Comparisons of Volatile Organic Chemical Content of News, Sheetfed, and Heatset Ink Formulations

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ABSTRACT: Volatile organic compound (VOC) contents of news, sheetfed, and heatset inks were evaluated by using different methods, and comparison of data with significant differences is reported. Environmental Protection Agency (EPA) Method 24, EPA Method 24A, and Bay Area Method 30 were the methods used. Ingredients of news inks were tested with Method 24, and experimental and calculated percentage VOC values of formulated inks were compared. Along with United States Department of Agriculture's 100% vegetable oil-based inks, commercial vegetable oil-based, and petroleum-based inks were used for comparison. Significant differences between methods, colors, and sources are discussed.

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KEY WORDS: Heatset ink, news ink, petroleum resin, sheetfed ink, vegetable oil, volatile content.

In the ink industry, a volatile organic compound (VOC) is defined as any organic material in an ink that will "eventually evaporate from the ink, regardless of the time it takes to evaporate." In this study, the following major types of news, sheetfed, and heatset inks were evaluated for VOC: (i) commercial petroleum-based news ink (1); (ii) Newspaper Association of America (NAA) hybrid soy oil-based news ink (2); (iii) United States Department of Agriculture (USDA) 100% soy oil-based news ink (3); (iv) USDA's soy oil-based sheetfed and heatset inks (4,5), (v) commercial soy oil-based sheetfed and heatset inks; and (vi) commercial petroleum-based sheetfed and heatset inks. VOC analyses of news ink and sheetfed inks were done by using United States Environmental Protection Agency (EPA) Method 24 (ASTM D2369-92), EPA Method 24A (ASTM D2369-92), and Bay Area Method 30 (ASTM D5328-92) (6). Method 24 was used to test the heatset ink samples. Here we report the comparison of results from different methods and the overall evaluation of these results.

EXPERIMENTAL PROCEDURES

A sample of each ink was heated under controlled conditions, and the amount of weight loss was measured by the difference in weight before and after heating. The most commonly used test method is EPA Method 24. This method specifies heating the sample at 110°C for 1 h in a forced air oven. Method 24A specifies a test condition of 120°C for 4 h under partial vacuum (~510 mm Hg) or 120°C for 24 h in a forced-air oven. Bay Area Method 30 specifies heating the sample at 40°C for 1 h in a forced-air oven. In addition to using Method 24, ingredients of inks were tested and percentages of VOC values for inks were calculated for comparison. Experiments were done in triplicate on three different days.

News ink vehicles included alkali-refined soybean oil (obtained from Archer Daniels Midland, Decatur, IL), USDA soy news ink vehicle (Gardner-Holdt viscosity of W-X) (7), NAA hybrid soy oil news ink vehicle (2) [prepared at National Center for Agricultural Utilization Research (NCAUR)], and commercial news ink vehicle (1) (prepared at NCAUR). Inks were formulated by mixing each of (i) USDA soy news ink vehicle (Gardner-Holdt viscosity of W-X) (7) and (ii) NAA hybrid soy oil news ink vehicle (2) and National Association of Printing Ink Manufacturers (NAPIM) commercial petroleum news ink vehicle (1) with 18, 25, 27, and 9% by weight of black, yellow, red, and blue pigment, respectively.

Sheetfed ink samples included three USDA soy-based sheetfed inks (USDA I, II, and III), formulated with USDA's soy-based vehicle (1) and carbon black 400R, Kerley Soy 40, and Kerley 40$^+$, respectively; soy-based commercial sheetfed ink (Commercial I) and petroleum-based commercial sheetfed ink (Commercial II, III) from two different manufacturers; two USDA soy-based heatset inks (USDA I, II) formulated with USDA's soy-based vehicle (4) and carbon black 250R and Super 36, respectively, and soy-based commercial heatset inks (Commercial I, II) and commercial petroleum-based (Commercial III, IV) heatset inks from two different manufacturers.

Carbon black (Elftex 8, Regal 250, and Regal 400) was obtained from Cabot Co. (Boston, MA). Carbon black dispersions (Kerley Soy 40, Kerley 40$^+$, and Kerley Super 36) were obtained from Kerley Ink (Broadview, IL). Sunbrite Yellow AAA (Sun 273-3556), Lithol Red (Sun 210-4200), Lithol Rubine (Sun 2219-0688), and Blue 15 (Sun 249-2083) were purchased from Sun Chemical Co. (Cincinnati, OH). Pigment and vehicle were mixed with a Shar High Speed Dispenser (Fort Wayne, IN) Model D-10P, at 2500 rpm for one-half hour. Also, the pigments were mixed with alkali-refined soybean oil (obtained from Archer Daniels Midland) with a magnetic stirrer in a beaker for 1 h. Dispersion of the pigments

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TABLE 1
Percentage Volatile Organic Compounds (VOC) Analysis of News

Color and vehicle	Method used				
	EPA Method 24[b]		EPA Method 24A[c]		Bay Area Method 30[h]
	Experimental[d]	Calculated[e]	I[f]	II[g]	
Black					
USDA[i]	0.1b	0.1b	2.1	0.1b	0.0b
NAA[j]	0.4b	0.4b	1.8a	0.4b	0.0b
NAPIM[k]	19.2c	21.1b	23.9a	21.3b	5.0d
Blue					
USDA	0.0b	0.0b	1.7a	0.0b	0.0b
NAA	0.6b	0.5b	1.6a	0.0c	0.0c
NAPIM	23.4c	23.3c	28.1	24.5b	6.1d
Red					
USDA	0.2b	0.2b	3.0a	0.2b	0.0b
NAA	0.6c	1.2b	3.0a	0.6c	0.0d
NAPIM	19.1c	19.2c	24.2a	20.6b	5.4d
Yellow					
USDA	0.0b	0.0b	1.2a	0.0b	0.0b
NAA	0.1b	0.3b	1.6a	0.0b	0.0b
NAPIM	18.3c	18.0c	21.5a	19.4b	4.6d

[a]Means within a row followed by a different roman letter are different ($P < 0.05$) based on least squares mean separation.
[b]ASTM D-2369-92 (Ref. 6).
[c]ASTM D-2369-92 (Ref. 6).
[d]Ink formulation tested for VOC.
[e]Ink ingredients tested and ink VOC calculated.
[f]Forced-air oven, 120°C, 24 h.
[g]Vacuum oven, 120°C, 4 h.
[h]ASTM D-5328-92 (Ref. 6).
[i]United States Department of Agriculture (Ref. 4).
[j]Newspaper Association of America (Ref. 2).
[k]National Association of Printing Ink Manufacturers (Ref. 1).

was completed with a water-cooled three-roll mill (Brazington, NY).

The experimental design was a completely random design with replications. The data were analyzed with an analysis of variance for the factors method, source, and color and all possible interactions. The dependent-measured variable was percentage of VOC. Least squares mean separation was used for comparisons when resulting significant *F*-test statistics were obtained at the 5% level.

RESULTS AND DISCUSSION

Table 1 shows the average percentage VOC of black, blue, red, and yellow news inks and significant differences at the 5% level. Results from three different methods (EPA Method 24, EPA Method 24A, and Bay Area Method 30) were tabulated. Ingredients of ink were tested with Method 24 (6), and experimental and calculated percentage VOC values of formulated inks are given in Table 1 for comparison. In general, the 24A-I Method showed more percentage VOC for all colors and sources, and Bay Area Method 30 produced the least percentage VOC. Tables 2, 3, and 4 tabulate the overall means of percentage VOC analysis of news inks by different method, color, and source, respectively.

Overall, Method 30 showed the least amount of VOC, followed by the Calc. Method, and Methods 24A-III and 24A-I, respectively. For colors, Yellow had the lowest percentage VOC, and Blue had the highest, while Red and Black were intermediate and similar to each other. The NAA and USDA inks had less percentage VOC than the NAPIM.

Table 5 shows the average percentage VOC of the commercial and USDA's black sheetfed inks. Results were tabulated from three different methods: EPA Method 24, EPA Method 24A, and Bay Area Method 30. EPA Method 24 is the more widely used, but the other methods were tested for comparison.

TABLE 2
Overall Percentage VOC Analysis of News Inks by Different Methods[a]

Method	Mean percentage VOC
EPA Method 24 (exp)[b]	7.0c
EPA Method 24 (calc)[c]	6.8d
EPA Method 24A-I[d]	9.5a
EPA Method 24A-II[e]	7.3b
Bay Area Method 30[f]	1.8e

[a]Means within a column followed by a different roman letter are different ($P < 0.05$) based on least squares mean separation. EPA, Environmental Protection Agency. See Table 1 for other abbreviation.
[b]Ink formulation tested for VOC (ASTM D-2369-92).
[c]Ink ingredients tested and ink VOC calculated (ASTM D-2369-92).
[d]ASTM D-2369-92 (120°C, 24 h, forced-air oven) (Ref. 6).
[e]ASTM D-2369-92 (120°C, 4 h, vacuum oven) (Ref. 6).
[f]ASTM D-5328-92 (Ref. 6).

TABLE 3
Overall Percentage VOC Analysis of News Inks by Different Colors[a]

Color	Mean percentage VOC
Blue	7.3a
Red	6.5b
Black	6.4b
Yellow	5.7c

[a]Means within a column followed by a different letter are different ($P < 0.05$) based on least squares mean separation. See Table 1 for abbreviation.

TABLE 4
Overall Percentage VOC Analysis of News Inks by Different Sources[a]

Source	Mean percentage VOC
NAPIM	18.3a
NAA	0.7b
USDA	0.4c

[a]Means within a column followed by a different letter are different ($P < 0.05$) based on least squares mean separation. See Table 1 for abbreviations and sources.

TABLE 5
Percentage VOC Analysis of Sheetfed Inks

	Percentage VOC[a]			
		EPA Method 24A[c]		
Ink	EPA Method 24[b]	I[d]	II[e]	Bay Area Method 30[f]
USDA I[g]	1.8e	6.9e	2.5e	0.8b
USDA II[g]	2.6e	6.8e	2.7e	0.9b
USDA III[g]	5.2d	9.9d	7.3d	1.3b
Commerical I[h]	14.6c	23.7c	21.5c	1.3b
Commerical II[i]	22.9a	27.0b	24.9b	2.0b
Commerical III[i]	19.7b	29.2a	28.7a	4.0a

[a]Means within a column followed by a different roman letter are different ($P < 0.05$) based on least squares mean separation. See Table 1 for abbreviations.
[b]ASTM D-2369-92 (Ref. 6).
[c]ASTM D-2369-92 (Ref. 6).
[d]Forced-air oven, 120°C, 24 h.
[e]Vacuum oven, 120°C, 4 h.
[f]ASTM D-5328-92 (Ref. 6).
[g]USDA I, II, III—Sheetfed ink formulations with 400R, Kerley Soy 40, and Kerley Soy 40$^+$ (Ref. 1), respectively.
[h]Commercial sheetfed ink, soy-based.
[i]Commercial sheetfed ink, petroleum-based, from two different manufacturers.

Tables 6 and 7 tabulate the overall means of percentage VOC analysis of sheetfed inks by different methods and sources, respectively. Overall, Method 30 had the least amount of VOC, followed by EPA Methods 24, 24A-II (120°C, 4 h, vacuum oven), and 24A-I (120°C, 24 h, forced-air oven) ($P \leq 0.05$). Commercial III contained the most VOC, followed by Commercial II and I, whereas USDA III, II, and I contained significantly less VOC than the commercial sources ($P \leq 0.05$). Table 8 shows the average percentage VOC of the commercial and USDA's black heatset inks. From least to greatest VOC, the inks ranked USDA I < USDA II < Commercial III < Commercial IV < Commercial I < Commercial II.

TABLE 6
Means of Percentage VOC Analysis of Sheetfed Inks by Different Methods[a]

Method	Mean percentage VOC
EPA Method 24[b]	11.1c
EPA Method 24A-I[c]	17.3a
EPA Method 24A-II[d]	14.6b
Bay Area Method 30[e]	1.7d

[a]Means within a column followed by a different letter are different ($P < 0.05$) based on least squares mean separation. See Table 1 for abbreviations.
[b]ASTM D-2369-92 (Ref. 6).
[c]ASTM D-2369-92 (120°C, 24 h, forced-air oven) (Ref. 6).
[d]ASTM D-2369-92 (120°C, 4 h, vacuum oven) (Ref. 6).
[e]ASTM D-5328-92 (Ref. 6).

TABLE 7
Means of Percentage VOC Analysis of Sheetfed Inks by Different Sources[a]

Source	Mean percentage VOC
USDA I[b]	3.0e
USDA II[b]	3.3e
USDA III[b]	6.0d
Commercial I[c]	15.3c
Commercial II[d]	19.2b
Commercial III[d]	20.4a

[a]Means within a column followed by a different letter are different ($P < 0.05$) based on least squares mean separation. See Table 1 for abbreviations.
[b]USDA I, II, III—sheetfed ink formulations with 400R, Kerley Soy 40, and Kerley 40$^+$ (Ref. 1), respectively.
[c]Commercial sheetfed ink, soy-based.
[d]Commercial sheetfed ink, petroleum-based, from two different manufacturers.

TABLE 8
Means of Percentage VOC Analysis of Heatset Inks by Different Sources[a]

Source	Mean percentage VOC
USDA I[b]	1.3f
USDA II[b]	8.6e
Commercial I[c]	32.0b
Commercial II[c]	35.2a
Commercial III[d]	28.4d
Commercial IV[d]	30.7c

[a]Means within column followed by a different letter are different ($P < 0.05$) based on least squares mean separation. See Table 1 for abbreviations
[b]USDA I, II—heatset ink formulations with 250R and Super 36 (Ref. 1), respectively.
[c]Commercial heatset ink, soy-based, from two different manufacturers.
[d]Commercial heatset ink, petroleum-based, from two different manufacturers.

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