BIODEGRADATION OF NEWS INKS AND EFFECT OF PIGMENTS ON NEWS INK VEHICLE DEGRADATION

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Abstract: Commercial news inks consisting of soy or mineral oil with petroleum resins along with four colored pigments and USDA's 100% soy oil based ink consisting of modified soybean oil and pigment were subjected to biodegradation. Each ink sample was inoculated with mixed cultures of Aspergillus fumigatus, Penicillium citrinum and Mucor racemosus. Fermentations were allowed to proceed for 5, 12 and 25 days. Percent degradation, determined gravimetrically, was calculated based on vehicle. Results show that pigment slowed the degradation of ink vehicles, and neither the time nor the type of pigment played a significant role. In all cases USDA's ink degraded faster and more completely (for all four colors) than either partial soy oil based or petroleum based inks.

Introduction

The transformation of organic substances by living organisms is an important factor in determining their environmental fate. Biodegradation is the predominant mechanism for the transformation of many organic compounds in soil. After completing our study on biodegradation of news ink vehicles (Erhan

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and Bagby, 1993), knowledge of biodegradation of news inks and effect of pigments on news ink vehicle degradation are needed. In this study four colored (black, blue, yellow and red) news inks formulated with three major types of news ink vehicles; (a) commercial petroleum-based (Flick, 1985), (b) American Newspaper Publishers Association's (ANPA) partial soy oil-based (ANPA, 1988), (c) United States Department of Agriculture's (USDA) 100%, soy oil-based (Erhan and Bagby, 1991), were evaluated for biodegradation. We selected microorganisms that are commonly found in soil [Aspergillus fumigatus (NRRL 163), Penicillium citrinum (NRRL 1843) and Mucor racemosus (NRRL 5281)]. Here, we report results from that degradation study.

Experimental

Aspergillus fumigatus (NRRL 163), Penicillium citrinum (NRRL 1843) and Mucor racemosus (NRRL 5281), used in this study, were obtained from the ARS Culture Collection, National Center for Agricultural Utilization Research (NCAUR). The synthetic liquid medium used (Koritala et al., 1987) for growing microorganisms contained 2.0 g asparagine, 1.0 g dipotassium hydrogen phosphate, 0.5 g magnesium sulfate, 2.0 g dextrose, 5.0 mg thiamine hydrochloride, 1.45 mg iron (II) sulfate heptahydrate, 0.88 mg zinc sulfate heptahydrate and 0.23 mg manganese (II) sulfate monohydrate in 1000 ml of distilled water. This medium was adjusted to pH 5.7 using a solution of 1:3 phosphoric acid:water. Thiamine hydrochloride, zinc sulfate heptahydrate, magnesium sulfate, phosphoric acid and dipotassium hydrogen phosphate were obtained from Aldrich Chemical Company, Milwaukee WI. Manganese (II) sulfate monohydrate, asparagine, dextrose and iron (II) sulfate heptahydrate were obtained from Fisher Scientific Company, St. Louis, MO.

Culture medium (1000 ml) was sterilized in a 2800-ml flask by autoclaving at 120°C.

Two loopsful of microorganisms grown on yeast-malt agar slants were transferred to the sterile medium and to each flask formulated ink samples (4 g) were added. Then the flask and its contents were shaken (200 rpm) on a rotary shaker at 25°C for 5, 12 and 25 days. Duplicate and triplicate samples were inoculated with mixed cultures of above three microorganisms. The fermentations were terminated by refrigeration at 34°F.

Inks were formulated by mixing each (a) USDA soy news ink vehicle (Gardner-Holdt viscosity of w-x) (Erhan and Bagby, 1991), (b) ANPA soy oil news ink vehicle (ANPA, 1988) (prepared at NCAUR) and (c) commercial petroleum news ink vehicle (Flick, 1985) (prepared at NCAUR) with 18%, 25%, 27% and 9% by weight of black, yellow, red and blue pigment, respectively. Carbon black (Elftex 8) was obtained from Cabot Co. (Boston, MA). Sunbrite Yellow AAA (Sun 273-3556), Lithol Red (Sun 210-4200), Lithol Rubine (Sun 219-0688) and Blue 15 (Sun 249-2083) were purchased from Sun Chemical Co. (Cincinnati, OH). In the formulation of red ink 14.2% Lithol Red and 12.8% Lithol Rubine combination was used. Pigment and vehicle were mixed with a Shar High Speed Dispenser, Model D-10P, at 3000 rpm for 2 hours. Also above pigments were mixed with alkali-refined soybean oil (obtained from Archer Daniels Midland, Decatur, IL) with a magnetic stirrer in a beaker for 1 hour. These samples were used along with the ink samples for comparison. To determine residual lipid material, the fermentation broth was extracted 4 times with diethyl ether (200 ml). The combined ether extract was washed with water (800 ml) and then dried over anhydrous sodium sulfate. The ether solutions were filtered through silicone coated filter paper (obtained from Whatman Lab Sales, Hillsboro,

OR) into tared round-bottomed flasks. To assure quantitative transfer, the sodium sulfate was washed four times with ether. Then the ether was removed with a rotary evaporator, and the flasks and their contents were placed in a vacuum desiccator overnight. Recoveries were determined gravimetrically. Validity of extraction protocol efficiency was established in the absence of microorganisms.

Results and Discussion

The extent of biodegradation of the soybean oil-pigment mix and the news inks was determined by differences between that added to the fermentation and that recovered at termination. Calculations for degradations were based on content of starting vehicle in the formulated inks. Tables 1-4 shows the percent biodegradation of black, yellow, blue and red ink vehicles after 5, 12 and 25 days of fermentation with mixed cultures of Aspergillus fumigatus (NRRL 163), Penicillium citrinum (NRRL 1843) and Mucor racemosus (NRRL 5281). In all four colors degradation of vehicle was inhibited in the presence of pigment regardless of the amount or the type of pigment. In all cases ANPA's inks were effected the most, followed by commercial ink. In general (with a few exceptions) effect was decreased as the fermentation time progressed from 5 days to 25 days.

Table 5 tabulates the percent degradation for different vehicles and soybean oil (Erhan and Bagby, 1993). Comparison of biodegradation of soy oil and different vehicles with four colored inks show that in the presence of pigment for all four colors soy oil degradation was decreased an average of 11.9%, 10.3% and 2.6% during the 5, 12 and 25 days of fermentation. USDA's 100% soy oil based ink vehicles degradation was decreased 13.1%, 9.9% and 7.4% during the 5, 12 and 25 days of fermentation. Amount of decrease in

degradation observed in USDA's vehicle was very similar to soy oils for 5 and 12 days of fermentation but slightly higher for 25 days of fermentation. ANPA's vehicle degradation was dramatically lowered by the presence of pigments. The percent decrease in the vehicle degradation was 55.2%, 55.6% and 42.5% for 5, 12 and 25 days of fermentation, respectively. In the black ANPA ink, as the fermentation time progressed the effect of pigment on the vehicle degradation did not change. In the red ANPA ink effect was increased in 12 days but decreased at 25 days. The average decrease in commercial vehicle degradation in the presence of pigment was 35.2%, 36.4% and 29.4% for 5, 12 and 25 days of fermentation, respectively.

For all four colored inks, the average degradation of USDA vehicles was 45.5%, 41.9% and 42.1% greater than that for ANPA 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.

Thus, the USDA ink offers environmental advantage as well as, the other superior qualities previously described, i.e., no petroleum, less ruboff and lower cost than any commercial ink including the ANPA's partial soy oil based ink.

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TABLE 1
Percent Degradation of Black Inks and Soybean Oil-Pigment Mixture with Mixed Cultures of Microoganisms[a]

Fermentation period # of Days	Soybean oil-pigment[b]	Percent degradation		
		USDA[c]	ANPA[d]	Commercial[e]
5	81.6[f]	58.1	10.9	7.9
12	85.8	64.8	19.3	11.8
25	94.0	79.8	22.5	15.6

[a]Mixture of Aspergillus fumigatus (NRRL 163), Penicillium citrinum (NRRL 1843) and Mucor racemosus (NRRL 5281).
[b]Alkali refined soybean oil-black pigment mixture.
[c]USDA-formulated with 100% soy oil-based vehicle (Type I) (Erhan and Bagby, 1991).
[d]ANPA-formulated with partial soy oil-based vehicle (ANPA, 1988).
[e]Commercial-formulated with petroleum oil-based vehicle (Flick, 1985).
[f]Calculated based on initial weight of vehicle.

TABLE 2
Percent Degradation of Yellow Inks and Soybean Oil-Pigment Mixture with Mixed Cultures of Microoganisms[a]

Fermentation period # of Days	Soybean oil-pigment[b]	Percent degradation		
		USDA[c]	ANPA[d]	Commercial[e]
5	81.4[f]	58.4	11.4	8.3
12	84.6	64.6	27.8	11.8
25	94.6	78.3	46.2	16.6

[a]Mixture of Aspergillus fumigatus (NRRL 163), Penicillium citrinum (NRRL 1843) and Mucor racemosus (NRRL 5281).
[b]Alkali refined soybean oil-black pigment mixture.
[c]USDA-formulated with 100% soy oil-based vehicle (Type I) (Erhan and Bagby, 1991).
[d]ANPA-formulated with partial soy oil-based vehicle (ANPA, 1988).
[e]Commercial-formulated with petroleum oil-based vehicle (Flick, 1985).
[f]Calculated based on initial weight of vehicle.

TABLE 3
Percent Degradation of Blue Inks and Soybean Oil-Pigment Mixture with Mixed Cultures of Microoganisms[a]

Fermentation period # of Days	Soybean oil-pigment[b]	Percent degradation USDA[c]	ANPA[d]	Commercial[e]
5	84.4[f]	59.0	15.0	8.6
12	92.5	68.5	30.2	13.3
25	95.4	81.5	47.2	16.9

[a]Mixture of Aspergillus fumigatus (NRRL 163), Penicillium citrinum (NRRL 1843) and Mucor racemosus (NRRL 5281).
[b]Alkali refined soybean oil-black pigment mixture.
[c]USDA-formulated with 100% soy oil-based vehicle (Type I) (Erhan and Bagby, 1991).
[d]ANPA-formulated with partial soy oil-based vehicle (ANPA, 1988).
[e]Commercial-formulated with petroleum oil-based vehicle (Flick, 1985).
[f]Calculated based on initial weight of vehicle.

TABLE 4
Percent Degradation of Red Inks and Soybean Oil-Pigment Mixture with Mixed Cultures of Microoganisms[a]

Fermentation period # of Days	Soybean oil-pigment[b]	Percent degradation		
		USDA[c]	ANPA[d]	Commercial[e]
5	79.3[f]	60.0	16.1	6.8
12	83.0	67.5	20.3	12.0
25	95.1	78.7	34.1	14.7

[a]Mixture of Aspergillus fumigatus (NRRL 163), Penicillium citrinum (NRRL 1843) and Mucor racemosus (NRRL 5281).
[b]Alkali refined soybean oil-black pigment mixture.
[c]USDA-formulated with 100% soy oil-based vehicle (Type I) (Erhan and Bagby, 1991).
[d]ANPA-formulated with partial soy oil-based vehicle (ANPA, 1988).
[e]Commercial-formulated with petroleum oil-based vehicle (Flick, 1985).
[f]Calculated based on initial weight of vehicle.

TABLE 5
Percent Degradation for Different Vehicles and Soybean Oil with Mixed Cultures of Microoganisms[a]

Fermentation period # of Days	Percent degradation			
	Soybean oil[b]	USDA[c]	ANPA[d]	Commercial[e]
5	92.7	67.7	29.7	12.2
12	96.3	73.6	54.9	18.0
25	97.3	85.9	65.2	22.7

[a]Data from Erhan and Bagby, 1993.
[b]Alkali refined soybean oil.
[c]USDA-100% soy oil-based vehicle (mean value of Type I, II and III) (Erhan and Bagby, 1991).
[d]ANPA-partial soy oil-based vehicle (ANPA, 1988).
[e]Commercial petroleum oil-based vehicle (Flick, 1985).