

CONTROLLING BUFFERED FOUNTAIN CONCENTRATES

Abstract

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After dealing with the traditional pressroom method of (chemical) control of acidic lithographic fountain solutions the contribution is concerned with a system based on the electrical conductivity of advantageously buffered fountain mixes. Detailed basis of the above is given with that of a non-subjective comparative system - using purpose designed instruments suited to pressroom conditions and the responses of everyday dilutions of buffered concentrates. Data is shown in respect of a representative range of lithographic chemicals and concentrates as well as isopropanol and Techfont. It is suggested that standardised (constant pH) acidic fountain solutions, and a standard control system are feasible. Accuracy is achieved via monitoring instruments.

For forty years, it has been accepted that the acidity of the fountain solution needs to suit the printing process and operators have checked the pH of said fluids. (1) When apparently necessary, adjustment of pH has been done by altering the quantity of the chemicals (i.e. the fountain/etch concentrate) in the final solution. This method of control dates from the 30's. In 1945 for instance lithographers were following chemical formulas with 'the Ph measuring stick' (2). The pH parameter is still frequently used today to control the quantity of the chemical concentrates, at the same time as the degree of acidity (3). It is based on the view that unsuitable degrees of acidity can contribute to press problems.

Chemists of the 50's realised that some chemicals caused the fountain solutions to be slightly buffered and that this assisted press operators to keep the pH under control, i.e. near the chosen level - giving an apparently wider mixing tolerance, and making the printing operation less variable. When metal plates are used, acidity levels between pH4 and neutral are common, and in relation to anodised aluminium surfaces, levels between 4.5 and 5.5 (inclusive) are general. The corrosion resistance of these surfaces has enabled the widespread adoption of concentrates which produce strongly buffered fountain solutions.

Some 25 years ago it was demonstrated that with a (4) constant quantity of desensitising chemical, variation of acidity between pH4 and 7 can make no difference in the ability of a fountain solution to prevent plate scumming. It was likewise shown that the quantity of desensitising material in the fountain solution is a major factor in respect of the scum resistance of metal plates when the pH is constant. It follows that the traditional control system, which unavoidably changes the quantity of desensitising material(s) when adjusting the pH, is suspect in principle.

This contribution also points out:-

- a) that since the 60's surfactants have been introduced into fountain solutions to eliminate oxydation scumming, (5) this necessitating accurate control. To alter the amount of surfactant according to a logarithmic and unrelated variable (pH) parameter is not clever.
- b) that the accuracy of the current system is seriously hazarded by the everyday operating method which is

subjective and assesses the acidity with colourimetric indicator strips.

c) that strongly buffered acidic and neutral concentrates cannot be controlled by the traditional system (6).

The following suggests a basis for a better - purpose built and perhaps standardised - fountain control system for use with buffered fountain concentrates.

According to the degree of dilution, strongly buffered acidic concentrates can yield solutions with pH responses similar to those in figure 1. These were obtained whilst using a representative commercial concentrate diluted in accordance with proven recommendations using randomly chosen tap water. This significant percentage change has only a small effect on the pH, from 5.0 to 4.4. When more accurate percentage differences are required they cannot be discerned and achieved with certainty via the pH strip system. With short range strips the accuracy is little better than 0.5 pH unit (7). Therefore, the amount of desensitising and other chemicals can change considerably before it is likely to be detected by the traditional control system. With strongly buffered formulations this feature is much worse. This being demonstrated by taking undiluted citrate/gum concentrate buffered at pH 5.0, and finding its pH to be 4.9; after dilution to form 10% and 2% solutions the pH levels were close to 5.1.

Realisation that this feature is associated with the undoubted advantages obtained by using well buffered concentrates to achieve near constant pH, has lead to the development of a purpose built 'measuring' instrument which avoids the subjective technique as well as the pH

parameter. Howson-Algraphy have called their Mark I manual version a Fount Monitor (8). See illustration.

According to Selley (9) the electric conductivity of a solution of any strong electrolyte is roughly proportional to its concentration since it depends on the quantity of ions available to carry the current.

Whilst considering electric conductivity meters in the above context after the manner of Bates and Blom (10)(11) and Scarlett (12) the particular relevance in respect to buffered acidic concentrates of conductivity became apparent. It was noticed that the chemicals employed in buffered formulations in the quantities necessary to provide the correct lithographic and desired pH buffering properties, imparted readily measurable (and characteristic) degrees of conductivity to the press ready solutions. These being several times greater than the conductivities of straight water(s).

Representative conductivities of a random selection of 51 local waters are given in table 1, instrumentally corrected to international standard 25⁰C. Infrequently are they greater than 600 micro-seimens/cm ($\mu\text{S}/\text{cm}$). The histogram in figure 10 demonstrates this point. Assuming that this selection is adequate enough to indicate the general situation, the mean conductivity is (rounded - it is not critical) 400 $\mu\text{S}/\text{cm}$. This assumption is based on the histogram being accepted as a discreet approximation to a skewed normal distribution, see dotted line. These typical conductivities were obtained from nine countries.

Because such a distribution is to be expected, the given figures have been accepted as an adequate basis for the remainder of this appreciation and the adoption of 400 $\mu\text{S}/\text{cm}$ water as 'average' water.

Investigation found that a conductivity meter yielded read-outs in respect of press ready solutions of a significant number (greater than 20) of commercial acidic and neutral buffered concentrates, several times larger than those of the straight waters. It also showed that variations in conductivity of water from 'pure' ($10\mu\text{S}/\text{cm}$) to 'hard' ($600\mu\text{S}/\text{cm}$) had little effect on the magnitude of the relationship. Figure 2 shows typical magnitudes when using two different 600 $\mu\text{S}/\text{cm}$ waters, one made by adding magnesium sulphate and the other by adding sodium bi-carbonate to 'pure' water. At normal 1.5% dilution of the representative concentrate (13), the conductivity relationships are 2.7: 1 and 3.0: 1. Similar relationships were found when calcium sulphate, potassium nitrate and other chemicals were used to create different 600 $\mu\text{S}/\text{cm}$ waters. It can be seen that these compare well with the relationship obtained when local 600 $\mu\text{S}/\text{cm}$ 'hard' water was used.

The above lead to the modification of a conductivity meter to obtain a purpose built device for monitoring the quantity of buffered acidic concentrate in fountain solutions made with average water, thereby providing a comparative fount control system using an instrument designed to suit buffered fountain solutions and the requirements of every-day pressroom conditions.

Taking water with a conductivity of 400 $\mu\text{S}/\text{cm}$ (25°C) and using it to produce appropriate fountain solutions with numerous randomly chosen buffered concentrates (the dilutions according to the instructions of suppliers), the ensuing conductivities were found to approximate to 1800 $\mu\text{S}/\text{cm}$.

Adopting 1800 $\mu\text{S}/\text{cm}$ as a standard for buffered fountain solutions in average water and adjusting a conductivity meter to cause it to register near the middle of an expanded 0 to 3.000 $\mu\text{S}/\text{cm}$ range of electrical responses, provided the basis of a monitoring device. Because this adjustment made nonsense of the nomenclature of the scale and because it was apparent that electrical units are unnecessary and unsuitable for pressroom usage, the expanded scale was substituted by one of the same dimensions, reading 0 to 3 arbitrary fount monitor units. By this means the meter became a suitably accurate comparative monitor. Normal strength buffered fountain solutions registering close to the middle of the scale, weaker solutions reading significantly less and stronger solutions more.

In due course, with the object of providing a valid means of standardising the above, a standard buffered acidic fountain concentrate was obtained by adopting a simple (buffered pH5) formulation. This comprising well known lithographic chemicals.

Citric acid (mono-hydrate)	5g
Tri-sodium citrate (crystals)	17g
Water (demineralised)	93mls

yields a solution on dilution to 1½% by volume using 400 $\mu\text{S}/\text{cm}$ water, giving a conductivity very close to 1800 $\mu\text{S}/\text{cm}$. See figure 3. With this nominally standard concentrate and water registering between 10 and 600 $\mu\text{S}/\text{cm}$ the deviations in the read out (at the same dilution) were found to be small - within plus or minus 50 $\mu\text{S}/\text{cm}$.

Table 2 lists conductivities of appropriate dilutions of a representative range of twenty commercial buffered acidic and neutral concentrates using the same quality water, conveniently a 600 $\mu\text{S}/\text{cm}$ tap water. These vary between 1,000 and 2,300 $\mu\text{S}/\text{cm}$ and are on average 2.9 times the magnitude of the conductivity of the tap water.

Table 3 sets out conductivities obtained when various specimens were used with 400 $\mu\text{S}/\text{cm}$ water. The closeness of these determinations with those obtained when typical 'hard' and 'pure' waters are employed, shows that the variations arising from these differences in quality of water are small. This is important, because the conductivities of local waters change from day to day and a successful fount control system cannot be unduly sensitive to such variations.

Table 4 lists the conductivities of various chemicals commonly found in buffered acidic concentrates at dilutions close to those normally employed. Other materials (e.g. dyestuffs, biocidals and surfactants) can contribute to the conductivity of a diluted concentrate; however, the amounts of these are of necessity low. It can be seen that the presence of gum arabic has

negligible affect (also see figure 7).

The foregoing prompts the concept of a standard fountain /etch monitoring system for use with buffered concentrates. This is based on the fact that it is the quantity of the chemicals in the final buffered solution that governs plate and press performance. Chemical analysis having shown that buffered acidic concentrates supplied by the majority of manufacturers contain not dissimilar quantities of various materials from the same group of chemical compounds. The quantity of chemical present, being more accurately indicated via the electric conductivity principle (with a suitable device) than by the traditional and subjective colourimetric strip technique. Accuracy is important. (16).

The preferred device is not a straight conductivity meter. Although it employs the conductivity principle it does not indicate the electric conductivity of a fountain solution. It has been designed to be a simple comparative monitoring instrument suitably responsive to the concentration of chemicals in the damping solutions employed by press operators, avoiding the use of electrical terms unfamiliar to press-men and the unnecessary and confusing over-sensitivity of normal conductivity meters.

The scale of the instrument is not logarithmic and it indicates the degree of dilution of a concentrate when working with water of a reasonable quality i.e. with a conductivity between about 10 and 600 $\mu\text{S}/\text{cm}$. As such, due to differences and variation in water quality it is not

perfect, but experience has shown that the changes which cause a variation of plus or minus one sub-division (0.2 unit) and less, are not important. Variations greater than this usually relate to a shortfall or excess of fountain concentrate.

The monitor is therefore not a meter in the sense that the term meter implies precise scientific accuracy. It is a robust and specifically designed instrument for press room use. By employing it to check solutions on a comparative basis before they are used for printing, the operator can control the quantity of buffered fountain concentrate and the working characteristics much more accurately than is possible via the dubious pH indicator technique. This can be seen from figures 4, 5, and 6.

Figure 4 refers to a traditional buffered acidic citrate /gum arabic mixture, (13) as employed earlier in this contribution. Reasonably linear (and perfect linearity is not necessary), the marked relationship of the degree of dilution to the read-out of the monitor is obvious. The unimportant changes in pH, that cannot be reliably discerned by the subjective pH strip technique are shown.

Figure 5 relates to a different proven fountain concentrate containing mono-sodium phosphate and sodium EDTA. This yields working solutions buffered close to pH 4.5. Changes in the quantity of concentrate are easily seen on the monitor scale.

To add to the usefulness of this report figure 6 illustrates the case with a well buffered alkaline

concentrate (14). Again, the widely spaced fount monitor readings are easily determined.

Figures 7 and 8 indicate the responses obtained when the monitor is used with different quantities of simple, unbuffered and buffered concentrates. When these two figures are compared, the suitability of the device for use with buffered acidic mixtures is obvious.

Figure 9 shows a typical influence of increasing amounts of isopropanol. These relationships fit well with those published elsewhere in respect of the conductivities of mixes of water and isopropanol.

The slight influence that 1% of the GATF substitute for isopropanol has on the monitor read out is shown in table 5. Specimen 'V' is the alkaline concentrate (14) and 'I' is the citrate/gum concentrate (13).

In its Mark I (manual) form, the preferred instrument comprises a strong metal box having a large read-out dial and a proven electronic circuit. See figure 11. This is wired to a rugged and accurately made, inert carbon electrode conductivity cell using alternating current (to minimise cell differences, polarisation and proximity effects) and containing a thermistor which compensates to 25⁰ for variations in temperature between 10⁰ and 70⁰C. It is operated by push button.

Although not essential, it is recommended that it is used with well buffered concentrates of preferred pH. This avoids the necessity of constantly checking the pH of the working solutions.

Insufficient concentrate causes the instrument to read low (e.g. 0.7) and this can be expected to coincide with scumming and plugging as well as undue biological contamination of the press. Wasteful and excessive use of concentrate will cause the needle to veer to the right and register high - say 2.7. An unduly strong concentrate will have the same effect, and such a reading will relate to delayed drying, ink-water problems and premature image failure. The operating readings obtained when using typical buffered concentrates will be located near the centre of the scale.

To avoid problems due to the quality of water, the instrument can be used as a checking device. Very pure and natural 'soft' water usually register near zero, normal/average waters around 0.2, 'hard' water close to 0.3 and 0.4 whilst very 'hard' water returns a reading of 0.5 and even 0.6. When significantly different from 0.2 the final readings may (according to the chemistry of the concentrate) need to be appropriately higher or lower to obtain best performance. When near or at the extremes, i.e. zero or 0.6, it is recommended that a suitable so called 'soft' or 'hard' concentrate be used.

To express the latter readings in terms of approximate number of parts per million of 'total dissolved solids', 0 can be taken as 70, 0.2 as 200, 0.4 to be 330 and 0.6 virtually 460 ppm. (Note: Fount Monitor readings, conductivity readings and total dissolved solids determinations, have no precise relationship to water 'hardness' or 'softness').

For economy, the quantity of concentrate can be precisely adjusted to record suitably left of centre, in a position found by experience with the local water supply to provide adequate short and long term plate and press performance. When adverse press conditions prevail this may not be possible and it may be necessary to employ a suitably high reading. With weak concentrates the quantity used is likely to need increasing to obtain the best printing. (Of course, if the weak concentrate is appropriately cheaper the outcome may be unimportant). By employing a dilution which gives a reading only one subdivision lower - failing to show via the pH strip technique - a plant consuming say 3,000 litres of concentrate per year, would save the cost of 250 litres of concentrate.

A few words of warning are necessary. The probe needs to be kept clean - once per shift, and the device needs to be used with care in re-circulating/pan fountains due to possible slight effects of contamination by materials from paper and board (15). There can be no doubt however that it gives users the ability to check the performance of auto-dosing equipment and manual mixers, and that it is well suited for non-contact fountains e.g. spray.

Bearing in mind the need for accuracy and the trend towards uniform fountain solutions (16) the technique appears to provide a step towards appropriate standardisation. A down to earth feature of the fount monitor is that it enables users to make up consistent fountain solutions under day to day working conditions even when dosing equipment is defunct, or mal-adjusted or missing,

and when the capacity of the reservoir(s) are unknown.

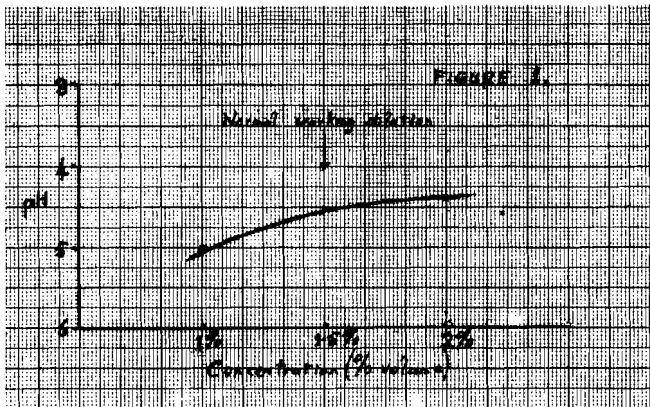
To summarise - the foregoing is concerned with a purpose designed comparative system for indicating the strength of buffered fountain solutions in press environments.

Thanks are necessary to the Directors of the Howson-Algraphy Group of Vickers PLC for their recognition of the importance of the foregoing in respect of plate and press performance. The provision of the necessary facilities and the co-operation of the analytical and technical departments must not be forgotten.

Note.

Because the electrical conductivity term seimens is the SI unit and considered to be more correct by electrical engineers than 'umhos', it has been employed in the above.

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Sample / Conductivity	Sample / Conductivity	Sample / Conductivity
1. 300	19. 55	37. 340
2. 518	20. 115	38. 360
3. 415	21. 250	39. 190
4. 320	22. 780	40. 890
5. 520	23. 290	41. 500
6. 120	24. 530	42. 1180
7. 1000	25. 600	43. 660
8. 291	26. 425	44. 920
9. 388	27. 600	45. 1150
10. 40	28. 600	46. 400
11. 365	29. 460	47. 450
12. 63	30. 460	48. 450
13. 161	31. 380	49. 600
14. 732	32. 610	50. 100
15. 354	33. 420	51. 115
16. 362	34. 510	
17. 480	35. 190	
18. 280	36. 420	

Samples 1 to 9 from reference 10

Table 1. Typical water conductivities.

Buffered Concentrate with 600 μ S/cm water	SP. Conductivity (μ S/cm) 25 ^o C
Specimen 'A' (2%)	1,400
" 'B' (tablets)	1,130
" 'C'	1,530
" 'D' (2½%)	1,610
" 'E' (3%)	1,330
" 'F' (3%)	1,160
" 'G' (6½%)	1,350
" 'H'	1,430
" 'I'	1,690
" 'J'	1,830
" 'K'	1,890
" 'L' (2%)	2,030
" 'M'	2,230
" 'N'	2,150
" 'O'	2,040
" 'P'	2,180
" 'Q'	2,330
" 'R' (4%)	1,340
" 'S' (4%)	1,250
" 'T'	1,380

TABLE 2 Press ready concentrations
(1½% volume unless different according to
published instructions).

Specimen	Sp/Conductivity ($\mu\text{S}/\text{cm}$) 25 $^{\circ}\text{C}$			Overall Variation	
	600 $\mu\text{S}/\text{cm}$ 'hard' water	400 $\mu\text{S}/\text{cm}$ water	10 $\mu\text{S}/\text{cm}$ 'pure' water	$\mu\text{S}/\text{cm}$	Found Monitor Unit
'A' (2%)	1,500	1,400	1,300	200	.2
'C'	1,530	1,550	1,450	100	.1
'D' (2½%)	1,610	1,530	1,510	40	.04
'E' (3%)	1,330	1,450	1,700	370	.37
'H'	1,430	1,310	1,430	120	.12
'I'	1,690	1,730	1,930	240	.24
'J'	1,830	1,740	1,650	180	.18
'K'	1,890	1,720	1,730	170	.17
'L' (2%)	2,030	1,970	1,930	100	.1
'M'	2,230	2,180	2,110	120	.12
'N'	2,150	2,030	1,980	170	.17
'O'	2,040	2,130	2,110	90	.09
'P'	2,180	2,030	1,880	300	.30
'Q'	2,330	2,310	2,530	220	.22
'R' (4%)	1,340	1,230	1,210	130	.13
'S' (4%)	1,250	1,230	1,160	90	.09
'T'	1,380	-	1,240	140	.14

TABLE 3. Typical variations 1½% v/v dilutions unless stated.

Chemical	S p/Conductivity (25° C)
Gum arabic	400
Cellulose gum	715
Citric acid (0.05%)	360
Tartaric acid (0.05%)	460
Phosphoric acid (0.025%)	680
mono-Sodium phosphate	1,080
di-Sodium phosphate	1,050
tri-Sodium phosphate	1,750
Sodium h-m phosphate	1,040
Sodium pyrophosphate	1,400
tetra-Sodium polyphosphate	2,500
Ammonium citrate	1,970
tri-Sodium citrate	1,900
Sodium tartrate	1,380
Potassium nitrate	2,460
Ammonium nitrate	3,170
Magnesium sulphate	1,320

TABLE 4. Fountain chemicals, (0.2%) solutions
in 400 μ S/cm water

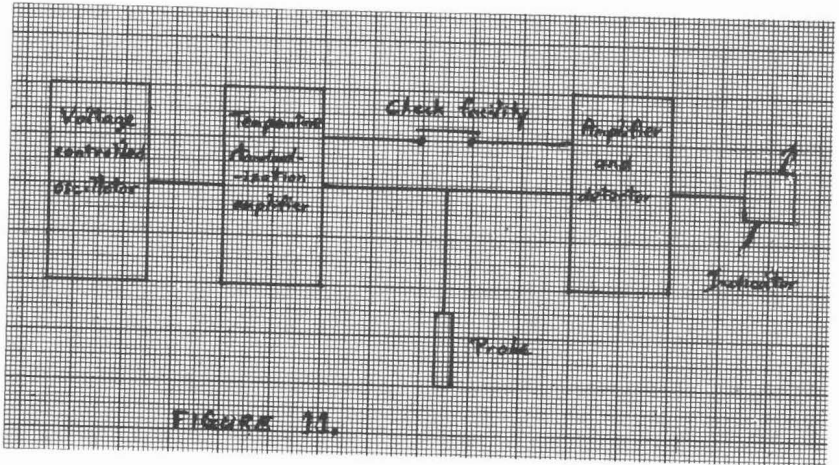


FIGURE 11.

Fountain Solution		Fount Monitor	
		with Techfount	without Techfount
2%	'C'	1.55	1.6
1½%	'H'	1.0	1.05
1½%	'I'	1.25	1.3
2%	'J'	1.8	1.9
1½%	'O'	1.7	1.75
1½%	'Q'	1.8	1.85
1½%	'U'	1.2	1.25
1½%	'V'	1.4	1.45

Table 5

