# VANISHING DOTS: CAUSES AND POSSIBLE CURES FOR NON-IMAGE PILING IN WEB OFFSET PRINTING

Bruce Blom Patricia Loel Robert Blake

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Abstract: During 1994-1995 several web heatset printers using 45#-60# coated paper reported premature loss of highlight dots necessitating a cleanup of the press. This resulted in excessive spoilage and lost production time. The cause of the problem has been identified as the build-up of coating and ink materials in the non-image area of the printing blankets. Some printers felt the problem was restricted to alkaline papers, but the data do not warrant this conclusion.

Two different, but not necessarily exclusive, mechanisms for the origin of non-image blanket piling and consequent loss of highlight dots ("vanishing" or "hollow" dots) have been proposed:

- Micro-pick of paper coating from the surface of the paper
- Dissolution of soluble calcium salts from the surface of the paper

In either case coating components, along with ink particles, accumulate in the non-image area of the blanket to the point where there is no longer efficient contact between the inked areas of the plate (in the highlight regions) and the corresponding area on the printing blanket.

Our results indicate that many of the commercially available fountain solutions "attack" the ink and cause it to become dispersed in the fountain solution. This can account for the presence of ink in the non-image area. We also find that the fountain solutions tend to be so acidic (pH  $\sim$  4) that calcium carbonate can be solubilized.

<sup>\*</sup> Mead Corporation, 232 Eighth Street, Chillicothe, OH 45601 614-772-3689

### Introduction

The problem of piling is not new, although causes may differ<sup>1</sup>. Unfortunately, "piling" is not a unique term; the specific type of piling needs to be defined in order to clarify what the problem actually is. In the present study we are referring to the accumulation of material in the non-image area of the blanket; we further clarify this by stating the type of piling we are investigating occurs on all units, including the first unit of the printing press and can, therefore, be encountered in single-color printing.

The problem encountered by several printers is illustrated in Figures 1A and 1B. Figure 1A shows a highlight region at the beginning of the print run, Figure 1B shows the same region after approximately 50 minutes of running time. Deterioration of the highlight and quarter-tone dots is clearly seen. Figure 2 shows pictures of the surface of blankets in the region of the quarter-tone. The actual printing area (the dot) is recessed from the surface of the non-image area. Figure 3 is an illustration of what we believe is occurring on the blanket surface.









FIGURE 2: McKay (blanket) #2, 2U halftone coating buildup in non-printed area. 200X (top) 350 (bottom). Z thickness 8-10µ



The left side of Figure 3 illustrates normal behavior; ink is applied to the plate, a portion transferred to the blanket, and a portion of that transferred to the paper. We have tried to illustrate that the surface of the ink film at the air interface is not a flat surface, rather it is a rough or irregular surface with peaks and valleys as a consequence of the ink splitting phenomenon. Because the blanket and paper are in such intimate contact (at least for the coated papers we are dealing with) there is 100% contact between the paper and the ink. This results in a continuous ink film appearing within the dot area.

The right side of Figure 3 shows what happens when there is a build-up of material in the non-image area. Eventually this material becomes so thick that there is no longer 100% contact between the irregular surface of the plate ink film and the blanket; where there is contact, from the peaks of the ink, there is ink transfer to the blanket and thence to the paper. In many cases there is clearly seen to be a "ring" or "doughnut" of ink. We believe this is due to the fact that the "well" on the blanket has beveled edges at the top; see Figure 2. Ink is postulated to be squeezed into this region during plate-blanket contact and then, because it is close to the new surface of the blanket, it is subsequently transferred (printed) during blanket-paper contact.

We have measured the thickness of the material that builds up on the blankets and find it to range from 7-13 $\mu$ m thick. This is impressive because one would assume that for a 1.5 $\mu$ m ink film thickness on the paper, there would be 3 $\mu$ m on the blanket and 6, $\mu$ m on the plate. Since ink feed is not changed during the run we have to assume that we are constantly presenting about 6 $\mu$ m of ink from the plate to the blanket. The fact that there are regions of solid ink still present within the "doughnuts" on the print suggests that by whatever mechanism, ink can still be transferred. Regrettably we have no data to show any correlation between the rate of build-up on the blanket and the appearance of the printed dot.

Analysis of the piled material on the blanket typically finds about 50% ink components, 50% paper coating components, notably the clay and calcium carbonate pigments. There is an indication that a small amount of latex binder from the paper coating is also present. Table 1 shows a comparison between the results obtained when running two different papers.

raper r i	Paper P5
ing Composition Typically 22% clay, Typica 6% CaCO <sub>3</sub> , 4% TiO <sub>2</sub> 25% C TiO <sub>2</sub>	lly 6% clay aCO <sub>3</sub> , 3%
material clay, TiO <sub>2</sub> , clay, C position Ca(MgFe)(CO <sub>3</sub> ) <sub>2</sub> ganic)*	aCO <sub>3</sub> , TiO
position Ca(MgFe)(CO <sub>3</sub> ) <sub>2</sub> ganic)* prganic component, about 50%, consisted prima ponents and a small amount (possibly) of paper	ril

\* the relative amounts of the pigments in the piled material are not the same as that of the paper coatings

X-ray analysis of the pigments indicated primarily kaolinite and calcite. Noteworthy is that the ratios of pigments indicated substantially more clay than calcium carbonate for both papers.

### Experimental

Prior to seeking the cause of the reported problem we felt it important to ascertain the extent of the problem and the conditions under which it might occur. In cooperation with two printers who had experienced the problem, the performance of a number of papers of varying coating composition was undertaken. The results are shown in Table 2.

As pointed out in Table 2, Printer #2 should be able to get approximately twice the number of impressions, all other things being equal, as Printer #1 for the same paper. For the five cases where such a comparison is possible, this was true for only two cases. For the other three cases, where Printer #2 could run in excess of 100,000 impressions, Printer #1 saw no change in performance. The image being printed certainly could be a factor; only when there are a significant number of fine screens being printed can the problem become apparent.

The other point clearly shown in Table 2 is that the performance of the paper does not appear directly related to the coating composition of the paper. This is important as at the beginning of this project there was a definite perception that "alkaline" papers, meaning those containing calcium carbonate in the coating, were more susceptible to the problem of non-image piling. The data in Table 2 suggest that this is not the case. In fact, Paper PI from Table 2, which ran so well at Printer #2, is the same paper as that in Table 1 (Paper PI). Running that paper on another press we were easily able to generate non-image piling.

Our conclusion at this point was that there are other factors affecting the performance of these papers and that an understanding of them might lead to some insights into the underlying causes of the problem. The most obvious starting point was to characterize the materials being used in the pressroom, and their interactions, and from there develop a working hypothesis.

## Materials

Paper, fountain solution and ink samples were obtained from Printers #1 and #2. Several additional commercial fountain solutions were also supplied by two manufacturers. Calcium carbonate used in our tests was Omya's. Hydrocarb 90.

	F	ield Result	s				
Impressions between Runnability** wash-up, thousands*			Coatin	ng Compo	sition		
PRINTER #1	PRINTER #2	Paper ID	PRINTER #1	Clay	<u>CaCO</u> <sub>3</sub>	<u>TiO</u> <sub>2</sub>	
23	100+	P1	medium	good	22	6	4
25	50	P2	medium	medium	17	9	3
28	NA	P3	good	NA	7	26	3
17	NA	P4	poor	NA	23	11	3
28	NA	P5	good	NA	6	25	3
27	50	P6	good	medium	25	0	2
20	100+	P7	medium	good	29	0	2
NA	58	P8	NA	medium	26	11	1
23	100+	P9	medium	good	30	0	2
NA = not a	pplicable.			·			
*Note that run twice as	because of di s long as Prir	fference in nter #1 for t	blanket diam the same amo	neters Printe	r #2 sho r	uld be abl	e to

Results

Paper

Paper testing was done in our lab using the NPA tester and methods<sup>2</sup>. Results are shown in Table 3.

For this particular set of tests wet pick was assessed by observing the urethanecovered blanket roller; its appearance was assessed versus photographic references of standards. Passes to fail is an indication of surface strength while the slope, which is the tack build with time, is an indicator of the rate at which ink solvent is absorbed into the upper layers of the paper coating. The latter two tests are conducted in the absence of fountain solution.

Papers Pl, P7, and P9 were the ones that had the best performance at Printer #2; interestingly they all have poor wet pick resistance, at least as measured by the method used here. All three are primarily clay-based coatings. Paper P6 is also a clay-based coating, but its pressroom performance is not as good.

Table 3. Paper Properties as Measured by NPA Methods				
Paper ID	Wet Pick*, Magenta ink	Passes to Fail	Slope, mean	
PI	4	6	4.6	
P2	1	7	4.6	
P3	1	7	4.9	
P <b>4</b>	1	4	9.55	
P5	2	7	5	
P6	1	5	4.8	
P7	5	4	11.3	
P8	1	7	5.6	
P9	5	5	6.4	
*1 = good.	5 = bad			

#### Fountain Solutions

Figure 4 shows the pH and conductivity characteristics of a number of different fountain solutions (from two suppliers) that are commonly encountered in the pressroom. Noteworthy is that these solutions have fairly consistent pH versus concentration characteristics. pH characteristics were largely unaffected whether dilution was in deionized water or mildly hard water (142mg/l as CaCO<sub>3</sub>); conductivities vary according to the actual salt concentration of the solutions.



Buffering and acidity characteristics were measured by titrating diluted samples with 0.1N sodium hydroxide; see Figure 5. The particular shape of any one curve is determined by the specific acids and buffering agents used in the formulation.



Table 4 summarizes the fountain solution data; we did note the volume of sodium hydroxide necessary to reach an arbitrary pH (5.5). The point here is that different solutions have varying capacities to resist changes in pH when alkaline materials are introduced. This buffering ability is quite large; a solution of hydrochloric acid of similar pH and comparable volume would be neutralized with less than one milliliter of sodium hydroxide. Solution A is being used at Printer #1, Solution G at Printer #2.

The solvents that were found reflect the types of materials being used as alcohol replacements, wetting agents, non-piling additives, etc. Not measured, but included in the percent non-volatile material, would be surfactants.

#### Inks

Table 5 summarizes the usual ink properties. Volatility is measured by drying the ink in an oven at 110°C for 1 hour. Inkometer data is collected at 1200rpm/90°F using a Thwing-Albert Inkometer. In general, the inks are similar.

Table 4. Fountain Solution Properties					
Solution	pH @ 4oz/gal	Volume of 0.1N NaOH to pH = 5.5 *	Solvents	% NVM	
Α	3.88	8.0cc	PG, BC	5.5	
В	3.57	7.7	PG,2-PE, +	9.4	
С	3.76	3.2	PG,BC	9.9	
D	4.06	3.4	PG,BC,2-PE	13.5	
Е	3.88	7.8	Acetic Acid + ??	24	
F	4.07	3.9	PG,BC	11.9	
G	3.79	5.4	not tested	12.2	
* for 50m	l of 4oz/gal F.S.		PG = Propylene Glycol BC = Butyl Carbitol 2-BE = 2-Butoxyethane	ol	

The most significant difference is in the lower viscosity / higher solvent content of the ink used by Printer #1.

Table 5. Ink Properties						
Ink	Ink % Volatiles Inkometer Data					
		Tack @ 1'	Slope @ 5'	Dry Time		
Printer #2	29	13.5	1.8	>10'	23"	
Printer #1	37	15	2	>10'	20.5"	
* Laray falling	g rod viscometer -	shorter drop ti	mes = lower v	iscosity		

### Material Interactions

While properties of the individual components are important, more often than not it is the interaction between components that plays a significant role in overall press performance.

### Ink/Water

Emulsification characteristics of inks and fountain solutions are felt to be of critical importance for proper lithography, but measuring this interaction is always problematic. For this study we elected to use the Kershaw tester<sup>3</sup>. This involves taking 25gm of ink and adding fountain solution slowly while stirring with a high shear mixer. A sensor monitors the applied torque. Torque increases occur as the amount of water (or fountain solution) dispersed in the ink increases; the torque drops suddenly when the ink can no longer absorb the water. Results are shown in Table 6.

Table 6. Ink-Fountain Solution Interactions						
Results of Kershaw Test						
Ink/Fountain Solution Combination Emulsification Capacity Torque						
Printer #2 - 4oz/gal	66ml	395				
Printer #1 - 4oz/gal	59	389				
Printer #1 - 8oz/gal	Printer #1 - 802/gal 58 410					

According to people experienced with this procedure, the difference in emulsification capacity between the Printer #2 ink/ fountain solution mixture and the Printer #1 materials is statistically significant. There is no statistically significant difference in the torque changes. The relevance of this method to press performance has not been validated, however. The difference between the printers inks is likely attributable to the difference in the rheology of the inks (Table 6). Note that for Printer #1 changing the concentration of fountain solution had no effect.

To clarify what, if any, adverse effects some of the fountain solutions might have on the inks, we took small amounts of each ink and put them in the various diluted fountain solutions (0.2 grams of ink in 10ml of 6oz/gal fountain solution in deionized water). They were then mixed in a laboratory ultrasonic cleaning bath; a notation was made whether ink became dispersed. in the fountain solution. All solutions were then allowed to sit for two days before being agitated again, this time for one minute. Typical results are shown in Figure 6; all observations are summarized in Table 7. It should be noted that simply mixing by hand was insufficient to cause the ink to disperse in the fountain solution.

# Printer #1 - Solution F (Table 7)



Printer #1 - Solution F + Alcohol Substitute



FIGURE 6: Effect of mixing ink and fountain solution

Table 7. Effect of Mixing of Ink and Fountain Solution   on Supernatant Appearance					
	mixing for 30" (ultrasonic)		samples from 1' ultrasonic	n preceding, additional mixing, two days later	
Esuntain Salutian	Using Ink From		Using Ink From		
Fountain Solution	Printer #1	Printer #2	Printer #1	Printer #2	
А	clear	clear	turbid	turbid	
В	clear	clear	turbid	sl. turbid	
С	clear	clear	turbid	turbid	
D	clear	clear	turbid	clear	
Е	turbid	turbid	turbid	increased turbidity	
F*	clear	clear	clear	sl. turbid	
F + alc. sub.	turbid	turbid	turbid	turbid	
G	turbid	turbid	turbid	turbid	
Water (deionized)	clear	clear	clear	clear	
15% IPA in water	clear	clear	clear	clear	
* "F" is a two-step system; unless indicated otherwise the data refers to the fountain solution itself, not the solution plus the alcohol substitute					

Our interest in this type of testing is because analysis of the piled material in the nonimage area on the blanket indicates that it is about 50% ink or ink components. To get to the non-image area it would have to come through the dampening solution. We are not certain whether the ink components are emulsified into the dampener solution on the press rollers or whether the ink components are leached from the ink at the ink/water interface on the printing plate. In the samples we have looked at it appears that the entire non-image area of the blanket is covered with piled material, not just the area surrounding highlight dots. Thus, the use of the intensive energy of the ultrasonic bath to simulate the mixing that would take place on the rollers of the press appears justified. Low energy mixing, as might be encountered with the Duke Water Pickup Tester, often used in the ink and fountain solution industry, is not representative, in our opinion, of the intense mixing found on a printing press.

We did allow two of these fountain solutions with the dispersed ink to evaporate in a watch glass; both became slightly tacky. One scenario might then be that the tacky ink residue accumulates on the blanket and begins to cause coating pick; piled material begins to accumulate. We have not confirmed this, however. Table 7 does show that isopropanol and water appears fairly benign. It would be interesting to see if it, or perhaps Fountain Solution "D", if only on an experimental basis, would increase the time between washes.

#### Ink/Paper

Our laboratory commonly measures ink-paper interactions using the NPA apparatus. Tables 3 and 8 contain the results of such testing using their standard, nondrying ink. A logical question is whether such results, using a non-drying ink, are representative of what would happen with a conventional heatset ink. Table 8 shows the results obtained using the actual inks from the customers along with three of the paper samples. The first point to note is the fairly low slope of the heatset inks when printed on a non-absorbing Mylar surface. This means that the tack rise due to evaporation is fairly low over the duration of the test (about 70"). For all examples note that the magnitude of the slope is fairly independent of the ink used ("Standard" is the non-drying ink); all inks rank the papers in the same order for absorptivity. Finally, we note that the Printer #1 ink gives slightly higher slopes versus the Printer #2 ink. This may be due to its higher initial tack and solvent content (Table 5). It is possible that the higher ink tack encountered with Printer # l's ink might be contributory to the fact that some of the papers do not run as well at that plant as at Printer #2.

	Table 8. Ink-Paper Properties						
	Tests Conducted Using Customers Heatset Ink						
		Slope					
Paper	Ink from Printer #2	Ink from Printer #1	Standard Ink				
P1	4.5	4.9	4.6				
P7	10.7	12.9	11.3				
P5*	6.2	6.8	7.7				
Mylar	0.6	0.7					
* this sampl	e was a slightly hi	gher basis weig	ht version of "P5"				

Fountain Solution - Paper (or calcium carbonate) Interactions

Table 9 shows the cold water extraction results for the paper samples. Clearly calcium is extracted from the paper even with plain water. At the pH of the test (close to neutrality) we are likely dissolving a soluble species, such as calcium hydroxide. Low values for the extractable calcium for Papers P6, P7, and P9 are consistent with the coating analysis in Table 2.

Table 9. Cold Water Extract Properties						
Paper	pН	Conductivity	Surface pH, Front	Surface pH, Back	Extractable Ca,ppm	
<b>P</b> 1	9.04	82	7.53	7.49	147	
P2	8.94	70	7.31	7.86	255	
P3	8.95	86	7.88	7.57	244	
P4	8.81	170	7.68	7.92	151	
P5	9,01	101	7.44	7.46	299	
P6	6.98	63	5.88	6.14	16	
P7	6.7	53	5.59	5.32	<15	
P8	8.18	119	7.01	6.96	235	
P9	6.72	55	5.31	5,84	<15	
P10	9.04	100	7.21	7.43	306	

Figure 7 shows the interaction between "press ready" fountain solution and calcium carbonate pigment. As might be inferred from the acidity of the fountain solutions (Figure 5 and Table 4), fountain solutions are much more aggressive than plain water and are obviously capable of dissolving the calcium carbonate itself. The pH of the fountain solutions rises to approximately pH = 8, where they can no longer dissolve calcium carbonate. Note that with the fountain solutions, the conductivity drops as the pH increases. This is not unexpected as the hydronium ion,  $H_3O^+$ , is the most mobile species contributing to the electrical conductivity of the solution.



The preceding tests are aggressive; some have argued that "total" calcium is not a relevant measure of a paper's propensity to contribute to non-image piling, rather it is "surface" calcium that is important.

We have attempted to simulate this by allowing a known volume of fountain solution to run down a fixed surface area of the various paper samples. Contact time was about 10 seconds; there was no obvious saturation of the paper itself. The results are shown in Figure 8. The important features of this graph are that calcium is definitely being solubilized by the fountain solution, but not by pure water. This suggests that for the "surface" calcium we are likely dealing with dissolution of calcium carbonate rather than a more soluble salt such as calcium hydroxide.

A comparison of these values versus the "total" calcium found by extraction shows only a very weak correlation.



### Discussion

As with many problems occurring in complex situations, such as pressrooms, often conflicting experiences and results are encountered. For example it is reported that this problem does not occur in Europe, where coated papers have been predominately calcium carbonate-based for years. Important differences between European and North American coated papers include the use of much higher synthetic binder levels in European papers. Other differences exist as well, including the routine use of fountain solutions normally running at pH ~ 5, while in North America pH ~ 4 is common. Another important difference is that in the US. the use of isopropyl alcohol has largely been eliminated and replaced by various substitutes; in Europe it is still widely used.

Other anecdotal information exists that suggests ink/dampening issues are important. Independent observations<sup>4</sup> found that piling could be minimized by decreasing the water feed to the plate. This approach required an increase the concentration of the fountain solution in order to maintain adequate levels of fountain solution chemistry. But, increasing the concentration of all the components was not the best approach, only the concentration of some of the components was called for, e.g. gum arabic. Additionally, it was found that chilling the fountain solution was beneficial. This may be due to lower emulsification taking place with increased ink viscosity.

While we do not claim to have conclusively identified specific causes for each printer's experience, we believe that the results gathered to date clearly show a pattern

- At the fountain solution pH's currently in use here in the US., not only are minor amounts of soluble calcium salts, such as calcium hydroxide and/or calcium sulfate, dissolved but also normally insoluble calcium carbonate. The solubility of calcium carbonate is dependent on pH; the higher the pH the lower the solubility.
- Fountain solution chemistry, particularly the isopropyl alcohol replacements, can be very aggressive towards inks. Ink becomes dispersed in the fountain solution<sup>5</sup> and is transferred to the non-image areas of the blanket. Isopropyl alcohol did not behave, in our tests, as aggressively as did the alcohol substitutes.

We suspect that a sticky layer of ink forms in the non-image area of the, blanket, as a consequence of ink-in-fountain solution emulsification brought on by adverse interactions between the ink and fountain solution. This sticky layer causes micropicking<sup>6</sup> of the surface of the paper; this picking may become excessive if the coating has been weakened by the dissolution of any calcium carbonate in the surface. The surprisingly small levels of calcium found in the samples we looked at (Table 1, paper P5) may be a consequence of the dissolution of the calcium carbonate.

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