Fount-free Printing

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Abstract: Fount-free offset (FFO) printing requires that the ink densities of the printed copy are a single valued function of the ink feeds. FFO process requires that the ink feeds be invariant over time and that some components of the ink be compatible with the media's non-image area. FFO processes further require that the transfer media be planographic with neither functionally raised nor depressed ink accepting areas. Such FFO processes are shown to enable closed loop color control technologies. DRUPA 2000 featured several displays that highlighted apparent FFO processes, including KBA's Cortina press demo, Sun/Heidelberg's "waterwashable" waterless ink demo on the QMXDI press and Presstek/Flint "single fluid ink" demo using the Anthem plate. We provide a historical review and characterization of these new processes and relate them to our definition of true fount-free processes.

Introduction

We shall begin the discussion of fount-free printing (FFO) with a definition: FFO is a printing process whereby the inks are of fixed composition as fed to the printing machine. The resulting ink densities on the printed copies from the printing machine are a single valued function of the ink feeds. FFO processes further require that the transfer media be planographic with neither functionally raised nor depressed ink accepting areas, but rather more or less "oleophilic" or "oleophobic" areas. We thus contrast FFO printing with

-Printing processes which employ technologies which "re-emulsify conventional inks" (which cannot be FFO processes because the recycled inks are adjusted in composition) AND

-Flexo and gravure printing processes, which require, respectively, functional raised or depressed ink acceptance areas on ink transfer media.

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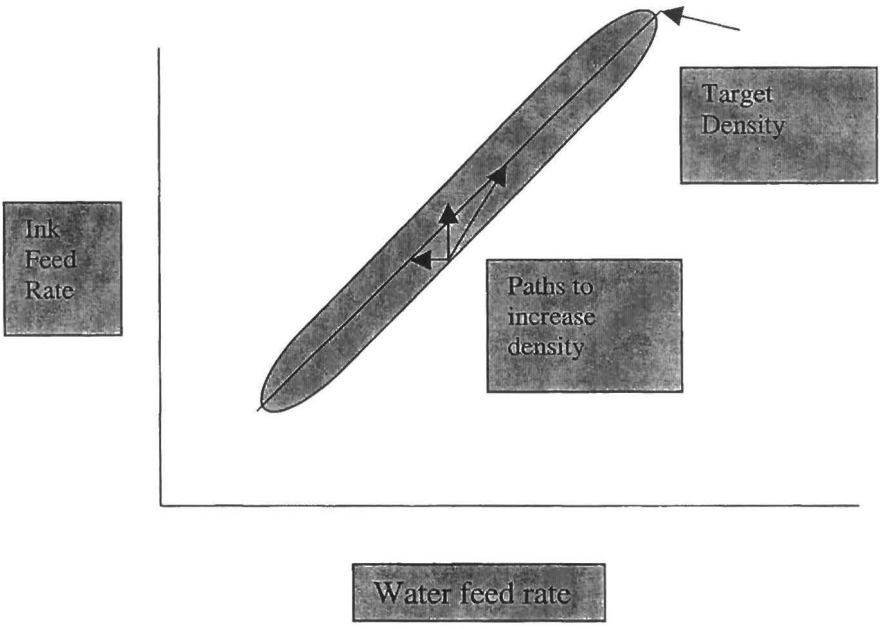
Why are fount-free processes of any particular importance? As discussed by Goodman (2000) they are enabling processes for closed-loop color control or "automated" offset lithographic presses. To see this consider the rather crude picture depicted in figure 1.

Figure 1. Crude Depiction of Conventional Lithography



The figure 1 depicts (gray-toned area) the region for a typical litho process where the ink/water emulsion is stable; no toning or image wash out. The target density line depicts the region where for a given ink feed rate there is a corresponding water feed rate which will print the desired ink density. (NOTE: The picture drawn is very oversimplified in that the function connecting ink density to feed rates is a complex function, not the simple linear curve, but it doesn't change the fundamental concept) Nevertheless, for any condition where print density is, for example, too low there are an infinite number of paths to bring the density back to the target as suggested by the arrows. The different paths correspond to diluting the ink emulsion but printing a thicker film or conversely concentrating the ink emulsion and printing a thinner film.

Therefore, we can say ink density printed by that conventional lithography is not a single valued function.

Conversely for any FFO process the process to adjust the desired ink density is a single-valued function of the adjustment to the ink feed rate. This single-valuedness provides a sure response for any control algorithm of the offset process thus enabling reliable closed loop color control.

Historical Review of Fount-free Processes- Waterless

Curtin (1970) described the first practical FFO technology. In his patent specification he suggested the key parameter defining his proposed one fluid ink process. "My invention comprises a printing plate having a background surface area with a sufficiently low adhesion...the adhesion of the ink to the inking roller and the cohesion forces between the ink particles are both greater than the adhesion between ink and said surface (that) the ink will not transfer to said surface." Curtin called such a property of the background surface abhesion. He further states, " For quality printing an abhesive material should have a release value of 30 or less." (He describes how one measures abhesive values, not discussed here) The crucial fact is that the inventor of the first feasible FFO process based his invention on finding unique abhesive materials for printing plate backgrounds.

In the early 70's, several companies patented FFO (waterless) processes, as described by Gipe (1972. 1973), Sorkin (1973), Gracia (1974) and Yoerger (1975). In 1977, Toray presented the first "Waterless" plate, the non-image areas being based on silicone chemistry, as described by Kobayashi (1975).

Nevertheless, despite these developments, there was a perception that abhesion, while a necessary condition for a successful fount-free process, was not a sufficient condition. Thus, in parallel, other FFO concepts were described. In 1975 two companion papers from Xerox, Pacansky and Becker (1975) and Gaudioso, et.al. (1975) presented a somewhat different view to explain the success of FFO processes (including Curtin's!). From Pacansky and Becker (1975) we can identify the " plate materials criteria for waterless lithography":

Non-image areas

-Must not dissolve in the ink solvent
-Must allow diffusion or swelling by the ink solvent
-Must not absorb the ink polymer

Image Areas

-Must not dissolve in the ink solvent
-Must not allow diffusion of ink solvent into the image surface
-Must have good adhesion to non-image areas

Ink

-Must contain a liquid that can diffuse into the master
-Ink polymer must NOT selectively deposit, adhere, adsorb or adsorb onto the non-image areas
-Ink polymer (+ pigment) must be selectively attracted to image not the ink solvent
-Ink polymer and ink solvent must be miscible

Compatibility according to Gaudioso related to the Hansen (1961) solubility parameter δ, a physical chemistry term which describes the relative chemical characteristic which leads to "likes dissolving likes" in conventional solution theory. They adopted the term weak fluid boundary layer (WFBL) theory to describe the splitting of the ink films within the ink solvent film rather than at the ink/plate interface preferred by Curtin. They related this solubility parameter to work of adhesion whereby ink release from the non-image area correlated with δ (ink solvent)- δ (ink polymer) multiplied by δ (ink solvent)- δ (non-image). Therefore, the release is best when δ (ink solvent) is between that for the ink polymer and non-image. Of course, ink solvent and non-image area must be fairly compatible to allow diffusion into the non-image. Thus, ink polymer and non-image parameters need to be as different as possible. However, as described in Gaudioso, et.al. , "Some degree of elastic behavior is also required for the ink to exhibit complete release". Chou (1996) further confirms this. That is, Ink must exhibit viscous flow for pumping/anilox feeding. Ink must exhibit elastic return during filament extension. Where Curtin taught that abhesion between ink and background was crucial, Gaudioso teaches that "swelling' of the background by ink solvent is crucial.

Figure 2 below depicts the crucial aspects of the weak fluid boundary layer (WFBL) model. [The original concept of the weak fluid boundary layer was proposed by Bikerman (1961) in order to explain adhesive rupture on polyethylene surfaces.]

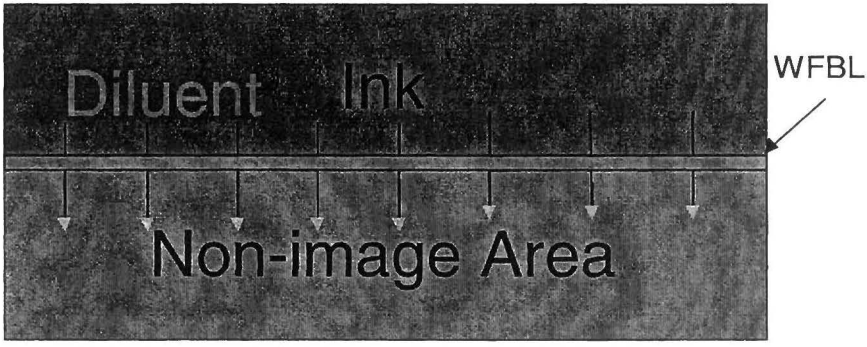


Figure 2. Depiction of Weak Fluid Boundary layer Model

Lanet and Gandini (1995) further elucidated on the ink solvent diffusion concept as regards the then current plate/ink technologies for waterless printing. They concluded based on DCA measurements that the WFBL model based on the diffusion concept was a viable explanation for the success of the technology at that time, "the diluents contained in typical waterless inks can readily diffuse into the non-image area of the plate, Therefore, the model described by Gaudioso in 1975 seems applicable to the actual waterless process..." They do, however, realize that the dynamics of an actual press may not be captured by the model as described by Gaudioso. Model studies on PTFE and other surfaces of different surface energies (De Grace, 1984) provided data on the dynamic aspects of ink release. Lanet (1997) showed as well that ink release from non-image areas is also possible for vegetable oil diluents having a less tendency to diffuse into the silicone surface (see comments below).

Confirming Tests of FFO-Waterless Processes

We have confirmed the key findings of the Grenoble group as regards the phenomena seen in currently commercial waterless plate processes. The two key facts from these data are shown in table 1 and figure 2.

Table 1. Swelling (wt in grams) of commercial silicone plate surfaces by Ink Solvents

	TWP	Emerald	Pearl Dry	TAN
Glycerol	-0.008	-0.022	-0.094	-0.018
Mineral Oil	0.586	0.492	0.692	0.554
Soy Oil	-0.014	-0.094	-0.094	-0.050

This table describes the fact that only mineral oil among typical litho ink solvent swells silicone i.e. is absorbed into silicone surfaces.

Figure 3. DCA of two different ink solvents on a silicone surface

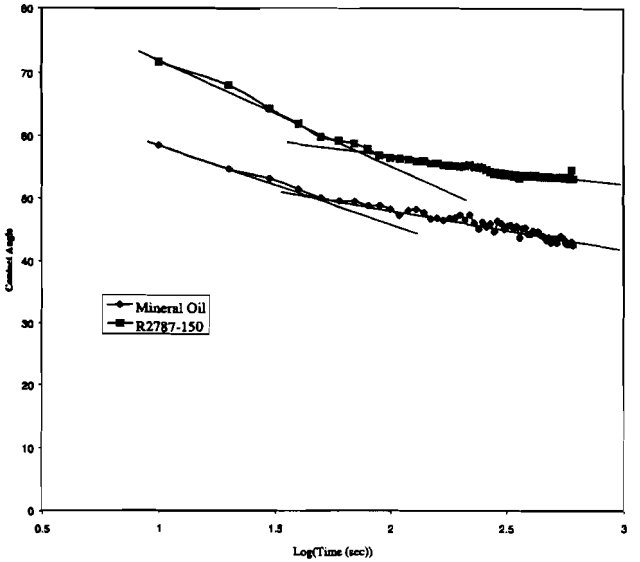


Figure 3 depicts the DCA following the method of Huang and Goodman (1995). The results closely follow those proposed by the Grenoble group. It shows two kinetic regimes: at short times the contact angle changes as function of spreading (advancing contact angle), however, after spreading reaches equilibrium the diffusion into the surface causes further decease in contact angles. What these data do not explain is the occurrence of clean prints on copies 1-5 in waterless printing... which is often seen. Or how certain "water washable" inks without a suitable ink diluent still can print cleanly under certain circumstances.

"Single Fluid Ink"

Recently, Kingman *et al.* published US patent 6140392 that disclosed a lithographic ink composition comprising acid-functional vinyl polymer and polyol phase. They claim that this particular composition can be used in lithographic printing without fountain solution, i.e. a "fount-free process." Kingman *et al.* disclosed the specific use of an acid functional vinyl polymer in the hydrophobic continuous phase of an ink emulsion. The "vinyl" polymer described in the patent is a relatively low molecular weight copolymer of styrene (hydrophobic monomer 63.6%), stearyl methacrylate (long chain hydrophobe pendant to backbone 23.9%), butyl acrylate (short chain hydrophobe pendant to backbone 7.7%), di-vinyl benzene (hydrophobic crosslinker 3.1%) and methacrylic acid (hydrophilic1.9%). Closer examination of the composition reveals architecture consistent with that of a polymeric stabilizer suitable for use

as an inverse emulsion (water-in-oil) stabilizer. Earlier "SFI" concepts are described in the patent literature.

In 1977 John Pacansky claimed a stabilized alcohol or water-in-oil ink emulsion comprising in part of 20-40% of a resin having polar segments which were miscible with alcohol/water and non-polar segments which were miscible in the non-polar phase of the ink. Pacansky suggested that the use of polymeric stabilizers could overcome difficulties associated with controlling the meta-stability of the ink emulsions previously stabilized with surfactants. Poorly stabilized ink/alcohol emulsions were observed to have broken down while standing (i.e. shelf-life stability) and/or prematurely on the ink rollers. Alternately, extremely stable emulsions tended to give poor printing results (i.e. high background/toning). Pacansky preferred the use of relatively small polyhydric alcohols such as ethylene glycol and the like. Polyhydric alcohols have been the preferred hydrophilic phase for lithographic ink emulsions according to patent literature.

In 1974, Alexander Spencer and Alfred Spicer obtained a patent for a lithographic printing ink that was produced by suspending ink in a hydrophilic medium that was characterized by a specific viscosity and rheology profile. It was claimed that a separate fountain solution was unnecessary. Spencer and Spicer preferred the use of liquid polyhydric alcohol (i.e. ethylene glycol) alone or in combination with water and optionally hydrophilic phase rheology modifiers. It was also suggested that it might be advantageous to include a spreading agent such as acetone, isopropyl alcohol or ethanol in the hydrophilic phase. Relative proportions listed in the patent (i.e. 5-60% of oleophilic phase) would suggest that both oil-in-water and water-in-oil ink emulsions could be produced using this technique.

In 1977, H.B. Parkinson patented a composition for a single step lithographic ink, which also utilized small polyhydric alcohols. This particular invention related the use of acid treated resins in combination with polyhydric alcohol to generate lithographic ink with specific rheology. Parkinson claimed that the strong mineral acid treatment of the ink resin imparted the improved properties in this field.

De Santo *et al.* also claimed the use of acid in a single fluid ink system. In this case phosphoric acid was claimed as a stabilizer. The other important features of their invention composition included a diluent with properties similar to fuel oil (No 1, No 2) and a polyol (i.e. ethylene glycol). De Santo *et al.* suggested that the phosphoric acid acted as an emulsion "facilitator" and stabilizer. It is not clear from this patent how the phosphoric acid acts as an emulsion stabilizer and it seems like a rather odd assignment for this particular molecule particularly at the levels that are preferred by De Santo. In any event, it appears that polyhydric alcohols are preferred over water ink emulsions for various reasons not the least

of which is the fact that these types of molecules do not evaporate as fast as water. However, a combination of water and polyhydric alcohols are claimed in most cases. Moreover, the ink emulsion patent literature contains examples of hydrophilic phases that were ultimately more complex than just a single polyhydric alcohol and/or a combination of a polyol and water. Hydrophilic phases used in ink emulsions optionally contain a) water b) polyhydric alcohols c) rheology modifiers d) desensitizer/phosphoric acid e) wetting agents f) hygroscopic agents g) anti-corrosive agents h) pH buffers i) surfactants j) chelating agents k) water soluble polymers.

Recently, Ohshima *et al.* patented an ink emulsion system which relates the use of an emulsified UV cure compound as well as a hygroscopic compound, glycol, triethanol amine and low HLB surfactant. In this case, the aqueous phase of the emulsion was preferred to be 60-80% by weight.

At DRUPA 2000 Flint presented a demo of a "single fluid" ink with Presstek Anthem (Rorke 2001) plate. However, the Single Fluid Ink concept (Generically) must overcome several challenges and questions:

-Single Fluid Ink (glycol/ink pigment ratio) MUST accommodate any kind of plate coverage.

-Emulsion MUST break-up on non-image but not in the roller train (provide suitable ink transfer).

-Amount of hydrophilic phase in the ink must be high (typically 30 to 50%) to keep the non-image area of a conventional plate free of ink.

-Do all conventional plates accommodate the requirements of Single Fluid printing?

-Do we need WFBL to form on the non-image?

-Do we need a unique abhesive layers for the glycol used in SFI (as on Anthem plate?) much as silicones for conventional waterless inks?

Water Washable FFO Inks

Water washable (WW) inks also introduce several issues. The goal of these technologies is to enable single fluid lithography, have zero VOC, no misting and be truly water washable and maintain compatible with existing press equipment. Nevertheless they present three big challenges:

-How to build viscosity of a water-based ink

-How to stabilize a water-based ink on the long ink train of an offset press.

-How to achieve instant drying after printing while maintaining stability on the rollers

The developers of these water-washable inks (Krishnan 2001) offer three possible solutions:

-Use a latex at pH=6.0 with a water-based gellant, not thickeners (which give poor film integrity) or fillers, like clays (which give poor gloss) or increased rosin ester content (which increases tack too much).
-Use a water-soluble linseed polyester, not a humectant like hydroxy ethyl ethylene urea (affects drying time) or an engineering solution, like a humidity chamber around the ink train (which is too hard to maintain)
-Use self-cross-linking micro-sized latex, which creates a drying mechanism by latex coalescence.

These results hint at both Curtin's and Gaudioso's models, i.e. that WW inks do not abhere to uniquely silicone plates. But, also, that linseed oil in the latexes may interact with the silicone to create a WFBL.

Summary

The idea of this paper is to describe three different potential FFO processes and review their historical development. The common elements are; for instance, the non-image areas need to be protected from the ink in all cases, regardless of the method of transport of that protecting material to the non-image area. The inks must possess high cohesive energies. They must contain "diluents" compatible with the non-image areas of the planographic media. These diluents may be linseed oil for water washable applications, glycol for SFI ink, mineral oil solvent for waterless. The non-image areas of the transfer media must be abhesive to the FFO inks. We may still need to do further work to understand whether image coverage is a factor in some "apparent" FFO processes.

We can say with confidence that for any FFO process that the opportunity for "closed-loop color control" is very real. Therefore, these processes need very detailed study and those, which are commercially feasible, robust and most compatible with installed capacity will become major operational processes in the near future.

Literature Cited

Bikerman, J.J.
1995 *J. Appl. Chem.*, **11**, 81 (1995)

Chou, S.M., Bain, L/J., Durand Jr., R. and Sanderson, E.
1996 International Printing & Graphic Arts Conference, *TAPPI Proc., 165*

Curtin, J.L.
1970 US Patent 3,511,178 (May 12, 1970)

DeGrace, J.H. and Mangin, P.J.
1984 Adv. Printing Sci. Tech., 17th IARIGAI 1983, Banks, W.H., ed, Pentech Press, 146 (1984)

De Santo, R.F., Carava, S.S., and Parkinson, H.B.
1991 US 4,981,517 (January 1, 1991)
Gaudioso, S.L., Becker, J.H., Sypula, D.S.
1975. "Mechanisms of Ink Release in Waterless Lithography", TAGA proceedings, pp. 174-194
Gipe, H.F.
1972 US 3,677,178 (1972)
1973 US 3,728,123 (1973)
Goodman, R. M.,
2000. "Waterless and Conventional Offset Lithography: A Realistic technical Comparison" Taga Proceedings, pp445-454
Gracia, R.F., Laughrey, R.A. and Tuohey, P.F.
1974 US 3,835,780 (1974)
Hansen, C.M.
1967 *J. Paint Techno.*, 39, N. 505, 104 (1967)
Huang, J.B. and Goodman, R.M.
1995. "Modeling Studies of Ink, Plate and Fountain Interactions by Contact Angle measurements," TAGA proceedings, pp.154-167.
Kingman, K.P., Balyo, R.A., Oberski, M.V.
2000 US Patent 6,140,392 (October 31, 2000)
Kobayashi, M. and Iwamoto, M.
1975 US 3,894,873 (1975)
Krishnan, R.
2001 private communication
Lanet, V., Blayo, A. and Gandini, A.
1997 "Elaboration and Characterization of Waterless Inks Containing Vegetable Derivatives," TAGA Proceedings, pp. 777-790
Lanet, V. and Gandini, A.
1995. "Characterization of surface energies of waterless plates," TAGA proceedings, pp. 1182-1193.
Ohshima, K., Imamura, M.,Taniguchi, K., Kawamura, E., Adachi, H.
2000 US 6,063,835 (May 16, 2000).
Pacansky, T.J. and Becker, J.H.
1975 "Materials Criteria for Waterless Lithography" Taga proc., pp. 195-219.
Pacansky, T.J.
1977 US 4,059,554 (November 22, 1977)
Parkinson, H.B.
1977 US 4,045,232 (August 30, 1977)
Rorke, T.P. and D'Amato, R.J.
2002 US 6,182,570 (Feb 6, 2001)
Sorkin, J.L., Kay, P.M. and Frishkorn
1973 US 3,775,115 (1973)
Spencer, A. and Spicer, A.L.
1974 US3,803,070 (1974)
Yoerger, W.E., McCabe, J.M. and Wright, J.F.
1975 US 3,859,090 (1975)