Ink-Setting Mechanism for Use on High-Performance Papers

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The papermaker and ink maker each have a challenge. The papermaker's challenge is to provide high-performance paper. The ink maker's challenge is to provide high-performance ink. How they do it is the discussed in this article.

High-performance coated papers are currently being produced on a global scale. This paper has enhanced properties improved via the use of next-generation coating mineral pigments. These pigments are synthesized to have well-defined sizes and shapes and overcome several limitations of older, mined minerals (clays, ground calcium carbonates, or ground calcium carbonates). Improvements include smoothness, opacity, brightness, and gloss. These new minerals can also change the print characteristics of paper and increase the rate at which offset ink sets, as inks designed for the older mineral surfaces may set too quickly and not achieve optimum gloss. As discussed below, an ink that would achieve high gloss with no set-off on both old and new mineral surfaces would give the printer flexibility and the ability to use the best paper for each job. To help with the design of such an ink, a new multi-phase mechanism for offset ink setting has been described and shown to hold promise for creating a high-performance ink to match the new high-performance paper.

High-Performance Paper

In the publication arena paper plays a double role. It is a physical structure that must survive conversion, shipping, handling, and storage. It is also a substrate that must interact with ink so as to provide accessible, attractive, and persuasive graphical information. The first role requires such properties as stiffness, fold resistance, color stability, brightness, gloss, opacity, and smoothness. The second role requires proper porosity for ink acceptance, holdout, setting, gloss, and optical density, with uniformity at the scale of visual resolution. In addition, today's market economics demand that these properties are provided at the lowest possible weight and material cost.

These roles require uniformity on the paper's surface. Since the wood fiber base stock is not uniform at a visually resolvable scale, coatings of fine mineral particles are applied. Clay, precipitated calcium carbonate, ground calcium carbonate (GCC), alumina, talc, and gypsum are the most common. The coating layer can be quite thin, as in the case of LWC (light-weight coated) paper or it can be thicker for better hiding and consist of several sequential applications. Economics also comes into play. In areas where coating is cheaper than fiber, coat weights are heavier.

Coatings are effective for several reasons. First, the typical coating mineral particle size is sub-micron. This is well below visual resolution, so larger base stock features can be filled in and visual uniformity is possible. This size is also in the range of the wavelength of light. This makes it relatively easy to produce an optically flat (protrusions are well below the wavelength of light) and glossy surface.

Second, the minerals in coatings are rigid and packed with pore space distributed among them. Pores create bulk and scatter light. More bulk means more coating volume and more smoothness and surface uniformity at the same coat weight. Light scatters when it encounters a boundary between materials with different indices of refraction. Every pore is defined by a set of air/mineral boundaries with a change in index of refraction so every pore scatters light. Scattering is essential because most inks scatter very little light back to the observer; they simply absorb certain wavelengths. The coating pores scatter the wavelength-depleted light that forms the image back to the observer. More scattering means more image intensity.

Third, coatings provide important subjective qualities. Gloss, brightness, and whiteness are associated with quality by most observers. People tend to connect the quality of the paper with the quality of the information on the paper. Advertising is more effective when the graphics exhibit accurate and intense color, high gloss, and uniform optical density.

Fourth, coatings provide a suitable base for ink. The coating pores remove solvent and, in the case of lithography, fountain solution, yet they reject the body of the ink so that it remains on the surface, where it is most efficient at absorbing light.

The last decade has seen a revolution in coating materials. Mined minerals are being replaced with synthesized minerals. Mined minerals tend to have broad particle size distributions (PSDs). They may contain visible amounts of colored impurity. Synthesized mineral particles, on the other hand, can be closely controlled in size and shape, and colored impurities can be excluded. It has been found that coating properties can be greatly enhanced when synthesized minerals are made uniform in size and shape.

Consider particle size. As the range in particle size is reduced, the packed pore volume is increased. This is illustrated in **Figure 1.** When a broad distribution of sizes is present, small particles fill pores defined by larger particles. When the PSD becomes narrower, these pores remain open. With more pores come more coating bulk and more light scattering. When the average size of the narrow distribution of particles is adjusted, gloss can be dialed in with little loss of the other properties.

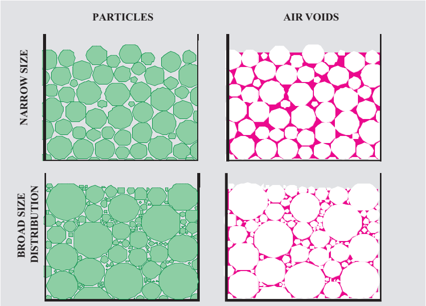

FIGURE 1. *Schematic showing that a narrower PSD (top pair) creates more pore volume with larger individual pores, advantages for coating bulk, and light scattering.*

Consider particle shape. Regular shapes can be aligned. For example, rods can be stacked like cord wood or dumped into a pile. The surface uniformity of these two configurations would differ greatly. Irregular shapes, like crushed limestone, present a similar surface, whether spread or dumped. Alignment allows a substantial improvement in smoothness and gloss.

Because of these paper property advantages, use of synthesized coating minerals with narrow PSDs and alignable shapes is growing rapidly. Foremost, among these is precipitated calcium carbonate (PCC). With PCC, the resulting paper exhibits superior brightness, smoothness, and gloss. However, the increased porosity of this improved coating has an influence on ink behavior.

High-Performance Ink

Consider an offset ink. It is applied as a paste with a cylindrical printing plate—a process that creates a substantial split pattern. To become glossy, this split pattern must level. Therefore, ink viscosity must rise slowly enough for leveling to become complete. Yet the ink must harden sufficiently to become resistant to transfer onto other surfaces. The rate at which this hardening occurs is called the setting rate. Generally, it is quantified as the viscosity of the ink film.

Offset inks for coated paper have co-evolved with broad particle size, distribution clay, and ground calcium carbonate coatings for many decades. The setting rate of these inks has been tuned for these mineral surfaces. If the ink set more quickly, leveling of its split pattern would be arrested and final ink gloss would be too low. If the ink set more slowly, it would transfer to and mark everything it touched—a phenomenon known as set-off. These unwanted behaviors define a window of operation for the ink. Resins and solvents are chosen so that the ink operates inside the boundaries of this window as defined by the clay/GCC-coated surfaces.

Narrow-PSD pigments, like PCC, demand a different window of operation for offset ink. The porous coating surface is more efficient at removing ink solvent from the ink. Accordingly, the ink sets more quickly on the open surface. Ink designed for a closed surface may not fully level, and ink gloss may be reduced.

Offset inks have been made to set more slowly so they will develop acceptable ink gloss on open surfaces formed with narrow PSD minerals, but these inks typically set too slowly and cause set-off when applied to closed clay surfaces. In other words, it is known how to shift but not how to enlarge the window of operation for an ink. This forces the printer to use paper with only one type of surface or to maintain different inks in inventory. Both options are limiting and costly.

New Ink-Setting Mechanism

The rest of this article will discuss the concept of offset ink with a broader window of operation; one that can produce high ink gloss and no set-off on both closed and open surfaces. Such inks are not available commercially, partially because the current understanding of the mechanism of ink setting is not detailed enough to provide design tools for the ink maker. Recently, a more detailed mechanism has been proposed as follows:

Offset inks are composed of colored pigment particles, polymeric resins, solvent oils (some able to cross-link), and functional additives. There is general agreement that ink-setting is initiated by separation and removal of oil from the ink film by absorption into the paper coating. Other oil-related changes occur, but more slowly or after a delay. Oxidative cross-linking in sheetfed ink has been found to occur over a much longer time scale. Oven evaporation of oil from heatset ink occurs at least a short time, say a second, after the absorption has begun.

Figure 2 shows the rate at which sheetfed ink gloss increases on three papers—one with a slow ink-setting surface, one with a fast ink-setting surface, and one in between. It can be seen that these papers differentiate within one second, and most of the gloss development occurs in the first few seconds.

Previous theories for offset ink-setting related viscosity directly to solvent/oil content of the ink. However, analysis of this theory indicates that nearly 90% of the oil content would have to leave the body of the ink in the first second to explain the fastest setting, lowest-gloss curve in **Figure 2.** This is based on estimates of how much viscosity growth is necessary to stop the leveling process, and how much oil removal would be needed to cause that viscosity growth if inks are simply dissolved resins with suspended color bodies, as proposed in previous setting models. Other evidence suggests that oil does not escape that quickly. For example, the tack of sheetfed ink increases smoothly for thirty seconds or more after application.

Accordingly, a new mechanism for offset ink setting has been proposed. It hypothesizes that offset ink contains several chemically distinct phases. Each phase has a distinct resin concen-

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tration, domain size, oil diffusion coefficient, and outer boundary. This and the initial setting sequence can be described with the aid of **Figure 3.** An ink out of the can probably has several phases in at least meta-stable equilibrium. These phases contain several ink resins and several solvent oils, as well as dispersed colorant in various proportions. However, the mechanism can be illustrated with just two phases—a phase with higher oil concentration and one with higher resin concentration—that also holds the dispersed colorant.

A key part of this multi-phase hypothesis is that the oil is initially distributed between a relatively mobile, low-viscosity phase and a highly viscous resin phase. There is probably not a pure oil phase and definitely not a pure resin phase. Immediately after the ink is applied to the coated surface, equilibrium is destroyed. Two oil flows are envisioned. One will leave the dilute resin phase and enter the coating; the other will leave the concentrated resin phase and enter the dilute resin phase. In a real ink, several such flows of different oils from different resin phases may occur.

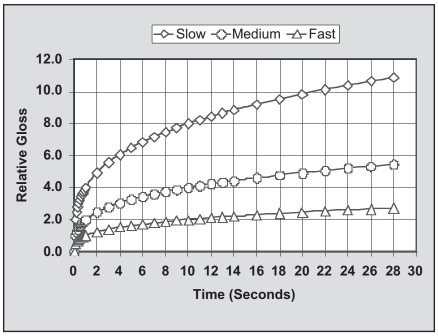

FIGURE 2. *Data showing the growth of offset ink gloss after application onto coated papers. Ink was applied with no emulsified fountain solution using a laboratory printer. The slowest gloss increase, triangles, occurred on an open surface formed with a narrow PSD pigment. The fastest gloss increase, diamonds, occurred on a closed surface formed with a broad PSD pigment. The middle curve occurred on a surface formed with a blend of broad and narrow PSD pigments.*

Mobile Phase Behavior. Two flows begin when oil imbibition into the coating begins. First is flow of oil into the coating pores primarily from the mobile phase, dV_1. In the mobile phase, oil can move relatively quickly, either by diffusion or convection, and the oil loss at the coating interface can quickly draw on oil from the upper ink surface and retard leveling. Oil movement through mobile phase channels explains the rapid response of upper ink surface viscosity to oil removal at the lower surface. As the mobile phase is depleted, the resinous phases begin to interact, or even coalesce, and phase invert, thereby allowing viscosity to climb well above its equilibrium value.

Concentrated Phase Behavior. When oil is removed from the mobile phase, oil begins to diffuse out of the resinous phase, dV_2, to replace the mobile phase loss. As oil leaves the resin phase, the resin phase shrinks. Oil moves slowly through the resin, so the escape rate can be high if the resin phase surface area is large and the resin domains are small, so the oil does not have to move far.

Solvent Loss Balance. Assume that the oil losses per unit ink area from the dilute and concentrated phases are dV_1 and dV_2, respectively. Three scenarios can be envisioned.

$dV_1 >> dV_2$. In this case, the mobile phase is rapidly depleted. Ink tack and viscosity skyrocket, and leveling is stopped prematurely, with low printed gloss. The concentrated phase coalesces with significant oil content still in place, which can later impede oxygen entry.

$dV_1 > dV_2$. In this ideal case, oil leaves the dilute phase somewhat more rapidly than it is replenished. Ink viscosity grows slowly enough for leveling to reach completion and quickly enough to avoid set-off. Once leveling is completed, concentrated phase oil content is low and oxygen entry is not unduly retarded.

$dV_1 = dV_2$. In this case, the surface pulls out oil only at the slow concentrated phase diffusion rate. The ink film remains too mobile, and ink marking and set-off can occur.

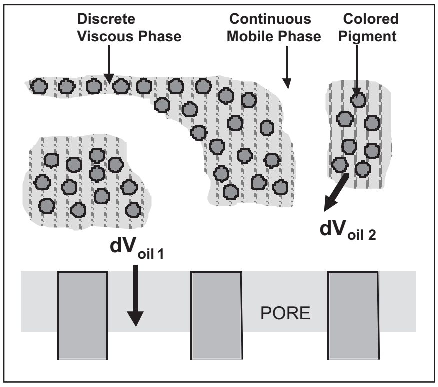

FIGURE 3. *Simplified schematic picture of the offset ink setting process. Two resin phases in the ink film and an escaping oil phase are shown. It is assumed that ink flows, because a low-viscosity continuous phase, allows the more viscous blobs of another phase to move past one another. Escaping oil (dV_1) comes mostly from the mobile phase. Viscosity depends on how quickly oil from the viscous blobs (dV_2) can replace the lost oil.*

Since there is a complete lack of data on actual ink resin and ink oil systems, exact quantification of the oil volume flows will be impossible. However, published diffusion and viscosity data from other systems were used with a minimum of parameter adjustment to estimate the effect that phase behavior will have. These calculations led to estimates of 23%, 26%, and 29% oil loss in one second into the slow, medium, and fast-setting papers in **Figure 2**. Though fraught with approximations, this mechanism gives much better estimates of oil-loss rate than previous mechanisms.

The important question is whether this theory can help an ink maker with widening the window of operation of offset ink. The theory describes the initial rate of ink-setting in terms of a number of adjustable ink properties: phase sizes and compositions, diffusion coefficients, and oil and resin properties, for example. Consider, for example, the radius of a typical resin domain at the instant of ink application to a paper surface.

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It can be seen in **Figure 4** that, as the radius of the hypothetical discrete resin domain decreases, viscosity growth on slow and fast surfaces becomes more similar. This means that the window of operation of the ink is widening. The range is not large (0.40–0.52), but it shows that an ink parameter can influence the relative effect of fast and slow surfaces on ink viscosity and, presumably, on ink gloss.

There are a number of other ink parameters that could be adjusted to change rates at which offset ink viscosity, tack, and levelness change in response to the media on which the ink is applied. With multiple phases, each with its own chemical makeup (resins, oils, pigments, additives), diffusion coefficients, relative solubility, viscosity, elasticity, and chemical potential, many design tools can be found for improved ink properties.

This offset ink-setting mechanism assumes multiple phases in the ink as a result of manufacturing method. An alternative is to propose that phase separation occurs only after the ink is applied to the paper. Implications of this possibility will be described in the next article in this series.

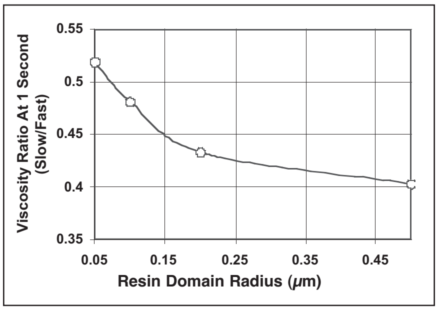

FIGURE 4. *Graph comparing offset ink setting rates on closed and open surfaces. If setting rates were identical, at one second, both viscosities would be the same and their ratio would be one. If the window of operation of the ink is very narrow, the closed (slow) surface will set the ink much slower than the open (fast) surface. Viscosity will remain low on the closed surface but will rise rapidly on the fast surface. The viscosity ratio at one second will be very small.*

Conclusions

Today's coated papers are being made using synthesized narrow PSD PCC coating pigments. These minerals provide chemical purity, bulk, light scattering, and alignment for improved brightness, smoothness, opacity, and gloss. The result is high subjective quality and high intensity and contrast in printed images.

The porosity advantage of narrow PSD-coating minerals affect offset ink-setting rate. Ink sets more quickly on these surfaces and, if the ink was designed for a low porosity surface, ink leveling can be retarded and ink gloss can be reduced.

An improved ink would work on both closed- and open-surfaced paper. It may be formulated with the aid of a newly proposed ink-setting mechanism. According to this mechanism, the width of the ink's window of operation can be increased by allowing oil sequestered in a viscous phase to more easily replenish oil lost from a more mobile phase. This could be done by making the viscous phase domains smaller.

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