

Pedro Fardim

*Instituto de Química, Universidade Estadual de Campinas, SP, Brazil
Present Address: Process Chemistry Group, Åbo Akademi University, Turku/Åbo,
Finland*

Abstract

Surface chemical interactions are important in many steps of paper manufacturing and converting and most of them are complex and not very well understood. Thus, many paper and coating formulations are designed according to an empirical trial-and-error approach. This work is the second part of a critical literature review concerning some interactions present in papermaking, coating and printing. In the first part interactions relating fiber surfaces and wet end chemicals were reviewed. In this second part, surface phenomena present in coating formulation and printing are discussed. Manufacture of paper is to create a surface. Different treatments, either mechanical such as calendering or chemical such as coating are applied to the paper surfaces in order to improve printability, optical properties, and strength. Coating is a mixture of minerals, colloidal particles and dissolved polymers which is applied onto the base paper surfaces requiring optimum flow properties, usually achieved with low solids and viscosity. However, high solids and viscosity are needed to obtain good printability and a uniform coating layer. A balance between coating application and printability must be found, and the understanding of surface chemical phenomena within coating formulation and rheology is required. A review concerning interactions between mineral particles with the dispersion media and also adhesion with latex particles is performed here. The influence of interactions between minerals, binder and co-binder on the coating water retention is discussed. Rheological properties and changes in coating color viscosity are interpreted using the DLVO theory. Formation and deposition of white pitch in paper machines are also discussed based in this theory. Interactions between printing inks and paper surfaces as well as penetration of the ink vehicle into coating layer are discussed in terms of Lucas-Washburn capillary model and thermodynamic work of adhesion. The concept of surface engineering is also suggested to be developed for coating formulation with the aim of improving adhesion with the paper base and eliminate problems such as varnish rejection, spots, cut dust and non uniform printability. The knowledge of surface chemical phenomena can be useful for the pulp and paper industry, not only for patents and product development, but also for improving in troubleshooting and customer support.

Key words: *Papermaking, coating, printability, surface chemistry, surface engineering.*

1. Produce a surface aiming at the best impression

Manufacture of paper is to create a surface. Different superficial treatments are used in the process aiming at the improvement of the

printability, optical properties and strength. These treatments can be mechanical, chemical or a combination of both and besides conferring greater economic value to the product, are primordial in a market of increasing

competitiveness. The different treatments used in the production of paper and the concept of printability are presented in the next section.

1.1 Superficial treatments in the paper manufacture

During the paper manufacture a set of well defined stages is followed. In the wet end section part of the machine the stage of flocculation occurs (Begnello, 1998, Swerin, 1995), followed by drainage and sheet formation on the wire screen. The next stages are the drying and the superficial treatment in the dry part of the machine. The main types of superficial treatments are surface sizing, calender in machine, coating, and super-calender.

Surface sizing and coating involve application of chemical components on the paper surface while calendering processes are only mechanical treatments. The surface sizing process consists of the application of a component layer that can be starch, polyvinyl alcohol, sodium alginate, carboxymethylcellulose, gelatins or glue. Sizing improves the fiber-fiber contacts by the fulfilling of empty pores and spaces and thus conferring better superficial strength and increasing the resistance to the water penetration (Verhoeff et al, 1963). Other polymers can be used mutually with the sizing agents aiming at the formation of a superficial film, as for example polystyrene films. Optical brighteners are also used to increase the brightness and whiteness of white papers.

Calendering in machine consists of running the dry paper onto a frictional area between two steel reels under pressure. This process undergoes a plasticization and compression of the paper, increasing

softness and being affected by parameters related to the humidity content, applied pressure and number of reels that the sheet passes. Coating is the application of a layer of ink prepared with pigments, adhesives, and other additives. This layer has the function to eliminate the lack of uniformity in the distribution of the printing ink that is caused by the surface roughness and sites susceptible to the capillarity in regions intra- and inter-fibers (Allem, 1998; Ström et al, 1995). The coating components form a complex mixture where the pigment has the highest ratio and each additive has a particular function. The needs and the amount of an additive are designed according to the end use purposes of the paper. Coating formulation is also directly related with the type and characteristics of the applicator available. The mechanical forces which the coating fluid is submitted during application are determinant for the formulation and also for a suitable process result (McGenity et al, 1992).

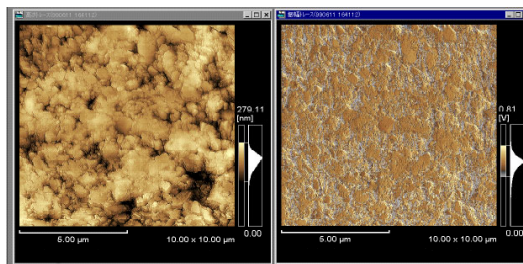


Figure 1. AFM image of a coated paper surface after calendering. Topographic (left) and phase (right) image (Fardim, 1999). Calendering process caused a superficial flattening which increased the directional light reflection.

The super-calendering process is often used off-machine for papers that already had been submitted to the coating process. It consists of running the paper between two reels under high pressure. The process is similar to the one of calendering, but it uses two types of reels, i.e., steel and a soft material, as for

example rubber. The purpose is to polish the paper surface and significantly increase the sheet specular gloss. Image obtained in Atomic Force Microscopy (AFM) of a coated paper surface after calendering shows a flattening of superficial plateaus in the topographical image (Fig.1). This flattening reduces the diffuse scattering of the light and increases the specular reflection, thus increasing the gloss (Fardim, 1999).

1.2 Printability: A Relevant quality parameter

Printability is a parameter related with the level of paper quality when it is printed. It is depend upon the capacity of the paper sheet in "accept" the ink solid particles in a uniform way, without formation of films with irregular thickness and also with good reproduction of images that contain small tonality variations. The printed dots must clear and defined without significant scattering and with absence of ink migration during multi color printing.

Evaluation of printability is made with specific tests, involving printing simulation in controlled conditions and image analysis aiming at to quantify bleeding, dot gain, tonality, interface color-color, optical density, color scattering, printed area and other parameters (Chen et al, 1995). Printing quality depends on paper characteristics, printing process, and the printing ink composition. The main printing processes in paper are: lithography, rotogravure, flexography, typography, electrostatic, ink jet, and digital. The printing ink is composed basically by colored pigments dispersed in a vehicle and both are specific for each printing process. For example, vehicles to be employed in rotogravure must have great capacity of penetration in the

structure of the paper while those vehicles to be employed in lithography require not formation of emulsion with water.

2. Coating and surface chemistry

Coating used in paper surfaces is a material composed by a complex mixture of components containing colloidal particles and dissolved polymers (Tab.1). A coating layer of approximately 10 g/m² is applied on the base paper in movement, generally using a transfer reel. The excess is removed by a steel blade and after coating transfer, the water is removed by treatment with heat in the drying section.

Component	Examples	Function
Pigments	Kaolin, Calcium carbonate, Titanium dioxide, Plastic pigments	Support a structure of fine porosity and form a surface which scatters the light.
Adhesives	Soluble in water (glues, starches, gums, casein, soy protein and others); Polymer emulsions (latex, poly-vinyl acetate, acrylates)	Bind the pigment particles between itself and the coating layer onto the paper. Fulfill pores between the pigments.
Additives for water repellence	Polymers urea formaldehyde	Make the coating less sensitive to water.
Plasticizers	Stearates, Paraffin emulsions	Improve the flexibility of the coating layer
Thickeners	Natural polymers Cellulose derivatives	Control rheological properties, viscosity, and water retention.
Dispersants	Poliphosphate s, Ligno-sulphonates Silicates	Optimize the pigment dispersion

Preservatives	Beta-naphthol formaldehyde	Prevent deterioration between different applications.
Anti-foams	Long chain alcohols	Control foam problems and eliminate air bubbles
Dyes	Direct dyes, Acid dyes, Colored pigments	Use in colored coating formulations

Table 1 - Typical components of the coating color formulation for printing papers and paper-boards (Scott et al, 1995).

During the coating color transfer, it requires excellent properties of fluidity, reached with low solids and viscosity. However, to get a dry layer of uniform coating and with good printability characteristics, high solids and viscosity are necessary (Van Gelder and Purfeerst, 1986), which on the other hand, can cause problems in the coating transfer such as deposits on the blade and coating marks (Reinbold and Ulrich, 1979). The needs are antagonistic and require a balance condition aiming at runnability and printability (Dahlvik, 2000). In terms of surface chemistry, the properties required during the coating transfer are those of a system in colloidal stability, while those excellent conditions of the coating layer and printability are observed when it has flocculation or particle aggregation and formation of macro-flocks (Grön, 1998). The knowledge of surface chemical interactions is important to achieve a balance between these trends.

2.1 Pigments and its interaction in the dispersion medium

Kaolin and calcium carbonate are the pigments generally used in coating formulation in Brazil and

Europe. Such pigments have differences concerning morphological properties, chemical composition, and surface charge. The latter plays an important role for colloidal stability and dispersion constancy. Pigment dispersion is the base of coating preparation, being the medium where the other formulation components are added (Alince and Lepoutre, 1980). Concentration of electrolytes and pH of the medium affect the dispersion, but specific characteristics of the pigment particles are also important (Sanders, 1992). The surface charge of calcium carbonate is negative and not dependent of pH, however this pigment can suffer decomposition in acidic media. The kaolin surface charge has different polarities between the face and the lateral of the particle, being negative in the face and positive in the laterals. The charge of the laterals is dependent of pH, being positive in acidic media and negative in alkaline media (Rand and Melton, 1977). The pH at the iso-electric point is approximately 7.5 and in values above of this pH, predominance of negative charge occurs at the laterals (Diz and Rand, 1989). In the acidic media the particle deposition is favoured due the electrostatic attraction between the positive laterals and the negative faces (Dollimore and Horrige, 1973). The electrostatic attraction can be enough to exceed the potential energy barrier, in accordance with theory DLVO, discussed in the part I of this revision. Presence of electrolytes in the medium also can favour the deposition due the compression of the double electric layer and reduction of the barrier of potential energy (Evans and Wennerström, 1999). In industrial applications, the pigment dispersions generally are kept in pH superior to 8.0 and a polyelectrolyte is used as dispersion

agent (Dahlvik, 2000). The polyelectrolyte is adsorbed at the particle surface and functioning as a protective agent. The mechanism for stabilization of the dispersion involves the increase in repulsion of the double electric layer, reduction of van der Waals attractive forces and effect of steric stabilization (Shaw, 1980). Use of dispersion agents reduces the effect of the concentration of electrolytes and pH of the medium in the dispersion, however, in extreme conditions the polyelectrolyte conformation is modified, affecting the adsorption and favouring particle deposition (Stenius et al, 1990).

2.2 Interactions between pigments, binder and co-binder

The system of coating components is subject to interactions particle-particle, particle-solvent, and particle-polymers. Different forces are involved in this system such as van der Waals attractive forces, electrostatic repulsions, steric stabilization and also mechanical network (Whalen-Shaw, 1989; Fadat and Rigdahl, 1986). It is important to stand out the characteristics of adhesion and cohesion between the mineral particles which form the coating base structure.

Coating formulation uses adhesives in its composition (Tab.1) in a proportion that can vary from 10-15 parts per 100 pigment parts. The function of adhesives is to promote the binding of pigment particles and between these and the base paper surface (Kline, 1993), therefore is also called binder. Styrene-Butadiene (SB) latexes are commonly used as coating binders in Brazil and Europe, especially for products destined to lithography printing due to the superficial strength and printability required,

but it can be also used for rotogravure and flexography.

Binders are spherical particles with diameter less than 1 μm and different chemical compositions of the sphere nucleus. The compositions can be of styrene-butadiene copolymer, styrene-butylacrylate copolymer, cross-linked styrene-butadiene, and others. The components ratio in the copolymer is generally 70 % of styrene and 30 % of butadiene or butylacrilate. The surface chemical composition of the binder spheres is also differentiated by the adsorption of acrylic acid or an anionic surfactant (Fig.2), which are used as stabilizing aids of the dispersion in water (Joanicot et al, 1993).

In ambient temperature, latex is an amorphous and viscoelastic material with a glass transition temperature (T_g) between -7 and 40 $^{\circ}\text{C}$, depending on component polymers. During the drying of the coating, latex is melt producing a film that embraces pigment particles on the surface and thus forming the paper coating. Adhesion between latex and inorganic pigments are influenced by the coating drying temperature, latex glass transition temperature, and surface properties of latex and pigment. Studies using AFM to measure superficial adhesion (Granier et al, 1994) had indicated that latex particles present higher work of adhesion with calcium carbonate than with mica and silicate plates. Latex presents acidic surface while calcium carbonate alkaline surface, this condition favours the adhesion between these particles. Silica has an acid surface therefore the observed adhesion is inferior to the one with calcium carbonate. In the case of kaolin, differences are observed between the crystal faces and laterals. Faces have character

more acid than the laterals and the pH at the isoelectric point of the kaolin surfaces has a value of 7.5 in comparison of 2.0 for silicate and 9.6 for calcium carbonate.

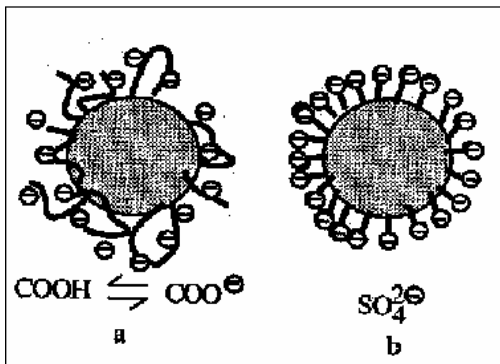


Figure 2. Binder spheres coated with acrylic acid (a) and anionic surfactant (b) (Joanicot et al, 1993).

Pigment particles are coated by a latex film when the temperature in drying conditions is higher than the latex T_g . Interactions between the film and the particle are dependent on the pigment superficial groups and the amount of acidic groups on the surface of the latex micro-sphere. A poor adhesion is observed in conditions of drying with temperature lower than the latex T_g , causing a partial surface coverage of the pigment (Granier et al, 1994). Beyond the pigment-binder interactions there is a third component which influences viscosity, water retention, the three-dimensional arrangement and the consolidation of the coating layer, as well as the gloss and printed gloss (Grön et al, 1998) that it is the co-binder or thickener (Tab.1). This component is generally a polymer soluble in water, for example carboxymethylcellulose (CMC), cationic and anionic hydroxyethyl cellulose (EHEC), and starches (Eriksson and Rigdahl, 1994). The amount of thickener used in coating formulation varies from 0.1 up to 1.5 parts for 100 dry pigment parts. Its effect on coating color viscosity is believed to be due to the capture of

water molecules by hydrogen bonding involving the hydroxyl and carboxyl groups of the polymer chain (Dahlvik, 2000).

A fraction of the restrained water is transferred to the paper surface during application, contributing for the adhesion between the base paper and coating layer (Young and Fu, 1991). However, if the amount of transferred water is very high, it can cause significant expansion of the fiber network or migration of latex particles and pigments (Malik and Kline, 1992, Engström and Morin, 1994). In cases where the water transference is very low, problems in the applied coating layer are observed (Barber, 1973). The effect of the thickener on the formation of a three-dimensional network in the dry coating layer is another important factor to be considered (Grön and Kuni, 1995). Employ of anionic starch, for example, does not contribute for formation of this kind of network, however, if cationic starch is used instead, a high interaction between this and the pigment particles is observed and conditions for a three-dimensional aggregation are achieved (Grön and Eklund, 1998). In case of CMC, a partial adsorption onto pigment particles was considered (Wang et al, 1996), which contributes for network formation. Presence of elastic flocks is also observed due to interactions between adsorbed and not adsorbed CMC (Whalen-Shaw and Gautam, 1990). These flocks are broken during the high shear conditions in coating application (Sandås and Salminen, 1991). Presence of high concentration of Ca^{2+} ions harms the water retention in coating colors which use CMC because this metal reduces the number of carboxyl groups available for the capture of water molecules (Dahlvik et al, 1997).

2.3 Rheological properties of coating colors

Coating colors are traditionally studied using rheology techniques. Rheology is the science of the flow and deformation of a substance that allows evaluate the performance of a coating color formulation during application. A long range of shear rate must be tested for a complete evaluation and this constitutes an experimental difficulty, once that the current measurement devices are suitable only for the extremes of low and high shear rates. The use of high-pressure capillary viscometers that employ extreme high shear (1000000 s^{-1}) was suggested (Gane et al, 1992) because coating is submitted to high shear rates in short intervals of time during the industrial application. Coatings are Non-Newtonian fluids (Krieger and Dougherty, 1957) or its viscosity varies with the shear rate (Tab.2). Coating components are particles not symmetrical that present size, form and cohesiveness as factors that affect the force necessary to put them into motion in a flow. These not symmetrical particles are suspended colloidal and other such as kaolin, calcium carbonate, and titanium oxide. Non-Newtonian fluids can be classified in different categories according to its response of shear stress as function of the shear rate variation (Fig.3).

Fluid type	Description	Examples
<i>Pseudo plastic</i>	Viscosity decreases with increasing in shear rate	Inks, emulsions and dispersions
<i>Dilatant</i>	Viscosity increases with increase in shear rate	De-flocculated solids, starch in water, clay in water, sand in water
<i>Plastic</i>	Fluid behaves as a solid under static conditions, but if a force is applied a flow is induced which can be either Newtonian, plastic, pseudo plastic or dilatant	Tomato ketchup
<i>Thixotropic</i>	Viscosity decreases as function of time under constant shear rate	Greases, printing inks and coating colors
<i>Rheoplectic</i>	Viscosity increases as function of time under constant shear rate	Rarely found

Table 2. Common categories of Non-Newtonian fluids (Schramm, 1994).

Paper coating is a thixotropic fluid and it must behave in a way that coating color flows only at the moment and at short instants after its application in conditions of high shear rates. The hysteresis behaviour of a coating color can be evaluated using a curve of shear stress versus shear rate (Fig.4). The flocculated structure of the fluid is destroyed as function of time during the shearing in a way that the viscosity is lower than the observed during the increase in shear rate. Flocks can reorganize again after the structure breakage and the time

needed to this restructure affects the return of viscosity to the previous values. If the flock restructure is achieved fast then viscosity keeps a constant platform, but if the linkages are restored slowly then the viscosity is reduced. The reestablishment of the linkages depends on the interface between the dispersed phase and the liquid phase and also on the shape of the particles in the dispersed phase.

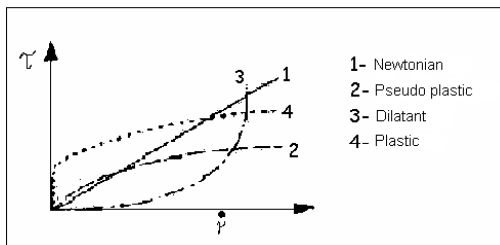


Figure 3. Illustration of the behaviour of different Non-Newtonian fluid categories as observed in plot a shear stress (τ) as function of shear rate ($\dot{\gamma}$) (Schramm, 1994).

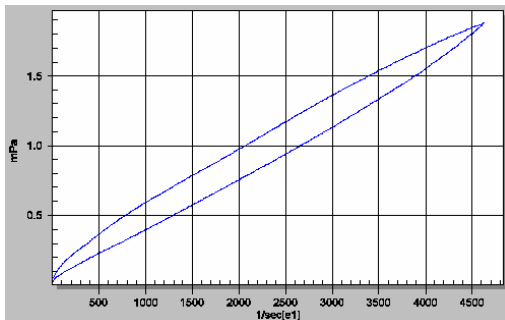


Figure 4. Thixotropic hysteresis behaviour of coating color observed in a plot of shear stress as function of shear rate (Fardim, 1999).

According to the curve of potential energy of DLVO theory, the barrier of free energy cannot be exceeded so that the system is remained in the dispersed form. However, a weak flocculation that keeps the dispersion occurs at the region of the secondary minimum. The formed flock is subject to the disruption due the action of shear forces, modifying the structure of the fluid and affecting viscosity. Brownian movement of particles can also generate collisions that provoke surpass on the free energy barrier and cause the

irreversible flocculation of the material. In this condition the production of a not homogeneous fluid occurs, causing changes in the rheological characteristics and significant viscosity reduction.

2.4 Coating and white pitch

"White pitch" is a deposit formed by coating components, generally originated from coated broke in the paper machine. The deposit many times contains latex, antifoams, pigment particles, and resins. This deposit reduces the machine efficiency due to the impregnation in the felt and consequent time off for cleaning. It can also occur in the coating application devices and cause coating marks or defects. During printing of a coated paper, "white pitch" can cause low resistance to wet and dry picking in off-set and thus many other printability problems.

Formation of "white pitch" involves flocculation of latex particles which can contain or not other process components. Cationic polyelectrolytes can be used to induce a flocculation of latex particles with pulp fibers and thus hindering the deposit formation. The surface phenomena involved both in deposit formation and well as on its remedy using polyelectrolytes are similar as it was already discussed in the part I of this review.

3. Surface chemistry and printability

Interactions between printing inks and paper involve a great number of surface phenomena. Printability parameters are affected by the physical structure of the sheet surface, as for example roughness and also by physicochemical parameters such as work of

adhesion and surface free energy. Many other parameters such as grammage, thickness, opacity, whiteness, brightness, formation and strength also affect printability.

Printing ink is composed by polymers, colored pigments and, vehicles which can be water, oil or organic solvent. The lithography printing process uses inks that contain oils as vehicle, while flexography can use water and oil. Organic solvents of low boiling points are used in rotogravure printing while digital photocopy processes do not use liquid vehicles. The ink jet printing generally uses a mixture of water and ethanol as a vehicle.

Interaction of the ink with the paper can be divided in three stages (Fig.5). In the initial stage (1) a fresh film of ink is placed on the sheet surface; in the intermediate stage there is an agglomeration of pigments to form a partially dry film and in the final stage there is a consolidation of a dry film with pigments agglomerated.

Mechanisms of drying of printing inks can be summarized in three main phenomena. Absorption of ink is the phenomenon that occurs when the vehicle penetrates the structure of the paper (A) and evaporation is the phenomenon that occurs when the vehicle evaporates to the atmosphere, with or without heating (C). Reactions of oxidation and polymerization also occur and the oxygen of air, a catalyzer, ultraviolet light or an electron beam can promote the cure of a polymer that assemble the pigments (B). In the drying process the three phenomena can occur with predominance of one of them, however, the increase in the printing speed has required the use of inks where the phenomenon of polymeric

cure dominates. This may have been due to the long time required for ink absorption and the consequent problems of solvent evaporation discharged to the atmosphere (Scott et al, 1995).

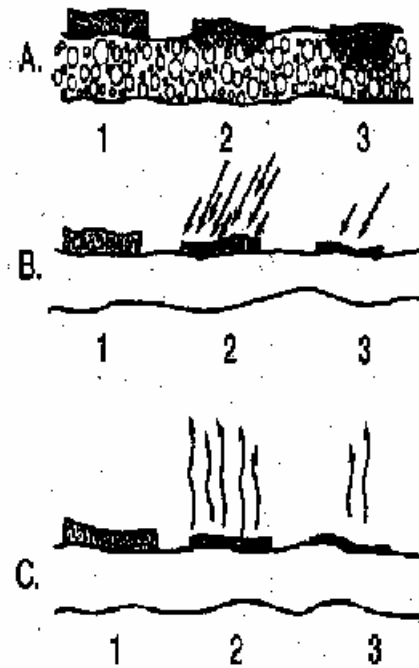


Figure 5. Different stages of printing ink drying at the paper surface (Scott et al, 1995). Vehicle penetration into the paper (A), cure by oxidation of polymers which aggregates the pigments (B), and vehicle evaporation (C).

Paper coating composition also affects the printing ink drying (Zang and Aspler, 1998). The adhesive used in coating color can reduce the penetration of water if its hydrophobic character or concentration is increased. The porous structure of coating also affects the penetration (Donigian et al, 1997). During printing, a part of the ink is immobilized on the surface by the paper roughness and in coated papers the roughness is limited, therefore the phenomena of ink drying have important performance. The penetration rate dh/dt of the vehicle in a cylindrical

pore of ray R is suggested by the equation of Lucas-Washburn:

$$dh/dt = R\gamma\cos\theta/4\eta b \quad [2.1]$$

Where h is the depth of penetration, t is the time, γ is the liquid surface tension, θ is the contact angle between the liquid and the wall of the pore and η is the fluid viscosity (Aspler, 1993). The term $\gamma\cos\theta/\eta$ presents good correlation with the ink jet printing quality using water based ink.

Water penetration in uncoated papers depends if the product was submitted to sizing or not. An inter-fiber absorption occurs initially being followed by the absorption of the fiber wall when the paper is not sized and the intra-fiber absorption is followed by the inter-fiber absorption when the paper is sized. The printing ink penetration occurs in a homogeneous mixture between pigment and vehicle; however, when the vehicle is oil based and contains a dissolved polymer it remains on the paper surface (Aspler, 1993).

Adhesion between components of printing ink and paper surface depends on the work of adhesion which is related with dispersion and permanent dipole forces between the molecules at the interface. The currently used expression to describe the work of adhesion (Berg, 1993; Erbil, 1997) considers acid-base interactions and formation of hydrogen bonding in a component W_a^{AB} and related interactions of physical character to the forces of dispersion in a component W_a^{LW} .

$$W_a = W_a^{AB} + W_a^{LW} \quad [2.2]$$

The component W_a^{LW} is termed Lifshitz-van der Waals and W_a is termed thermodynamic work of

adhesion. Such components can be estimated using values of surface tension and measurements of contact angle, with some approximations (Berg, 1993) for pure liquids. Nevertheless for multi component systems such as printing ink this estimative are complex. Interactions between the printing ink and the paper surface are still not much investigated. Research concerning the adhesion between the ink components and the paper surface has been started just for a few years (Wickman, 1998) using surface chemistry concepts. The development of new products and printing quality parameters are in many cases still performed using trial-and-error approach, frequently based in subjective methods.

4. Surface engineering, coating and printability

Surface modification of the base paper with purpose of increase the adhesion with the coating layer as well as the development of formulations of coating color and printing inks can be improved with the application of the surface engineering concept. Better adhesions between ink and paper can be achieved if thermodynamic parameters are combined considering the different printing and coating types. Problems usually observed such as spots, varnish rejection, formation of cut dust and non uniform printability could be eradicated in an objective and lasting way. Catalyzers for printing ink drying could be incorporated in the coating formulation, reducing the amount of vehicle used in printing and thus improving printability. There are many possibilities, including the formulation of "digital" coatings through the incorporation of conductive polymers, already available, and then make possible

the long-distance printing by using a micro-antenna on the paper surface.

5. Conclusion

Concepts of surface chemistry are practically involved in all stages of manufacture and printing of paper. Coating color formulation and its performance also present important surface interactions. Coating rheological properties which are important during application can be interpreted in some extent by the DLVO theory. Coating structure and its effects on printability can also be interpreted considering thermodynamic properties between mineral and adhesive particles. Paper printability can be investigated and be improved according to a surface chemistry approach, though many researches are still based on subjective methods of evaluation. The concept of surface engineering can also be applied in coating and printing ink formulations and thus makes possible the development of paper with higher economic benefits.

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