ENVIRONMENTAL ASPECTS OF VEGETABLE OIL-BASED LITHOGRAPHIC NEWS INKS

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Abstract: Lithographic news inks were evaluated for their potential biodegradation with Gravimetric method (using mixed cultures of soil microorganisms) and the "Modified Sturm Test" (using activated sludge). Commercial news inks consisting of vehicles prepared with petroleum resin base and either mineral oil or vegetable oil solvents were used for comparison. Results of both methods showed that the USDA inks degraded faster and more completely than either of the petroleum resin-based commercial inks. Also comparison of deinking properties and analysis of volatile organic compounds showed the superior environmental properties of the vegetable oil based inks over petroleum resin-based inks.

Introduction

The major environmental properties of printing inks are biodegradability, emission of volatile organic compounds (VOC) and deinkability. In our previous studies (Erhan and Bagby, 1993, 1994, 1995) three types of news ink vehicles, (a) commercial petroleum-based (Flick, 1985), (b) Newspaper

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Association of America (NAA, formerly the American Newspaper Publishers Association, ANPA), hybrid soy oil-based (ANPA, 1988), (c) United States Department of Agriculture (USDA) 100% soy oil-based (Erhan and Bagby, 1991), were evaluated for biodegradation. In the Gravimetric method, microorganisms that are commonly found in soil [Aspergillus fumigatus (NRRL 163), Penicillium citrinum (NRRL 1843) and Mucor racemosus (NRRL 5281)] were used (Erhan and Bagby, 1993). To evaluate the effect of pigments on news ink vehicle degradation, four colored inks (black, blue, yellow and red) formulated with the above three vehicles were degraded using the same microorganisms (Erhan and Bagby, 1994). Also the same formulations were degraded using the "Modified Sturm Test" (Organization for Economic Cooperation and Development) (OECD, 1981). In this method, test organisms were obtained from activated sludge, and the extent of degradation was determined by measuring carbon dioxide evolution.

In this paper we report results of our recent volatile organic compound (VOC) analysis study of the above mentioned news inks. In the ink industry, VOC is defined as any organic material in an ink which will "eventually evaporate from the ink, regardless of time it takes to evaporate." The 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) are the three major methods used for VOC emission evaluation of printing inks. Comparison of results from different methods will be made.

We also summarize the results of deinkability studies conducted at Western Michigan University, Kalamazoo, Michigan (Rosinski, 1995). The recycling of both pre-consumer and post-consumer recovered paper is on the rise. The success of many paper

recycling efforts depends on the "deinkability" of the printed product. USDA's 100% soy oil-based and commercial 60% soy oil based news inks were evaluated with regard to the environmental impact of the deinking process (residue), the success of the deinking and the effect of ink film aging on the process.

Experimental

Detailed information on experimental biodegradation procedures was given in our previous papers published at Technical Association of the Graphic Arts (TAGA) Technical Conference Proceedings (Erhan and Bagby, 1993, 1994 and 1995).

To test for VOC, a sample of the ink was heated under controlled conditions, and the amount of weight loss was measured by the difference of 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 hour in a forced air oven. Method 24A specifies a test condition of 120°C for 4 hours under partial vacuum (~510 mm Hg) or 120°C for 24 hours in a forced air oven. Bay Area Method 30, specifies heating the sample at 40°C for 1 hour in forced air oven. Experiments were done in triplicate on three different days. The experimental design to evaluate two soy ink formulations with respect to deinking efficiency and sludge composition can be found in the paper titled "The Aging and Deinking of Soy Printed Newsprints" (Rosinski, 1995).

Results and Discussion

Biodegradation: In the Gravimetric Method, the microorganisms consume the various substrates at markedly different rates and with different levels of completeness. After 25 days, soybean oil is nearly completely

degraded, while, USDA's 100% soy oil-based vehicle degraded 82 to 92%, commercial hybrid soy oil-based and petroleum based vehicles degraded 58 to 68% and 17 to 27%, respectively (Erhan and Bagby, 1993).

Degradation of the ink vehicles was inhibited by the presence of pigment regardless of the amount or the type of pigment. In all cases NAA's inks were affected the most, followed by the petroleum based inks. For all four colored inks, the average degradation of USDA vehicles was 45.5%, 41.9% and 42.1% greater than that for NAA vehicles and 50.9%, 54.1% and 63.7% greater than that for petroleum based vehicles at 5, 12 and 25 days of fermentation, respectively (Erhan and Bagby, 1994).

In the Modified Sturm Test, the amount of carbon dioxide (CO_2) produced by the test sample was measured and expressed as percent of the theoretical CO_2 it should have produced. Percent theoretical CO_2 (TCO_2) was calculated from the carbon content of the test compound. In this method, test samples giving ≥60% yield of TCO_2 in 28 days are regarded as readily biodegradable. If biodegradation started before day 28 but had not plateaued at day 28, the test was prolonged until the plateau is reached. In this study, the experiment was continued for 73 days and using the formula below (Eq. 1), percentage TCO_2 evolved was calculated for 3, 6, 10, 14, 28, 35, 42, 53, 63 and 73 days.

$$\% TCO_2 = \frac{\text{mg } CO_2 \text{ produced}}{\text{mg test material added in test} \times \text{mg } TCO_2/\text{mg test material}} \times 100 \quad \text{(Eq. 1)}$$

The rates of biodegradation for both NAA and petroleum inks were very slow as was observed with the Gravimetric method. Soy oil-pigment mix and USDA inks took an average of 36 and 38 days to reach 60% TCO_2 while NAA and

petroleum inks did not reach 60% TCO_2 even after 73 days. Extrapolation showed that it would take 240 days for NAA and 420 days for petroleum inks (Erhan and Bagby, 1995).

VOC Analysis: Table 1 shows the average % VOC of black, blue, red and yellow news inks. Results from three different methods namely EPA method 24, EPA method 24A, and Bay Area Method 30 were tabulated. Using method 24 ingredients of inks were tested and results are tabulated in Table 2. Experimental and calculated % VOC values of formulated inks are given in Table 1 for comparison. Results showed very good agreement. In Table 1, results obtained with method 24A, using two sets of reaction conditions are tabulated. In method 24A, samples are placed in a forced air oven at 120°C for 24 hours or a vacuum oven for 4 hours. Percent VOC's resulted from reaction conditions of 120°C, 24 hours in forced air oven were higher. The third method, Bay area method 30 resulted in the lowest % VOC for all inks tested. Overall data show that USDA's 100% soy oil-based ink showed the lowest % VOC, followed by the NAA ink. On the other hand, NAPIM's commercial petroleum based ink formula showed the highest % VOC in every color with all methods. These results once again demonstrated the advantage of using soy oil in the news ink formulations. These accepted VOC test methods are not very sensitive at low VOC levels. Additional studies are proceeding to determine if the differences between the USDA's 100% soy oil-based ink and NAA's hybrid soy oil-based ink are significant. Although we have not investigated the level of peroxidation that may have occurred with the raw soybean oil contained in the inks, it is possible that method 24A (24 hours), in particular, would give spurious results.

Deinking: The results of the study (Rosinski, 1995) are as follows:

- The aqueous wastes generated for both 100% soy and hybrid soy (60%) inks are not classified as a hazardous waste under the Resource Conservation and Recovery Act.

- Biological Oxygen Demand (BOD) was greater for the 100% soy formulation over the entire 6-month period.

- BOD continually increased over the aging period in agreement with the ink vehicle biodegradation results.

- Chemical Oxygen Demand results were similar for all samples and consistent over the 6-month period.

- Brightness of the reformed deinked paper indicates that an increase in soy oil content does not affect deinkability over the aging period.

- Image analysis indicated that USDA 100% soy ink was removed more completely than the hybrid soy ink, even after 6-months aging.

- There is no significant yield loss in either soy formulation over the 6-month time frame.

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TABLE 1. Percent Volatile Organic Compounds (VOC) Analysis of News Inks

Color and Vehicle	Method Used: EPA Method 24[a] Experimental[d]	EPA Method 24 Calculated[e]	EPA Method 24A[b] I[f]	EPA Method 24A I[g]	Bay Area Method 30[c]
Black					
USDA[h]	0.09	0.14	2.14	0.11	0.00
NAA[i]	0.38	0.38	1.80	0.40	0.00
NAPIM[j]	19.16	21.13	23.92	21.34	4.99
Blue					
USDA[h]	0.00	0.01	1.68	0.00	0.00
NAA[i]	0.63	0.53	1.46	0.00	0.00
NAPIM[j]	23.39	23.31	28.13	24.53	6.10
Red					
USDA[h]	0.16	0.19	2.98	0.17	0.00
NAA[i]	0.58	0.58	3.01	0.56	0.00
NAPIM[j]	19.08	18.88	23.36	20.58	5.37

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TABLE 1 (continued)

Color and Vehicle	Method Used: EPA Method 24[a] Experimental[d]	EPA Method 24[a] Calculated[e]	EPA Method 24A[b] I[f]	EPA Method 24A[b] I[g]	Bay Area Method 30[c]
Yellow					
USDA[h]	0.00	0.01	1.12	0.00	0.00
NAA[i]	0.07	0.35	1.15	0.00	0.00
NAPIM[j]	18.27	19.21	22.10	19.42	4.55

[a] ASTM D-2369-92. [b] ASTM D-2369. [c] ASTM D-5328-92. [d] Ink formulation tested for VOC. [e] Ink ingredients tested and ink VOC calculated. [f] 120°C, 24 hr, forced air oven. [g] 120°C, 4 hr, vacuum oven. [h] United States Department of Agriculture (Erhan and Bagby, 1991). [i] Newspaper Association of America (ANPA, 1988). [j] National Association of Printing Ink Manufacturers (Flick, 1985).

TABLE 2. % VOC Analysis of News Ink Ingredients
Using EPA Method 24

Ingredients	% VOC
Soybean oil[a]	0.00
Heat bodied soybean oil[b]	0.00
Picco Resin[c]	0.00
30% Blend of Picco Resin and soybean oil[c]	0.57
50% Blend of Picco Resin and soybean oil[c]	0.44
Magic oil (#47)[d]	100.00
EXX-Print 7220[d]	2.08
Carbon Black (Elftex 8)[e]	0.75
Blue 15[e]	0.13
Lithol Red[e]	0.40
Lithol Rubine[e]	1.05
Diarlide Yellow[e]	0.03

[a] Alkali refined soybean oil (Erhan and Bagby, 1991). [b] Gardner-Holdt Viscosity w-x (Erhan and Bagby, 1991). [c] ANPA, 1988. [d] Flick, 1985. [e] (Erhan and Bagby, 1992).