A Paper to be Presented at the 1990 TAGA Annual
Conference in Kansas City, 1-4 April 1990.

PHYSICO-CHEMICAL CHARACTERIZATION OF FOUNTAIN SOLUTIONS CONTAINING IPA AND SUBSTITUTING ADDITIVES

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Abstract: The Laboratory has applied physico-
chemical methods to test fountain solutions in
which the surface tension has been reduced with
isopropanol or surfactants. The objective was to
replace isopropanol by commercial additives of
fountain solutions.

The compatibility of some systems - printing inks
and fountain solutions - has been outlined on a
pilot scale. Full-scale printing tests have been
made to evaluate the practical possibility of
replacing IPA.

INTRODUCTION

In lithography, the main task of the fountain
solution is to keep the non-image areas of the
plate free of printing ink throughout the run
without interfering with the inking of the image
areas. This is achieved by forming a thin water
film in the non-image areas of the plate to
prevent the transfer of ink into these areas /7/.

Depending on the fountain system, the fountain
solution is transferred either to the plate or
through the inking system. The most common devices
for spreading the water are brush dampeners,

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rotating disk dampeners, turbo dampeners, roller dampeners and spray bar dampeners. The methods of application are shown in Figure 1.
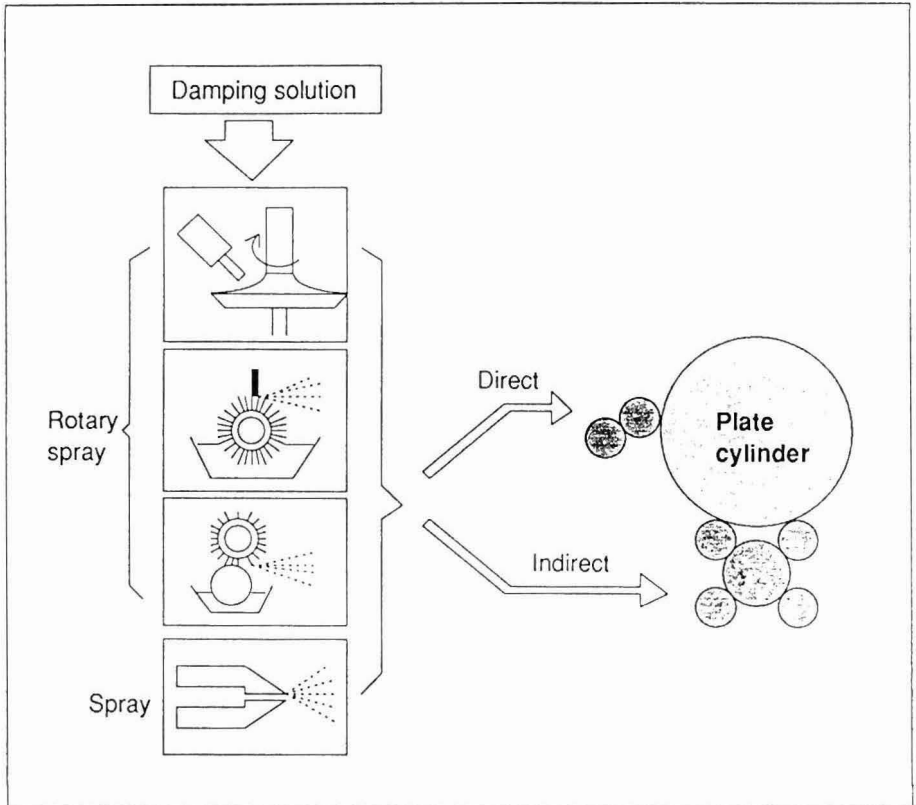

Figure 1. Comparison of the fountain techniques.

In all systems some fountain solution is returned to the inking unit from the plate, where it has to be emulsified in the ink to avoid an excess of surface water on the inking rollers. A surplus of surface water reduces the transfer of ink causing "water marks".

To provide for a feasible emulsification and to spread the fountain solution rapidly over the non-image areas, the surface tension of the fountain solution has to be low. This is achieved most

efficiently by adding 5 to 20 per cent of isopropanol (IPA). IPA is suitable because it dissolves in water fast and homogeneously.

However, environmental and economical aspects have forced printers all over the world to look for substitutes for IPA. The first group of substituting additives tested consisted of surfactants. Their normally high dynamic surface tension has been their principal limitation, i.e. their effect on the surface tension is too slow compared with the physical phenomena in the nip. This is caused by the slow orientation of the macromolecules at the interface, a formation of micelle, and attraction between the hydrocarbon chains.

This is the report on a study of some of the aspects of IPA replacement in fountain solutions /8/. The principal lithographic properties of commercially available substitutes have been tested and full-scale printing trials have been made with some substitutes. The purpose has been to define a useful substitute in physico-chemical terms.

METHODS AND MATERIALS

Laboratory tests

Surface chemical measurements

The **dynamic surface tension** (γ_{DYN}) of the fountain solutions was measured with an instrument based on the oscillation jet principle /1/. With this instrument the measuring range in the surface age is from 1 to 15 or even 20 ms. The measurements were carried out at a temperature of 23 ^{O}C and the results are given at a surface age of 5 ms.
Static surface tension (γ) was measured with a du Noüy ring-tensiometer at room temperature (25 ^{O}C). In these measurements the surface age was 1 minute. The conductivity and pH of the fountain solution were also measured.

The **surface energy of the inks** (γ_{INK}) - including dispersion ($\gamma_{INK,d}$) and polar components ($\gamma_{INK,p}$) - was determined by Kaelble's method /3/ (the relation between these terms is $\gamma_{INK} = \gamma_{INK,d} + \gamma_{INK,p}$). A drop of the test liquid is placed on the ink surface and the contact angle of the drop is determined with Lorenzen & Wettre's Contact angle instrument. The surface tension properties of the ten test liquids range from completely nonpolar (n-hexadecane) to highly polar (water). The surface energies of the inks were calculated by a computer programme based on the algorithms given in the reference /4/.

By measuring the contact angles of a fountain solution on an ink surface it is possible to use Young's equation to calculate the **interfacial tension between the ink and the fountain solution** /5/. When a drop of a liquid is placed on a solid surface, the forces on the three-phase contact surface can be expressed by the equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta \qquad\qquad (1)$$

where γ_{sv} is the surface energy of the solid
γ_{sl} is the interfacial tension between liquid and solid
γ_{lv} is the surface tension of the liquid,
θ is the contact angle of the liquid drop on the solid surface.

To determine the interfacial tension between inks and fountain solutions, the contact angle tests were carried out at a room temperature of 23 $^{\circ}$C.

Emulsification tests

The emulsification tests were carried out by first mixing 50 g of ink and about 50 ml of a fountain solution for half a minute. The amount of water emulsified in the ink was determined by weighing the ink sample after pouring the surplus water back into the water vessel (at the beginning of the test the total amount of the fountain solution was 200 ml). The test was continued by adding 50

ml of water into the ink vessel and by mixing for a certain time. The procedure was repeated until the 5 mixing periods had been completed and, correspondingly, 5 levels of emulsification had been reached. The mixing periods were 0.5, 1, 2, 4 and 8 minutes and the testing temperature was 25 °C.

This kind of an emulsification test is based on the Surland-method and it is made with a **DUKE Ink-Water Emulsification Tester.** The test, normally based on a 10-minute test period with 1-minute steps, is widely used and has been recommended as an ASTM Standard Test Method /2/. The reason for cutting the test periods was the number of emulsification tests.

Materials

The inks used in the investigation were two 4-colour heatset ink series (inks V and M) and one 4-colour sheetfed offset ink series (ink S). 11 commercial additives of fountain solutions were tested using concentrations of 3 percent by volume. The solutions were further diluted by adding isopropanol (IPA): 5 percent by volume and 10 percent by volume.

Printing tests

Performance

Full-scale printing tests were carried out in a 4-colour heatset press (Lithoman IV) equipped with an indirect Dahlgren dampener. The fountain solution normally contains a commercial additive A and IPA, but in the test IPA was replaced step by step by additive R. The printing conditions have been presented in Table 1. Printed samples were collected and measured as a function of the concentration of the fountain solution.

Table 1. The conditions of the heatset printing
         tests.

	Normal	Test
Printing ink	M	V
Paper (g/m^2)	Coated 115	Coated 60
Fountain solution,	A 3/IPA 10	R 4/IPA 4
additive/IPA (%)		R 4.5/IPA 0
Plate	Kalle P61	Kalle P61
Blanket	Reeves Alto	Reeves Alto
Running speed (m/s)	6	8

The printed samples contained a 4-colour test
scale with 25, 50 and 75 per cent halftones and a
compact tone.

Image analysis

An image analysis of the printed samples was made
by the three halftones of the test scale. The
instrument contained a microscope connected by a
camera to a monitor and a PC. The computer program
used in the analysis provided 19 different para-
meters with standard deviations for a halftone
shown in the monitor. The parameters were

Area	Colour deviation
Perimeter	Colour mean
Rounded perimeter	Edge width
Hole count	Edge gain
Other area count	Mean radius
Raggedness	Deviation of mean radius
Square raggedness	Moment angle
Circular raggedness	Moment ratio
Voidiate	Screen tonal value
Blur	

We chose blur, voidiate and the screen tonal value
(dot size) to assess the printing quality.

RESULTS AND DISCUSSION

Laboratory tests

The surface tension measurements (static and dy-
namic) were carried out with the 11 commercial
additives, which are recommended by their manu-
facturers as total or partial substitutes for IPA.
The results of the measurements are in figure 2.
As can be seen, the static surface tensions of the
substitutes are level with or even lower than
those of pure IPA-solutions (50.0 and 42.2 mN/m),
whereas the dynamic values of 3 percent solutions
are mostly higher. The dilution by IPA reduces the
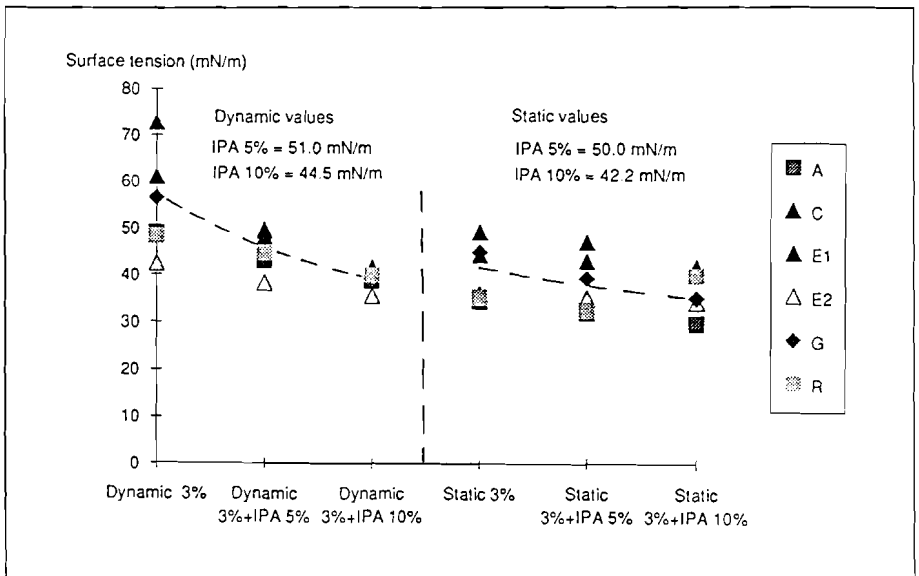values rather effectively.

Figure 2. The results of the measurements of
surface tension.

Table 2. The results of the tested ink/fountain
         solution combinations.

Fountain solution	Surface tension (mN/m)	Conductivity (mS/m)	pH	Dynamic surface tension (mN/m)	Interfacial tension (mN/m)			
					V/Y	V/M	V/C	V/B
R 3%	35,3	144,0	3,4	48,3	15	14	15	19
R 5%	33,2	218,0	3,3		14	9	13	16
R 3% + IPA 5%	32,6	127,0	3,4	44,6	16	15	15	18
G 3%	44,9	145,0	5,1	56,5	18	16	14	19
G 5%	43,5	224,0	5,0		16	17	14	17
G 3% + IPA 5%	39,3	127,0	5,2	47,9	17	15	16	19
					Interfacial tension (mN/m)			
					M/Y	M/M	M/C	M/B
A 3%	34,5	128,0	4,7	49,0	14	14	12	14
A 5%	32,9	193,0	4,7		11	14	11	12
A 3% + IPA 5%	29,9	110,0	4,9	43,0	14	19	15	16
E1 3%	35,9	125,0	3,8	42,4	14	16	12	12
E1 5%	31,8	192,0	3,7		13	16	13	14
E1 3% + IPA 5%	35,2	108,0	3,8	38,3	15	15	13	16
R 3%	35,3	144,0	3,4	48,3	15	15	14	16
R 5%	33,2	218,0	3,3		12	14	12	13
R 3% + IPA 5%	32,6	127,0	3,4	44,6	14	15	13	13
					Interfacial tension (mN/m)			
					S/Y	S/M	S/C	S/B
E2 3%	44,3	270,0	4,1	61,0	17	18	13	13
E2 5%	42,4	396,0	4,1		16	18	14	12
E2 3% + IPA 5%	43,1	210,0	4,3	48,2	12	15	11	12
C 3%	49,2	101,0	4,7	72,7	18	25	13	19
C 5%	48,7	140,0	4,6		18	24	14	17
C 3% + IPA 5%	47,1	77,0	4,8	49,6	21	20	12	22

Table 3 shows the properties of the tested inks,
coded V, M and S. The symbols Y, M, C and B stand
for the colours of the inks, i.e. yellow, magenta,
cyan and black.

Viscosity was measured with a Ferranti-Shirley
cone/plate viscometer at a shear rate of 100 1/s.
The highest viscosities were naturally obtained
with ink S, i.e. sheetfed inks. It can also be
observed that there is no correlation between the
colours of different ink series.

The same applies to the surface energy values: The highest surface energy of ink S is in cyan, whereas in ink M it's magenta and in Ink V yellow. This shows the big difference between the ink properties of different inks. The values of the relative polarity have been calculated by the equation

Relative polarity (%) = $(\gamma_{INK,p}/\gamma_{INK})$ * 100   (2)

This gives a better picture of the real differences between the inks which may be expected to influence ink behaviour in printing. As can be seen, the lowest polarity is in ink V/M and highest in inks S/C, M/B and M/M.

Table 3. The properties of the tested inks.

Ink code / colour	Ink viscosity 100 1/s (Pas)	Surface energy (mN/m)	Relative polarity (%)
V/Y	21,7	33,8	21
V/M	36,2	24,9	3
V/C	27,1	31,6	18
V/B	28,9	29,1	20
M/Y	32,6	29,5	14
M/M	27,1	33,5	23
M/C	25,3	29,9	19
M/B	32,6	31,7	23
S/Y	56,1	32,9	19
S/M	73,3	30,9	13
S/C	42,1	35,2	28
S/B	51,6	29,6	11

The emulsification tests were carried out with six of a total of 11 additives of fountain solutions. The combinations and the results of the measured properties are shown in Table 4. The emulsification tests were performed as a function of the mixing time and the results may be considered as exponential functions of the mixing time in the formula

$$E = E_{max}(1-\exp(-kt)) \tag{3}$$

where E_{max} = maximum emulsification (%)
k = emulsification coefficient
t = mixing time
E = measured emulsification (%).

Table 4. The results of the emulsifications tests.

Fountain solution	Emulsification coefficients / E=Emax(1-exp(-kt))							
	V/Y		V/M		V/C		V/B	
	k	Emax	k	Emax	k	Emax	k	Emax
R 3%	0,9	35,2	0,9	35,2	0,3	48,2	2,2	30,6
R 5%	0,4	40,6	0,4	33,1	0,4	43,4	2,1	31,5
R 3% + IPA 5%	0,4	40,3	0,4	33,8	0,3	44,4	0,9	36,0
G 3%	0,3	44,8	0,3	38,6	0,2	55,0	1,5	36,7
G 5%	0,3	41,5	0,3	35,7	0,2	61,9	1,4	34,9
G 3% + IPA 5%	0,3	39,2	0,3	40,2	0,3	50,7	1,5	35,3
	M/Y		M/M		M/C		M/B	
	k	Emax	k	Emax	k	Emax	k	Emax
A 3%	1,1	40,2	0,5	52,5	0,8	48,6	0,4	56,5
A 5%	1,1	46,3	0,6	55,2	0,7	45,2	0,5	51,2
A 3% + IPA 5%	0,6	44,5	0,2	61,2	0,4	49,7	0,2	64,9
E1 3%	0,3	47,3	0,3	49,3	0,3	57,0	0,2	61,3
E1 5%	0,4	41,4	0,4	44,1	0,4	52,4	0,2	55,3
E1 3% + IPA 5%	0,2	51,8	0,3	52,2	0,3	55,2	0,2	52,6
R 3%	0,5	43,5	0,3	56,8	0,5	46,5	0,1	81,8
R 5%	0,8	37,4	0,4	47,1	0,5	44,6	0,2	65,1
R 3% + IPA 5%	0,4	44,4	0,2	67,6	0,4	43,3	0,2	64,6
	S/Y		S/M		S/C		S/B	
	k	Emax	k	Emax	k	Emax	k	Emax
E2 3%	0,1	114,3	0,7	61,0	0,1	238,1	0,8	43,4
E2 5%	0,2	101,4	0,9	51,4	0,0	356,4	0,6	44,4
E2 3% + IPA 5%	0,2	87,3	0,8	47,0	0,1	256,8	0,4	46,2
C 3%	0,2	96,4	0,5	63,1	0,1	272,8	0,7	44,7
C 5%	0,2	87,0	0,6	58,6	0,1	280,9	0,7	45,2
C 3% + IPA 5%	0,1	106,2	0,6	55,3	0,1	339,1	0,5	42,1

Figures 3 and 4 show the emulsification curves with 4 ink/fountain solution combinations. The dotted line is the fitted curve according to the equation (3). As can be seen, the properties of the inks and fountain solutions influence the emulsification tendency of inks. By comparing the curves in Figure 3, we can see that E_{max} increases when IPA is added to the fountain solution. The emulsification rate, on the other hand, decreases,

i.e. coefficient k is smaller with the IPA
solution. This was observed in quite a large
number of the tested combinations (Table 4).

Figures 3 and 4 also show the influence of
different fountain solutions on the emulsification
of the same ink: with solution R the ink M/B
emulsifies more slowly and more than with solution
A. The surface tensions, both dynamic and static,
are identical with these solutions, but the pH of
solution A is higher than the pH of solution R. On
the other hand, when comparing the curves in
Figure 4 it can be seen how strongly the ink can
influence the emulsification. The interactions
between the inks and the fountain solutions are
quite complex, and the emulsification tendency of
an ink cannot be predicted by an emulsification
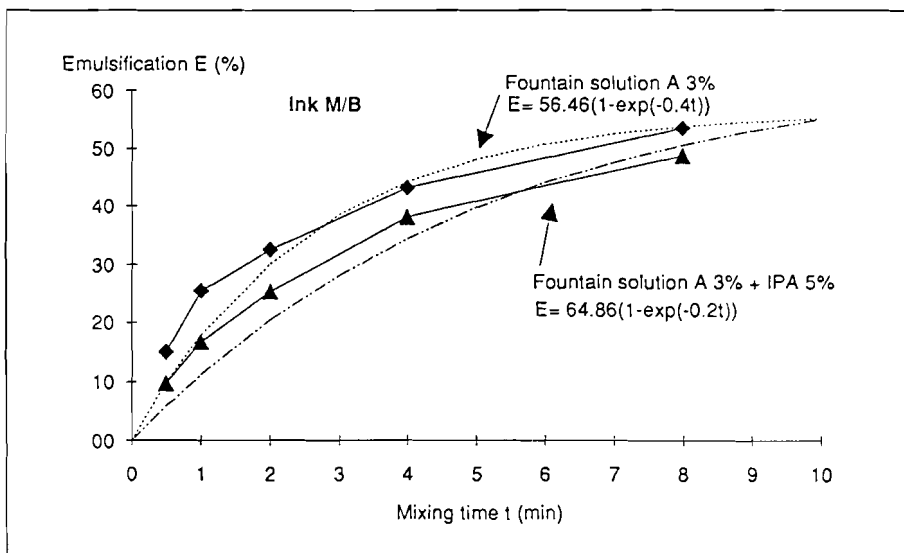test of one fountain solution.

Figure 3. The emulsification curves of the ink M/B
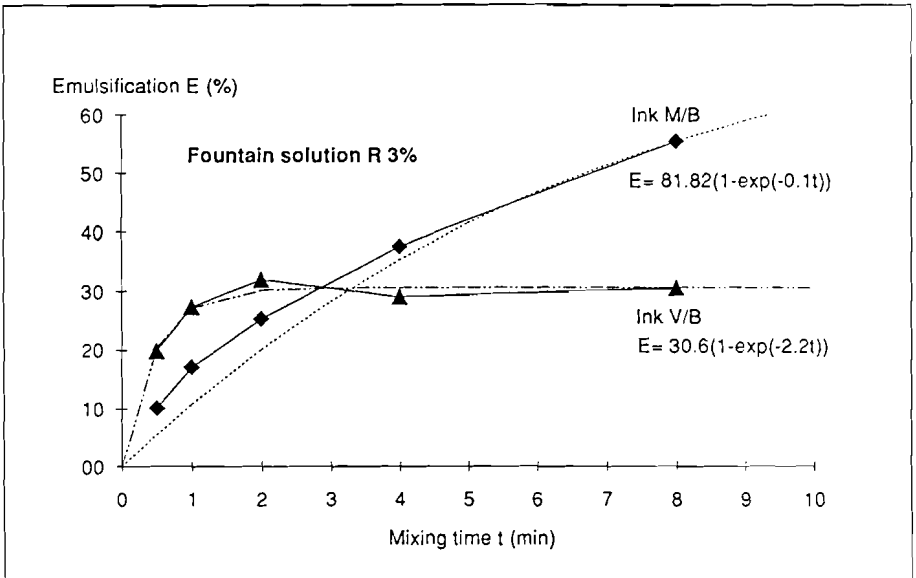with fountain solutions A and A + IPA.

Figure 4. The emulsification curves of the
    fountain solution R with the inks M/B and V/B.

Full-scale printing trials

Printing quality was assessed by the results of
the density measurements and by the parameters of
the image analysis. The relative contrast was
calculated by the densities of the 75 % halftone
and the compact tone. The relative contrast and
some of the most important parameters of the image
analysis are in Table 5.

Table 5. Assessment of the printing quality.

Parameter	Halftones, cyan colour,			NORMAL
	25	50	75	
Dot size (%)	26.4	51.5	75.7	
Voidiate (%)	0.22	0.24	0.13	
Blur (%)	0.11	0.06	0.05	
Relative contrast				0.40

Table 5. Assessment of the printing quality.

| | Halftones, cyan colour, | | | R/IPA |
	25	50	75	
Dot size (%)	33.5	67.9	88.2	
Voidiate (%)	1.57	3.94	2.56	
Blur (%)	0.28	1.10	0.41	
Relative contrast				0.19
				R
Dot size (%)	36.2	59.8	83.6	
Voidiate (%)	0.83	2.34	1.36	
Blur (%)	0.47	0.74	0.40	
Relative contrast				0.21

From the results we can see that in the black
colour the dot size increases when IPA is
eliminated. In the other colours, however the dot
size is highest with R/IPA and lowest when Normal.
The situation is similar with the voidiate. The
blur is very intensive in the middle tones,
especially with cyan and yellow. The relative
contrast is highest in Normal and R, too, is
better than R/IPA.

We have previously tested the additive R in
combination with news inks. Rather wide tolerance
ranges were obtained for the water feed with
blankets and plates of low polarity in the image
areas /9/.

SUMMARY

The compatibility of some lithographic systems -
i.e. printing inks and fountain solutions with and
without isopropanol - have been studied on a
laboratory scale and with full-scale printing
trials in a heatset line.

It has been observed that the time-dependent
emulsification of a certain fountain solution in a

model, i.e. containing the emulsification rate (k) and the hypothetical maximum emulsification capacity (E_{max}). Both parameters can be easily determined by a Duke test.

Inks with a high emulsification capacity (E_{max}) show a low viscosity and a high polarity. The correlation between the emulsification rate (k) and the ink rheology was more obscure: in one set of inks a high viscosity corresponded to a high emulsification rate.

The dynamic surface tension of the fountain solution indicates how fast the additives reduce the surface tension when a new interface has been formed. It is considered to be of utmost importance to the fast interactions in the printing nips. However, only weak correlations were observed with emulsification parameters (E_{max}, k) have been seen. On a laboratory scale, the emulsification behaviour seems to be governed mainly by ink viscosity, while the fountain solution plays only a minor part.

In the full-scale printing trials in a 4-colour heatset press with the Dahlgren fountain system the printing quality was better with IPA than with a commercial additive. The difference can be clearly seen in the dot size of the middle tones.

Although we still have only little experience in replacing IPA by commercial additives, it seems that IPA can be eliminated or its concentration decreased in most fountain systems. Printing trials and compatibility tests of the materials are however necessary.

There have been difficulties in printing by modern presses with the Dahlgren fountain system. Especially gum arabicum may precipitate from an additive into the fountain system thus causing disturbances. The washing of rollers and blankets

additive into the fountain system thus causing
disturbances. The washing of rollers and blankets
is also more difficult without IPA because alcohol
is a good solvent of printing inks.

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