SOLVENT EVAPORATION FROM WEB OFFSET HEATSET PRINTS II--A STUDY OF IMPORTANT VARIABLES

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Abstract: It was recently demonstrated that a thermogravimetric analyzer could be modified to model the function of a web offset heatset drying oven.[1] Given that this technique could potentially be very useful, a study was made of some of the variables that may be important in solvent retention. The effect of these variables on weight loss was examined. Some of the variables studied included heating rate, final temperature, solvent composition, ink color, and resin composition. The data collected to date indicates very little dependence of solvent loss on heating rate. This was surprising and possible explanations are currently being investigated. A dependence of solvent loss on final temperature is indicated. Not surprisingly, studies on a sample containing soybean oil showed a large effect on solvent evaporation. An effect on solvent retention is also observed with high boiling hydrocarbon distillate cuts. Solvent retention shows no dependence on ink color.

INTRODUCTION

A lot of attention has recently been paid to the quantities of hydrocarbon solvents retained in ink films. This is due to recent environmental legislation and concerns voiced by the Environmental Protection Agency (EPA). These concerns are not limited to one type of ink but to any ink containing low-boiling, organic solvents which may be potential VOCs (volatile organic compounds). Ink manufacturers have been attempting to reduce VOCs in their inks, in response to this

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legislation by either developing inks with less solvent or by using high-boiling, low-VOC (or no VOC) solvents such as soya oil. As a result of this legislation and the EPA concerns, a large amount of work aimed at trying to determine the quantities of solvents retained in ink films has recently begun. Techniques used to study solvent evaporation vary from oven tests on thick films in aluminum pans, to tests done on thin films on paper in a thermogravimetric analyzer (TGA). Solvent extractions of actual prints run on a press and then subsequent analysis of the prints is also being used to determine the quantity of retained solvents. All of these techniques have some problems associated with them. A technique utilizing the TGA has been chosen for this work since the problems associated with using this instrument are minor compared to the problems encountered with the other techniques. Therefore, the problems associated with using the TGA are more easily addressable.

Although there is interest in determining retained solvents in different types of inks, the discussion in this paper is limited to web offset heatset inks. Previous estimates of retained solvent concentrations vary. An EPA Guideline Series report estimated that 50% of the total ink solvent present was retained on the web after printing.[2] The solvent, which is usually a hydrocarbon distillate cut with a boiling range of approximately 450° - 520° F, typically constitutes about 30% of the total ink by weight. Another early study estimated that only 6-7% of the solvent originally present in the system was retained on the web.[3] A study which I reported last year estimated that 20-25% of the solvent originally present was retained in the ink film.[1] This value may be highly dependent on several variables. This study was meant to address some of these variables and to determine whether any dependence of solvent retention or solvent evaporation on these variables is observed.

The object of this study is to determine the dependence of solvent evaporation or retention on the variables of interest. The quantity of solvent retained in an ink film on the substrate was determined under varying conditions. When possible, conditions approaching those observed on a WOHS press were utilized. The substrate used for all experiments in this report was aluminum foil.

In this paper, free solvent refers to volatiles in an ink which can evaporate, and does not include solvent which appears to be permanently trapped in the ink film. The trapped solvent may have a very low vapor pressure due to Raoult's Law. The total solvent in an ink refers to all of the volatiles present in the ink including the solvent which may be trapped.

Results indicate that there is no dependence of weight loss on ink color. Resin composition, however, does effect the amount of weight lost. Likewise, solvent composition effects weight loss, as one would expect. A somewhat surprising observation was that different heating rates have no effect on the quantity of weight lost or the amount of retained solvent. Weight loss data at heating rates below 100° C/min were imprecise. Final temperature does effect the amount of weight lost as expected. The dependence of weight loss on these variables will be explored more fully in the following sections.

EXPERIMENTAL

The solvents used in the following studies include Magiesol 47 oil, Magiesol 52 oil, and Soya Oil. The Magiesol solvents were obtained from Magie Bros. Oil Company. The Magiesol 47 oil is a hydrocarbon distillate cut whose components have boiling points between 464° and 520° F. Likewise, the Magiesol 52 is also a hydrocarbon distillate cut, but the boiling points of its components are between 520° and 580° F.

The resins used in the resin composition study included Lawter UR-185 phenolic modified rosin ester, Neville LX1082-280 hydrocarbon resin, and Akzo Filtrez 360 Maleic modified rosin ester.

The inks used were standard web offset heatset inks produced internally. The inks were emulsified with a two-part fountain solution using a model 134-1

VWR variable speed electric stirrer.

Thermogravimetric analyses were done on either a DuPont model 951 thermogravimetric analyzer or a modified DuPont model 951 thermogravimetric analyzer. The TGA is interfaced to an IBM PS/2 model 60 microcomputer using DuPont Thermal Analyst 2000 software which collects and processes the data.

RESULTS AND DISCUSSION

The ink used for this study was a web offset heatset (WOHS) magenta which was approximately 30% solvent and emulsified with approximately 30% water. The TGA consists of a furnace a microbalance, and associated electronics. The instrument measures weight loss as a function of temperature. The values reported in this paper are the percent weight lost relative to the total emulsified ink weight. Any values reported for solvent retention will assume that approximately 65% of the weight lost will be due to water and the other 35% will be ink solvent. This is the approximate value observed in our previous work.[1]

One of the variables studied was final temperature. The weight loss at several final temperatures in the range of interest was examined. The results are shown in Figure 1. A tabulation of the results is shown in Table 1

TABLE 1

WEIGHT LOSS	FINAL TEMPERATURE
27.8% ± 3.5	100° C
38.1% ± 3.3	125° C
38.9% ± 8.8	150° C
46.6% ± 3.9	175° C
55.6% ± 21.4	200° C

Table 1--Solvent loss values and standard deviations for dependence on final temperature.

along with the standard deviations. The samples were heated at rates such that the same amount of time elapsed before each sample reached its final temperature. The values were fitted to both

FIGURE 1

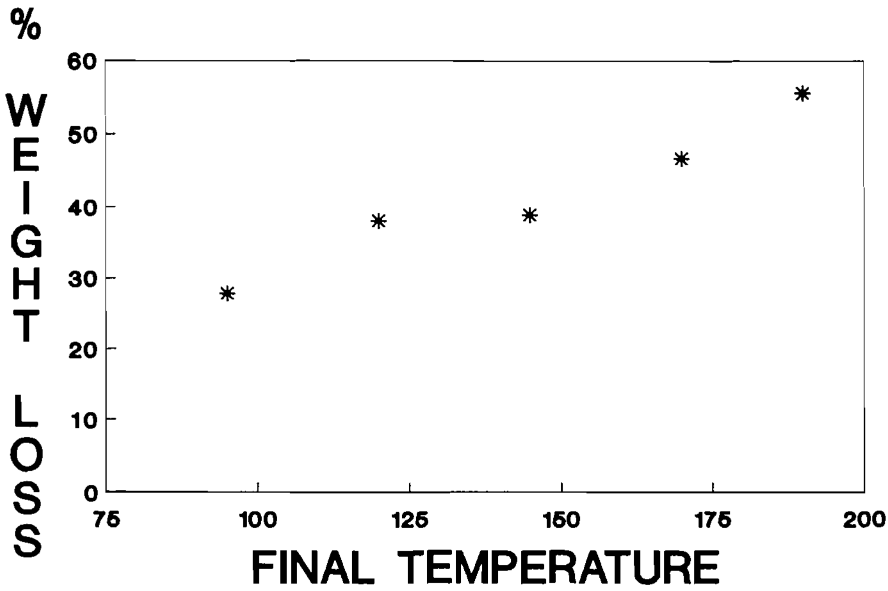

Figure 1--Dependence of solvent loss on final temperature.

TABLE 2

		Avg. % Deviation
EXPONENTIAL:	$Y = 15.5 * EXP(6.62x10^{-3}X)$	4.7%
LINEAR:	$Y = 0.266X + 3.11$	4.9%

Table 2--Equations and % deviations for lines which best fit final temperature dependence of solvent loss results.

exponential and linear curves. The results are shown in Table 2 along with the equation for the line. These two equations provided the best fit to the data. All corrected data in the rest of this report will be normalized to 150° C using the above results. This allows for comparisons between samples whose only difference is their final temperature. Values obtained by fitting data to both of the above equations were typically very similar and well within experimental error. The dependence of weight loss on final temperature under press conditions is very important to know. The conditions used in this report are similar to those observed on a press in most cases.

Another factor studied was heating rate. The results of examining the dependence of weight loss on heating rate were surprising. No dependence of weight loss on heating rate was observed. The results which were not corrected for final temperature are shown in Figure 2, while the

FIGURE 2

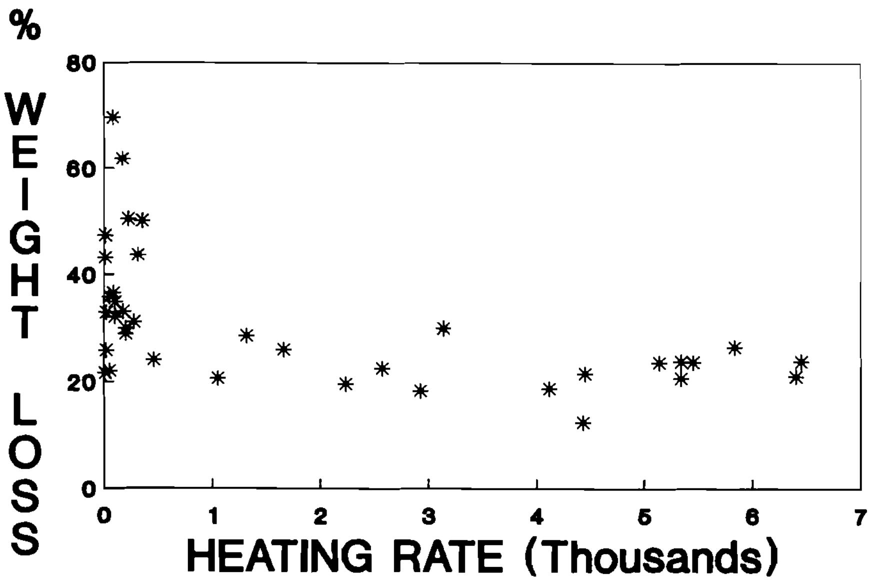

Figure 2--Dependence of solvent loss on heating rate without correcting for final temperature.

results corrected for final temperature using the linear equation are shown in Figure 3. Averages of the weight loss values over different temperature ranges for both the corrected and uncorrected weight losses are shown in Table 3 along with the standard deviation of the data. These results may indicate that limited solvent diffusion through the

FIGURE 3

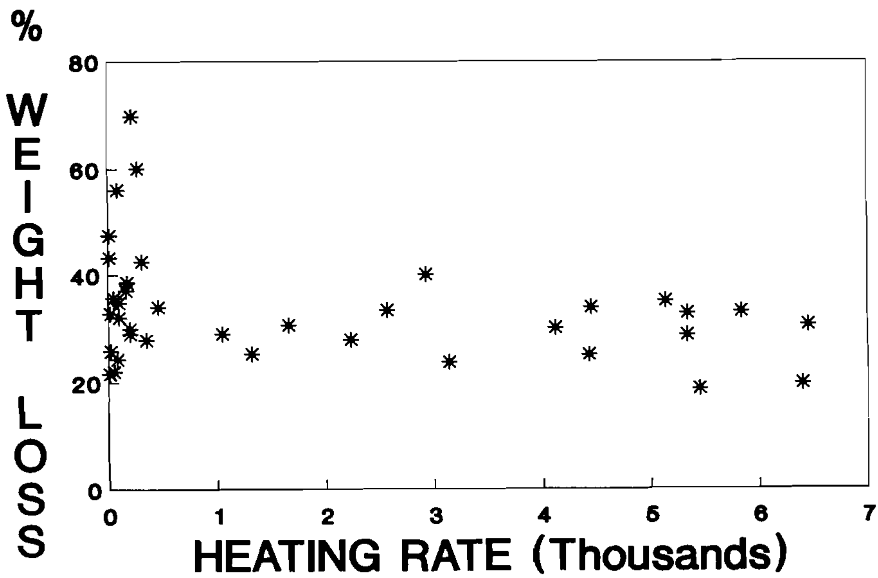

Figure 3--Dependence of solvent loss on heating rate after correcting for final temperature using the linear equation.

ink film is not important at the heating rates studied. The highest heating rates used are still 3000°-4000° C/min slower than the heating rates experienced on a fast WOHS press. Therefore, on the press diffusion of solvent through the ink film may be important. However, given the results of previous work, diffusion does not seem to be a factor at press heating rates.[1] Most of the experiments at high heating rates had final temperatures greater than 150° C. This is obvious from the above statistics. A decrease in percent volatiles in the temperature corrected data is seen.

Another variable examined was resin composition. Several varnishes were made containing just resin and solvent with a small amount of tridecyl alcohol (TDA) to enhance

TABLE 3

Uncorrected	
$T < 100°$ C	34.3% ± 12.3
$T \geq 100°$ C	35.8% ± 6.0
$100°$ C $\leq T \leq 4000°$ C	35.6% ± 5.2
$100°$ C $\leq T \leq 5000°$ C	35.3% ± 5.6
Corrected (Linear)	
$T < 100°$ C	34.3% ± 12.3
$T \geq 100°$ C	31.6% ± 6.6
$100°$ C $\leq T \leq 4000°$ C	32.7% ± 6.4
$100°$ C $\leq T \leq 5000°$ C	33.2% ± 6.7
Corrected (Exponential)	
$T < 100°$ C	34.3% ± 12.3
$T \geq 100°$ C	30.7% ± 7.0
$100°$ C $\leq T \leq 4000°$ C	32.0% ± 6.8
$100°$ C $\leq T \leq 5000°$ C	32.8% ± 7.0

Table 3--Weight loss values and standard deviations for select temperature ranges for heating rate dependence of solvent loss studies.

dissolution of the resin in the solvent. Three resins were studied, a phenolic modified rosin ester, a maleic modified rosin ester, and a hydrocarbon resin. All three were dissolved in Magiesol 47 oil and the TDA. The ingredients of all three varnishes were combined in the following proportions: 50% resin, 45% Magiesol 47 oil, and 5% TDA by weight.

The results of the weight loss experiments are shown in Figure 4 for both the temperature corrected (linear) and uncorrected results. The weight losses from the phenolic and maleic varnishes were within experimental error identical. The weight loss from the hydrocarbon resin was much lower. The weight losses and standard deviations for the various resin solutions are shown in Table 4. The data shows that the phenolic and maleic resins release solvent more easily than the hydrocarbon resin. Given these results, we can conclude that the higher the concentration of

FIGURE 4

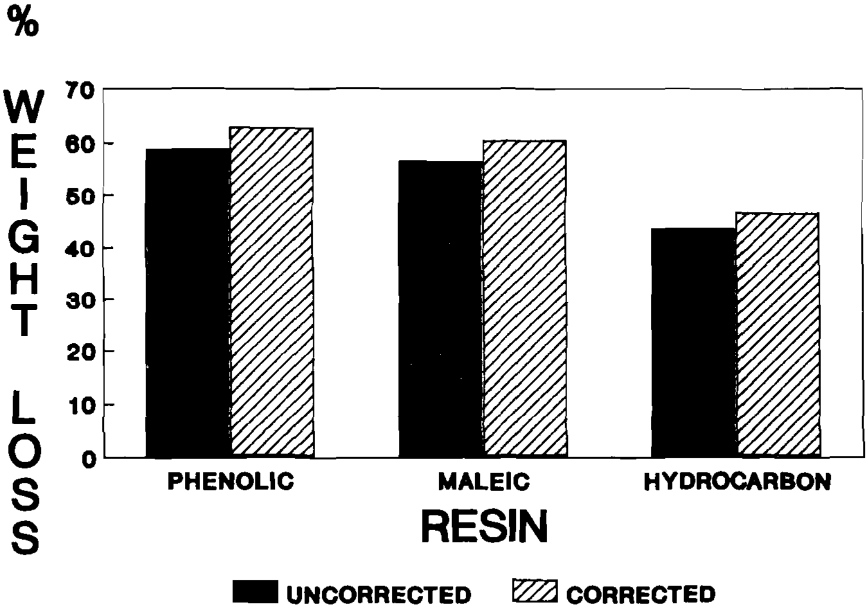

Figure 4--Affect on weight loss of resin composition.

TABLE 4

Uncorrected

Resin	% Weight Loss
Phenolic	58.9% ± 1.6
Maleic	56.6% ± 4.5
Hydrocarbon	43.5% ± 8.6

Corrected

Resin	% Weight Loss
Phenolic	52.6% ± 1.7
Maleic	60.2% ± 4.7
Hydrocarbon	46.4% ± 9.1

Table 4--Values for weight loss and standard deviation as resin composition is varied.

hydrocarbon resin in an ink, the more solvent will be retained. More work needs to be done before these results can be confidently applied to inks. Making the samples more "ink like" and studying combinations of resins would be very useful. This work is in progress.

The next variable studied was solvent composition. Three solvents were examined, Magiesol 47, Magiesol 52, and soya oil. Again, varnishes utilizing each of the three oils were prepared. The resin used in each of the varnishes was the same maleic modified rosin ester used above. The concentrations used were the same as above: 50% resin, 45% solvent, and 5% TDA by weight.

The weight loss results are shown in Figure 5

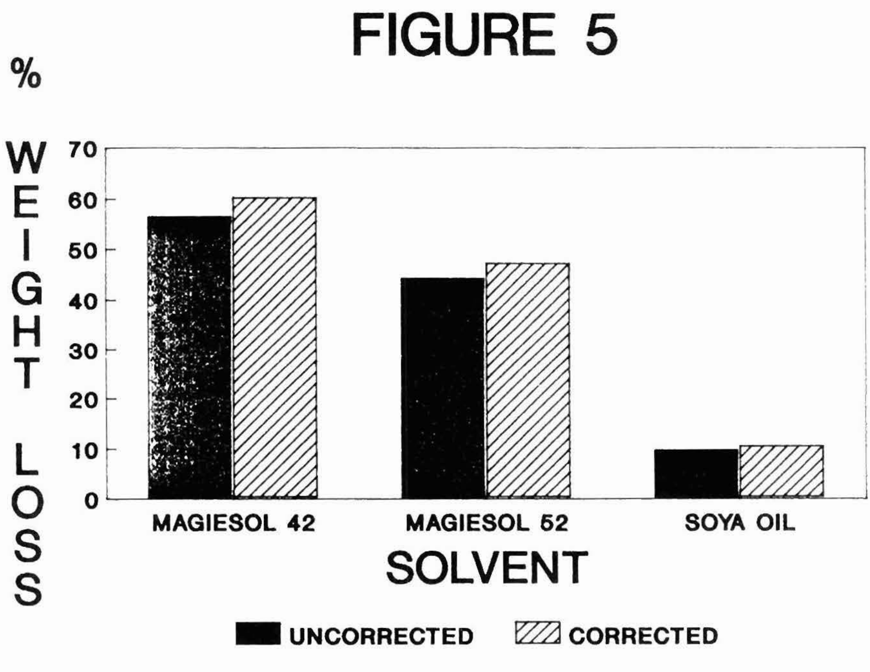

Figure 5--Weight loss as a function of solvent composition.

for the temperature corrected (linear) and uncorrected data. The temperature corrected data utilized the linear equation. The individual values with the standard deviations are shown in Table 5. A weight loss of greater than 50% is observed for the varnish made with the Magiesol 47. Obviously, either some resin components which had not fully reacted are volatilizing, the resin is cracking, or both are occurring. The quantity of resin volatilizing could be estimated from the soya oil weight loss. If we assume that no soya components evaporate and that all of the TDA present does evaporate, the weight loss greater than 5% (from TDA) will be due to the resin. Using the above assumptions and the soya oil varnish weight loss results, approximately 5.5% of the weight loss is due to resin components. Using the above data for solvent loss and given a solvent or

TABLE 5

Uncorrected

Solvent	% Weight Loss
Magiesol 47	56.6% ± 4.5
Magiesol 52	44.3% ± 9.3
Soya Oil	9.80% ± 5.9

Corrected

Solvent	% Weight Loss
Magiesol 47	60.2% ± 4.7
Magiesol 52	47.1% ± 9.9
Soya Oil	10.5% ± 6.3

Table 5--Weight loss values and standard deviations when solvent compostion is changed.

solvent mixture with a known boiling range, a solvent loss can be estimated. More work to make sure that this data can be applied to inks with confidence needs to be done. This future work includes making a series of samples containing pigments and other typical heatset ink components in concentrations similar to those observed in inks. Again, samples which are more "ink like" and which contain solvent mixtures should be studied. This work is in progress.

Weight loss as a function of ink color was also studied to determine whether the lighter colors like yellow reflected more heat and thus retained more solvent. The results are shown in Figure 6 and in Table 6. It is obvious from the

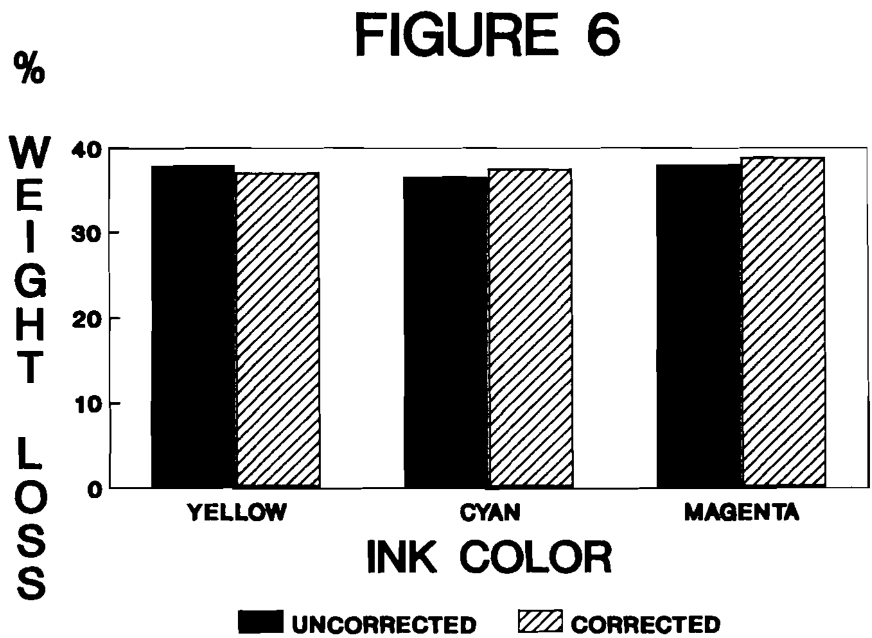

Figure 6--Dependence of weight loss on ink color.

results that no differences (within experimental error) in weight loss exist between different colors. The inks used were similar except for the pigment. The amount of emulsified fountain solution in each was approximately 30%.

The effect of cooling rate on solvent weight loss was also examined. There was no observed dependence at the rates used. The cooling rates used varied from approximately 100° C/min. to approximately 300° C/min.

CONCLUSION

This study could be of importance for printers

TABLE 6

Uncorrected

Color	% Weight Loss
Magenta	38.0% ± 11.5
Cyan	36.6% ± 8.0
Yellow	37.9% ± 10.9

Corrected

Color	% Weight Loss
Magenta	38.8% ± 14.2
Cyan	37.5% ± 3.3
Yellow	37.0% ± 12.6

Table 6--Weight loss values and standard deviations for different ink colors.

and manufacturers of printing equipment, especially given the increasing concern over solvent emissions. The conditions used closely model those observed on a printing press. If we assume that the proportion of water lost to solvent lost is 65% water to 35% solvent, the above results indicate that approximately 20-25% of the ink solvent originally present is retained in the ink film after the sample is heated to 150° C, regardless of the heating rate. This non-dependence on heating rate is important because it implies that no kinetic limitations (i.e. slow diffusion) are present at the heating rates used. The heating rates observed on printing presses are slightly higher than those used in this study, but given the results of previous work, this non-dependence on heating rate appears to also hold at WOHS press dryer heating rates.[1]

The results of the solvent dependence tests, although expected, may still have some limited usefulness for predicting solvent weight losses as a function of solvent boiling point. Likewise, the resin dependence studies may have some limited usefulness for weight loss predictions. Both of these studies will be more useful as more experiments are done using systems which more closely resemble true WOHS inks.

Some doubt had existed on whether different ink colors influence solvent loss. The results in this paper indicate that solvent color does not influence solvent loss.

Future work will include measuring solvent losses on various papers and further exploring resin and solvent dependence on more "ink-like" systems. Other variables studied will include amount of emulsification and gaseous environment (O_2 vs. N_2), in order to examine the effects of oxidation. This work could also be expanded to include other types of heatset inks.

This technique is very useful for modeling ink volatility on a WOHS press. The technique, given the above results, could now be considered routine, since modifications to obtain high heating rates are no longer required. This technique can be accurate and inks can be evaluated quickly. These advantages make this a very desirable and sensible technique. This technique may help printers determine how to maximize solvent evaporation in the oven in order to have less retained solvent, or it may help ink manufacturers make inks with fewer VOCs to make it easier for printers to meet government specifications. Comparisons to oven test methods such as EPA method 24 will eventually be made to determine the validity of using such oven test.

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