

Fate of EDC-CCl₄ (75:25) Residues During Milling and Oil Extraction of Soybeans^{1,2}

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ABSTRACT

When soybeans were fumigated with ethylene dichloride-carbon tetrachloride (75:25, EDC-CCl₄), a residue of each component of this mixture remained in both the hull and interior portion of the treated soybeans. Residues found in the various milling and processing fractions of the fumigated soybeans indicated that toasting removed the residues from the hulls but that steaming involved in the flaking process did not remove residues from dehulled soybeans. Fumigant residues from the

flakes passed into both the miscella and extracted marc and were subsequently detected in the recovered hexane from both of these fractions. The solvent-free oil and meal products contained no residues. Accumulations of residues in the recovered hexane could present a contamination problem to the soybean processor as he depends upon the continuous reuse of hexane in his oil extraction process.

Only in the past 5 years has there been a yearly carryover of soybeans requiring substantial storage at all marketing levels—farm, CCC bins, local elevators, and soybean-processing plants. Numerous reports received and investigated by the Mid-West Grain Insects Investigations Laboratory indicate that this increased storage of soybeans has resulted in some severe infestations by the Indian meal moth, *Plodia interpunctella* (Hübner), throughout Mid-Western States; in addition, damage by the cowpea weevil, *Callosobruchus maculatus* (F.), to stored soybeans has been reported in South Carolina. Very infrequently damage by insects to stored soybeans has been recorded in the literature. Holman and Carter (1952) sampled soybean storages over a 2-year period but failed to detect the granary weevil, *Sitophilus granarius* (L.), or the rice weevil, *S. oryzae* (L.). Other species typical of corn storage were observed, particularly the Indian meal moth, which is acknowledged as being commonly found in stored soybeans. Previously Heape (1966) reported a serious infestation of bagged soybean seed by the cowpea weevil in Nigeria.

No tolerances for fumigants or insecticides for post-harvest treatment of soybeans have been established. Although the ethylene dichloride-carbon tetrachloride (EDC-CCl₄) mixture used in the study reported here is now exempt from the requirement of an established tolerance for postharvest application to stored grain, no information is available concerning what happens to EDC-CCl₄ residues during milling and oil extraction of treated soybeans.

A cooperative project was developed between the USDA Mid-West Grain Insects Investigations Laboratory, at Manhattan, Kans., and the Northern Regional Research Laboratory, headquarters for the Northern Utilization Research and Development Division, Peoria, Ill., to fumigate and to process treated soybeans to determine residue levels in the various milling and processing fractions.

MATERIALS AND METHODS.—Fumigation Procedures.—About 400 lb of 'Clark' variety soybeans were fumigated in an 8-bu-capacity tower constructed from a

20-in.-diam metal duct. The tower was mounted in a swinging cradle to permit easy tipping for removal of the soybeans. An aeration system consisting of a screened false floor in the base of the tower, 2-in.-diam flexible return duct, and a low-capacity fan recirculated the fumigant upward through the tower. The rate of air movement through the soybeans was 1/2 ft³/min per bu of soybeans. The fumigant was recirculated for 1 hr.

The fumigant was released into an evaporation chamber, made from 2-in.-diam pipe, and inserted in the return duct circuit. The chamber was wrapped with electric heating tape and maintained at 200°F so that the liquid fumigant would volatilize better before its contact with the soybeans in the tower.

The temperature of the soybeans was 25°C and their moisture content was 12.0%.

The fumigant was a mixture by volume of 75% EDC and 25% CCl₄ applied at a dosage equivalent to 6 gal/1000 bu of soybeans.

After a 72-hr exposure the tower cap was removed and the soybeans were aerated for 1 hr to remove the interstitial gas concentrations. The unsealed soybeans were allowed to stand overnight before transfer to fiber drums and transport to the Northern Laboratory at Peoria for processing.

Milling and Extraction Procedures.—Fig. 1 is a flow diagram of the process. The fumigated soybeans metered to process at 60 lb/hr were cracked through 6-in.-diam corrugated rolls at 0.075-in. clearance into a double screen shaker, where the feed entering the top screen (3/16-in. perforated plate) and the "overs" leaving the bottom screen (14-mesh) were aspirated to remove free pieces of hull. "Fines" through the 14-mesh screen were not aspirated but were combined directly with the product. The hulls were sampled for analysis and then toasted in a batch cooker by heating to 85°C, steaming 20 min at 25% moisture, drying 45 min, and discharging at 17% moisture.

The dehulled meats were heated with live steam to 77°C and flaked at a moisture content of 9–10% through 12-in.-diam smooth rolls to 0.007- to 0.008-in. thickness. Total retention time from cracking to flaking was approximately 12 min.

The flakes were extracted in a countercurrent immersion-type extractor (Kennedy 1946) having 20 extraction stages and a retention time of 45 min. Hexane (commercial grade) preheated to 60°C was introduced countercurrent to the flakes at a 1:1

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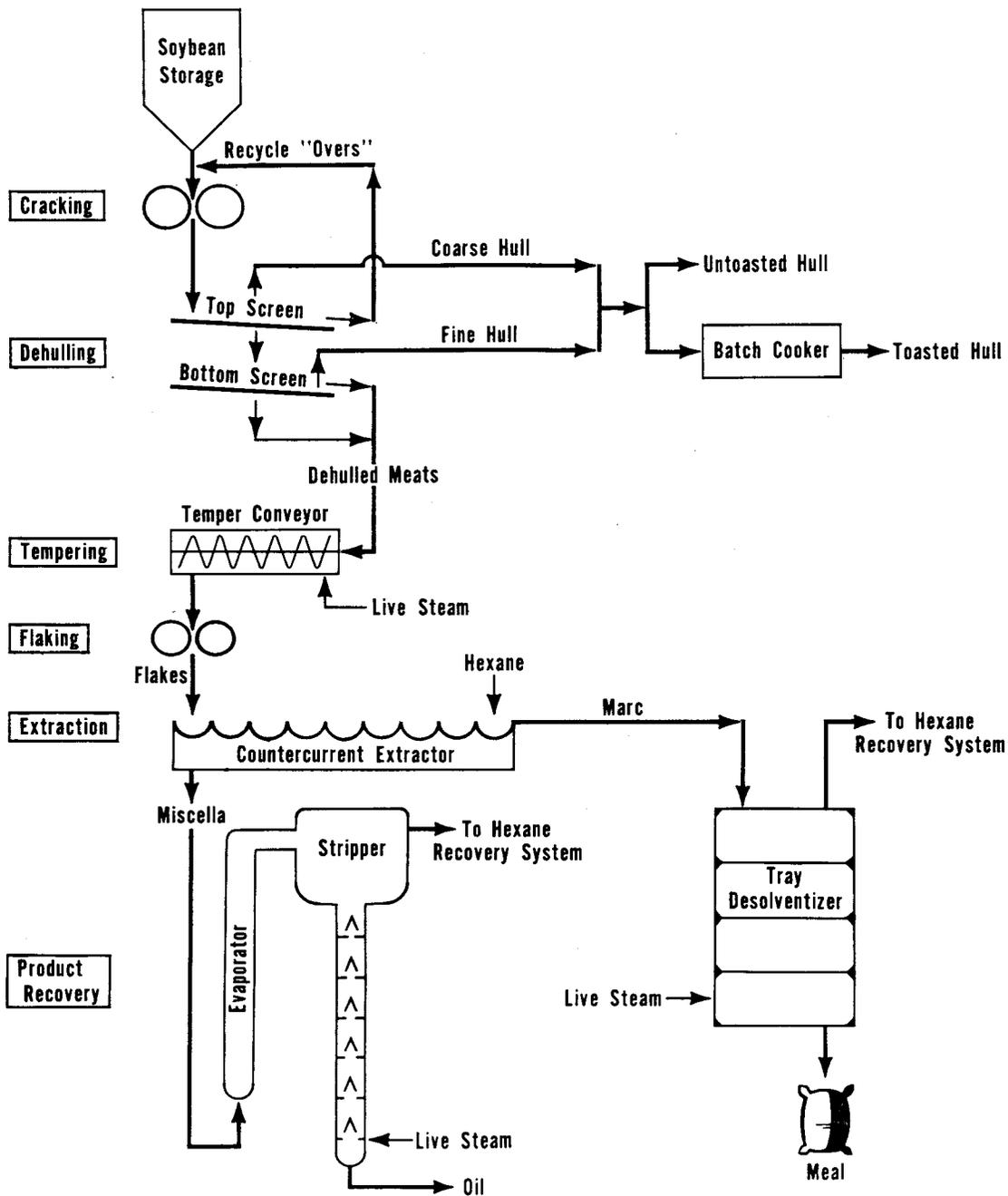


FIG. 1.—Soybean milling and extraction flowsheet.

weight ratio. The solvent temperature in the extractor was maintained by a circulating water bath in the bottom of the unit. Spent flakes were drained on an inclined conveyor and discharged to a 4-tray desolventizer. Live steam was introduced in the bottom tray to aid solvent removal. Retention time was approximately 20 min, and the desolventized meal left the unit at 116–121°C.

The oil was desolventized in an Artisan⁵ evapora-

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tor-stripper of the "disk and donut" type in which 132°C steam was passed countercurrent to the downward flow of oil in the stripper leg. Product oil left the unit at 127–132°C. Stripper vacuum was maintained at 18 in. of mercury absolute pressure.

The total solvent inventory for the run was 350 lb of which approximately 40% was recycled during the 6.5-hr run.

Control Run.—Approximately 300 lb of soybeans from the same lot but not treated with fumigant were processed under the same conditions as de-

Table 1.—Process analyses of fumigation run.

Component	Percent				NSI ^a	Urease activity ^b
	Moisture	Fat	Protein	Fiber		
Beans to process	8.9	18.4	38.2	4.4	85	2.3
Hull from aspirator ^c	9.1	3.8	12.5	31.6	—	—
Defatted meal	3.1	0.5	56.2	2.6	50	2.0

^a NSI = nitrogen solubility index.

^b pH change with 0.2-g sample of defatted meal.

^c Hull recovery was 7.6% of the whole soybeans processed.

scribed for the fumigated beans. Samples were taken at the same process points as for the main run and were checked for fumigant content.

Analytical Methods.—Residue analysis of total volatile organic chlorine and of carbon tetrachloride were conducted by the Stored-Product Insects Research and Development Laboratory at Savannah, Ga. The residues were determined by a colorimetric method described by Ramsey et al. (1957).

Analyses for moisture, crude fat, protein, and fiber were conducted according to Official AOCs Methods (Anonymous 1969). Nitrogen solubility index (NSI) was determined by the method of Smith and Circle (1938), and urease activity by the AACC procedure (Anonymous 1962).

RESULTS.—The analyses of whole beans, hull, and defatted flakes indicated in Table 1 indicate hull and oil removal typical of commercial operations. Since the meal was desolventized but not toasted (as in plants producing meal for animal feed), a low level of cooking was obtained; this level was reflected by a high urease activity and NSI in the meal produced.

When soybeans were fumigated with EDC-CCl₄ (75:25), a residue of each component of this mixture remained in both the hull and interior portion of the treated soybeans (Table 2). Slightly higher EDC residues and lower CCl₄ residues were recovered in the hulls than in the whole soybeans. Toasting removed these residues from the hulls. However, the steaming involved in the flaking process was ineffective in removing residues from dehulled soybeans. Total volatile organic chlorine residue present in the flakes before oil extraction was 70 ppm. This residue passed into both the miscella and marc leaving the extractor and was detected in the solvent recovered from these process streams. The solvent-free oil and meal products contained no residue.

Corresponding samples from the control run reported in Table 2 as "untreated control samples" were free of fumigant. No fumigant contamination was found in either the hexane or the raw soybeans used for this study.

DISCUSSION.—The persistence of the EDC-CCl₄ residues through the flaking process suggests that even very low levels of fumigant will remain in flakes from treated soybeans entering the extraction system.

Accumulation of residues in the recycled hexane resulting from extended periods of processing of fumigated soybeans could present a contamination problem to the soybean processor, since he depends upon the continuous reuse of hexane in the oil-extraction process. The extent to which fumigant residues can accumulate in the recycle hexane is limited to an equilibrium value at which the rate of fumigant residue added to the system is equal to the rate

of fumigant residue lost through the plant's solvent recovery system. The percent F_(D), representing the percent of fumigant residue in the recycle hexane at equilibrium, can be calculated from the relationship: 100 F ÷ SR where: F = pounds of fumigant as chloride added to the extractor per day, S = pounds of solvent lost each day, and R is the ratio

$$\frac{\% \text{ by wt of fumigant in solvent vapor lost}}{\% \text{ by wt of fumigant in liquid hexane recycle}}$$

Application of this equation to a plant processing 100 tons of soybeans/day (93 tons of flakes containing 70 ppm chlorine), with a solvent loss of 1 gal/ton of flakes processed, and R = 0.5 (from Raoult's Law) indicates an equilibrium fumigant residue concentration as high as 5.1% as organic chlorine or 6.6% as EDC-CCl₄ might be possible under these conditions.

The number of days required to reach this equilibrium value can also be estimated. The percent of fumigant residue in the recycle hexane at any day of operation "D" is given by percent F_(D) =

$$\left(\frac{100 F}{SR} \right) \left[1 - \exp \left(\frac{-SRD}{S_r} \right) \right]$$

where S_r is the weight of solvent in the plant work tank (assumed for a 100 ton/day plant to be 5500

Table 2.—Residues of EDC-CCl₄ (75:25) in milling and processing fractions of soybeans fumigated by the recirculation method at a dosage of 6 gal of mixture/1000 bu.

Sample	Fumigant residue as ppm chloride ^b		Total volatile organic chloride
	EDC ^c	CCl ₄	
Whole beans	51	19	70
Hulls from aspirator	60	10	70
Toasted hulls	0	0	0
Flakes to extractor	60	10	70
Miscella ^d	3	44	47
Hexane recovered from oil	41	35	76
Oil	0	0	0
Hexane recovered from meal	41	35	76
Meal	0	0	0
Untreated control samples	0	0	0

^a EDC-CCl₄ = ethylene dichloride-carbon tetrachloride.

^b Minimum residue capability of the method is 1 ppm. 0 values, therefore, indicate the lowest detectable amount of residue.

^c EDC data obtained by difference of total chloride and CCl₄ analyses.

^d Oil in hexane solution from the extractor.

lb). The number of days required to reach equilibrium can then be estimated by substitution of D values until the calculated fumigant residue concentration approaches the equilibrium value. In this example about 3 months would be required.

It seems unlikely that soybeans containing 70 ppm organic chlorine residue would be processed continuously over a period of several months; therefore, the equilibrium value would probably never be reached. Whether meal and oil products free of fumigant residue can be produced when the recycle solvent contains even a few percent of fumigant, however, has not been demonstrated. Further investigation should be made to determine whether any undesirable reactions occur between the fumigants used and soybean components.

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