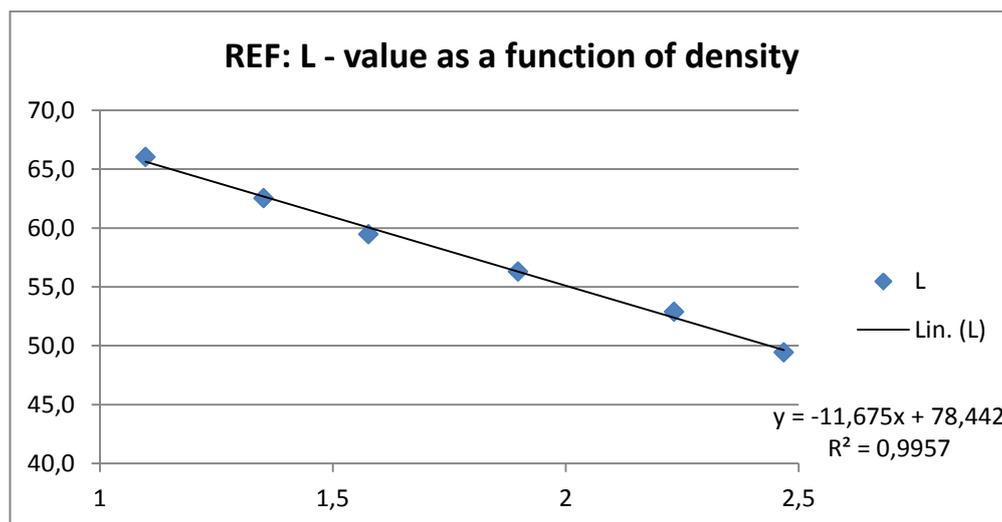


Figure 69: L-value as a function of density in reference ink.

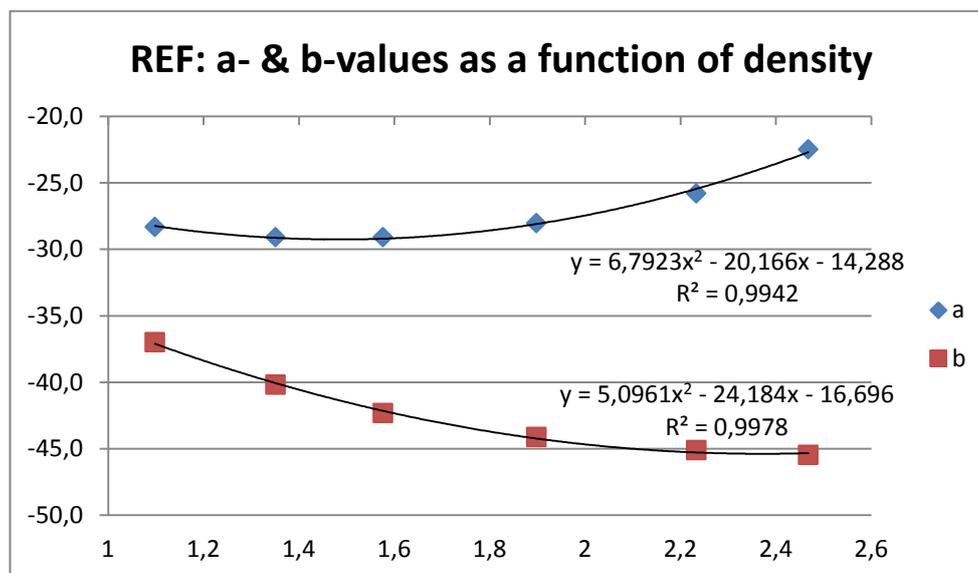


Figure 70: A- & b-values as a function of density in reference ink.

### Colour difference

As a part of the results part of this study, colour difference calculations was conducted for the purpose of to find out whether the fillers will affect in the colour. First the Lab-values were calculated in the point of reference (target density) and from these values the colour differences were calculated with the most basic of the tolerance method; the CIE1976 colour difference formula, explained in chapter 5.2.4. Also the following differences in the colour were determined:

- $\Delta L$  which represent the difference in lightness/darkness value: positive is lighter and negative is darker than standard.
- $\Delta a$ ; the difference on red/green axis: positive redder and negative greener.
- $\Delta b$ ; the difference on yellow/blue axis: positive yellower and negative bluer.
- $\Delta C$ ; the difference in chroma: positive more saturated and negative duller.
- $\Delta H$ ; the difference in hue, which depends on the quadrant: 1st: positive yellower and negative redder; 2nd: positive greener and negative yellower; 3rd: positive bluer and negative greener; 4th: positive redder and negative bluer. (Color Communication 2007: 15.)

## 8 Work process

### Preliminary tests & test plan

Prior starting the actual test series, preliminary tests were performed to ensure the successful test results. First the ink material to be tested, SunLit Diamond, was tested in IGT printability tester without any additives. This was to ensure that the ink will run properly in the testing machine and for the purpose of rehearsing the accurate use of the testing machines. These preliminary tests went fine and no obstacles occurred.

After the runnability of the ink in IGT was assured, the screening tests were performed, conducted at Sachtleben in Pori mill. This was a test to study the dispersing properties of the ink and the addition of  $\text{BaSO}_4$  in the ink. Dispersion was carried out using an automatic muller of Ault & Wiberg illustrated in Figure 71.



Figure 71: Automatic muller, Ault & Wiberg (Kulmala 2010b: 1).

With the information provided from the preliminary tests, the actual tests were decided to begin with cyan series and proceed with yellow and magenta. From the  $\text{BaSO}_4$  offering, 2 different Blanc fixe products were selected to the tests. Also a reference ink, milled ink without any additional additives, and an ink with competitive filler, treated kaolin, was chosen to be tested.

Three different filling rates were chosen; 4, 8 and 12 %.

### **Workflow for the test series**

The preparations of ink batches were performed at Sachtleben in Pori mill; the ink and filler were weighted, milled and then collected from the muller. These steps are illustrated in Figures 72 and 73. After the preparations at Sachtleben Pori mill, the ink was packed in small glass jars and send to the printing laboratory of Metropolia University of Applied Science.



**Figure 72: Application of the ink and filler on the muller (Kulmala 2010a: 1).**



**Figure 73: Collection of the milled ink (Kulmala 2010a: 2).**

The test strips were printed on IGT –printability tester at the printing laboratory of Metropolia. The IGT –printability tester is introduced in chapter 6 and the operation principle of IGT is described in appendix 1. After the test strips were printed, they were

let in place to dry for approximately 24 hours. This was done to standardize the measurement results. Experience in practical applications has shown that for example the density will decrease over the time but after 6 hours no significant decreasing will appear. With cyan the density will decrease approximately 0,15 units in 6 hours. In addition to density, also the colour co-ordinates, i.e. Lab-values, may change substantially after ink drying. The criteria according to the ISO standard are exclusively dry values. (Seidel 2010: 2; Vesalainen 2009: 42.)

After the drying period measurements were performed for the test strips. First the density values were measured after which Lab-values and gloss measurements succeeded. All the measurement data was tabulated to be used for the determinations which were the next step of the work process. Following the graph constructions and calculations needed for the determinations the results were interpret and the effects of fillers analyzed.

## 9 Results

In this chapter, the results constituted from the experimental part are discussed. For convenience of the result handling, only the results worthy of remark are presented in this chapter. When considering the results provided in this chapter one should keep in mind the following:

- As the tested inks were pre-treated, milled, the results are comparable only among themselves, and no comparison should be done with external results or standards, such as ISO 12647-2.
- The pre-treatment, milling, was done for the reference ink as well, to make it comparable to the inks with additional fillers. Thus, again, no comparisons should be made with external results or standards, not even with the reference ink.
- For practical reasons, the addition of the fillers to the ink material was done adding it on top of the ink and via milling it with the original ink material. As

this is not the proper way to fill the ink, the results have to be considered as indicative.

- The fact that the ink already contained filler (4% kaolin) was ignored.
- For the time being a limiting factor, the results from this study are based on only one tested ink colour, cyan. Hence no generalization should be made, as any information about the behavior of the yellow and magenta inks are not available.
- Again, as for the time allowed, no repetitions of the tests were possible to perform. Thus the results should be considered carefully, and again, only as indicative.
- The IGT-printability tester used offered no opportunity to use dampening solution; hence no information is available whether the fillers impact on ink/water emulsification which is substantial part of the offset lithography.

For facilitate the handling of the results, abbreviations were used as follows:

- REF: Reference, milled ink not containing any additional filler;
- BF1 4%/8%/12%: Blanc fixe 1 – filling rates 4, 8 & 12 %;
- BF2 4%/8%/12%: Blanc fixe 2 – filling rates 4, 8 & 12 %;
- Kaolin 4%/8%/12%: competitive filler, kaolin- filling rates 4, 8 & 12 %.

## 9.1 Ink requirement

As in more detailed described in the chapter of Determinations, ink requirement is defined as the quantity of ink required for reaching a given level of optical density on the print. As a rough principle, the smaller the number the better; the less the ink is needed to produce the required density and/or colour, the better it is. However, other parameters such as gloss procurement must also be taken into consideration; no real advantage can be accomplished if the quality properties have to be compromised too much. As the results for ink requirement following matters were considered:

- Does the filler affect on the ink requirement in the target density?
- If so, what is the effect on increasing the filler content?
- If there was any effect, why would this effect appear?

- Does the different filler material have different effect, regardless the filling amount?
- If so, how are these effects differing, and what would be the reason for these differing effects?
- Concluding all of the above, what would be the best, and worst, filler to be used?
- The cost factor; when considering the cost of filler compared to the cost of pigments/ink material, is it worth of using?

As explained in chapter of determinations, to study the contribution of different fillers and filling rates to ink requirement, the ink requirement values has to be determined in a fixed point of reference. As the density of an ink film is still the most common way to control the colour and thickness of an ink film, it is advisable to determine the ink requirement as a function of density and calculate the values for the target densities chosen. The target density used in this study was chosen by the recommendations by the Technical research Centre of Finland (VTT), and for cyan ink, printed on light weight coated paper it is 1,45 (+/- 0.5) (Table 31).

### **General view**

If the spacing effect was to succeed, it was possible to expect positive results from the ink requirement determinations. This would mean that the ink requirement would stay in the same level with the reference ink, or in the most positive scenario even be decreased. However, it has to be remembered that the ink where the filler was milled in, was ready make ink and already contained 4 % of filler. That 4 % has been chosen for some particular reason; maybe because it was tested that above that limit the spacing effect does not grow in its efficiency anymore, or perhaps for the reason that after exceeding the limit of 4 % the properties of the ink were compromised too much. This is something only the developer of the ink knows, but as said, there must be some reason behind it. And for that reason, and because the ink requirement is in a substantial relation to the pigment concentration of an ink, it was presumable that at least no efficient spacing effect could probably occur anymore. Nonetheless, even with no increase in ink requirement it was constituent to find out how much ink would be

required to produce the target density, in which all the quality parameter were measured.

Adding the filler to the ink obviously has an effect to the ink requirement for a specific target density. In regard to the expectations of the change in ink requirement relating to the filling rate, the most positive results were gained from using the Blanc fixe 1 and the competitive filler, kaolin. As illustrated in Figure 74, in general it can be seen that from the Sachtleben products, Blanc fixe 1 outperformed Blanc fixe 2 in all the filling rates. This was expected due to the smaller particle size of Blanc fixe 2. The competitive filler performed slightly better than Blanc fixe 2. When interpreting these results, one must be careful and the possibility of errors and process variation cannot be ignored.

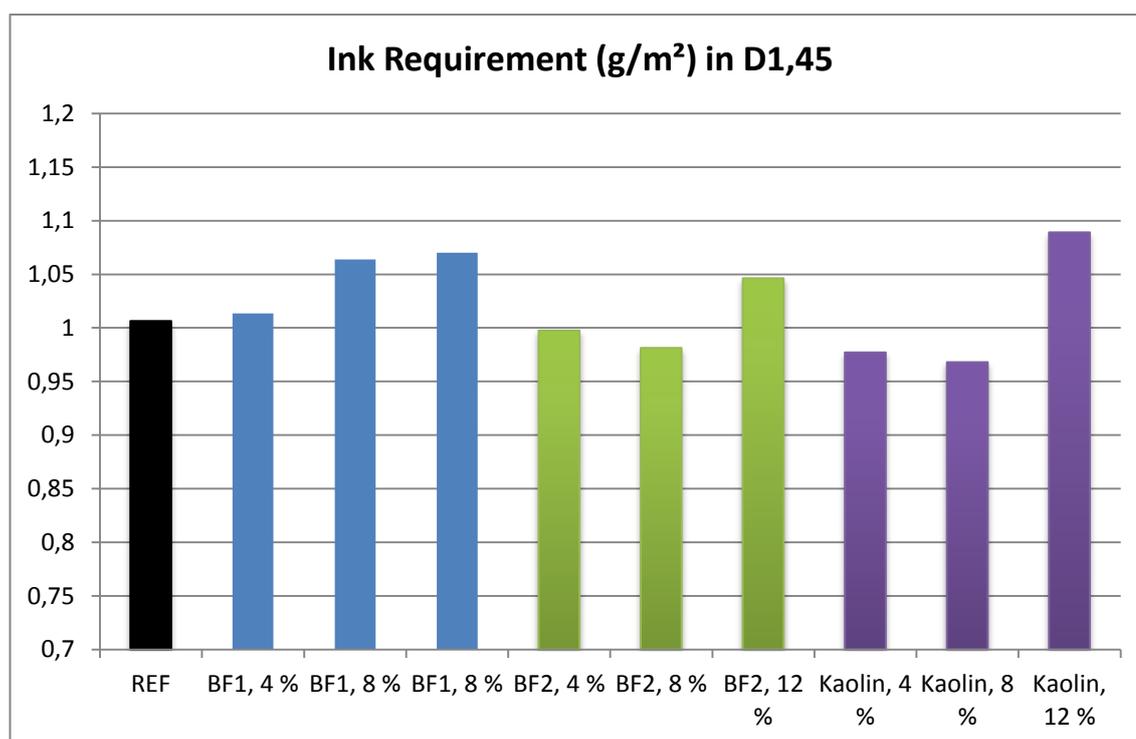


Figure 74: Ink requirement in target density.

Interestingly enough both of the Blanc fixe 2 and kaolin fillers produced descent in the ink requirement when the filling rate was either 4 or 8%, and jumped off to increase when the filling rate was increased to 12%. To confirm this, ink requirements were calculated in other densities as well; the average change in ink requirement is illustrated in Figure 75. These very positive results can be interpreted either as a success in the pigments spacing or can be ignored as a process variation and effects of measuring

errors. In my opinion, no hasty conclusion should be drawn; however, these results indicate positively to the direction that further tests will be worthwhile.

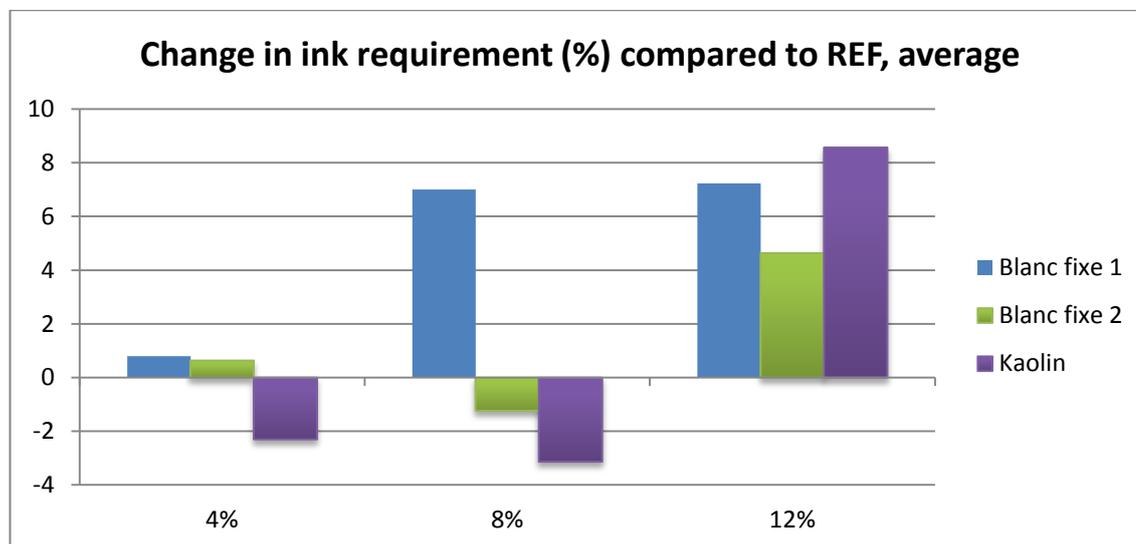


Figure 75: Average change in ink requirement (%) compared to reference ink.

### Blanc Fixe 1

As already stated above, Blanc fixe 1 was the only filler behaving so that with the increase in the filler content, also increase in the ink requirement happened commensurately.

The increase in ink requirement between filling rates 4 and 8 % was relatively much bigger than what was between 8 and 12%. This can be seen from the Table 34 with the ink requirement results for Blanc fixe 1. Adding up the process variation and measuring errors, these results can be simplified by stating that considering the inaccuracies, the ink requirement of Blanc fixe 1 4% was approximately equal to that with reference ink, and the ink requirements of 8 % and 12% filling rates were in practice the same with each other. So the question is that, what is the significant factor that makes the ink requirement jump when the filler content is doubled from 4 to 8%, but then again, stays moderate even the filler content is increased from 8 to 12 %. This observation is illustrated in Figure 76.

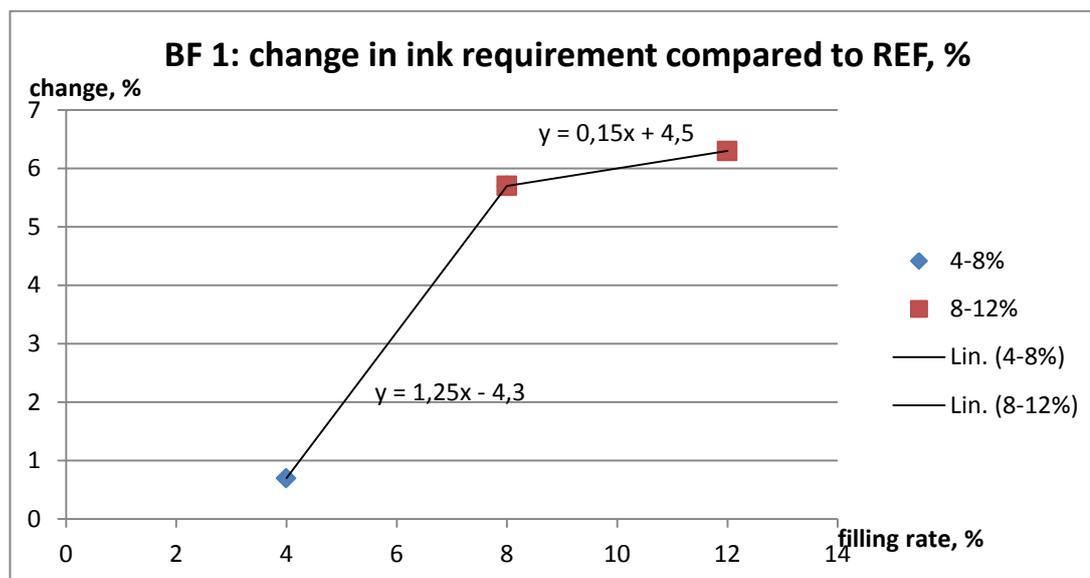


Figure 76: Change in ink requirement (compared to reference ink) of Blanc fixe 1 as a function of filling rate.

The conclusion from the results of Blanc fixe 1, with a particle size of approximately  $1\mu\text{m}$ , might be that the particle size is too large for the spacing to succeed in desirable way; not enough filler particles are available to space all pigment particles which results as increased ink requirement for the efficiency of pigment particles cannot be increased. In addition, particle size itself is defining factor in the matter of ink density, as described in chapter 3.2.1.

However, what is positive; the small amount of 4 % is quite neutral for the result of ink requirement which means that as long as it does not affect to the print quality too decreasingly it can be used to lower the cost of the ink. The only data points we have are the data from the filling rates of 4, 8 and 12 % which means that we don't know whether the relation between the filler content and increase in ink requirement is as linear as it is illustrated in Figure 75. It might be as well that the change is very moderate between the filling rates of, for instance, 4 and 6 % and only then the steep rise in ink requirement would take place. To find this out, more data points are needed.

### Blanc fixe 2

The ink requirement change in Blanc fixe 2 is illustrated in Figure 77. Unlike with Blanc fixe 1, Blanc fixe 2 shows decrease in the ink requirement compared to reference ink. This is the case with filling rates 4 and 8%, but when the filling rate is increased to 12%, the ink requirement jumps and becomes increasing compared to reference.

This might be a positive result from successful spacing of the pigments in ink with the filler. The particle size on Blanc fixe 2 is approximately  $0,7 \mu\text{m}$ , smaller than what Blanc fixe 1 has ( $1,0 \mu\text{m}$ ). The indication from this could be that the particle size is small enough to execute a felicitous spacing of the pigment particles. However, the threshold for increasing the pigment scattering efficiency is somewhere above 8% but significantly under 12 % of filling rate.

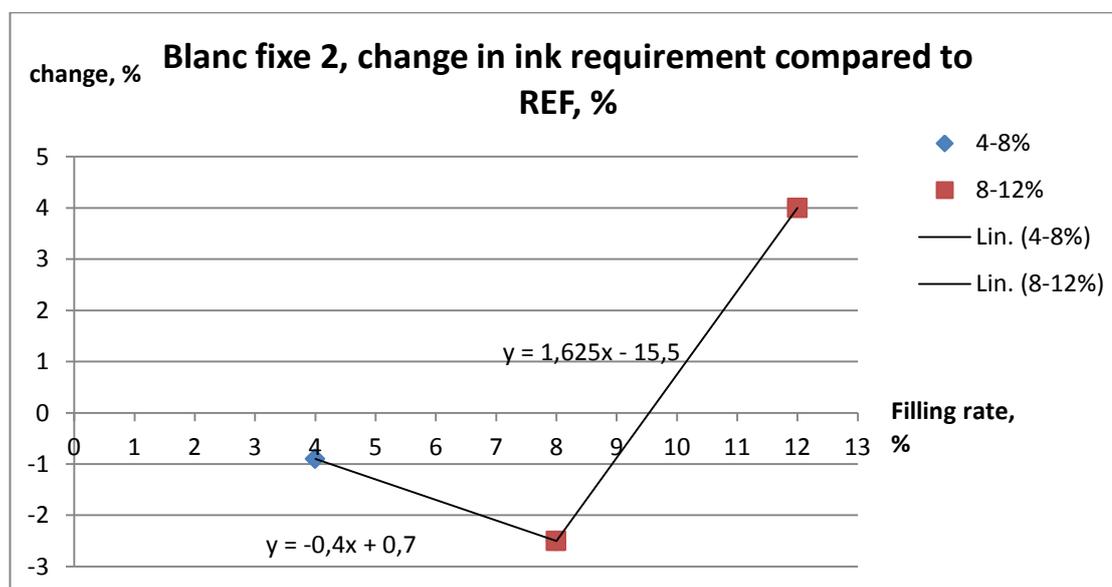


Figure 77: in ink requirement (compared to reference ink) of Blanc fixe 2 as a function of filling rate

### The cost factor

As the single biggest motive behind this study was to examine whether the relatively high cost pigments could be replaced by the filler pigments, the final optimum filling rate will be dependent also on the cost of the particular filler pigment. However, it is not certain that the ink requirement, as a function of filling rate, behaves as a linear function, as described in Figures 76 and 77; having only three data points is not enough to certify that assumption. Also, if one would like to find the optimal filling rate using the variables of pigment and filler cost as a factor, the behaviour of the change in ink requirement compared to the filling rate should be known much more exact. Also, one should bear in mind that there is still the question about optimization with the effects of filler content on print quality.

What we can do, however, is to calculate approximate results for the use of filling rates 4, 8 and 12%. These calculations are still somewhat vague, but indicative. The following results take into account only the cost of an ink and filler material, ignoring all the other properties of the corresponding ink mixture that will be discussed later in this chapter. The calculations of costs are based on the material costs tabulated in Table 35.

**Table 35: Cost of the materials**

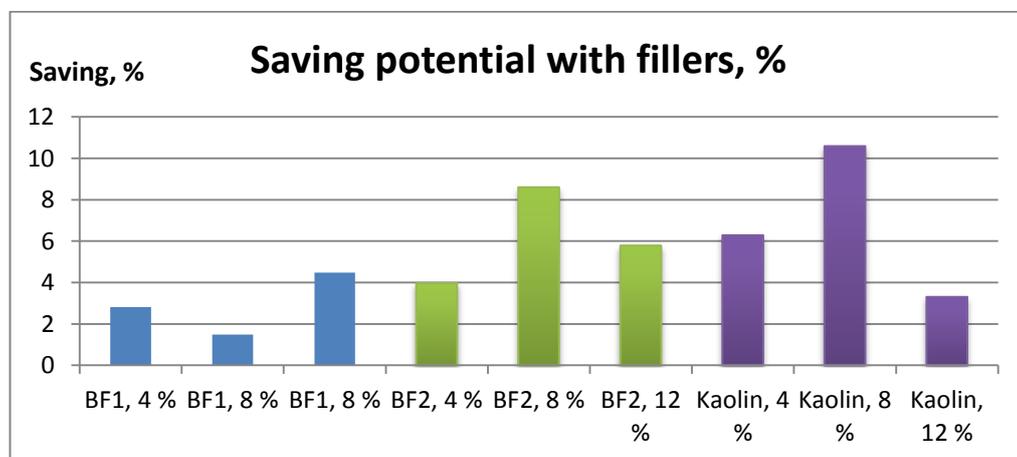
Material	Price per kilo (€)
SunLit Diamond, cyan ink	6,0
Blanc fixe 1	0,9
Blanc fixe 2	1,3
Kaolin	0,7

The costs are calculated for the ink requirement in the target density of 1.45. The following equation is used:

Cost of the mixed ink material =  $a \times (1 - b) \times \text{ink price} + a \times b \times \text{filler price}$ ,  
where:

- $a$  = ink requirement ( $\text{g/m}^2$ )
- $b$  = filling rate (0,04; 0,08 and 0,12)

As a summary of results, Figure 78 is provided.



**Figure 78: Saving potential with different fillers.**

## 9.2 Set-off and print through

As can be seen from Figure 79, no specific correlation between filler content and set-off in target density was discerned. This is mainly because the ink quantities of a certain ink in the target densities vary. Another factor influencing this is most likely the measurement of set-off; the printed ink film of set-off area is nothing but constant causing large variation. This is illustrated in Figure 80 In addition, the changes were small in their absolute numbers, hence it can be said the fillers did not affect the set-off (significantly).

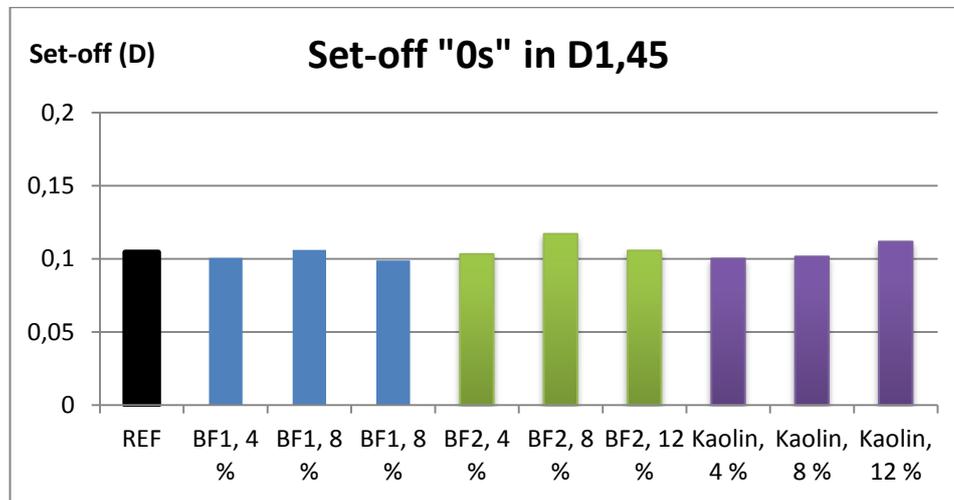


Figure 79: Results of set-off "0s" in target density

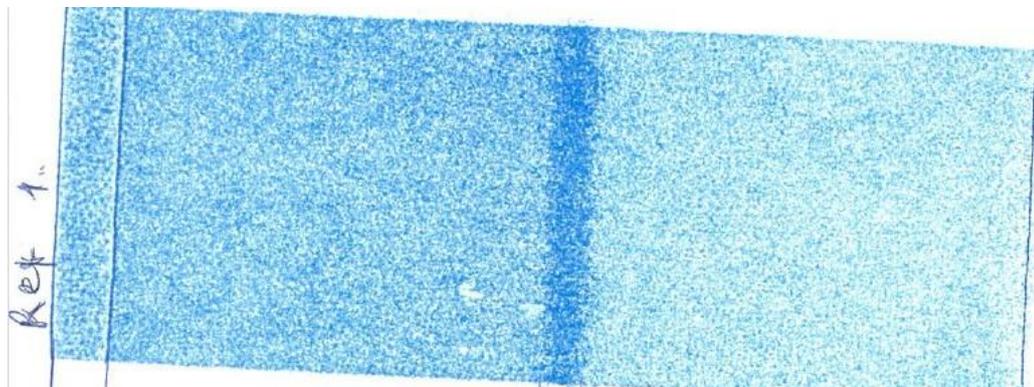


Figure 80: Printed test strip (set-off) of reference ink in density of 2,5.

As describe in the chapter of determinations, the ink quantity will govern the results of density. Hence, the set-off values were determinated also as a function of ink amount. As can be seen in Figure 81, there is still no correlation between filler content and set-off.

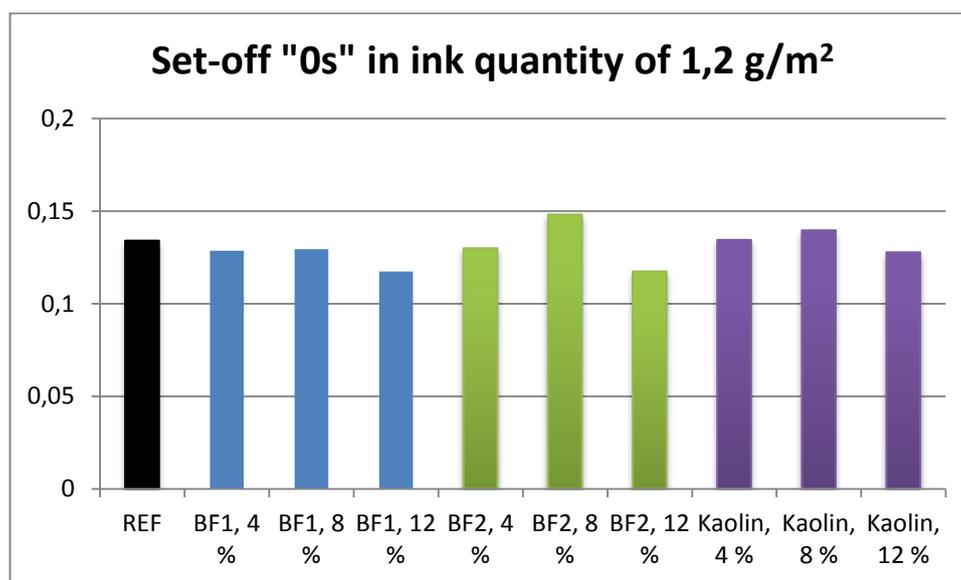


Figure 81: Set-off "0s" in ink quantity of 1,2 g/m<sup>2</sup>.

### Print through

The measurement of changes in print through did not succeed as expected. Clearly the paper used in test was thick enough not to allow any variation in print through even in commensurate to high versus low density, let alone to the relation with fillers. Thus no results are to be expounded.

### 9.3 Gloss

Modification of inks, e.g. adding fillers, is always balancing between the cost and different ink properties. One important factor to consider is gloss, which typically is a much desired property for high quality print. As a summary of the results gloss 60° values calculated in the target density 1,45 are illustrated in Figure 82.

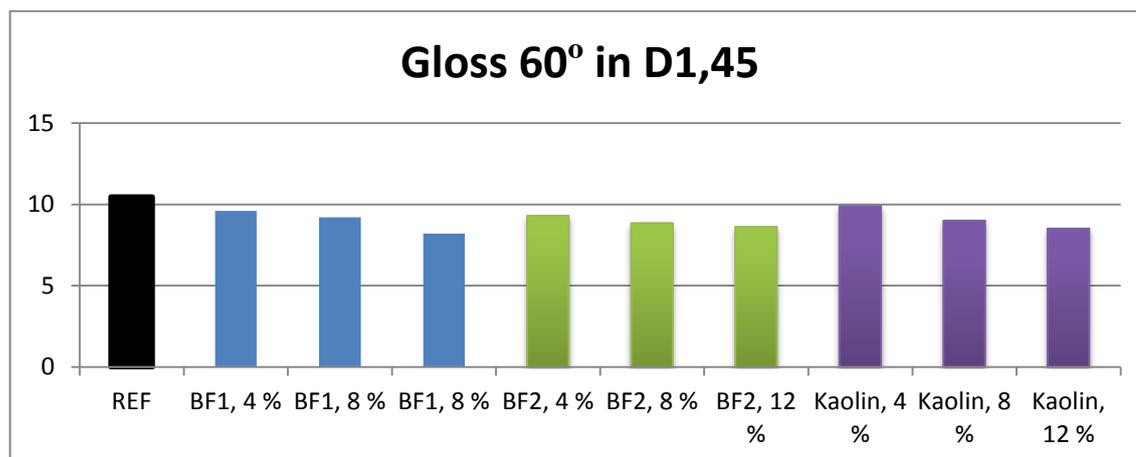


Figure 82: Gloss 60° in target density.

As seen from Figure 82, there is some reduction in gloss when the filler content increases. Percentually the reduction in gloss relatively to the filler amount is between 5 and 20 percent, but then again, increase in absolute numbers is not too high in any case. Gloss anyhow is relatively small and the ink materials should be tested on more glossy papers to reveal any possible significant reductions.

Reduction in gloss when adding, and increasing the filler content may be a result of the particle size distribution of the fillers; too much coarse pigment particles are detrimental to gloss. It might also be affected by poor dispersion and pigment wetting, resulted from the milling process, as they will cause light scattering within the ink film which then reduces the gloss.

Another explanation might be the fact that the gloss giving element, vehicle, is reduced relatively in the ink when an amount of 4 to 12 percentage of weight is compensated by the filler. This might be also the reason for that kaolin with a smallest particle size of 0,4  $\mu\text{m}$  did not perform hardly any better than other fillers; with decreasing particle size specific surface area is also decreasing, demanding more vehicle component to wet the pigment particles completely. It is also identified that the inhomogeneous distribution of ink components throughout the printed ink film may have an influence to a low gloss, as this can correlate with lower surface resin content.

## 9.4 Colour

In L-value no significant alternation in the slopes of the linear trend curves was noticed. This denotes that no affect is contributed from the filler and the filling rate to the decrease speed of the L-value. The decrease itself is predictable in its basics. This can be seen in Figures 83 and 84 and especially in their trendline equations with their slopes.

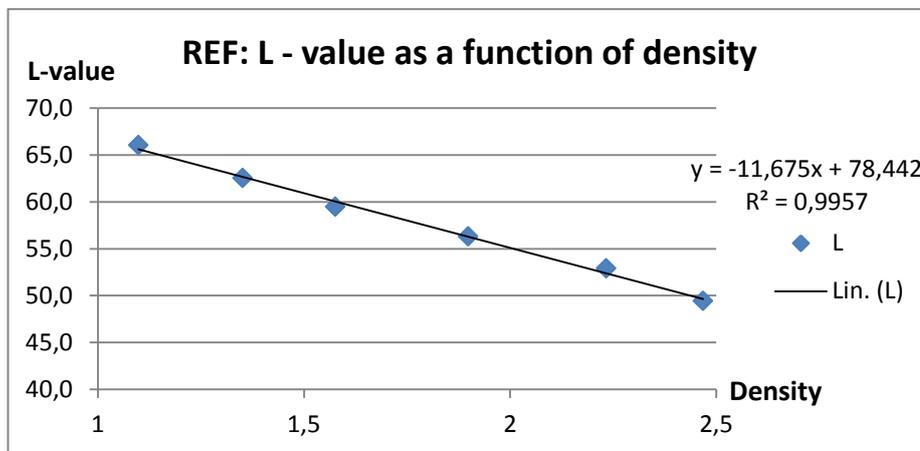


Figure 83: L-value as a function of density in reference ink.

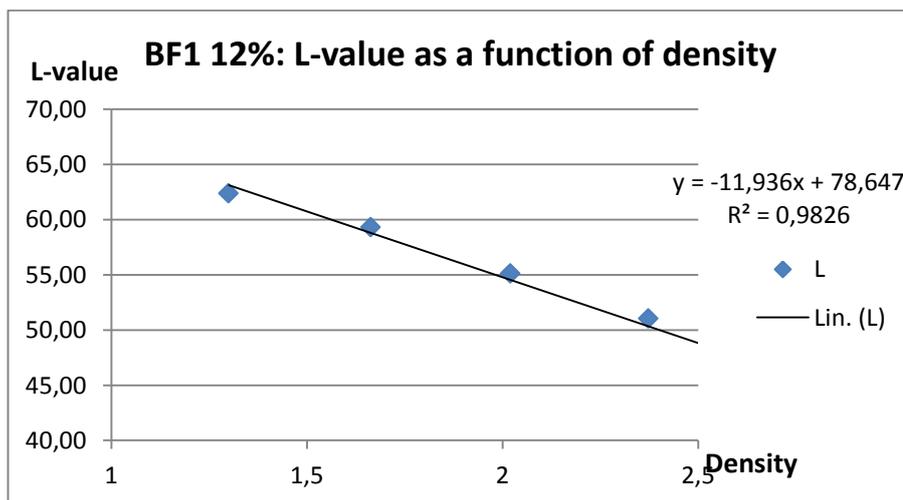


Figure 84: L-value as a function of density in Blanc fixe 1 12%.

Also in the Lab-values calculated in target density 1,45 no coherent change commensurate to different fillers and filling rates was perceived. This is illustrated in Figures 85 and 86. This was good news.

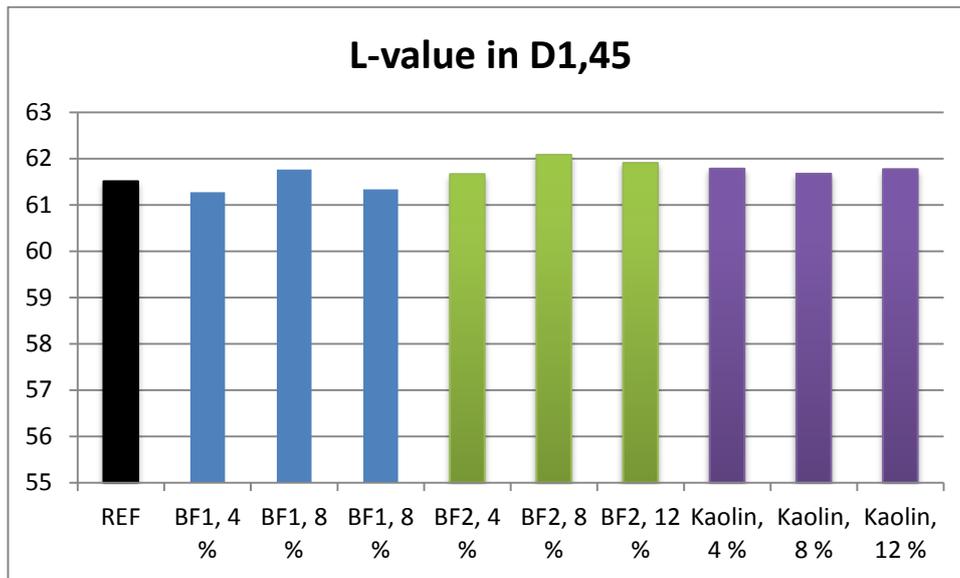


Figure 85: L-value in the target density.

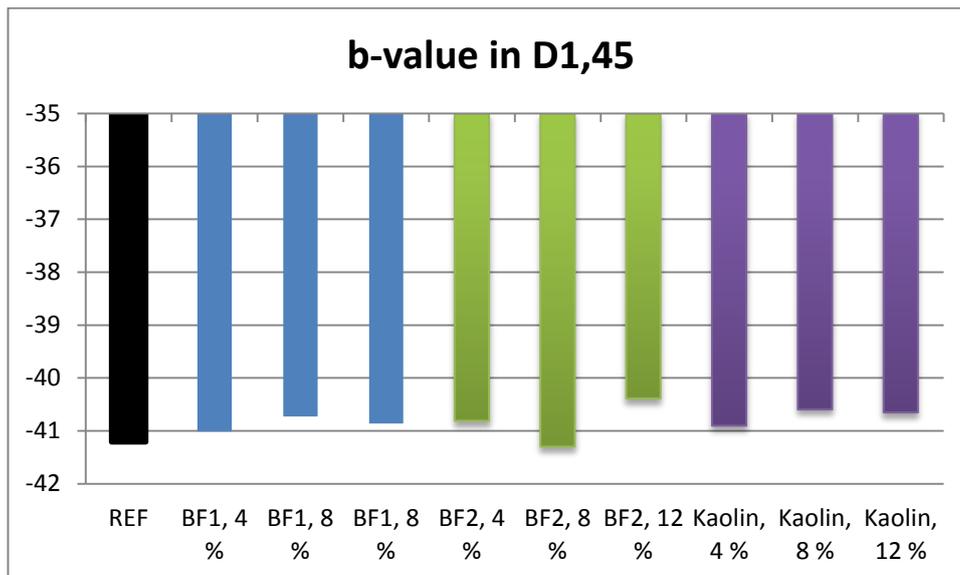


Figure 86: b-value in the target density.

### Delta E & delta H

Calculations of delta E and delta H were adhered to the equations of CIE76. Calculations indicated no significant colour differences as the delta E values stays under 1,2 (Figure 87). And what is even in more importance is that, referred to the ISO standard 12647-2 where the delta E value for process inks is tolerated until 5, the results are much better than acceptable. As a conclusion it can be stated that fillers do not affect

ink colour noteworthy, though slight increase in colour difference in consequence of filler rate increase is evident.

This conclusion is backed up also from the perspective of absolute colour difference, hue difference (delta H). As illustrated in Figure 88, some variation in hue can be observed, but it is minor, and stays clearly below the acceptable thresholds in ISO 12647-2; according to ISO, a maximum tolerance of 1.5 is permitted in gray areas and 2.5 in the primary colours.

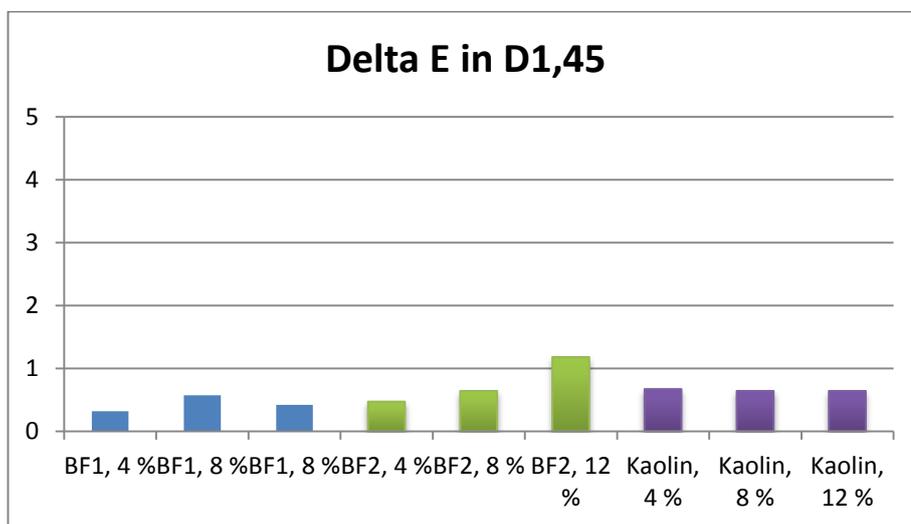


Figure 87: Delta E CIE76 in target density.

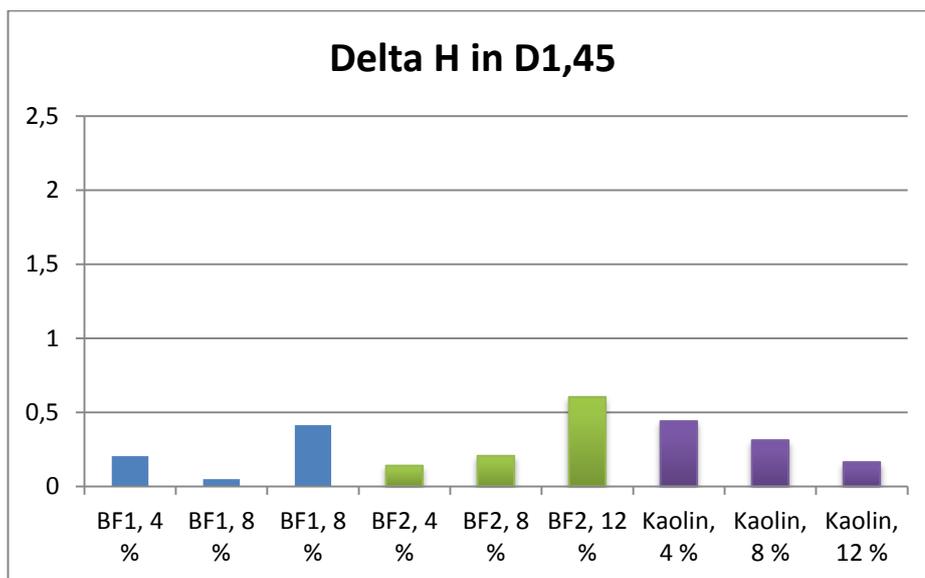


Figure 88: Delta H CIE76 in target density.

## 10 Summary and conclusions

Printing industry is one of the branches where the price accounts for a vast share of competitiveness of the companies. This accounts for the perennial demand for lower end-product prices, which in turn inevitably leads for request of cost reduction of the raw materials. To be able to reduce the price of printing ink, where the cost of the pigment material can be accountant for more than what all the other ingredients together are, it is essential to exploit the possibilities to compensate the pigment loading of the ink. To fulfil this purpose, less-expensive filler pigments from a variety of sources, such as calcium carbonate and aluminium silicate, are used. This is also what the barium sulfate products of Sachtleben, the orderer of this thesis work, are aim to successfully perform.

This study was conducted to find out whether it is beneficial to use the barium sulfate based Blanc fixe products as a filler material in offset inks. Prior to this study there was no knowledge about the use of Blanc fixe in printing inks, thus the main object of this study was to find out whether it is rational to open this market area for a wider study. This main objective was achieved, indicating that it is worthwhile to proceed within this area of interest. Best performer from the Blanc fixe products was Blanc fixe 2 with the filling rate of 8 %; money saving potential of almost 10 %, without affecting the print quality crucially.

Regardless of the positive results, there are still a lot of open questions around the subject, and further studies are required to cover these. In the first instance, as only cyan ink was covered within this study, all of the process coloured should be tested in the future; it is not, by any means, straightforward to say how for example yellow ink will behave under the influence of barium sulfate. Secondly, as time and resources being a limited factor, it should be viewed whether to continue the study only with the best performer, Blanc fixe 2, and only with a narrow range of filling rates to find the optimum. In the next phase of the studies, the filler should be added to ink without any existent filler content, and it is also advisable to perform the adding during the real ink manufacture processes

It is noticeable that the inks from different manufacturers can differ substantially in their formulation. From this point of view it would be important to test some other ink series from another manufacturer. What should be also acknowledged is that in the context of this study inks were tested in IGT-printability tester, without any dampening solution. Thus, no comments can be made concerning the ink/water emulsification. This should most definitely take into account when considering the circumstances of the further studies.

From the important properties of ink there are some critical ones that should be include in the next step of the studies. Rheological properties are one of those; offset process is very dependent of right kind of rheological properties, such as viscosity and tack, and ignoring them is not advisable. A matter of record is that fillers might have an effect on rheological properties: for example kaolin ASP 101 (filler in the ink used in the tests) is used not only as filler, but also to increase the viscosity of inks. Tack is also very relevant for the overprinting printing processes. From the other properties of ink, a scrub-test would be beneficial to execute. Blanc fixe is known for its good abrasion resistance in paints, and if these benefits could be brought into inks it would most certainly mean added value for the customers.

This study has already been tapped in the light of the preliminary results; it was rather safe to start the mouth-to-mouth marketing of these products when the results indicate such positive news. However, no hasty conclusions should, and have not, been made, which is why this project is to continue, conducted by Sachtleben in Germany, Dusseldorf.

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## **Appendix 1: IGT part list**

### **Part list of the IGT AIC2-5**

The IGT AIC2-5 printability tester consists of the parts listed below. The parts are marked in Figure 89 accordingly.

1. On/Off –switch (operation)
2. Signal light for mains voltage
3. Switch for speed (low/high)
4. Switch for interval time (timer)
5. Display for interval time
6. Button for lengthening the interval time
7. Button for shortening the interval time
8. Speedometer
9. Start button for the sector
10. Scale of the printing force for the lower printing disc
11. Front holder for the test strip (and for the possible covering)
12. Lower printing disc
13. Installation slots
14. Lower printing axis
15. Lifting reel for the lower printing disc
16. Upper printing axis
17. Lifting reel for the upper printing disc
18. Upper printing disc
19. Scale of the printing force for the upper printing disc
20. Brush
21. Switch for speed type (constant/increasing)
22. Signal light: on when the sector is in an accurate starting position
23. Adjuster of the printing force for the upper axis
24. Test strip

- 25. Covering
- 26. Back holder for the test strip (and for the possible covering)
- 27. Sector
- 28. Adjuster of the printing force for the lower axis
- 29. Start button for the engine
- 30. Speed adjuster with a locking knob
- 31. Switch for the main current

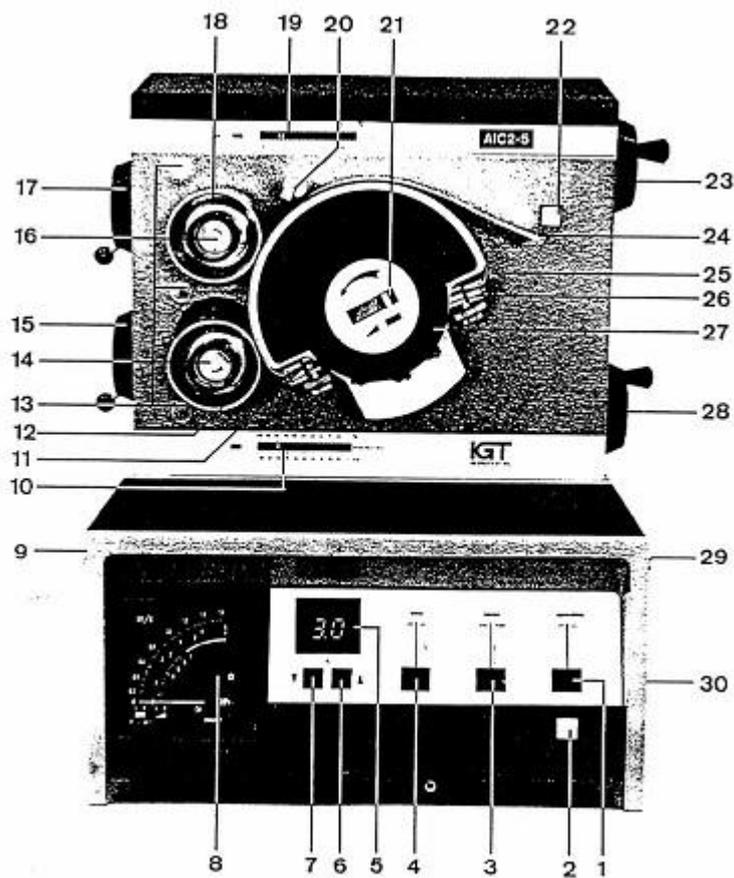


Figure 89: IGT (Vahander 2007: 28-29).

## Appendix 2: IGT operation principle

### Inking of the print disc

Inking of the printing disc is done via the inking Unit. The IGT AE Inking Unit (Figure 90) used at Materopolia printing laboratory is a slow running inking unit, now out of production as high speed inking units has become more general. The AE Inking consist of two inking arrangement enabling two different colours or types of ink can be used simultaneously. And in addition, as one inking arrangement can hold two printing discs, AE inking unit can be used to ink a maximum of 4 printing discs simultaneously. The technical design of this inking unit enables the user to make a large number of prints without adding ink or pick test oil and without heating up the device significantly and without influence of misting. (Inking Unit AE.)



Figure 90: Inking unit AE.

Print proofs are usually needed from 5 to 6. The printing is started with a high amount of ink. When the ink is applied to the inking unit it is recommended to use an ink pipette (Figure 91) as it increases the accuracy of application of ink and therefore inking, thereby enhancing the performance of the tests. When using the ink pipette, it is important that it is not to open it straight away to the required volume and then attempted to fill the hole up with ink. If done so, it is likely to have air bubbles in the pipette and therefore an inaccurate measurement. (IGT AIC2-5 2002; Todd: 1994: 250-251.)



**Figure 91: Ink pipette.**

To measure the ink correctly, a small amount of ink should be taken on the end of a palette knife and, with the ink pipette closed, dab the ink on to the top of the pipette so that it will be covered by the ink. During filling, the ink is to be agitated by moving the palette knife up and down. This helps liquefy the ink and also prevents air bubbles being trapped in it. The pipette should be overfilled by 0,2 to 0,3 ml. When the required amount has been attained and the pipette closed, it should be checked if any air is trapped in the ink by turning the screw until ink flows out of the opening. This additional ink should then be wiped off immediately. If it happens that ink remains to come out of the aperture, it is a sign of air inside in the pipette, thus the pipette must be refilled. (Manual IGT ink pipette 2001: 2; Todd 1994: 250-251.)

The pipette is filled by ink amount 1,5 ml. After filling of the pipette, the ink is applied evenly across the width and circumference of the distributor roller, illustrated in Figure 92. After the machine is started the lever is released by letting it down. That will elicit the distributor roller and inking rollers, rubber and to be in contact with each other, the fester drum, the rubber roller and the big metaldrum.



**Figure 92: Inking unit AE of Metropolia printing laboratory.**

The colour will be given 3 minutes to even out. Meanwhile the clean printing disc is weighted (Figure 93) and the reading is marked down. After weighing the printing disc is placed to the inking unit's holder. A click voice is heard when the disc is properly placed. This is important to notice as if the disc is not steadily in its place, it might fall during the inking and will be easily damaged.



**Figure 93: Weighting of the clean print disc.**

Following the 3 minutes that the inks film is levelled out, the printing disc will be inked for 45 seconds by setting it down in contact with the rubber roller. After 45 seconds the disc is lifted up and released from the holder. Now the disc will be weighted again and the reading is marked down.

### *Printing the test strips*

The 150° sector of IGT serves as a printing cylinder, to what against one or two printing discs are pressed to, and where the strip of test paper is attached to. The paper strip is attached from its front edge to the (uncovered) front holder of the sector, straightened and then drawn and attached to the back holder of the sector. On both sides of the sector there are holders with double chin where a possible cover and the test strip are placed. For the various tests, there are a range of different coverings the impression cylinder can be provided with. The holders will hold the cover and test strip still preventing them to slide. (IGT AIC2-5 2002; Leach & Pierce 2007: 838; Vahander 2007: 27.)

As the set-off is measured as well, one of the printing discs needs to be covered with a strip of the same paper that is used for printing. The paper strip is attached to the disc with pieces of tape. After that the disc is situated on the lower printing axis. When the set-off disc and the strip of paper on the sector are on place, the sector is turned counterclockwise until a red signal light turned on. The inked printing disc is placed on the upper printing axis. Figure 94 illustrates the situations until this phase.



**Figure 94:** IGT-printability tester; ready for printing.

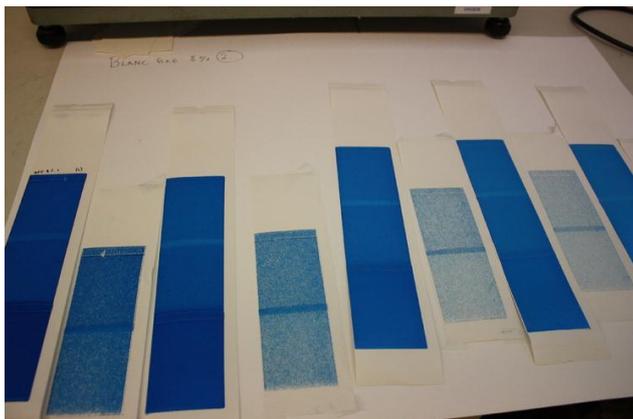
The next step is to set the printing force for both the upper and the lower axis. The printing force is adjustable from 50 to 1000 N. The printing force is set by first adjusting the force from the reels on the right hand side, then locking the pressures on from the reels left hand side and doing the last adjustment form the right hand side reels.

The printing force used in the tests series of this study was 650 N and the printing speed was constant, 1 m/s. (IGT AIC2-5 2002; Leach & Pierce 2007: 838; Vahander 2007: 27.)

When two printing discs are used, the distance between two prints is 70 mm. When the speed appointed in is 1 m/s, the time between the two sequential prints is 0,008s. During one print cycle it is possible to use 2 different intervals and the printing can be stopped in the midway using the timer. The first interval is determined by the printing speed, as described above. The second interval is comprised by the printing speed plus the interval determined using the timer. This interval can be set between 0,2 and 9,9 seconds. When setting the highest possible speed, interval times of 0,014 can be achieved. If it is desired to achieve longer intervals than 9,9 seconds it can be executed by making the first printing with one disc and after a predestined time (timing with a stopwatch) carrying out the other printing with another disc. So being, it is possible to set practically all the interval times of the printing presses. (IGT AIC2-5 2002; Leach & Pierce 2007: 838; Vahander 2007: 27-28.)

To start the printing, the power button is pressed down until required speed is obtained. Still holding the power button down, the print button is to be pressed. Both of the buttons has to be pressed down until the sector has rotated and the printing is completely done. The printing takes place in the upper nip, after which the fresh proof is immediately (0,008 s) pressed against the set-off paper. The second interval is set up for 9,9 seconds. (Vahander 2007: 27.)

After both intervals the printing is done and the printing pressures are set free and the printing disc released from the axis. Now the printing disc will be weighed again and the result marked down. The strip of tested paper and set-off paper will be then set free from the sector and disc, and attached to a sheet of paper to dry up (Figure 95). The printing disc will be cleaned with solvent.



**Figure 95:** Test strips are let to dry out.

After the first printing the yield of the ink will be decreased. This is done by removing approximately 50 % of the ink from the distributor roller. After decreasing the ink amount, it will let to equalize for 2 minutes. And like the first time, the inking disc will then be inked for 45 seconds.

These steps will be repeated until the density of the test strip will be under the target density. After all the required test prints are done, all the equipment will be carefully cleaned with solvent (Figure 96).



**Figure 96:** Cleaning of the print disc.