Research and Development

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SEPA Project Summary

Treating Chlorinated Wastes with the KPEG Process

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The two reports summarized here describe development of the alkali metal polyethylene gylycolate (APEG) chemical technology to dechlorinate hazardous hydrocarbons in soils and its application at four demonstration sites: field-scale application to contaminated soils on the island of Guam pilot-scale demonstration in Moreau, New York; and drum-stored contaminated materials at the Bengart & Memel site in New York and in Omaha, Nebraska. The Omaha site involved tetrachlorodibenzo-p-dioxin (TCDD) in waste herbicides.

Equipment for the field-scale application on Guam included a steam-jacketed mixer, a steam-generating plant, and a condensate collection system. Approximately 15 yd³ of contaminated soil (with concentrations averaging 3535 ppm Aroclor 1260) were batch treated with potassium polyethylene glycolate (KPEG). The polychlorinated biphenyl (PCB) concentrations were reduced by more than 99%, with no individual PCB congener exceeding 2 ppm.

The reports provide detailed information about preparation of contaminated soils before treatment, equipment and reagents used during treatment, and analyses done before, during, and after treatment. Potential users are given sufficient information of the KPEG process to ascertain which version of the process is best suited for a particular site.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the

research projects that are fully documented in two separate reports (see Project Report ordering information at back).

Introduction

The two reports concern a chemical dechlorination process that employs a reagent, typically prepared by reacting a base (e.g., potassium hydroxide) with one of several polyethylene glycols (e.g., PEG 400). Early laboratory- and drumscale studies are described that proved the feasibility of the KPEG technology to treat PCB-contaminated soils. In-depth descriptions are given of the KPEG-process demonstrations that have been done to date.

A typical laboratory-scale procedure for dechlorinating polychlorinated dibenzo dioxins (PCDD)- and PCB-contaminated soil involves mixing potassium hydroxide (KOH) and polyethylene glycol-400 (PEG-400, average molecular weight of 400 Daltons) to produce the reagent KPEG. This KPEG reagent is mixed with the contaminated soil, heated to approximately 150°C (302°F), and maintained at that temperature while being continuously stirred for 1 to 4 hr. Excess reagent is then decanted, the soil is neutralized with acid and rinsed two or three times with water, and the decontaminated soil is discharged.

The reaction of the KOH and PEG-400 produces an alkoxide (ROK) (Equation 1), which in turn reacts with one of the chlorine atoms on the aryl ring to produce an ether (ArCl_{n-1} OR) and potassium chloride (KCI) salt (Equation 2). Replacement of the chlorine atom on the aryl ring with an ether-linked PEG

detoxifies the compound. The dechlorination process is described in Equations 1, 2, and 3:

ROH + KOH
$$\longrightarrow$$
 ROK + H₂0 (1)
ROK + ArCl_n \longrightarrow ArCl_{n-1} OR + KCl (2)
 $\stackrel{\triangle H}{\longrightarrow}$ Ar Cl_{n-1} OH + CH₂ =
 $\stackrel{H}{\downarrow}$ - OR (3)

Pilot-Scale and Field-Scale KPEG Treatment Demonstrations

Four site demonstrations of the KPEG process are discussed. A pilot-scale demonstration was conducted at the Moreau, New York, site, and a field-scale demonstration was conducted at the Guam site. At the Bengart & Memel site in New York and a site in Omaha.

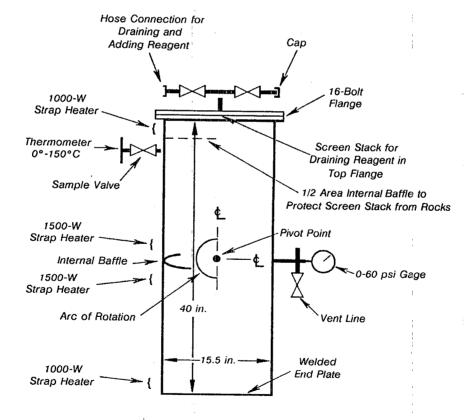
Nebraska, drum-treatment demonstrations of the KPEG process were conducted. Discussions of these four site demonstrations should assist potential users of the KPEG process with sufficient information to assess which of the four versions of the KPEG process is best suited for implementation at a particular site.

Pilot-Scale Demonstration of KPEG Process in Moreau, New York

The objectives of the demonstration at the Moreau site were to document that the KPEG reagent could effectively dechlorinate PCBs to acceptable levels at the 40-gal scale (from hundreds and thousands of parts per million to less than 3 to 4 ppm) and to gather process data that would subsequently be used to design a larger (2-yd³ or 400-gal) reactor. The test at Moreau was not intended to be a site cleanup; only a small portion of the contaminated soil was treated as part of the test.

The Moreau site was formerly a drag strip. The drag strip was oiled periodically, and some of the oil used for this purpose was transformer oil containing PCBs. The PCB concentrations in the soil at the site ranged from nondetectable up to tens of thousands parts per million. The pipe reactor (Figure 1) used during the pilot-scale tests was constructed from a 40-in. length of 16-in. steel pipe. It was mounted on a stand that allowed it to rotate about the indicated pivot point, and because it rotated through an arc of 180° in about 10 sec, mixing inside the pipe was gentle. A baffle along the side of the pipe (midway down its length) redirected the flow of slurry along the pipe wall and enhanced mixing.

Four electric heating straps heated the reactor. One 1000-watt heating strap was wrapped around the top of the reactor, and another was wrapped around the bottom. Both straps were about 10 in. wide. Two 3-in.-wide 1500-watt straps were wrapped around the center portion of the reactor



Removable Insulation Is Used During Operation

Figure 1. Reactor detail for the Moreau, New York pilot-scale demonstration.

During the reactor operation, temperature and pressure were recorded every 15 min. The reactor motion and its direction were controlled by a hand-held switch; therefore, during the entire time the reactor was operating, someone held the switch and manually reversed the reactor's direction at the end of each 180° turn.

Vapor from the reactor was vented through a small fan-cooled condenser (Figure 2). The condenser condensate was collected in Condensate Drum No. 1, which was vented to an ice condenser consisting of a coil submerged in an ice bath that drained to Condensate Drum No. 2. Condensate Drum No. 2 was vented through an activated carbon canister to remove any trace volatiles before atmospheric discharge.

The treatment procedure involved preparing the solvent PEG mixture—dimethylsulfoxide (DMSO), triethylene glycol methyl ether (TMH), and PEG-400 [ratio 2:1:1]—in a 55-gal drum. The soil, solvent mixture, and 45% KOH solution were then loaded into the reactor and mixed. The reactor was heated to 150°C, and the samples were withdrawn by removing the thermometer and pouring the slurry (~50 g) out of the thermometer insertion port.

Altogether, four runs were made with this reactor. Table 1 lists the reactor contents for each of these runs. After the samples were taken out of the reactor. both soil and reagent were analyzed for PCBs. The reductions in PCB concentration in the soil achieved during Run No. 1 ranged from 93.9% to 99.8% and averaged 98.3%. The PCB reduction in the remaining three runs (Runs 2 through 4) was greater than 99%. PCBs were also found in the recovered reagents, generally at higher concentrations than those in the soil; this indicated that although the PCBs were being extracted from the soil into the liquid phase, chemical dechlorination was not yet complete. The PCB concentrations in the reagent were 0.16 ppm in Run 1, 74.8 ppm in Run 2, 72.4 ppm in Run 3, and 4.25 ppm in Run 4.

Field-Scale Demonstration of KPEG Process in Guam

The U.S. Navy Public Works Center on Guam was selected for the field-scale demonstration of the KPEG chemical dechlorination system. The PCB concentrations in the soil at the site averaged 3535 ppm, with "hot-spots" as high as 45,860 ppm (4.59%). Soil contamination (found primarily in a nearby storm

drainage ditch) was the result of leaks from a transformer rework building and waste PCB stored outside the building. Excavated, contaminated soil was stored in a 12.2- by 18.3-m (40- by 60-ft) metal building with a heavy rubber liner erected on a concrete pad. Also another 30.5- by 30.5-m (100- by 100-ft) concrete pad was poured for the installation of the field-scale KPEG treatment system.

Soil and particles smaller than 1/2 in. were passed through the screens and collected separately so that particles would not be jammed in the mixer.

Laboratory studies of contaminated soil samples from Guam determined the soil's potential for KPEG treatment and established the reagent formulation and other operating parameters. Figure 3 is a simplified mechanical flow diagram of the KPEG system at Guam. As illustrated, the mixer was the primary component of the system in which the chemical dechlorination process occurred. An extensive pipe network connected the ancillary equipment with each other and with the mixer.

The principal components of the Guam KPEG treatment system (mixer, platform, liquid reagent loading system, heating system, nitrogen system, condensate collection system, process cooling system, reagent collection system, and ventilation

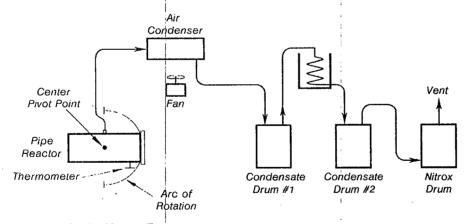


Figure 2. Equipment arrangement for the Moreau Test.

Table 1. Material Charged to Reactor, in Pounds

Run	Soil	Sulfolane	DMSO	ТМН	PEG-400	45% KOH	Total Liquid
1	33.5	0.0	11.0	5.5	5.5	11.0	32.9
2	32.5	0.0	10.0	5.0	5.0	10.0	30.0
3	34.0	0.0	12.0	6.0	6.0	12.0	35.9
4	39.0	15.0	0.0	7.5	7.5	13.0	43.0

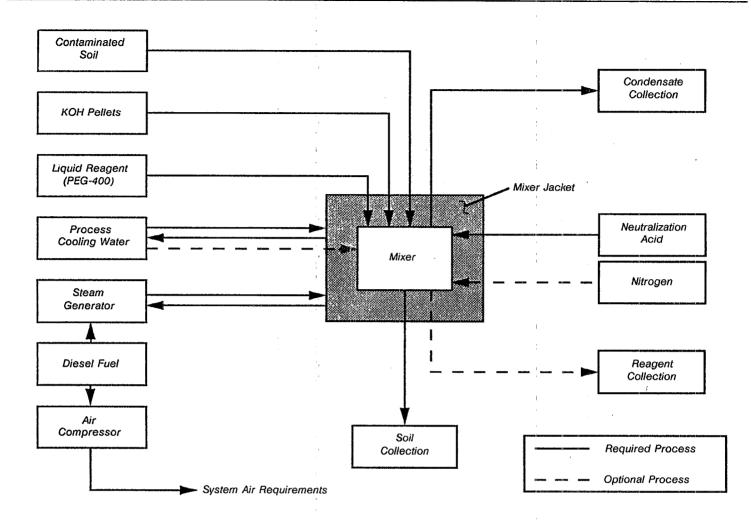


Figure 3. Mechanical flow diagram of KPEG field-scale treatment system.

system) are described in detail in the full report.

Six 55-gal drums were placed on a metal pallet, the pallet was positioned in the metal building next to the stockpiled soil, and the soil was shoveled into the drums. The six drums of soil were relocated to the scale, where a small forklift with a drum-lifting attachment placed them on the scale. A grab sample was collected from each of the six drums of soil. These samples were placed in a container and mixed thoroughly to provide a homogeneous sample for PCB analysis.

A crane hoisted the drums of soil, and two persons on the platform used the manual chainfall on the drum lifter to dump the drum contents into the mixer. After every second drum of soil was loaded, the mixer was turned on for a short time to disperse the soil evenly throughout the mixing cylinder.

After all the soil was loaded into the mixer, the components of this KPEG (PEG 400 and KOH) formulation were added. The mixer was run at low speed (30 rpm) while the PEG-400 was pumped into it; this allowed thorough dispersion of the PEG-400 and KOH to initiate the first reaction shown in Equation 1. When the reagents and soil were completely mixed, the mixer was switched to high speed (60 rpm). The vent line from the mixer to the condensate collection system was opened, and the fan condenser was turned on.

The steam-generating plant was ignited and 80-psi steam was circulated through the mixer jacket. The mixer contents reached 150°C in approximately 2 hr, and the temperature and mixing were maintained for 4 hr. At the end of 4 hr, the steam generator and mixer were shut down, the fan condenser was turned off,

and the contents were allowed to cool overnight.

After cooling overnight, all the treated batches of soil were neutralized with concentrated sulfuric acid and discharged. Samples were collected from the sample-collection port, and the slurry pH was measured. If the collected sample had a pH in the 6 to 9 range, it was also used as the posttreatment soil sample. The treated soil and reagents used in the treatment process were discharged into the soil-collection hoppers pending analytical results.

A high-pressure (2000-psi) water washer was used to decontaminate the process equipment, and the resulting water was collected in 55-gal drums. The collected condensate and water were passed through a series of cartridge filters and activated-carbon canisters. The treated water was then collected, sampled, and held until results of

analyses for PCB contamination were obtained. Treated waters with nondetectable PCB concentrations were either collected by a liquid transport truck and discharged into the sanitary sewer treatment plant or pumped back onto the hot zone.

PCB analyses employed an EPAdeveloped field-screening method, which was followed with a more vigorous, corroborative analysis. A review of treated soil analytical data from both analyses indicated that the destruction of the total PCB concentration exceeded 99%. In both sets of data, however, analysis of each of the congener peaks showed that a tetrachiorobiphenyl congener concentration in a portion of the treated batches was slightly above the R&D permit requirement of 2 ppm or lower per PCB peak. The batches containing greater than 2 ppm of the tetra congener were loaded back into the mixer, mixed with the new KPEG formulation of 1.3 moles KOH and 1.0 mole PEG-400, and retreated. Analytical results of the retreated batches indicated the tetra congener in each batch was well below 1 ppm.

Drum Treatment Demonstration of KPEG Process at Bengart & Memel Site, New York

The preceding two KPEG demonstrations were performed to prove the effectiveness of the KPEG process at larger scales and to promote the development of a full-scale system. The demonstrations described in this section and the one that follows concern the in situ treatment of smaller quantities of contaminated materials that may have already been placed into drums for storage. This process offers an alternative to the costly and hazardous process of emptying drums of hazardous materials.

When Bengart & Memel, Inc., a wholesaler of nonferrous scrap metals, dismantled PCB transformers and capacitors. PCBs were released into the soil. In the mid-1970's, soil samples from this site contained PCB concentrations exceeding 50 ppm. Soil sampling and analysis indicated that PCB concentrations were excessive in seven locations on the property. As part of the remedial program, the contaminated soil was excavated and placed in 166 55-gal steel drums. Because of a consent order deadline, only 51 drums of soil were treated in this demonstration. All the remaining drums were shipped, unprocessed, directly to a landfill.

During the KPEG treatment process, a weighed quantity (typically 150 to 170 lb) of a single-phase reagent mixture (2:2:4:9:5—PEG:TMH:DMSO:45% KOH: water) was added to each of the soil drums. A bimetal thermometer was inserted into the 3/4-in. bung on each drum cover, and the drums were heated from the bottom to ensure that all of the soil contaminants would react. The soil temperature was monitored 9 to 12 in. below the top of the drum, and the soil temperatures were typically maintained between 105° and 110°C for several hours.

The drums were vented to a central condenser system with a capacity of 16 drums (see Figure 4). During heating, vapors exited from the drum through an insulated flexible line connecting the 2-in. drum bung with the main header. Because part of the header was icejacketed, much of the water vapor was condensed and drained directly into a 55gal holding drum. The remaining vapor was drawn through an air-cooled radiator (used as a condenser), which also drained liquid to the 55-gal holding drum. An ice-jacketed scrubber containing a dilute sodium hypochlorite solution (for odor control) trapped most of the remaining condensables. From the scrubber, the vapor passed through a 55-gal drum filled with a mixture of activated carbon and containing a molecular sieve. A vacuum pump provided negative pressure for the vapor control system.

A 30-in. auger attached to a hand drill was used to collect treated soil samples from the drums. Four samples (one from the center, one close to the drum wall, and two spaced between the center and wall) were collected from the drum by penetrating the soil as deeply as possible with the auger.

After the treated soil had been decontaminated, the soil had to be brought from a highly alkaline to a neutral pH by the addition of dilute acid.

Soon after the KPEG treatment (October 1986), EPA determined the concentrations of PCBs in selected drums. A second group of drums was sampled and analyzed in February 1987 after the reagent had been in contact with the soil for 5 mo. Group 2 included fresh samples from the drums that EPA found contained PCB concentrations exceeding 50 ppm, samples from treated drums not analyzed by the EPA, and one soil sample that contained less than 50 ppm when EPA analyzed it. The low-concentration sample was analyzed to check the potential reaction progress in drums with PCB concentrations below 50 ppm. A comparison of the reduced concentrations reported in February with the October results indicated that the reaction continued during the holding period.

A review of treated-soil analytical data indicated that PCB concentrations were reduced from 108 to 27 ppm (a 75% reduction). The PCB levels in the soil in one drum with an initial concentration of 1300 ppm were reduced to 78 ppm (a 93% reduction).

Drum Treatment Demonstration of KPEG Process at an Omaha, Nebraska, Site

This 1987 EPA study was designed to demonstrate the effectiveness of the KPEG process for treating drummed, contaminated herbicide wastes containing dioxins. The contaminated waste contained 17,800 ppm 2,4-D, 2800 ppm 2,4,5-T, and 1.3 ppm 2,3,7,8-TCDD.

The KPEG reagent used in this demonstration was prepared with PEG and KOH. The field-scale testing of the KPEG technology was performed on one 20-gal batch of the contaminated waste.

The treatment equipment consisted of a 55-gal drum, a clamp-on heating band, and a stirring motor. The drum containing the KPEG reagent and the contaminated waste was heated to a temperature of 70° to 85°C for 2 days while being continually stirred. After 2 days, the heater was turned off and the reaction mixture was allowed to cool to ambient temperature. The treated waste samples were then analyzed to determine the posttreatment concentration of the contaminated waste.

Table 2 presents the analytical results of samples collected before treatment and after the first and second treatments. The KPEG treatment reduced the concentration of 2,3,7,8-TCDD in the waste to less than the detectable range. The concentrations of both 2,4-D and 2,4,5-T were reduced by 98%.

Conclusions

The pilot-scale KPEG demonstration in Moreau, New York, represented the first attempt to dechlorinate PCBs in a reactor/mixer at a scale larger than that used in the laboratory. Results of the demonstration indicated that PCBs could be reduced by an average of 98.3% (reductions ranged from 93.9% to 99.8%).

The field-scale demonstration at Guam proved the effectiveness of the KPEG technology for treating soils with initial PCB concentrations averaging 3535 ppm

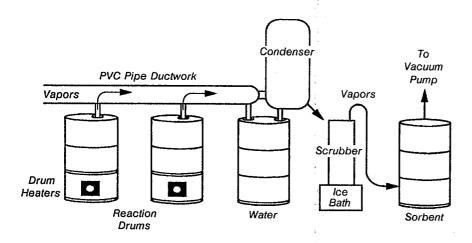


Figure 4. Central condenser system, KPEG drum treatment demonstration, Bengart & Memel, Buffalo, New York.

Table 2. Drum Scale Treatment of TCDD, 2,4-D and 2.4,5-T

		Concentration is	Paraont		
Contaminant	Conc. in Untreated Waste, ppm	First Treatment, ppm	Second Treatment, ppm	Percent Reduction of Contaminants	
TCDD (2,3,7.8)	1.3	0.086	ND*	99.99	
2,4-D	17,800	9,000	334	98.12	
2,4,5-T	2,800	1,700	55	98.04	

*ND = None Detected

(3260 to 3828 ppm). PCB concentrations were reduced to an average concentration of 6.74 ppm (1.01 to 13.9 ppm), which represents an average reduction of 99.84% (99.58% to 99.98%) with no resolvable PCB congener exceeding 2 ppm (after retreatment). The process implemented in Guam was successful in its treatment of PCB-contaminated soil without the use of DMSO or TMH.

The KPEG process used at the Bengart & Memel site successfully reduced PCB levels in soil contained in 55-gal drums to below the 50-ppm control limit set for the soil at the site.

The drum-scale KPEG process at the Omaha site proved to be capable of degrading 2,3,7,8-TCDD, 2,4-D, and 2,4,5-T. Initial concentrations of 1.3 ppm 2,3,7,8-TCDD, 17,800 ppm 2,4-D, and 2,800 ppm 2,4,5-T were reduced to concentrations of none detectable, 334 ppm,

and 55 ppm, respectively. The demonstration also proved the effectiveness of KPEG without the use of DMSO or TMH.

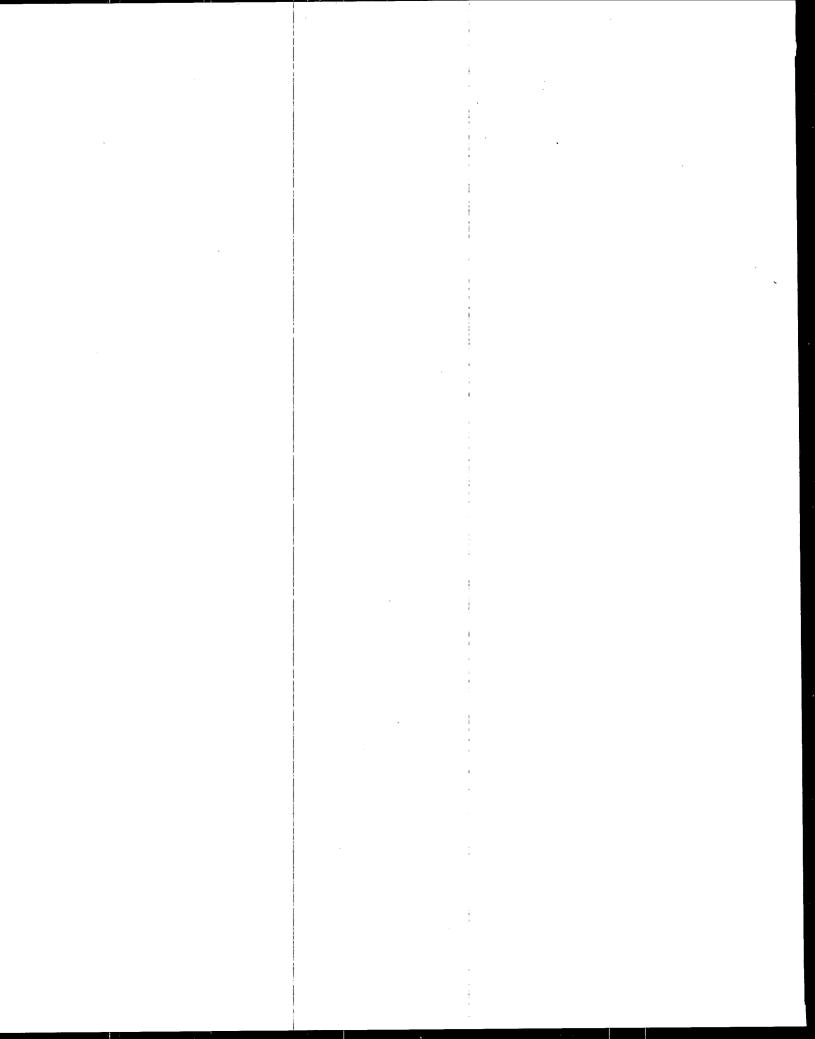
Recommendations

The following recommendations were made concerning the field-scale KPEG system:

- The system should be used at additional sites to provide more background data on the technology.
- Additional field-scale demonstrations should be done in an attempt to optimize the reagent formulation and operating parameters.
- The labor intensity of the system should be reduced by modifying it with materials handling equipment and automation.

- Attempts should be made to identify alternative equipment manufacturers that may be capable of further increasing the efficiency of the system.
- Design of a full-scale, fully portable, self-supportive KPEG treatment system should be initiated for soils contaminated with halogenated aromatic compounds.
- Efforts should be initiated to delist the KPEG-treated soil judged to be "clean" per the requirements of the R&D permit.

The full report was submitted in fulfillment of Contract No. 68-03-3413, Work Assignment No. 1-2, and IAG RW17933910 by PEI Associates, Inc., under the sponsorship of the U.S. Environmental Protection Agency.



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T. D. Ferguson and C. J. Rogers are the EPA Project Officers (see below).

The complete reports entitled "Field Applications of the KPEG Process for Treating Chlorinated Wastes" (Order No. PB 89-212 724/AS: Cost: \$17.00, subject to change), and "Comprehensive Report on the KPEG Process for Treating Chlorinated Wastes" (Order No. PB 90 163 643; Cost \$23.00, subject to change) will be available only from:

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