Food Packaged in Paper Treated with Pyrethrins Protected from Insects

INSECT-PROOFING PAPER

Laboratory Evaluation of Pyrethrins-Piperonyl Butoxide Formulations

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Three formulations of pyrethrins with piperonyl butoxide were applied to natural kraft paper in order to determine comparative insect-proofing properties. The formulations—a wettable powder slurry, a petroleum oil solution, and an emulsion—were applied at three dosage levels. Samples of the paper were analyzed for piperonyl butoxide and were evaluated biologically immediately after, 6 months after, and 1 year after treatment. There was no loss of piperonyl butoxide during the 1-year period. Biologically the treated paper, regardless of length of time after treatment, afforded protection against boring insects for 2 months to more than a year, depending on the dosage and the type of formulation used. Untreated kraft paper, in comparative tests, was penetrated by insects in an average of 5 days.

The increased use of paper bags and packages as containers for cereals and other foods during recent years has accentuated the ever-present problem of protection of these foods from insect contamination. The infestation and contamination of packaged foods by insects result in appreciable losses to the manufacturer and the consumer. In a review of the problem Gray (*8*) has presented results from a leading manufacturer showing an average of 8.4% of hot-roll mix packages infested by insects over a period of 1 year, with infestations as high as 14 to 19% in August and September. The majority of these infestations were caused by penetration of the packages by grain and cereal insects.

Although correct sealing of the containers serves as one of the most important means of preventing entry, it does not afford protection against the boring insects. As pointed out by Linsley (*11*), the incorporation of toxic or repellent chemicals in the paper coverings of packages offers one of the most promising approaches to the problem.

In an extensive study, Essig and his coworkers (*5*, *6*) concluded that many so-called repellent chemicals showed promise of giving protection against insect penetration. Cotton (*3*) obtained good experimental results with potassium chromate applied to multiwall paper bags. Block (*1*) and Frings (*7*) reported a number of inorganic salts, selected on the basis of "taste repellency," to be very effective, and Chamberlain and Hoskins (*2*) found that some commonly used insecticides, as well as certain dinitro compounds, gave extended protection against insect penetration when applied to paper.

Jones, Kerbey, and Incho (*9*) recently reported on the use of a combination of pyrethrins and piperonyl butoxide for the insect-proofing of paper and paper products, and Gray (*8*) has stated that this combination is one of the most promising developments for preventing insect penetration of packaged food products. The pyrethrins–piperonyl butoxide combination presents the added advantages of having an excellent record of safety toward warm-blooded animals (*12*, *13*) and of possessing pronounced residual life when held under normal storage conditions. The present laboratory study was made to evaluate more critically the influence of formulation and dosage on performance over the period of a year.

Methods and Results

For the laboratory evaluation of paper treated with combinations of pyrethrins and piperonyl butoxide, 1-square-foot samples of machine-finished northern kraft having a basic weight of 80 pounds per ream were coated with these materials in a wettable powder slurry, a petroleum oil solution, and a water emulsion (10 sheets per treatment). The slurry was formulated by the addition of water to a powder containing 1.67% pyrethrins, 16.67% piperonyl butoxide, and 6.66% petroleum oil impregnated on 50% Barden clay and 25% Celite 209. The petroleum oil solution was made by dilution of a concentrate composed of 6.67% pyrethrins plus 66.67% piperonyl butoxide and the water emulsion by dilution of a concentrate of 4% pyrethrins, 40% piperonyl butoxide, 10% emulsifier, and 50% petroleum oil.

Application of the slurry to the paper surfaces was accomplished with a "rod coater," while the oil solutions and water emulsions were sprayed on with a De-Vilbiss atomizing spray gun (No. 24) operated at an air pressure of approximately 2 pounds per square inch. Since the practical deposit found to be effective in preventing insect penetration of paper products was 5 mg. of pyrethrins in combination with 50 mg. of piperonyl butoxide per square foot, theoretical deposits of this amount, as well as one half and two times this amount, were applied (Tables I and II). The treated paper samples were allowed to air-dry in the laboratory for about 24 hours. During a portion of this drying period the treated surfaces were exposed to artificial light, but upon drying they were stored in darkness between sheets of aluminum foil for the duration of the test period. A temperature of 80° ± 2° F. and a relative humidity of 50 ± 5% were maintained in the laboratory throughout this study. Portions of the papers were taken at the specified intervals for biological and chemical tests.

Two methods of biological testing of the treated papers were used. For evaluation of the rate of knockdown of the various treatments "surface activity" tests using flour beetles were made. In this method red flour beetles, *Tribolium castaneum* (Hbst.), were confined to the treated surfaces under Petri dishes and observations made of the per cent knockdown at various time intervals (Figure 1). Two replicates of 50 beetles were exposed to each treatment and the average per cent knockdown was determined after 2, 4, and 24 hours' exposure. The tests were repeated after the papers had aged for 2, 4, 6, and 12 months.

The results of these tests (Table I) showed that, in general, the slurry treatment was superior to the oil solution and the water emulsion in knockdown effectiveness. Also, the papers treated with the oil solutions showed superiority in knockdown to those treated with the water emulsions except at the highest dosage (10 mg. of pyrethrins plus 100 mg. of piperonyl butoxide per square foot). Although the coatings at one half the recommended dosage (2.5 mg. of pyrethrins plus 25 mg. of piperonyl butoxide per square foot) resulted in good initial knockdown after an exposure of 24 hours, the surface activity of all treatments decreased after 4 months. At the recommended dosage of 5 mg. of pyrethrins plus 50 mg. of piperonyl butoxide per square foot, both the slurry-type treatment and the oil solution retained good knockdown effectiveness for 12 months, while that resulting from the water emulsion declined after 4 months. Treatments made at twice the recommended dosage all resulted in good knockdown throughout the 12-month aging period.

For evaluation of the resistance of the treated papers to actual insect penetration, the procedure followed was essentially the same as Method A adopted by the Technical Association of the Pulp and Paper Industry (*14*). In this test a treated paper was placed on the top of a half-pint Mason jar, with the treated side outward, and the cap, from which the entire center had been removed, was placed on the jar. The jar was then inverted in a metal tray containing a layer of wheat infested with approximately 200 last instar cadelle larvae, *Tenebroides mauritanicus* (L) (Figure 2). About 40 additional larvae were added every 10 days. Five replicates were used for each sample of treated paper and daily observations were made to determine the first attempted penetration and the first complete penetration of the paper by a cadelle larva.

Table I. Surface Activity Tests of Kraft Paper Treated with Pyrethrins and Piperonyl Butoxide

(Red flour beetles. Averages of 2 tests of 50 beetles per test)

Type of Formulation	Theoretical Deposit, Mg./Sq. Foot: Pyrethrins	Theoretical Deposit, Mg./Sq. Foot: Piperonyl Butoxide	Exposure Period, Hours	Average % Knockdown at Treatment Age: 6 days	2 months	4 months	6 months	12 months
Slurry	2.5	25	2	3	13	14	10	2
	2.5	25	4	31	...	41	20	6
	2.5	25	24	97	98	97	66	81
Oil solution	2.5	25	2	3	11	16	6	1
	2.5	25	4	9	...	37	10	10
	2.5	25	24	91	86	91	28	57
Emulsion	2.5	25	2	4	3	6	0	0
	2.5	25	4	17	...	14	2	1
	2.5	25	24	95	47	46	8	1
Slurry	5.0	50	2	39	35	62	48	34
	5.0	50	4	74	...	86	70	73
	5.0	50	24	97	99	100	96	97
Oil solution	5.0	50	2	5	10	41	12	9
	5.0	50	4	42	...	74	38	21
	5.0	50	24	96	97	98	84	84
Emulsion	5.0	50	2	21	4	6	0	0
	5.0	50	4	53	...	17	4	1
	5.0	50	24	94	89	95	18	5
Slurry	10.0	100	2	48	49	85	78	39
	10.0	100	4	82	...	93	96	77
	10.0	100	24	100	100	100	100	98
Oil solution	10.0	100	2	14	20	37	26	5
	10.0	100	4	48	...	66	54	34
	10.0	100	24	97	98	98	90	86
Emulsion	10.0	100	2	31	30	46	28	7
	10.0	100	4	68	...	89	60	33
	10.0	100	24	99	98	99	98	92
Untreated control	...	...	2	0	0	0	0	0
	...	...	4	0	0	0	0	0
	...	...	24	0	0	1	0	2

Table II. Insect Penetration Tests of Kraft Paper Treated with Pyrethrins and Piperonyl Butoxide

(Cadelle larvae. Results are averages of 5 tests)

Type of Formulation	Theoretical Deposit, Mg./Sq. Foot		Fresh Treatment, Av. No. Days		Treatment Aged 6 Months, Av. No. Days	
	Pyrethrins	Piperonyl butoxide	To first attempt	To penetrate	To first attempt	To penetrate
Slurry	2.5	25	20	210	6	223
	5	50	37	. . .[a]	63	. . .[b]
	10	100	130	. . .[a]	166	. . .[b]
Oil solution	2.5	25	10	68	7	99
	5	50	19	130	16	186
	10	100	12	330	14	224
Untreated paper check	. . .	. . .	2	5	1	10
Emulsion	2.5	25	4	37	1	60
	5	50	6	121	3	108
	10	100	9	193	3	207
Untreated check paper	. . .	. . .	1	3	1	10

[a] No penetrations to date (580 days).
[b] No penetrations to date (400 days).

The data in Table II show the effectiveness of the slurry, oil solution, and water emulsion formations in preventing insect penetration immediately following application and after aging for 6 months. It is significant that the treated papers were fully as resistant 6 months after treatment as when freshly prepared. Here, as in the surface activity tests, the slurry-type treatment was superior to the oil solution and water emulsion sprays. In the tests of the fresh treatments the untreated papers were penetrated in an average of 3 to 5 days, while those treated at the recommended dosage (5 mg. of pyrethrins and 50 mg. of piperonyl butoxide per square foot) by the slurry method had not been penetrated in over 1.5 years of continuous exposure. At approximately the same dosage the oil solution and water emulsion treated papers were penetrated in an average of about 4 months.

The paper samples treated at one half the recommended dosage with the slurry type formulation were penetrated in about 7 months, the oil solution in 2 months, and the water emulsion in 1 month. At twice the recommended dosage no penetration of the papers treated with the slurry have occurred to date (580 days); the oil solution treatments were penetrated in 11 months and the water emulsion in 6 months. Rather conclusive evidence of the superiority of the slurry-type treatment may be seen in these tests, since the protection period with this treatment at one half the recommended dosage was about equal to that of the water emulsion applied at twice the recommended dosage and approximately 1.6 times as long as that of the oil solution treatment at the recommended dosage.

Chemical analyses of the treated paper samples for piperonyl butoxide were made to determine the actual insecticide deposits applied by each of the treatments and as a further check on the loss of insecticide due to aging (Table III). Analyses were made on freshly treated samples and on samples aged for 6.5 months and for 1 year. To obtain a representative sample for chemical assay a narrow diagonal strip was cut from each treated sheet. These were composited into two lots, each representing 0.5 square foot, and analyzed separately employing the method described by Jones and coworkers (*10*). The analytical figures reported in this study thus represent an average of two extractions. In addition, the Cueto-Dale method (*4*) for the determination of pyrethrins in paper coatings was used for evaluation of the approximate pyrethrins content after the treated papers had aged for 1 year. Although no initial analyses were made by this method, the results obtained after 1 year of storage are roughly in agreement with the piperonyl butoxide values.

The results of the chemical analyses given in Table III show that no apparent loss of either piperonyl butoxide or pyrethrins took place when the papers treated with the three types of formulations were stored under laboratory conditions for 1 year. Because of the methods of application employed, it was not possible to confine the sprays within the square foot area; consequently it is not surprising that the analyzed values for the oil solution and emulsion sprays were somewhat less than for the slurry treatment. These differences contributed to, but certainly did not completely account for, the superiority of the slurry treatment.

Summary and Conclusions

In laboratory tests three formulations of pyrethrins and piperonyl butoxide were applied to machine-finished northern kraft at three deposit levels, and then evaluated chemically and biologically at

Figure 1. Surface activity tests

Red flour beetles confined to treated papers

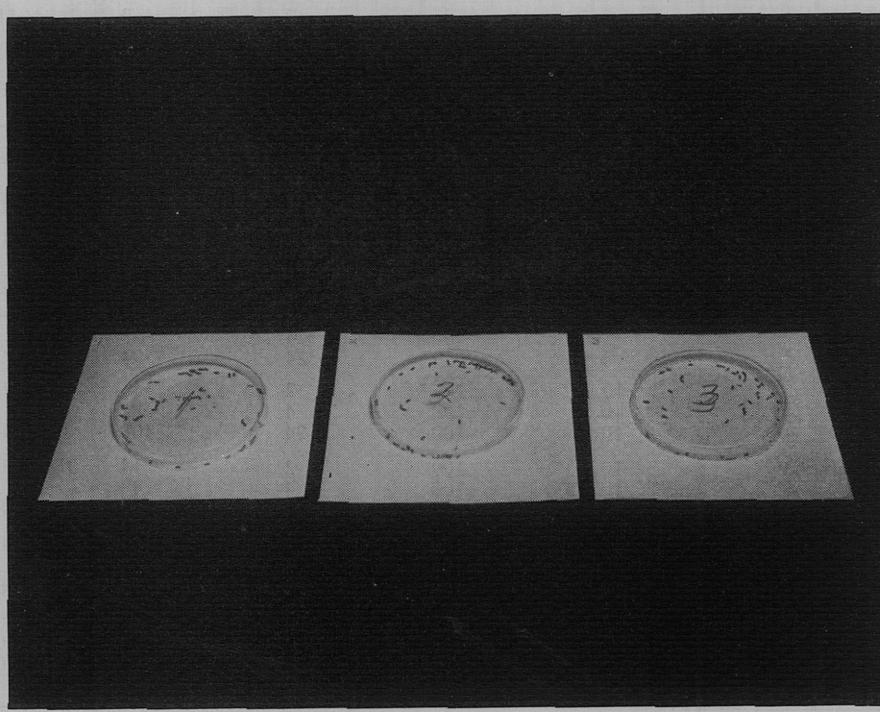

Figure 2. Insect penetration tests

Papers in jars at top of picture have been penetrated

intervals over a period of 1 year. A wettable powder, an oil solution, and a water emulsion were applied at rates to provide theoretical deposits of 2.5, 5, and 10 mg. of pyrethrins plus 25, 50, and 100 mg. of piperonyl butoxide, respectively, per square foot.

Chemical analyses of these papers for piperonyl butoxide conducted a few days, 6 months, and 1 year after treatment showed that the actual deposits were reasonably close to the theoretical values when initially applied and that storage for 1 year resulted in little or no reduction. Determination of pyrethrins at the end of 1 year showed that there had been no appreciable loss during the storage period.

Samples of the same papers used for chemical assay were employed in two types of biological tests. The first of these, the surface activity test, was designed to determine the immediate knockdown effect on insects that might crawl on treated papers. Results at the usually recommended dosage of 5 mg. of pyrethrins plus 50 mg. of piperonyl butoxide per square foot, employing the red flour beetle, showed that the wettable powder was the most effective treatment and the oil solution was nearly as effective. When aged up to 1 year there appeared to be little or no loss in effectiveness of the wettable powder treatments. There was a slight loss of activity of the oil solution treatments at 6 months whereas the water emulsion showed a pronounced reduction in effectiveness.

The second technique, the penetration test, was designed to evaluate the various treatments against insects that actually bore through packaging materials. Employing cadelle larvae, it was demonstrated that fresh wettable powder treatments were superior to the oil solutions or water emulsions by a greater margin than was noted in the surface activity tests. When the treated papers were aged for 6 months, there appeared to be no reduction in effectiveness. Thus, at the recommended rate of application the wettable powder treatments have remained effective against cadelle larvae for more than 1 year, but the untreated papers were penetrated in about 1 week. By comparison, the oil solution and water emulsion formulations remained effective for 4 months, a period that in many instances would represent more than the normal shelf life of packaged foods.

Table III. Chemical Analyses of Kraft Paper Treated with Pyrethrins and Piperonyl Butoxide

(Averages of duplicate analyses on 5 treated samples)

Type of Formulation	Theoretical Deposit, Mg./Sq. Foot: Pyrethrins	Piperonyl butoxide	Analyzed Piperonyl Butoxide Deposit, Mg./Sq. Foot, at Treatment Age: 21 days	6.5 months	1 year	Analyzed Pyrethrins Deposit 1 Year After Treatment, Mg./Sq. Foot
Slurry	2.5	25	24	22	21	4
	5.0	50	58	56	60	7
	10.0	100	107	108	114[a]	11
Oil solution	2.5	25	20	18	20	4
	5.0	50	35	36	40	6
	10.0	100	74	80	84	10
Emulsion	2.5	25	17	20	18	4
	5.0	50	40	34	39	9
	10.0	100	80	80	88	14

[a] Analysis of one set of treated papers only.

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