FACTORS DETERMINING THE EFFICIENCY OF LITHOGRAPHIC INKS

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Abstract: The rate of emulsification theory and the laboratory test deduced from it has become a useful tool for the industry. Problems in reproducing results are discussed and remedies suggested.

It is shown that the emulsification curves relate to the rates of change in the emulsified ink's flow properties, to the shear stability of the emulsion formed, to ink tack increase and to ink transference, mist and sling.

The effects of the dampening solution's pH and electrical conductivity on the emulsification rate are investigated, together with the effects of alcohol or alcohol substitute addition to the dampening solution (ds).

It is suggested that electromagnetic phenomena determine the preferential wetting of surfaces on the press.

Finally, the discussed ink/ds parameters are put in relation to commercial efficiency.

Introduction

The rate of emulsification theory (Surland 1967 and 1980) proposes that it is essential for the lithographic process that the ink has a capacity of emulsifying dampening solution into its body. Substantial evidence was given that an off the press emulsification test, determining the rate of emulsification of the particular dampening solution into the particular ink, gave results which essentially predicted the efficiency of the pair on the press. It was postulated that the rate of emulsi-

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fication curve is a result of opposing factors, P_+= emulsion former, and P_-=emulsion breaker, as expressed in the equation: $W + O \ (\rightleftarrows) \ W/O$ where the arrows are considered vectors, respectively, for P_+ and P_-, and W=dampening solution and O=ink. (Figure 1.)

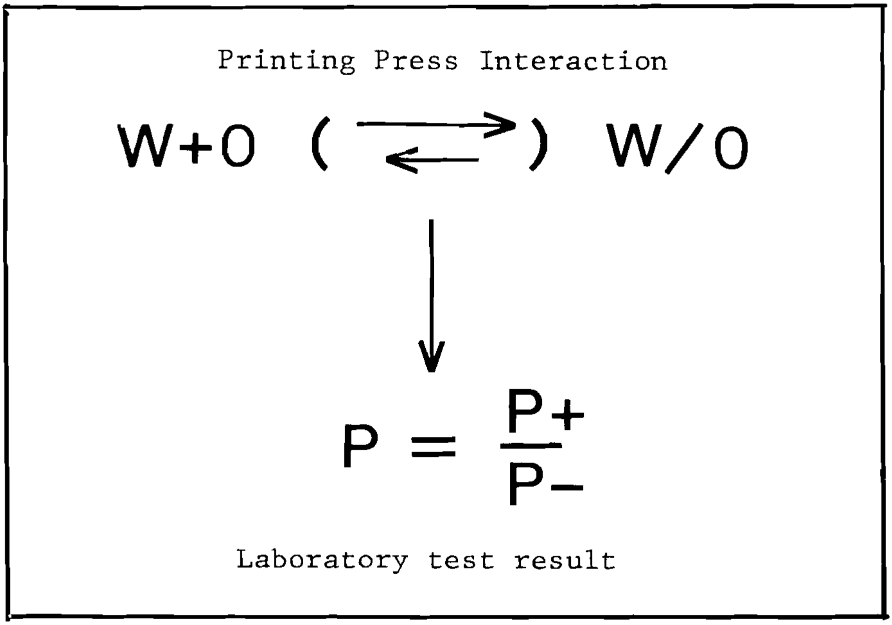


Figure 1. The rate of emulsification theory

On the press, P_+ must always be larger than P_- to preserve the necessary emulsification capacity. The test results have shown that with the most efficient lithographic pair, ink and dampening solution, P_- is initially very small in relation to P_+, but should approach a constant value, $\frac{P_+}{P_-}=1$ at a point on the curve (a,b) where $(a)\sim 5$, and well beyond the situation reached on the press.

This presentation will analyze reasons why some operators fail to obtain results which can be interpreted in a meaningful manner. Then, as apparently it is not the ink itself as applied to the press, but rather an on the press formed emulsion, together with the unemulsified dampening solution, which are producing the printed image, the progressive emulsion rheology changes and parameters affecting the emulsion formation, stability and breakdown will be discussed.

An observation indicating that electromagnetic phenomena involving para- and diamagnetism might determine the preferential wetting of metals or their compounds is presented.

Finally, the ink/ds parameters investigated are viewed in relation to pressroom performances.

Parameters Affecting the Emulsification Test Results

Introduction

Private communications, as well as results obtained from "round robin" testing with various procedures stipulated by an ASTM committee, have revealed that although many operators benefit from meaningful and reproducible results, others do not.

Figure 2 shows the results with the same ink and dampening solution but with deviating test procedures, one adapted by a printing house in Europe, the other by "standard procedure".

The difference in these results warrants a discussion of which procedure parameters affect the results most significantly.

A. Mixer Geometry

The adapted equipment for the standard procedure involves a Sunbeam "Mixmaster" modified for the test. A flat bottom mixing bowl is placed on a larger diameter freely-revolving turntable and two opposite-driven mixing blades (90 RPM) each contact the bottom of the bowl over their most possible width (45 mm) and conform to the bend of the bowl to its vertical side. Properly aligned, the bowl will and should, during the test, slide from side to side on the turntable, allowing the mixing blades to scrape ink off the side of the bowl. The center distance of the mixing blades is 42 mm. This geometry assures efficient mixing of virtually all the ink volume during the test.

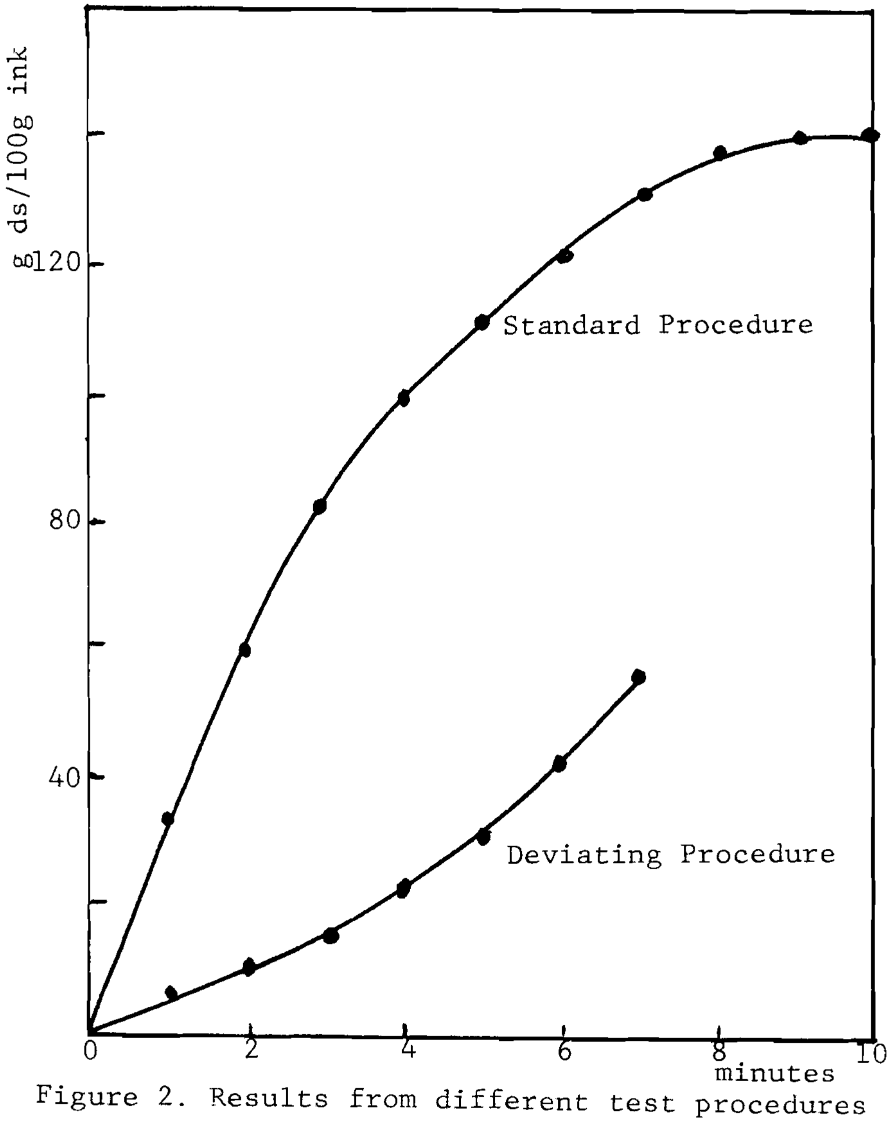


Figure 2. Results from different test procedures

The non-standard procedure (Figure 2) used one mixing blade only and a hand-held paper cup as container. Figure 3 shows test results from the standard procedure versus the comparative result using only one mixing blade. Some years ago, a mixer intended for emulsification testing was marketed. In some way the geometry was similar to the "standard geometry", with two mixing blades in a steel bowl. However, the bowl was placed in a fixed center position and revolved with a speed around 4.5 RPM. Initially, the bowl had an indentation in the bottom excluding about 5.7 cm^3, or more than 10 percent of the ink volume, from the mixing procedure. Also, the mixing blades were curved on the bottom, allowing for a contact width each to the bowl bottom of only 34 mm, against 45 mm with the standard equipment, indicating a relative mixing efficiency of 74 percent.

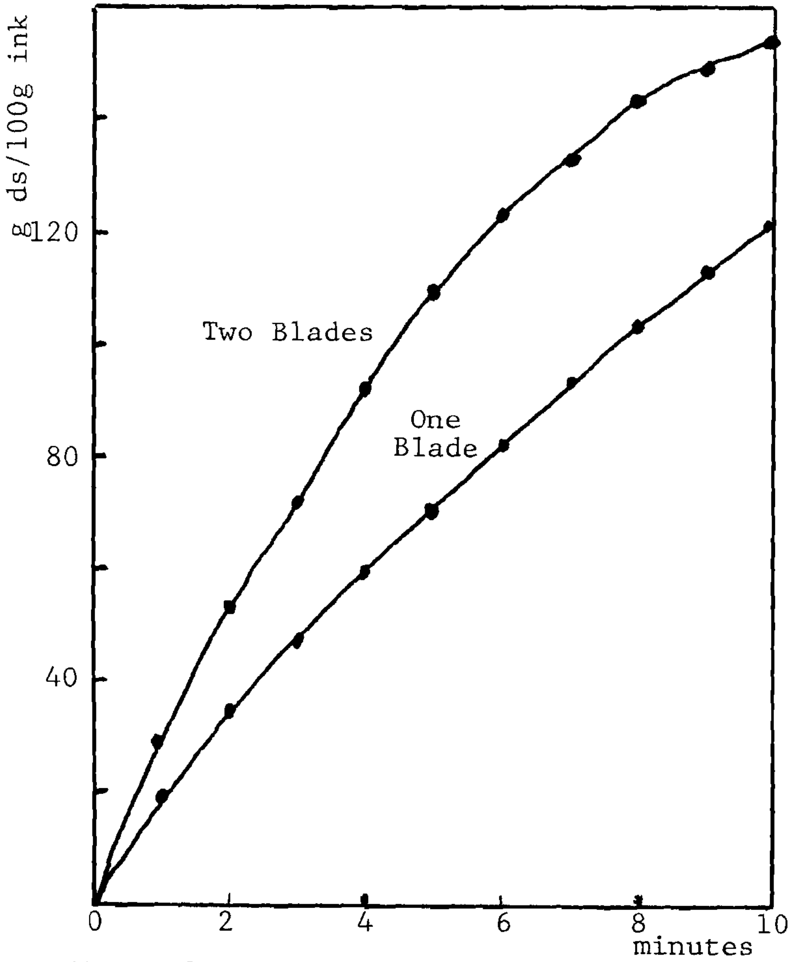


Figure 3. Results with two (normal) and with one blade

Figure 4 shows a comparison of repetitive results with the "commercial" versus the "standard" equipment.

The steeper increase between the 5 and 10 minute results with the commercial mixer indicates that this mixer involves less of the total ink volume than the standard equipment.

	Emulsification, g sol./100 g ink			
	Commercial		Standard	
	5 min.	10 min.	5 min.	10 min.
	43.2	56.0	55.5	58.0
	42.8	49.2	55.0	58.5
	41.8	52.0	54.6	59.2
	42.4	53.4	54.6	59.2
Average	42.6	52.7	54.9	58.7
Extreme Deviation	1.4	6.8	.9	1.2

Figure 4. Comparative Results

Although much of the deviation in results could be explained by the geometrical differences discussed above, the center distance between the commercial mixing blades is 37 mm (42 mm with the standard). This, together with the fixed center position of the bowl, causes the closest reach between the blades and the bowl side to be about 5 mm (0 mm with the standard because of sliding). Subsequently, a wall of ink can be built up against the side of the bowl. Whether this volume will participate in the emulsification procedure depends entirely on its flow and adhesive properties. Dependent on the particular ink's state of emulsification, the formed emulsion might or might not be able to gradually incorporate the geometrically unreachable ink volume. Consequently, the initial emulsification numbers will be relatively low and the curve form will approach a straight line, rather than an equilibrium curve as can be obtained with the standard equipment. Figure 5 illustrates this. A rather freely-flowing news ink was tested with alkaline solution: (1) with the commercial mixer, where the bowl and mixing blades were changed to standard geometry; (2) with the same mixer, where also the fixed center bowl geometry was changed to the standard one with a freely-revolving turntable; and (3) with standard equipment. It is seen that the results (2) and (3) are very close.

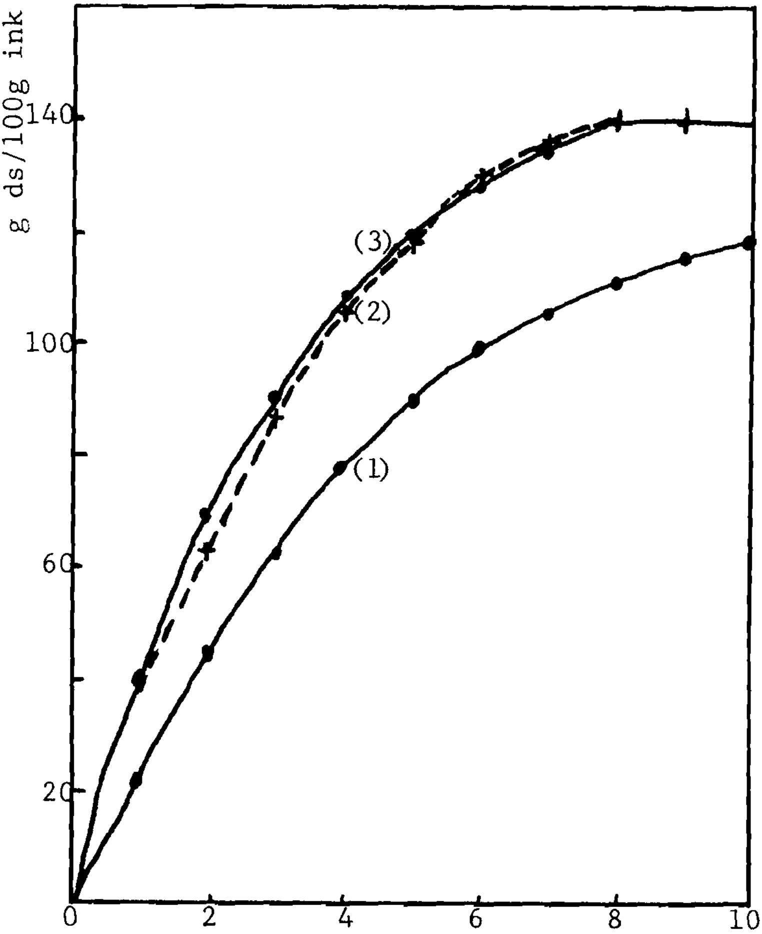


Figure 5. Results with different geometry

When the geometry is acceptable, it is recommended to recheck the horizontal and vertical alignment of turntable, bowl and mixing blades. The latter should be adjusted to a position where the blades, during mixing, just touch the bowl bottom, rather than letting the entire weight of the mixer head rest upon the turntable. It is recommended to adjust the blades while a piece of paper is placed between the blade and bowl.

B. Prestirring of the Ink

It has been observed that with highly thixotropic inks, the initial readings can be far too low unless the ink has been stirred well in advance. Therefore, prestirring without incorporation of air is recommended as part of the standard procedure.

C. Addition of the Dampening Solution

With the standard procedure, it is recommended to add the solution in increments of 15 ml from a 100 ml reservoir prior to each mixing period. Occasionally it is necessary to add more, at the initial steeper increase of the emulsification curve. The attempt is to assure a reasonably constant surplus of unemulsified solution during the test. When 50 ml or more solution is added at one time, it has often been observed that large volumes of ink, torn loose from the main inkbody, sail around in the solution without being submitted to emulsification. This will have similar effects as those shown in Figures 2 through 5.

D. Mixing Speed

With the standard equipment it was found that 90 RPM was the fastest practical mixing speed. Above that, the loss of dampening solution by splatter increases steeply. As the readings depend on the number of revolutions, it is essential that the speed is kept constant. This was easily possible with the Sunbeam mixer and Temple motorspeed control originally used. However, later changes in both equipment parts made it necessary to monitor the speed manually, which can be done successfully, but is impractical. Recently, Sunbeam engineers have submitted an experimental gear-controlled mixer, which, in connection with an automatic timer, monitors the speed at 90± 1/3 RPM without external equipment.

E. Separation of Free Solution

It has been observed that some operators, when separating the surplus unemulsified solution between the mixing periods, vigorously stir the material with a pallet knife. This, obviously, can be the cause of significant error on the result.

To obtain interpretable results, the mixer--and not the operator--shall do the mixing work. If necessary, which it usually is not, to move the ink to release a large pocket of entrapped solution, this should be done extremely slowly so as not

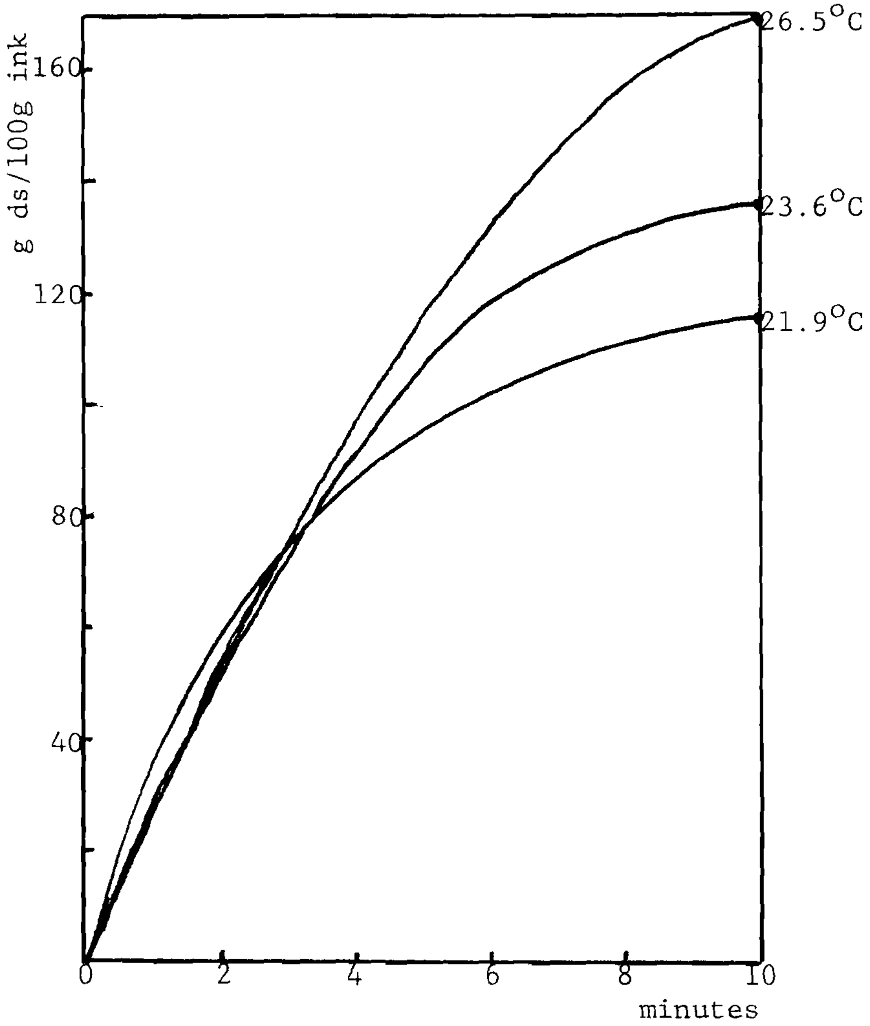


Figure 6. P as a function of temperature

to change the degree of emulsification during that process. Other operators spend much time, many minutes, in order to conscientiously remove the tiniest droplet from the ink surface. This can also be a cause for error, and is at best insignificant for the test result. It is strongly recommended that only one minute should be spent for the separation process. Knocking the bowl to force water from the surface should not be done, as it tends to break the emulsion.

F. Testing Temperature

Figure 6 shows three test results with the same news black ink and alkaline dampening solution. All the tests were conducted at room temperature, approximately 22.7°C. One was done with the normal starting temperature of ink and solution at 25°C. With the two other tests, the materials had a starting temperature at 5°C and 50°C, respectively. Probably the emulsion temperatures at the end of the test (Figure 7) give an indication of the emulsification capacity, b_{max} as a function of the temperature.

$$\frac{\Delta b_{max}}{\Delta t} = \frac{168-117}{26.5-21.9} = 11.1$$

b_{max} at the 25°C end temperature is seen from Figure 7 to be 152, and the variance is then: $\frac{11.1}{152} \times 100 = 7.3\%$ for each °C deviation from standard temperature.

With test media at varying ambient temperatures (22.2-27.8°C) a gel varnish and a heatset black gave, respectively, 3.04 and 1.79, corresponding to the variances of $\frac{3.04}{48} \times 100 = 6.3\%$, and $\frac{1.79}{27} \times 100 = 6.6\%$ per °C deviation.

Besides the ambient temperature, heat of friction and evaporation have an effect on the temperature of the test media. Figures 8 and 9 show the results of simulated emulsification tests. The test media were at 25.0°C, and the stainless steel bowl and mixing blades (162.3 + 210.2= 372.5g) at ambient temperature 23.5°C initially.

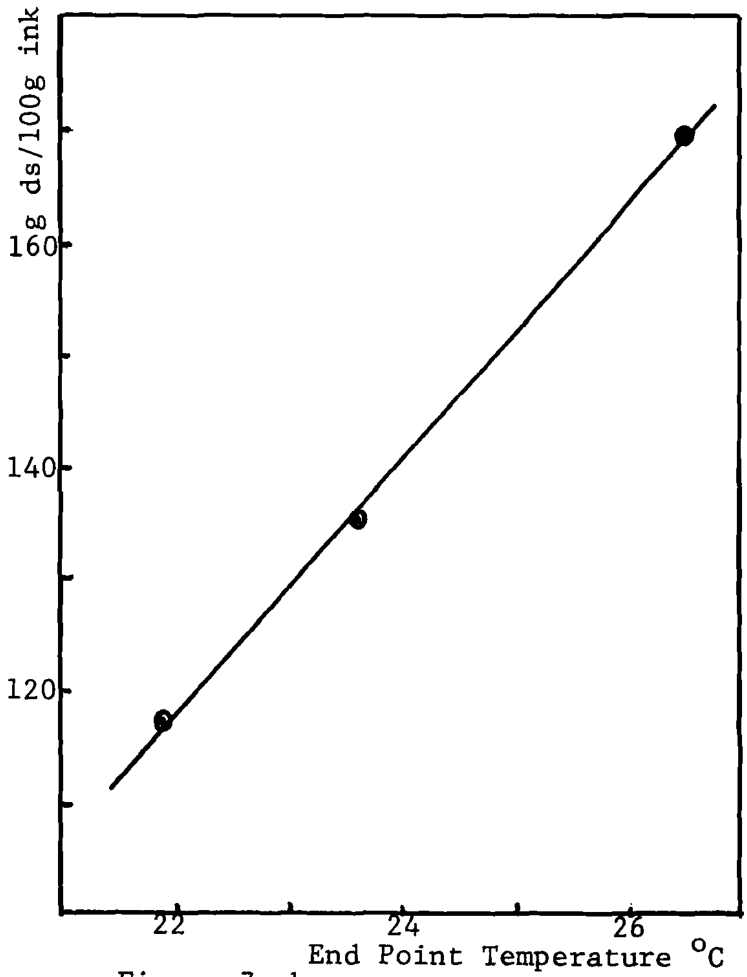


Figure 7. b_{max} versus temperature

When the end temperature is within a close range of 23.5°C, and the loss of dampening water to evaporation is about 1g, a crude calculation estimates the magnitude of the parameters determining the temperature change in the media during the test at:

Initial media temperature:	25.0
- Thermal loss to bowl and blades:	0.5
+ Frictional heat:	1.7
- Heat of vaporization:	2.7
= End point temperature	23.5°C

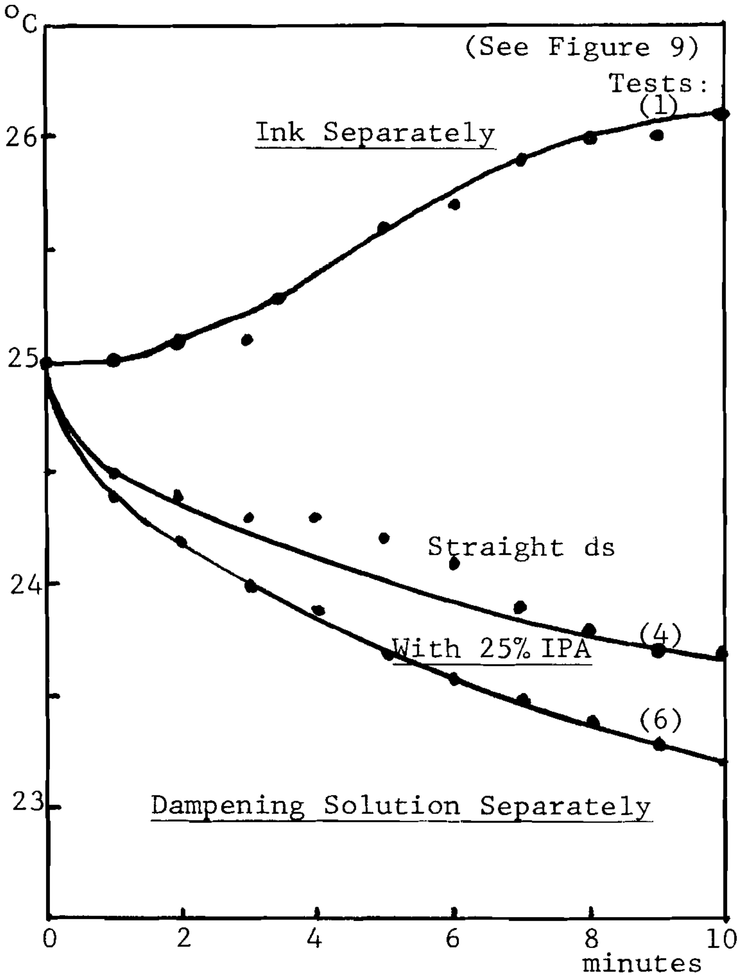


Figure 8. Temperature effects of friction and evaporation

G. Gravimetric Versus Volumetric Determination

A loss of dampening solution during the test due to transfer, splatter and evaporation in the range of 2.5-6g must be expected. (Figure 9.) The loss is essentially independent of the maximal emulsification, b_{max}, and introduces an error when the emulsification is determined as volume loss. The magnitude of the error is inversely proportional to b_{max}. E.g., if b_{max} varies in the range of 140-30, the maximal error varies in the range of 8-40 percent.

This type of error is prevented when the emulsification is determined as weight gain of the ink phase, and therefore a gravimetric rather than a volumetric determination was recommended for the standard procedure.

Test	Material	Mixing Periods	Time Spacing Minutes	Initial Material Temp. °C	End Point Temp. °C	Ambient Temp. °C	Material Loss g	
							Evaporation	Total
1	50g Litho News Black	10 x 1 min.	45	25.0	26.1	23.9	-	-
2	"	1 x 10 min.	10	25.0	26.4	23.5	-	-
3	"	none	10 45	25.0	24.6 23.7	23.4	-	-
4	100g Dampening Solution	10 x 1 min.	45	25.0	23.6	22.7	1.07	3.49
5	"	none	45	25.0	23.5	22.7	1.00	1.00
6	100g Solution with 25 Vol. % IPA	10 x 1 min.	45	25.0	23.2	22.7	1.95	5.61
7	"	none	45	25.0	23.8	22.7	1.53	1.53

Figure 9. Tests with ink and dampening solution separately

Conclusions

The analyses indicate that the major errors in the emulsification test results can be prevented by these precautions:

A) The mixer geometry should be such that virtually all of the ink volume is exposed to emulsification at any time during the mixing periods.

B) The ink should, prior to the test, be brought to a state of agitation similar to that in which it is on the rollers of a printing press.

C) The dampening solution should be added in increments in the attempt of maintaining a constant surplus volume of unemulsified solution; this volume should be significantly lower than the ink (or emulsion) volume to ascertain efficient and reproducible emulsification.

D) The mixing speed should be kept constant at 90 RPM.

E) Manual stirring, or knocking the bowl, to separate unemulsified solution between the mixing periods, should be absolutely excluded.

F) As the temperature of the test media has a significant effect, ink and dampening solution and, preferably, also the bowl and the mixer blades, should be brought to standard temperature, 25.0°C, before the test, and the ambient temperature should be close to the same.

G) The emulsification should be determined gravimetrically to prevent the error introduced by volumetrical determination.

Emulsification Curves Versus Rheology Changes

Introduction

It might be difficult to visualize why an ink exhibiting a P_C emulsification curve (equilibrium at (a,b) where (a)$\sim$5 minutes) performs better on the press than, for example, with a P_B curve ((a) $>$10 minutes) when the two curves corresponding to the rate of emulsification established on the press could be identical. (Figure 10.) It has been shown (Surland 1980) that the abscissa for the equilibrium point appears to be directly proportional to the water balance range on the press. With a non-equilibrium curve, this range is very narrow.

Discussions with many ink production people have revealed that because their P_B inks "work on the press", they fail to understand the significant benefit with a P_C ink. The success or failure of the commercial process depends on the width of the performance margin of many components where ink, dampening solution, plate, press, paper and craftsmanship are the most important ones. If

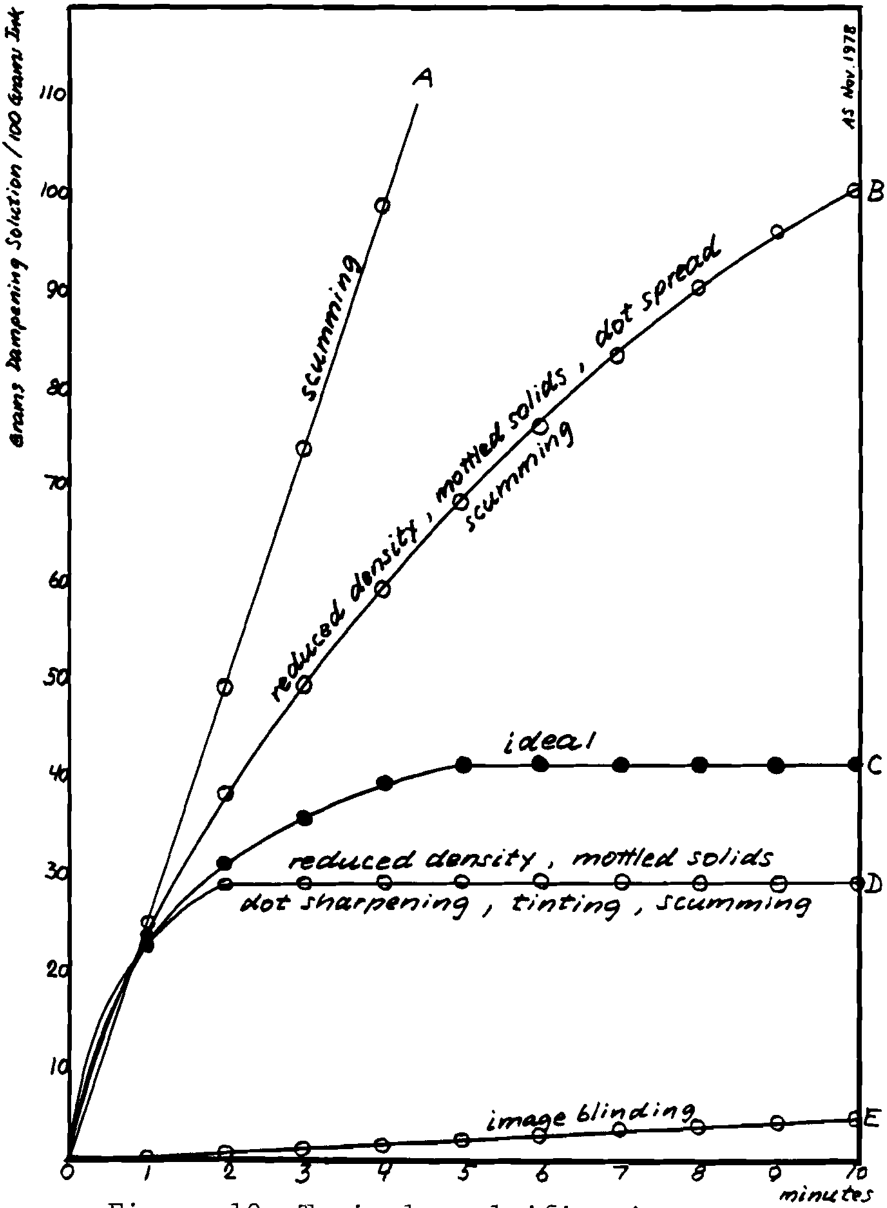


Figure 10. Typical emulsification curves

each component has its maximal performance margin, which is hardly ever the case, the P_B ink will probably "never fail", (although records of printed waste might show otherwise). However, if

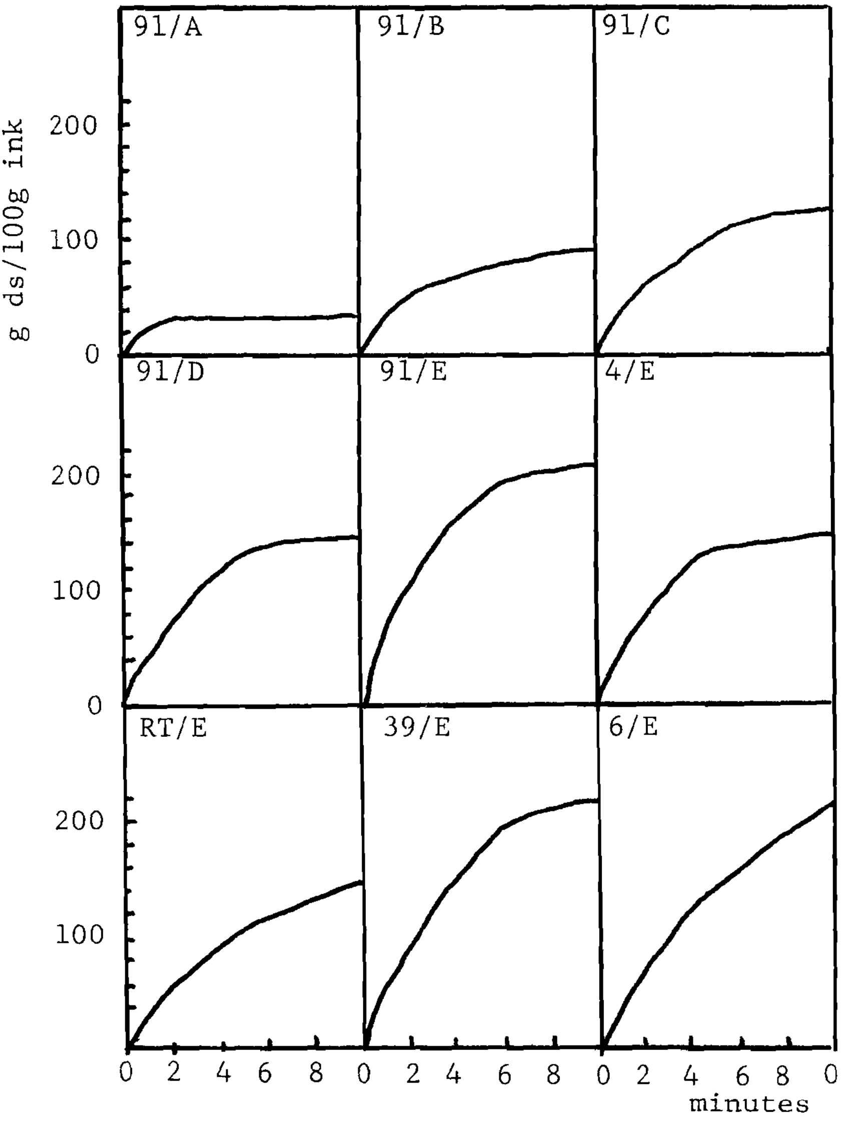


Figure 11. Emulsification curves with various news ink/dampening solution combinations

a combination of narrow performance margins occurs with other components, the ink's rate of emulsification could be the one parameter determining the difference between success or failure. This is supported by the fact that production people often complain that their inks performing "perfectly" at one account, fail badly at another one under apparently the same conditions.

The following investigation is aimed to help the ink makers to understand better the significance of the proper emulsification characteristics and thereby help the printing industry with more efficient production.

(a_x, b_y)	Laray Viscosity		(a_x, b_y)	Laray Viscosity		(a_x, b_y)	Laray Viscosity	
	Poises	Yield		Poises	Yield		Poises	Yield
No. 91A			No. 91D			RT		
0, 0	20	151	0, 0	20	151	0, 0	20	62
1, 23	20	191	1, 45	22	206	.25, 10	20	115
1.5, 28	21	219	2, 76	23	403	.5, 20	20	186
2, 32	Break		2.5, 89	23	449	1, 38	20	254
No. 91B			2.75, 94	Break		1.9, 60	21	301
0, 0	20	151	No. 91E			2.5, 70	21	467
1, 31	20	189	0, 0	20	151	3, 76	Break	
2, 50	20	345	1, 56	21	436	No. 39		
2.5, 56	21	420	1.5, 85	23	561	0, 0	22	135
3, 61	Break		1.75, 98	23	759	1, 43	24	357
No. 91C			2, 104	Break		1.5, 78	24	474
0, 0	20	151	No. 4			1.6, 83	24	743
1, 37	21	291	0, 0	23	79	1.75, 90	Break	
2, 60	23	369	.25, 15	23	105	No. 6		
2.5, 69	24	439	.75, 37	23	119	0, 0	19	145
2.75, 74	Break		1.5, 60	23	143	1.25, 55	24	771
			1.75, 69	23	219	2.1, 80	24	1862
			2, 74	Break		2.75, 100	24	3236
						3, 105	Break	

Figure 12. Rheology changes with emulsification

Progressive Emulsion Rheology

Viscosity Changes

Figure 11 shows the emulsification curves for various news blacks with different dampening solutions. The pH and conductivity of the 100 ml solution were measured before the test and, when possible, also after the test. (Figure 13.) When the equilibrium point (a,b) was not reached within the testing period, "(a,b)" was estimated by a probable graphic extrapolation.

Using the method as described (Bassemir 1981), a Laray viscometer was used to determine the ink's viscosity and yield value, respectively, in poises at 2500 sec.$^{-1}$ and dynes/cm^2 at 2.5 sec.$^{-1}$. Figure 12 shows the Laray data on the straight inks and on their emulsions with the respective solutions corresponding to their progressive emulsifications. This way a Laray emulsion break point (a_x,b_y), defined as the point after which the Laray yield value decreases, was determined for each ink/dampening solution combination. The emulsions were made by manual stirring.

Figure 13 tabulates the test data. The emulsion shear stability is shown as:

$$E_s = \frac{a_x \times b_y}{a \times b}$$

and the flow stability as:

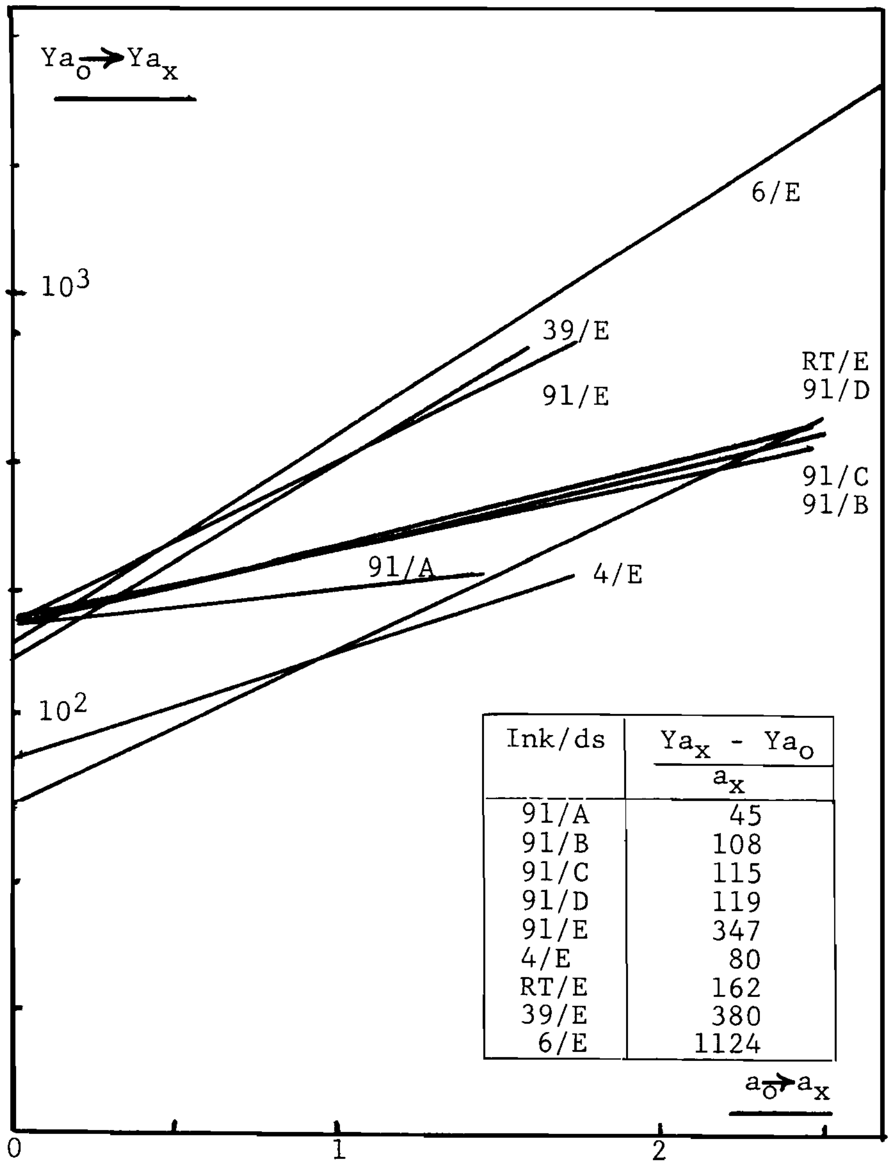
$$F_s = \frac{Y(0,0) \times V(a_x,b_y)}{V(0,0) \times Y(a_x,b_y)}$$

, where Y and V are the Laray numbers for yield value and viscosity measured respectively at (0,0) and at the emulsion break point $(a_x b_y)$.

Litho Offset News Blacks		Dampening Solution		Emulsification Test Results Equilibrium Point	Laray Emulsion Break Point	Relative Emulsion Shear Stability	Relative Flow Stability
Ink	Solution	pH	mho/cm x 10^3	(a,b)	(a_x,b_y)	E_s	F_s
91	A	2.91-3.05	1.50-1.40	3, 34	1.5, 28	.41	.72
"	B	7.25-7.25	1.13-1.15	10, 94	2.5, 56	.15	.38
"	C	9.98-9.01	1.31-1.21	8, 124	2.5, 69	.17	.41
"	D	10.82-8.99	1.35-1.10	7, 142	2.5, 89	.22	.39
"	E	11.48	1.97	8, 204	1.75, 98	.11	.23
4	E	11.45-9.89	2.01-1.63	5, 140	1.75, 69	.17	.36
RT	E	11.45-9.32	2.01-1.62	"13, 152"	2.5, 70	.09	.14
39	E	11.48	1.97	"12, 220"	1.6, 83	.05	.20
6	E	11.45	2.01	"20, 285"	2.75, 100	.05	.06

Figure 13. Equilibrium point versus relative emulsion and flow stability

Figure 14 shows the yield value increase within the a_x x b_y area.



Ink/ds	$\frac{Ya_x - Ya_o}{a_x}$
91/A	45
91/B	108
91/C	115
91/D	119
91/E	347
4/E	80
RT/E	162
39/E	380
6/E	1124

Figure 14. Yield value changes $a_o \rightarrow a_x$

Tack Changes

Figure 15 shows tack/time curves of Ink No. 91, its emulsions with solution (D), and with addition of TiO_2 pigment. The latter was ground into the ink on a roller mill to exclude air bubbles. The tack was determined on a Reed Inkometer (Thwing - Albert Manual). It is seen that the initial tack reading is higher with increased dispersed phase, regardless of whether this consists of water droplets or solid pigment. However, the solids dispersion curve remains equidistant from the original, while the emulsion curve intersects at a time inversely proportional to the degree of emulsification. Obviously, water is lost passing through the nips. In step with this, the splitting film becomes thinner, resulting in decreasing tack readings.

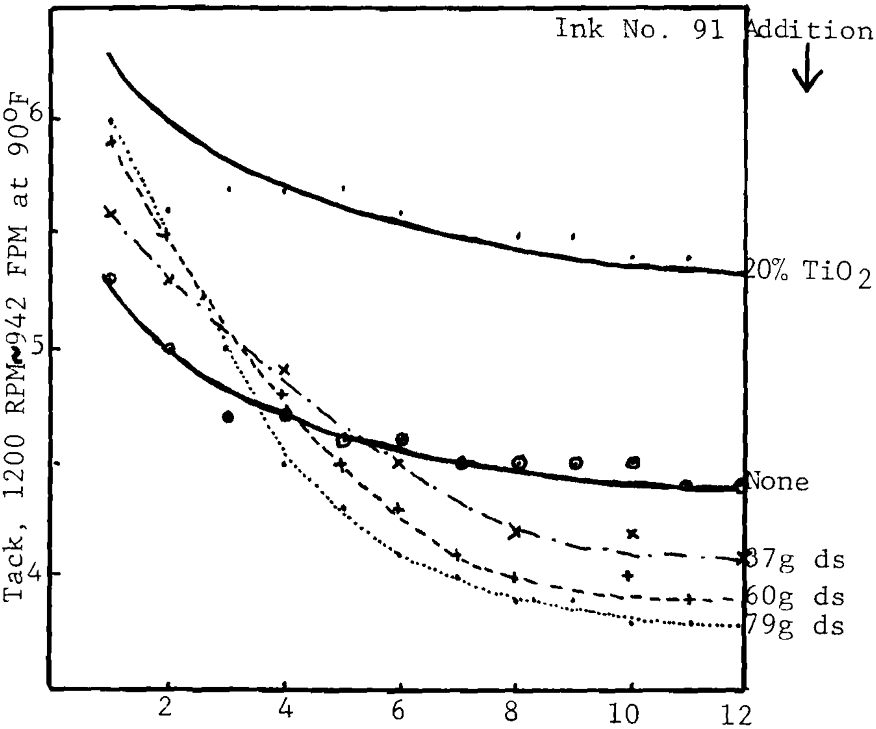


Figure 15. Tack with increasing emulsification, and with pigment addition

Figure 16 shows the tack curve with the No. 6 ink and 6/E emulsion. Again, the emulsion shows the highest initial tack, but the much later intersect with the original indicates much higher emulsion stability than with the No. 91 ink. Apparently this is in conflict with E_s, Figure 13. However, E_s describes the emulsion stability at relatively high shear (Laray) in relation to the stability at relatively low shear (Emulsification Test). On the Inkometer, only loss of water occurs and $p=\frac{P_+}{P_-}$ determines the loss rate. Therefore, when $P \gg 1$, the loss rate is much smaller than when P rapidly approaches 1 (equilibrium curve), and the emulsion stability under relatively high shear is proportional to P.

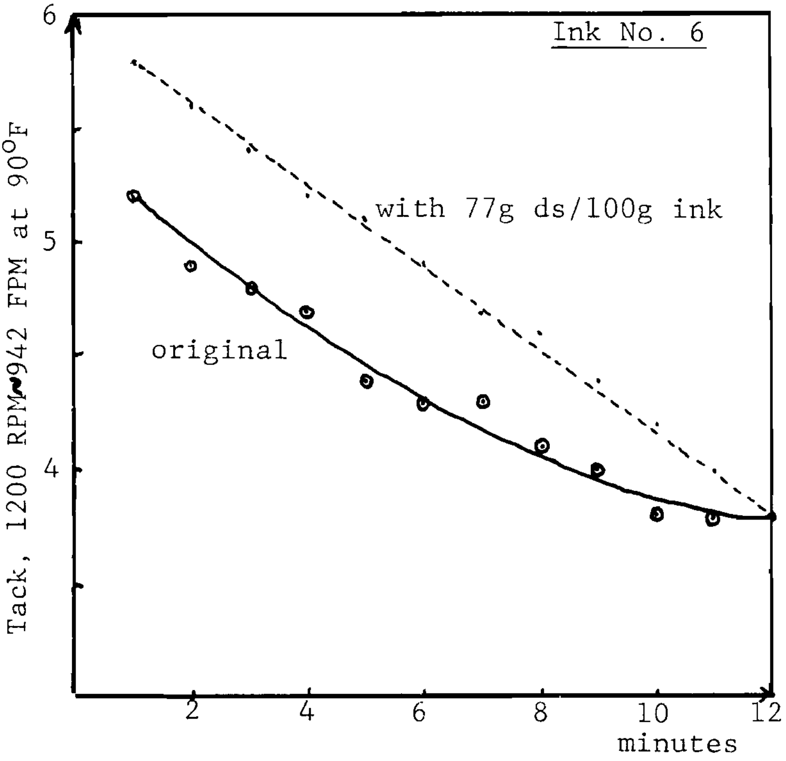


Figure 16. Tack stability with "Low Es ink"

To visualize the happenings during the filamentary ink transfer process at the nip exit, a "cubic splitting model", Figure 17, is suggested.

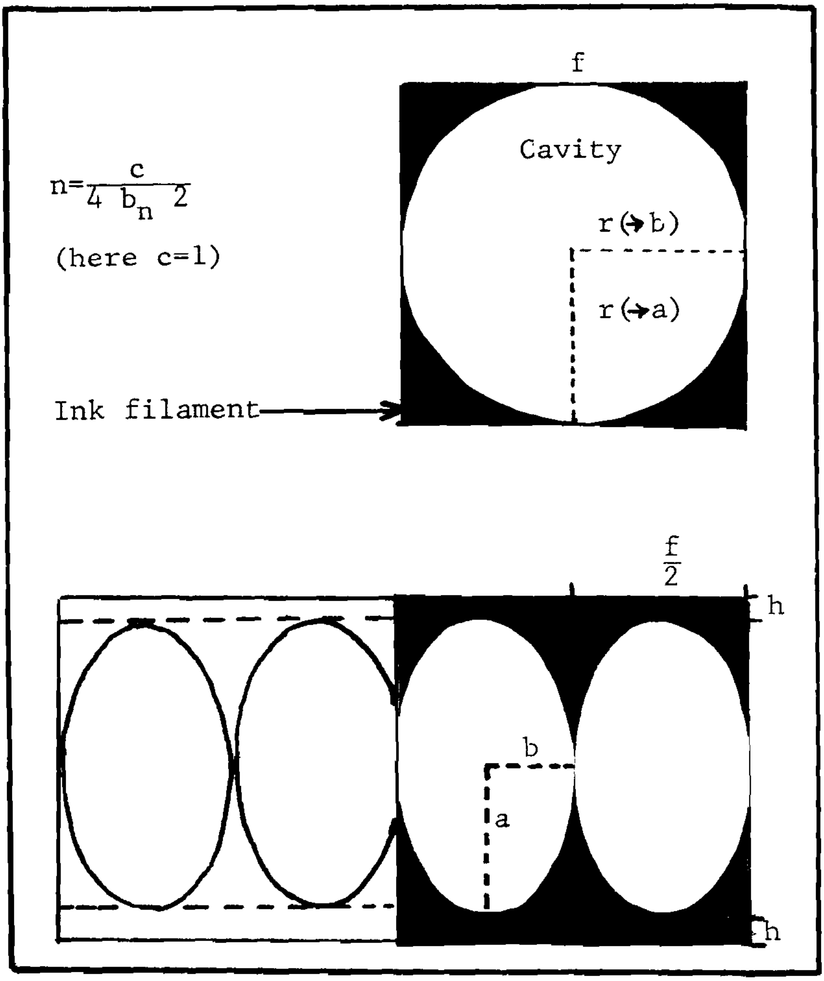


Figure 17. Cubic film splitting model

The largest cavity in the cube with the dimension f can be visualized as a sphere with the radius $\frac{f}{2}$. All the ink volume in the cube is then collected in one single filament "at its moment of splitting". The ink volume can be considered constant; therefore, when the number of cavities in the cube increases, they will take the form of ellipsoids, which, "at the moment of filament split", do not touch the horizontal end planes in the cube. As the cavity number equals the filament number n, it can be seen that, with increased filamentation, an even ink film increasingly

thicker (h) will theoretically be collected on the horizontal planes, and less of the ink volume will be contained in the filaments.
$h_n = \frac{f}{2} - (\frac{f}{2} b_n)^{\frac{1}{2}}$ where $b_n = \frac{1}{2n^{\frac{1}{2}}}$. This might explain the tack increase with increased n as introduced by an increase in disruptive "particles", whether they consist of water, pigment or even gas.

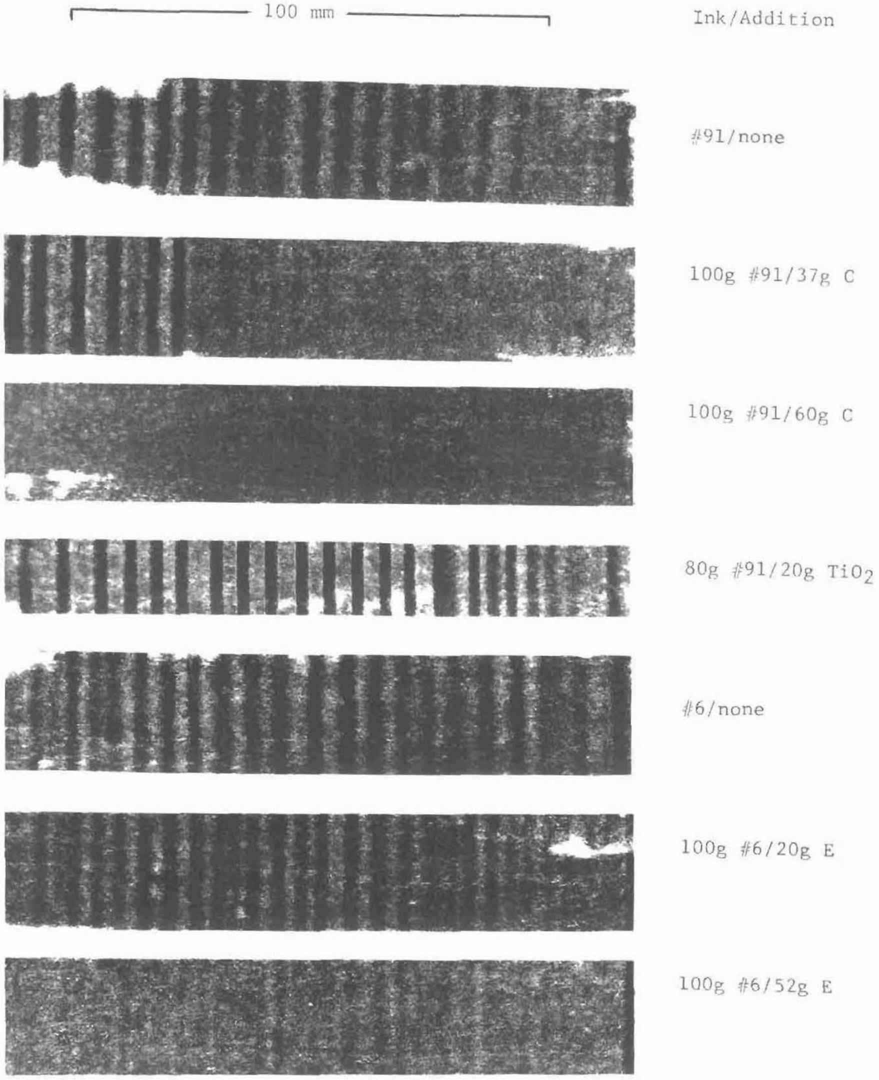


Figure 18. Inkometer rib formation

Figure 18 shows contact prints of rib formation produced by running the investigated materials for two minutes with the oscillating roller disengaged. (Unfortunately, the ink with the TiO_2 addition was run on another Inkometer for five minutes, so the rib numbers for this are not comparative.) Figure 19 shows the calculation of f', the rib distance, and n', supposedly proportional to n, the filament number or frequency, as well as the tack reading.

Ink/Addition	Length mm	Rib Count	f' mm	$n' = \frac{10^3}{(f')^2}$	Tack 1 min.
91/none	132	22	6.0	28	4.8
91/37g C	130	25	5.2	37	5.1
91/60g C	83	19	4.4	52	5.4
91/20% TiO_2	122	21	5.8	30	5.8
6/none	100	17	5.9	29	4.6
6/26g E	108	23	4.7	45	5.0
6/52g E	120	29	4.1	59	5.3

Figure 19. f' and n' of rib formation

The numbers are plotted, Figure 20. It appears that the tack, at least for the emulsions, is proportional to n'. To determine the proportional effect of h, n, V, Y or other parameters, future studies are required.

Figure 21 shows ink sling, or non-airborne ink droplets, and the airborne ink mist. These recordings were made by holding a paper pad under the Inkometer, supported in the back by the circulation tank and held up against the Inkometer front bar. The ink sling was measured during the first 10 seconds and recorded as the unevenly distributed deposit outside the bar. The ink mist was measured during the interval 70 - 100 seconds and recorded as the evenly distributed deposit inside the bar.

A comparative rating clearly shows that both sling and mist were inversely proportional to the increased disruptive "particle" concentration (pigment or water droplets).

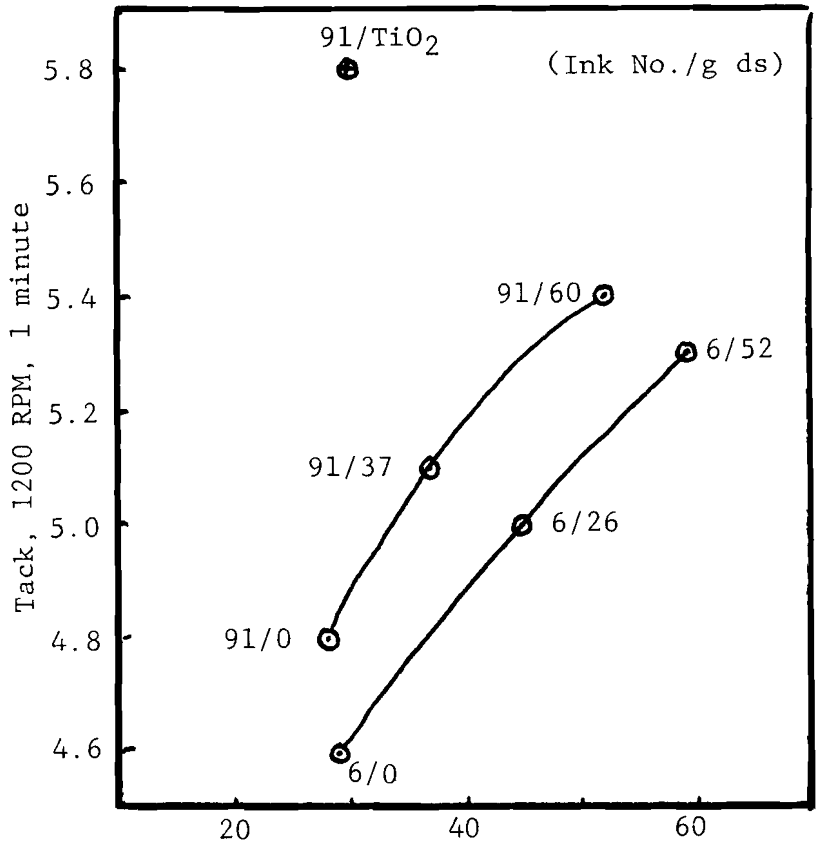


Figure 20. Tack versus n'

Conclusions

A) Different ink/ds pairs produce different emulsion curves.

B) The tack, viscosity and in particular the yield value increase with increasing emulsification.

C) The ink fly, sling and mist, decrease with emulsification.

D) Emulsified ink transfers more evenly than unemulsified ink.

E) Ink/ds pairs with equilibrium emulsification curves show significantly less change in rheology than pairs with non-equilibrium curves.

Ink	Sling	Mist	Addition
No. 91	4	5	none
No. 91	1	4	37g ds/100g ink
No. 91	0	1	60g ds/100g ink
No. 91	2	1	20% TiO_2
No. 6	3	6	none
No. 6	1	4	26g ds/100g ink
No. 6	1	3	52g ds/100g ink

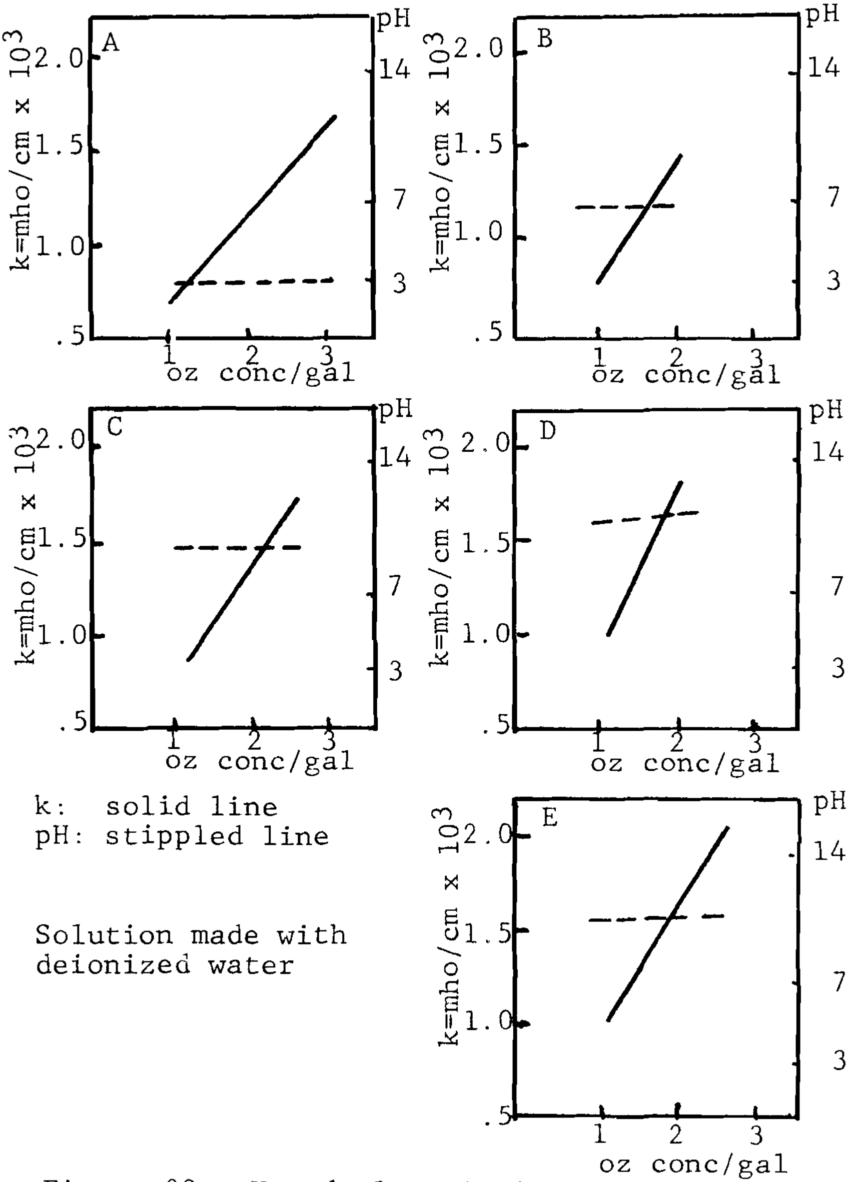
Rating: 0 - 6 ∼ none → moderate

Figure 21. Ink sling and ink mist

Effects of the Dampening Solution

pH and Electrical Conductivity

The pH and conductivity as functions of concentration, together with the buffering curves for the dampening solutions used in the rheology study, are shown. (Figures 22 and 23.)



Solution made with deionized water

Figure 22. pH and electrical conductivity of the dampening solutions

From Figure 13 it can be seen that (b) is essentially proportional to the product of pH and conductivity (k), as given in mho/cm x 10^3. The constant (C) involves many parameters, but is con-

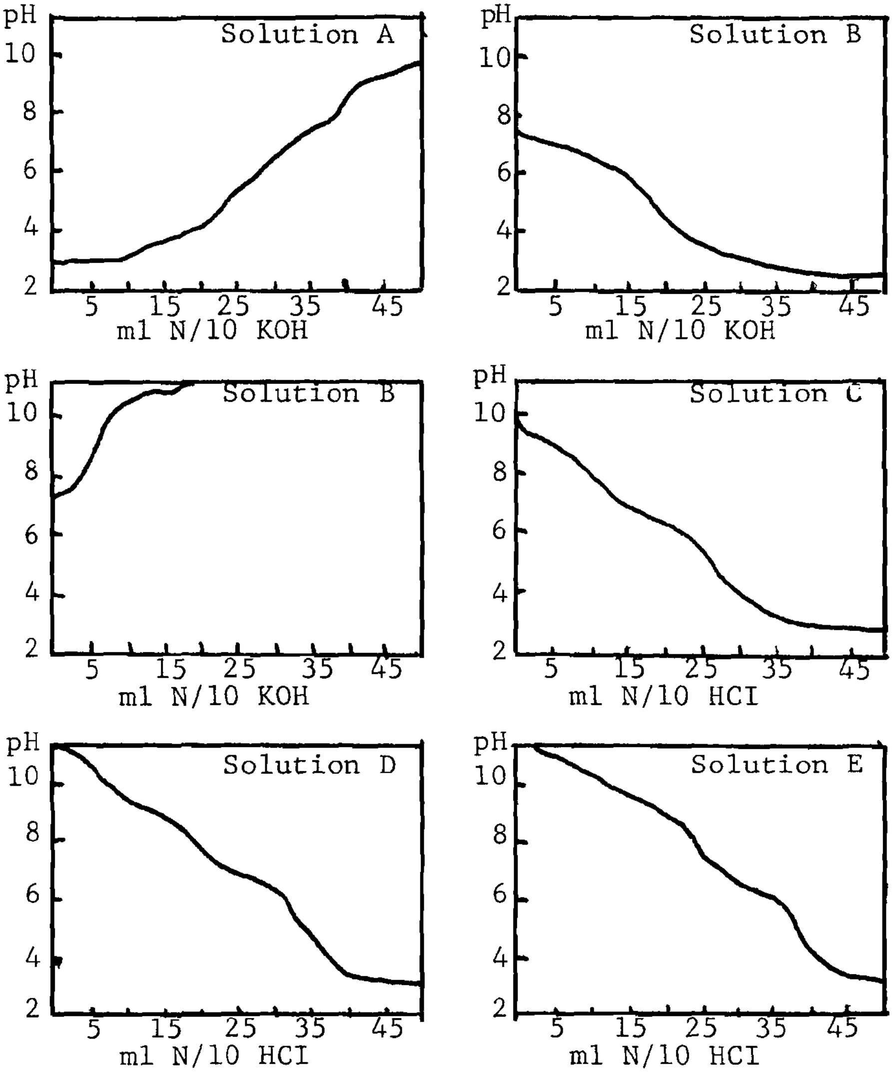


Figure 23. Buffering curves (with 500 ml dampening solution)

sidered here only as the sum of an ink and a dampening solution constant ($C_i + C_{ds}$). An estimation of the relative magnitude of $C=C_i + C_{ds}$, when $C_{ds_A}=0$ is shown on Figure 24.

Ink/ds	b	pH	k	pH x k	$C=\frac{b}{pH \times k}$	Cds	Ci
91/A	34	2.91	1.50	4.4	7.7	0	7.7
91/B	94	7.25	1.13	8.2	11.5	3.8	7.7
91/C	124	9.98	1.31	13.1	9.5	1.8	7.7
91/D	142	10.82	1.35	14.6	9.7	2.0	7.7
91/E	204	11.48	1.97	22.6	9.0	1.3	7.7
4/E	140	11.45	2.01	23.0	6.1	1.3	4.8
RT/E	152	11.45	2.01	23.0	6.6	1.3	5.3
39/E	220	11.48	1.97	22.6	9.7	1.3	8.4
6/E	285	11.45	2.01	23.0	12.4	1.3	11.1

Figure 24. Parameters determining the emulsification capacity b

It appears that b depends dominantly on the pH and conductivity of the dampening solution, to a large degree on the ink formula and to some degree on a content of surfactants in the dampening solution. When b for a given ink is known with one dampening solution, it can roughly be predicted for another one, using the equation b=C x pH x k; $b' = \frac{b}{pH \times k} \times pH' \times k'$.

Considering $P=\frac{P_+}{P_-}$, P_+ is proportional to the concentration of anions (e.g. OH^-) while P_- is proportional to the concentration of cations (e.g. H^+).

Alcohol and Alcohol Substitutes

The T.A.G.A. paper (Surland 1980) showed (in Figure 10) the form of the emulsification curves for two sets of process inks determined with straight acidic dampening solution (= ds A) and with the same solution containing 25% of isopropyl alcohol by volume. The actual data in terms of the equilibrium point (a,b) are given in Figure 25.

The strongly reduced a x b area with the alcohol addition, in particular with the "marginal" inks, indicates that, in general, significantly improved performance is effectuated by the alcohol. None of the substitutes had nearly the same effect in this regard. Some of these have been found to act as solvent for the inks, which must be considered as an unwanted quality.

Ink	Equilibrium Point (a,b)		a x b (+IPA) / a x b (-IPA)
	-IPA	+IPA	
WB	4,31	4,36	1.16
WR	13,69	7,54	.42
WY	8,52	3,33	.24
WK	12,37	3,31	.21
SB	13,80	3,35	.10
SR	12,58	4,40	.23
SY	10,45	5.35	.39
SK	5,36	4,31	.69

Figure 25. The effect of alcohol addition

Conclusions

A) The dampening solution and its concentration can be monitored by pH and conductivity measurements.

B) Acidic dampening solutions appear to be relatively well buffered, while neutral or alkaline solutions appear to be poorly buffered.

C) The emulsification capacity of an ink/dampening solution pair is proportional to the pH and conductivity of the dampening solution, and to particular ink and dampening solution constants.

D) Of additives reducing the surface tension of acidic dampening solutions, isopropyl alcohol, as added in larger volumes than the "alcohol substitutes", has a significant effect of improving the emulsification characteristics of in particular "marginal" pairs.

Differential Affinities of Surfaces on the Press

As so frequently stated in the literature, the roller and image-forming surfaces on the press, in regard to their affinities to ink or water, are essentials for the efficiency of the printing process. It is well known that in competition with each other, water will preferentially wet surfaces like zinc oxide, steel, aluminum and chromium; while oily ink will preferentially wet rubber and copper. (Bassemir and Bean 1979) have shown that barium and calcium deposited on the plate image area causes plate blinding. In other words, barium and calcium wet preferably with water. From the time when lead driers were used in oxidative inks, it is known that lead deposited on the non-image area on the plate caused scumming. Lead is preferentially wetted with oil. (Adams 1956) determined the contact angles of a 5 percent oleic acid solution in mineral oil on metals. Figure 26 shows the data with the metal elements plotted in a "hydrophilicity" diagram. Assuming that the 90° angle divides the elements with regard to preferential wetability, it was attempted

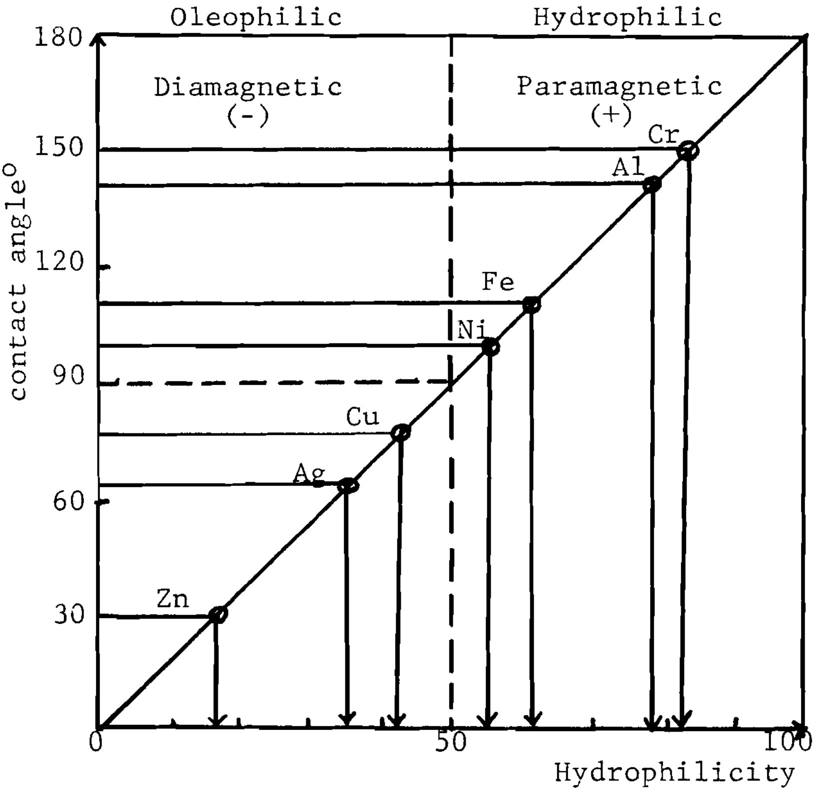


Figure 26. Electron spin as probable determinator of hydrophilicity

to relate this difference to elementary constants. It was immediately seen that all the rather oleophilic elements were diamagnetic, while the rather hydrophilic elements were paramagnetic. Time limits prevented further studies in this area, but if the principle proves true, it could be extended to select elements or compounds to create more efficient lithographic plates than is the case today. Also, the indication would be that electromagnetic phenomena play a basic role in surface affinities.

Conclusion

The indication is that surfaces built up of molecules with "unpaired" electron spin (paramagnetic) wet preferably with water, while surfaces built up of molecules with "paired" electron spin (diamagnetic) wet preferably with oil.

Correlation Between Laboratory Results and Commercial Printing Efficiency

Introduction

To relate the findings discussed above to actual printing, and to illustrate the significant impact of the results on its efficiency, the following examples from commercial printing are given:

Ink and ds Water on the Press

(MacPhee 1979) estimated that the ink film thickness on a print is around 1 micron, corresponding to an ink film on the form rollers of 2.5-3.5 microns. On the plate the ink film was 2-3 microns and the ds water film about .5-1 microns.

(Fuerst 1982) found that ink accumulated by a Dayco Color Separator from the formroller on a web press, according to a Carl Fischer titration, contained 20 percent water. The press speed was reported as 1400 FPM, the ink was a heatset publication process red, and the ds water acidic with an alcohol substitute. The ink coverage was estimated to be about 8 percent solids. Figure 27 shows the emulsification curve with the materials used, and the point on the curve (.75,25) corresponding to 20 percent water. Related to the test equilibrium point (a,b)=(2.5,39), the indication is that on the press the degree of emulsification will correspond to the degree of emulsification obtained within the first minute or two by the laboratory test.

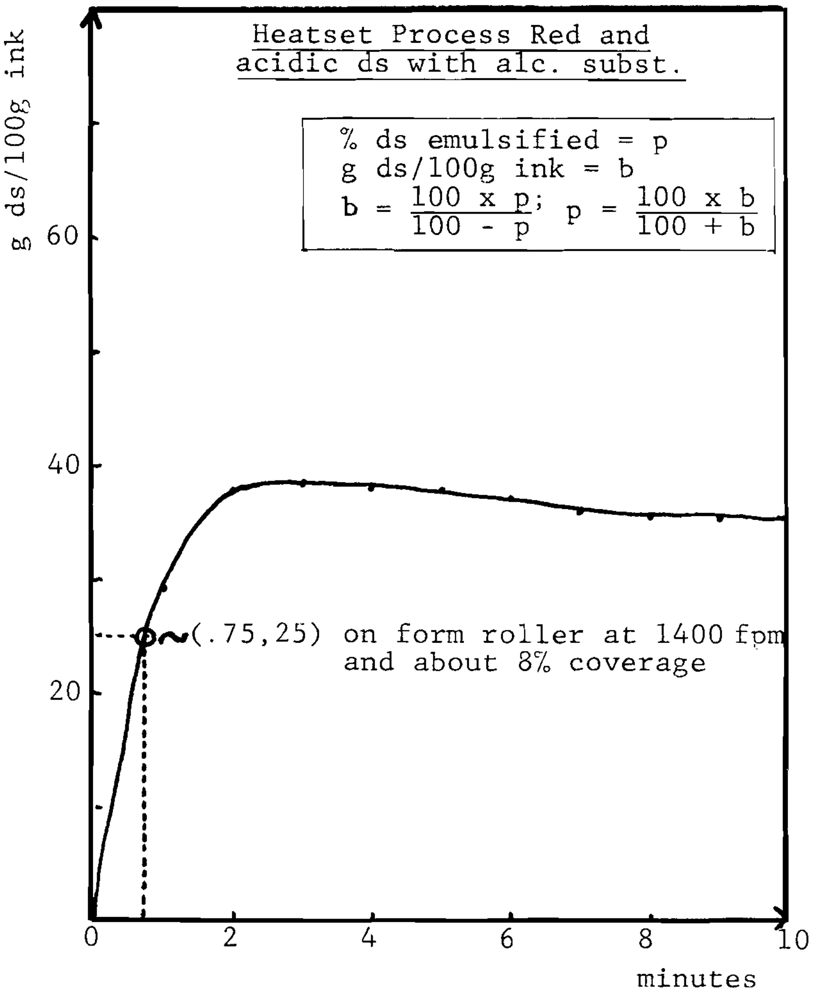


Figure 27. Approximate press emulsification versus laboratory curve

Interference of Surface ds Water with Ink Trapping

Figure 28 shows a process print with green specks on a brown suede jacket. The specks are produced in different spots for each subsequent print, and are caused by the lack of transference of red ink in the speck areas (.5-1 mm). Figure 29 shows the same print with lower web tension. Although the specking trend can still be noticed, the problem was alleviated to a tolerable degree.

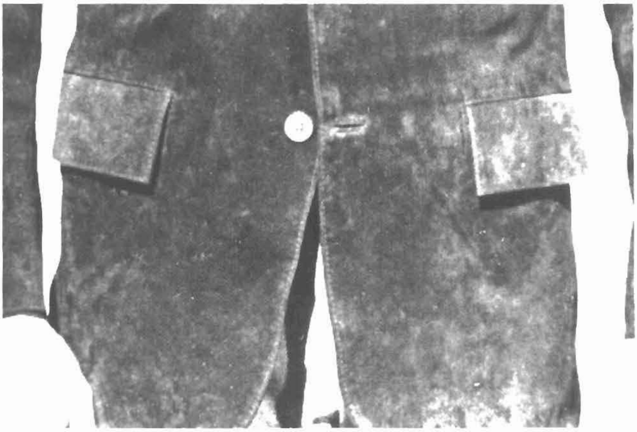


Figure 28. Trapping specks at higher web tension

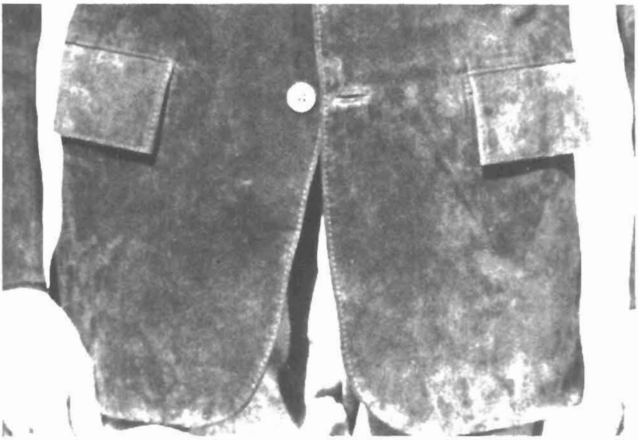


Figure 29. Trapping specks at lower web tension

Figure 30 shows the emulsification curves with the material used. It is noticed that the red ink shows a curve which can be classified as a P_{DE} type, which would not only tend to carry more water on its surface, but in addition its formed emulsion would tend to break under shear. It will then seem that water droplets over the red ink on the blanket produce the spot-wise lack of transfer. With the slacker web, the web clings to the blanket, (more wrap-around) a slightly longer time,

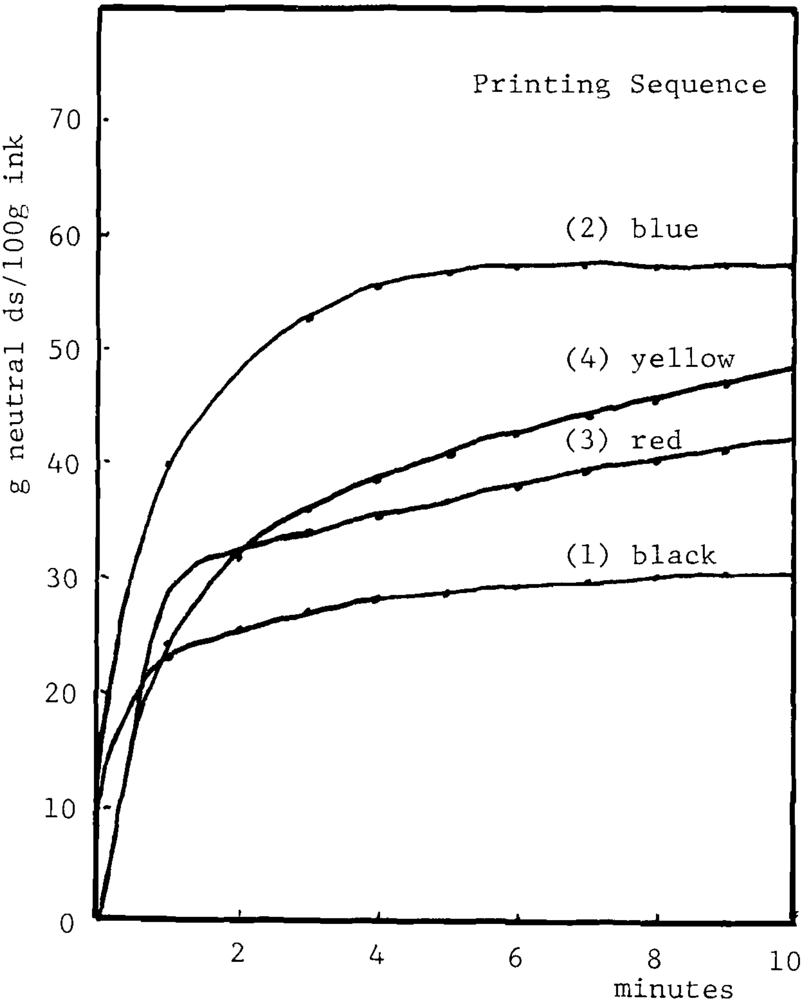


Figure 30. P of process inks where the red produced green specks due to poor trapping

enough for more of the surface water to be absorbed into the paper, allowing for better ink transfer. The problem was permanently eliminated with a red exhibiting a more ideal emulsification curve.

Contamination of Chromium Dampening Roller

A severe case of "ink contamination" was investigated. Figure 31 shows the emulsification curves

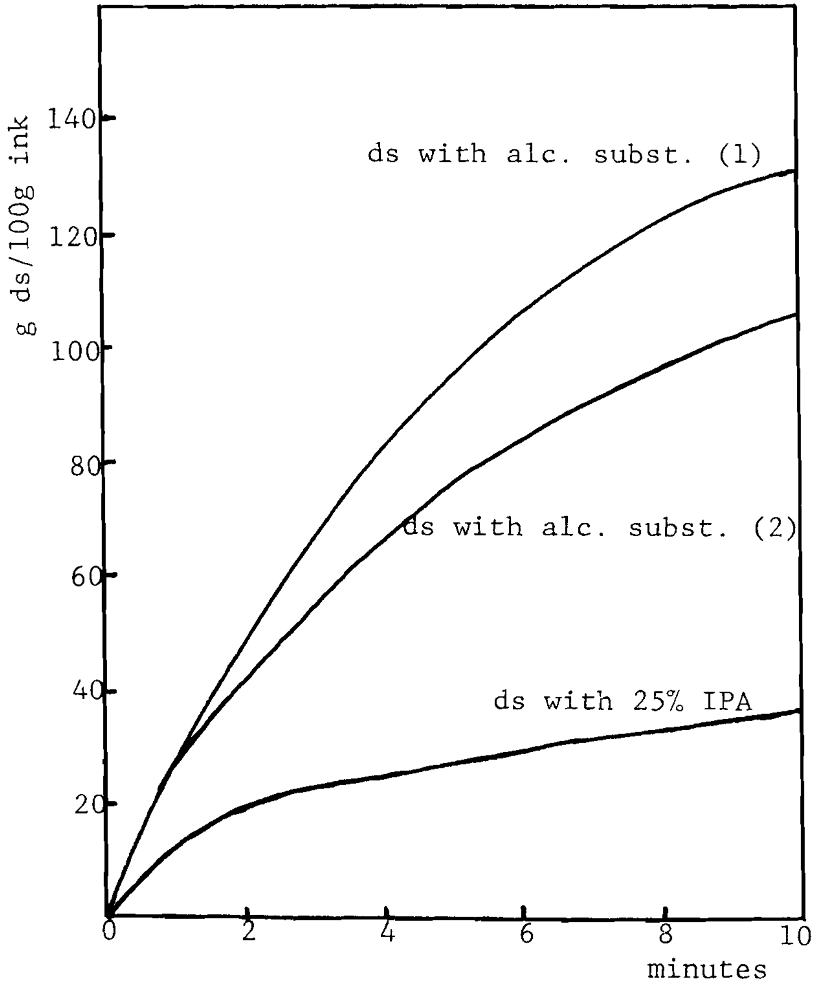


Figure 31. P with the same ink and ds; but with different ds additives

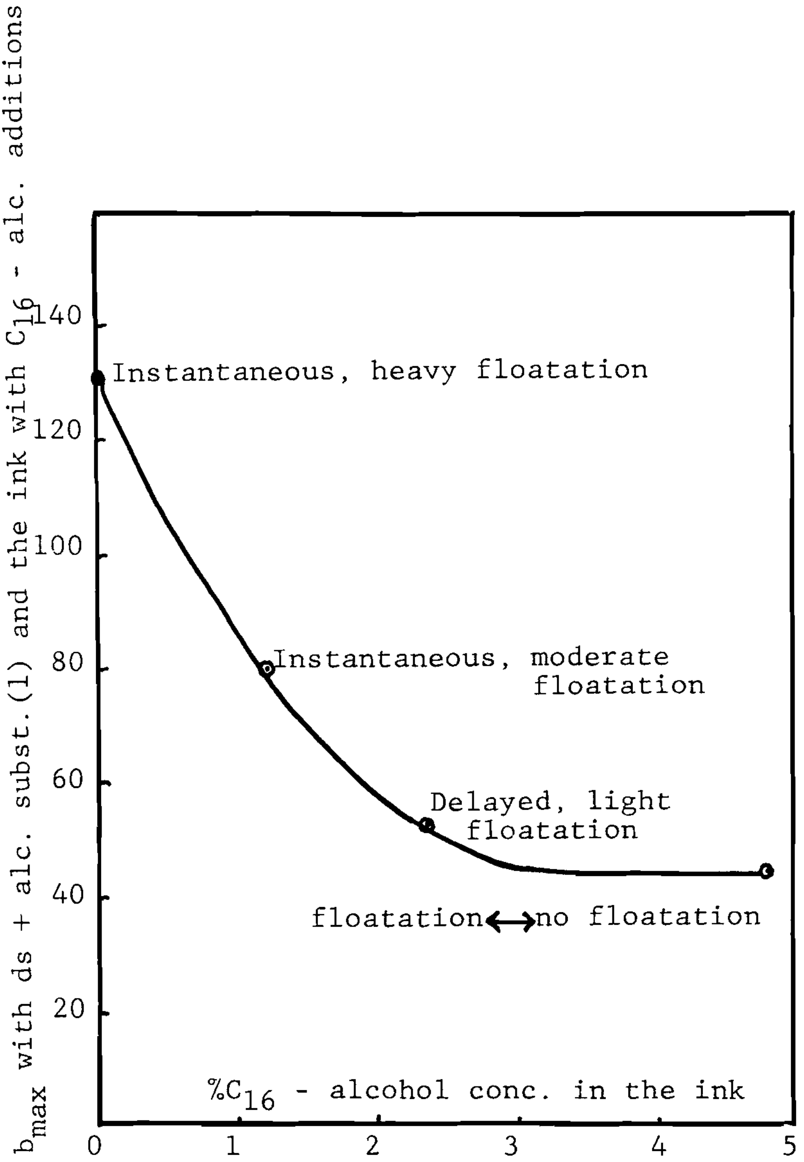


Figure 32. Chromium dampening roller contamination by ink floatation

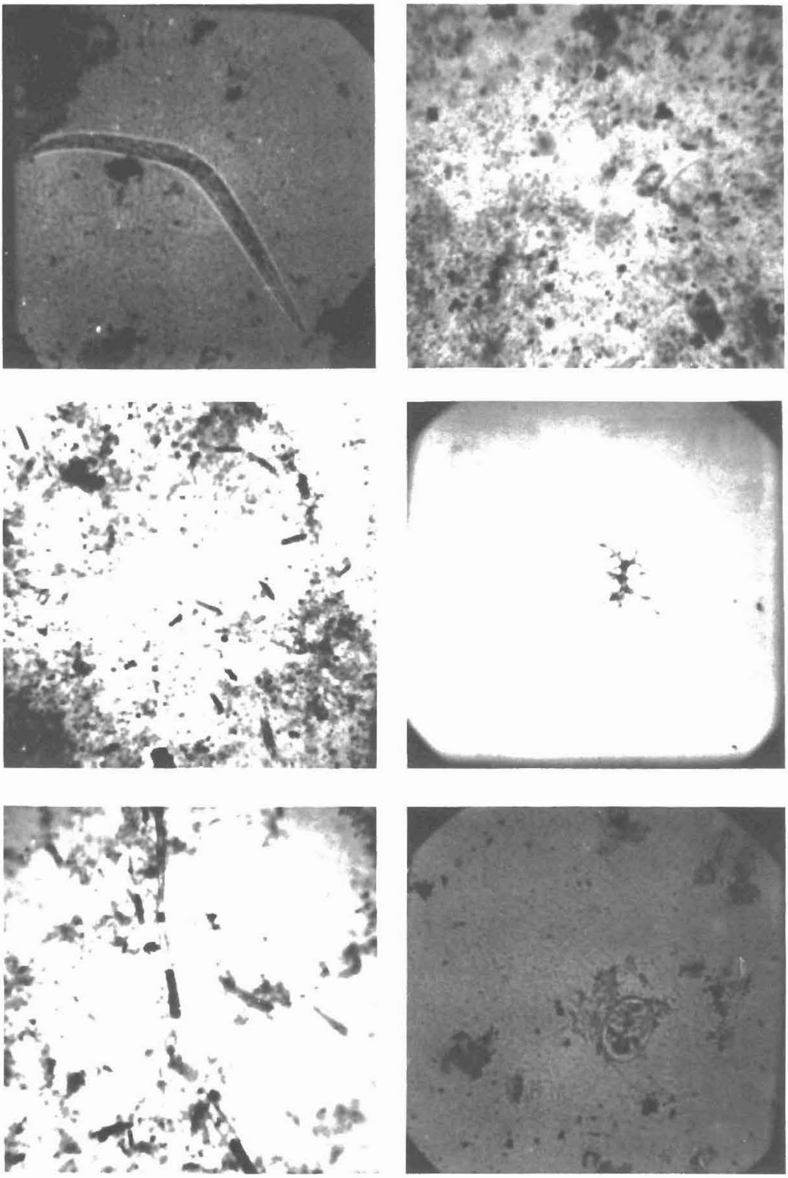


Figure 33. Microbial contamination of alkaline dampening solution

with the materials in question. These results indicate that the ink is "marginal" in performance; substitute (1) is the same and substitute (2) only slightly better. Isopropyl alcohol appears to be the most effective additive. This was confirmed by letting a droplet of the ink fall through the surface of the different solutions. With substitute (1) an instantaneous separation of a relatively heavy, and pigment-containing layer, was noticed on the surface. With substitute (2), the separation was slightly retarded and not so heavy. No separation was noticed with the alcohol. The separated "film" must be expected to be "electromagnetic" enough for attraction to the chromium surface on the dampening roller.

Figure 32 shows the end point results from emulsification test with substitute (1), the poorest, as a function of increasing addition to the ink of a C_{16}-alcohol. The surface separation from the ink was prevented with about 3.2 percent addition.

Microbial Contamination of Alkaline ds

Severe toning was encountered with news printing and a recirculating dampening system. It showed that the dampening solution which started out with a pH of 11.02 changed to 6.50 only by circulating about 40 gallons ds for an hour without printing. The pH change would be equivalent to the addition of about 1g hydrochloric acid per gallon ds. However, it was not the PVC piping which broke down by some strange mechanism to release acid. P. Ernest proved in the laboratory that the rich population of microorganisms with the PVC as substrate, by their life cycle, could produce the acid equivalent for the change of pH. Figure 33 shows examples of the population. Obviously, the toning problem was a result of the strongly reduced emulsification capacity with the lowered pH, and it was solved with a one-way dampening system and an ink like the previously mentioned No. 91 ink. Most likely, the problem would not have occurred with a well-buffered dampening solution.

Laboratory Performance Parameters Related to Commercial Reputation

Figure 34 shows the inks', and dampening solutions', (as evaluated, Figure 11) actual performance characteristics. It is seen that the performance could virtually be predicted by the form of the emulsification curves alone. However, if a performance parameter $P' = E_x$ x F_x x (a x b), where the single factors were discussed previously, is introduced, it is seen that this parameter gives a numerical value in good correlation with the known performance of the ink/ds pairs.

Ink/ds	Characteristics	Es	Fs	a x b	Performance Parameter $P' =$ Es x Fs x a x b
91/A	tinting, scumming linting, plate wear	.41	.72	102	30
91/B	no complaints	.15	.38	940	54
91/C	no complaints	.17	.41	992	69
91/D	excellent performance, excellent lay, no set off on turnbars	.22	.39	994	85
91/E	no complaints	.11	.23	1632	41
4/E	no complaints	.17	.36	700	43
RT/E	inferior to 91/D	.09	.14	1976	25
39/E	severe tinting	.05	.20	2640	26
6/E	scumming and tinting	.05	.06	5700	17

Figure 34. Performance parameter P' as related to actual performance

Emulsion Inks

(Lindqvist 1980) quoted a Scandinavian ink manufacturer who stated several years earlier regarding emulsion inks, "Who would like to buy such an amount of water in a tin?" Figure 35 shows a commercial heatset print with process inks containing 25 percent pre-emulsified water produced in 1975. Although several hundred thousand pounds of this ink type were sold around that time, the system was ahead of its time. Presently, far more stringent control on the ink materials have been introduced, and better understanding of technology necessary for manufacturing such ink systems developed, so emulsion inks ought soon to have a strong comeback. In this presentation, it has been shown that, by far, more even ink transfer can be obtained with emulsion inks. The early experience also showed that a far lower web temperature was required for drying emulsion inks. The visible smoke caused by the condensation of hydrocarbon solvent vapors was reduced, if not eliminated. In addition to this, some of the water is lost on the press as vapor, which has a substantial cooling effect on the roller train and thereby reduces the viscosity changes of the ink on the press. (This effect would be even more pronounced with letterpress inks.) The emulsion will tend to eliminate ink mist and sling. So, with the many advantages, the money spent on "water in the can" might come back many times as higher printing efficiency.

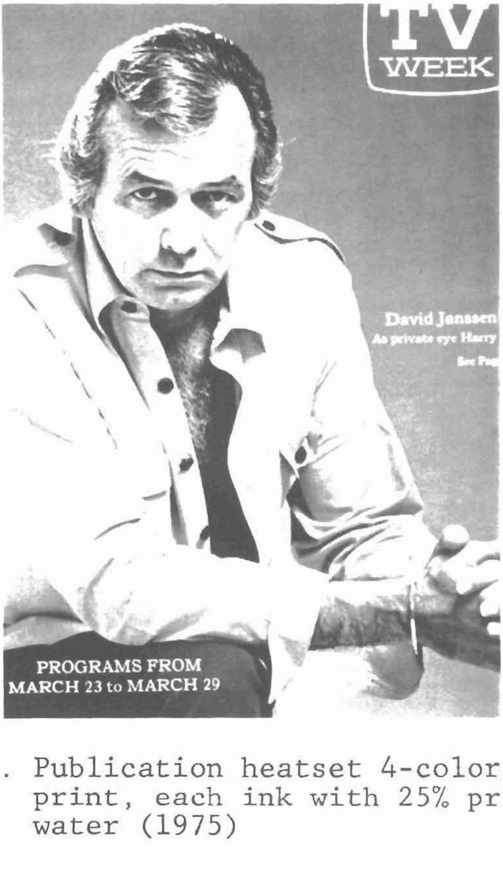


Figure 35. Publication heatset 4-color process print, each ink with 25% pre-emulsified water (1975)

Summary:

The rate of emulsification with the ink/dampening solution pair determines essentially the efficiency of the lithographic printing process.

The rate can, with good approximation, be predicted from the laboratory emulsification test (Surland 1980) when the proper equipment and procedure are used.

With emulsification, the ink viscosity, tack and in particular the yield value increase significantly.

The rheology changes are controlled with inks reaching emulsification equilibrium, which puts a ceiling over the changeability.

Ink emulsified to a certain degree transfers more evenly, mists and slings less and minimizes temperature increase on the roller train.

The dampening solution and, in particular, its pH and electrical conductivity, have a pronounced effect on the degree of emulsification, which, with good approximation for a particular ink, can be predicted from these parameters.

Isopropyl alcohol addition to the dampening solution, in general, improves the emulsification characteristics. "Alcohol substitutes" have far less effect in this regard.

Electromagnetic phenomena might well have significant effect on the efficiency of the lithographic process as determined by preferential wetting of the critical surfaces.

Inks with a guaranteed quantity of emulsified water, (pre-emulsified) maintaining equilibrium emulsification curves, would appear to greatly improve the efficiency of the lithographic printing process and to be generally far superior to inks whose degree of emulsification at the moment of printing depends on accidential circumstances.

Definition of Terms

$W + O \rightleftarrows W/O$: press interaction between ds and ink

$P = \frac{P_+}{P_-}$: emulsification test interaction between ds and ink

P_+ : vector determining emulsion build-up

P_- : vector determining emulsion break

P_A : $P_+ \gg P_-$, b_{max} large, $a \gg 10$

P_B : $P_+ > P_-$, $a > 10$

P_C : $P_+ > \rightarrow = P_-, a \sim 5$

P_D : $P_+ > \rightarrow = P_-, a \ll 5$

P_E : $P_+ \geq P_-$, b_{max} small

P_F : $P_+ > P_- \rightarrow P_+ < P_-$ (possible suffix to the other curves)

(a,b) : emulsification test equilibrium point ($P_+ = P_-$)

b_{max} : maximal emulsification during the emulsification test

(a_x,b_y) : Laray emulsion break point; the last point with increased yield value

V : Laray viscosity, poises at 2500 $sec.^{-1}$

Y : Laray yield value, $dynes/cm^2$ at 2.5 $sec.^{-1}$

Materials used: inks : 91, 4, RT, 39, 6 (News Blacks)

ds : dampening water: A acidic, B neutral, C, D, and E alkaline

Heat of vaporization : 540 cal./g

Definition of Terms - Continued

thermal capacities, cal./g/°C :

$$\begin{aligned}&\text{ink} \sim .4\\ &\text{ds} \sim 1.0\\ &\text{steel} \sim .107\end{aligned}$$

$E_s = \frac{a_x \times b_y}{a \times b}$; $\frac{\text{Laray emulsion stability area}}{\text{Emulsification test emulsion stability area}}$

$$F_s = \frac{V(a_x, b_y) \times Y_{(0,0)}}{Y(a_x, b_y) \times V_{(0,0)}}$$

k : electrical conductivity of ds in mho/cm x 10^3

$P' = E_s \times F_s \times (a \times b)$: ink performance parameter

f : model cube dimension

$n = \frac{c}{4\ b\ 2}$ = number of filaments in model cube (Figure 17)

$b_n = \frac{1}{2n^{\frac{1}{2}}}$ = the horizontal cavity axes in the model cube

f' : Inkometer rib spacing, mm at 2 minutes

$n' = \frac{10^3}{(f')^{\frac{1}{2}}}$, proportional filament number (if n is a function of f')

$h = \frac{f}{2} - (\frac{f}{2}\ b_n)^{\frac{1}{2}}$: the increasing ink film thickness on the horizontal end planes in the model cube with increasing n

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