UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

May 31, 2002

**MEMORANDUM:**

**Subject:** Efficacy Review of a Supplemental Data Discussion to Support an Experimental Use Permit for "Frog Mineral Reservoir"
EPA Reg. No. 53735-EUP-R
DP Barcode: D282794
Case No.: 070675

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**Applicant:** King Technology
530 11th Avenue, South
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**Formulation:**

| Active Ingredient(s) | % by wt |
|---|---|
| Silver (ionic, from 0.5% AgCl) ..... | 0.37% |
| Inert Ingredients ..... | 95.50% |
| Total | 100.00% |

## I BACKGROUND:

The registrant, King Technology is applying for an Experimental Use Permit (EUP) to conduct swimming pool field studies on their product Frog Mineral Reservoir. The product is designed to be used with chlorine to eliminate bacteria, prevent algae and help maintain a neutral pH in swimming pools. The product would allow the chlorine residual to be reduced from 0.6 ppm to 0.4 ppm available chlorine, yet maintain its effectiveness as a swimming pool disinfectant. The product is installed in the recirculation system of the pool whereby the water flowing through the system passes through a bed of granular calcium carbonate coated with silver chloride. Hydrated silver ions are then released into the recirculating water. The hydrated silver ions have a low level of biocidal effectiveness and while this is not sufficient alone to maintain the disinfectant level in a swimming pool, it does allow a reduction in the amount of available chlorine needed to properly disinfect the pool.

An experimental use permit (EUP) for swimming pool products is needed to confirm the findings from presumptive efficacy testing conducted in the laboratory studies. The testing under the EUP employs actual field conditions and requires the product to be tested in outdoor swimming pools for an entire swimming season (4-12 months).

A previous efficacy review (dated March 22, 2002) on the presumptive laboratory efficacy test, MRID No. 454488-02 was conducted for the purpose of an experimental use permit (EUP). However, this review yielded no evidence that the use of the product contributes to disinfection at reduced chlorine levels. Additionally, the 0.4 ppm available chlorine was comparable to the chlorine control in killing the target microorganisms even in the absence of additional silver ions, the proposed use of 3000 gallon indoor pool was not acceptable for testing the efficacy of the product under actual field conditions, and the proposed use of one bather for 15 minutes per day for 5 days a week was not reflective of actual use conditions and unacceptable.

This submission included an additional supplemental efficacy data discussion with 13 references to support King Technology's discussion.

## II USE DIRECTIONS (For Experimental Use Only):

The Frog Mineral Reservoir is part of a complete pool care system when used correctly with 0.4-1.0 ppm chlorine levels will eliminate bacteria, prevent algae and help maintain a neutral pH in swimming pools.

This product should only be used in the Frog Cycler. Check the Frog Mineral Reservoir (FMR) label to make sure you have the correct FMR for you Frog Cycler. Use only the factory recommended FMR. Use of any other product could result in damage to pool equipment or surface, unsafe pool conditions, fire or explosion. Do not use this product for more than 6 months.

## III AGENCY STANDARDS:

Numerous factors influence the concentrations necessary for disinfection of swimming pool water in practical applications: numbers of swimmers in the pool; frequency of use; frequency with which water is changed; general weather conditions; and types and degree of organic contamination of the water by the swimmers themselves (e.g., suntan lotions and oils) and by various debris. Therefore, a two-phased study (presumptive laboratory testing and confirmatory field testing) is required.

(1) Laboratory test requirements. Presumptive efficacy of swimming pool water disinfectants may be substantiated with data derived from the AOAC Method for Water Disinfectants for Swimming Pools or with slight modifications (e.g., pH) thereof, against both *Escherichia coli* (ATCC 11229) and *Enterococcus faecium* (ATCC 6569).

(2) Performance standard for laboratory test. The lowest concentration of the test germicide providing results equivalent to those of the sodium hypochlorite control is the lowest concentration of the product that can be considered effective.

(3) Field test requirements. In addition to the laboratory test requirements referred to above, confirmatory efficacy data shall be derived from in-use tests under an Experimental Use Permit in at least two swimming pools. The tests must be conducted for an entire swimming season (4 to 12 months).

(4) Performance standard for field test.

The product, when used as recommended in swimming pool water, should demonstrate that not more than 15% of the samples collected shall fail to meet the following bacterial indices.

(i) The standard plate count at 35° shall not exceed 200 colonies per 1.0 ml.

(ii) The most probable number of coliform bacteria shall be less than 2.2 organisms per 100.0 milliliter. When the membrane filter test is used there shall be no more than 1.0 coliform organisms per 50 ml.

(iii) The most probable number of entercoccal organisms shall be less than 2.2 organisms per 100.0 milliliter. When the membrane filter test is used there shall be no more than 1.0 enterococcal organisms per 50 ml.

## IV SUMMARY OF SUBMITTED SUPPLEMENTAL EFFICACY DATA DISCUSSION:

The information provided was submitted in response to the April 10, 2002 meeting between Agency Representatives and King Technology. The purpose in providing this information was to supplement previously submitted presumptive efficacy testing of the Frog Mineral Reservoir using the AOAC Official Method 965.13 for Water Disinfection for Swimming Pools.

The argument presented in the submitted discussion was the action of silver and chlorine is synergistic in that the rate of killing is greater than would be anticipated if either silver or the halide (at a reduced concentration) were to be used alone.

King Technology submitted a number of references to support their argument of silver being an effective microbicide. The references were as follows:

U.S. EPA's Registration Eligibility Document of Silver (U.S. EPA RED 738-R-93-005, June 1993), the efficacy of silver for disinfection is acknowledged in this document. The Agency has registered at least forty silver-based compositions or products as pesticides. Six of the registered products are for use in pools and spas.

1. F. X. Abad, R. M. Pinto, J. M. Diez, and A. Bosch, Disinfection of Human Enteric Viruses in Water by Copper and Silver in Combination with Low Levels of Chlorine, Department of Microbiology, University of Barcelona, 08028 Barcelona, Spain, Applied and Environmental Microbiology, July 1994, pp. 2377-2383.

2. Amit Gupta, Maria Maynes, and Simon Silver, Department of Microbiology and Immunology, University of Illinois, Chicago, Illinois 60612-7344, Applied and Environmental Microbiology, December 1998, pp. 5042-5045.

3. Lee K. Landeen, Moyasar T. Yahya, Susan M. Kutz, and Charles P. Gerba, Department of Microbiology and Immunology, University of Arizona, Tucson, AZ 85721, Water Science Technology, Vol. 21, No. 3, pp. 267-270, 1989.

4. Xian-Zhi Li, Hiroshi Nikaido, and Kurt E. Williams, Silver-Resistant Mutants of *Escherichia coli* Display Active Efflux of Ag+ and Are Deficient in Porins, Department of Microbiology and Division of Infectious Diseases, University of Saskatchewan, Saskatoon, Saskatchewan S7N 5E5, Canada, and Department of Molecular and Cell Biology, University of California, Berkeley, California 94720-3206, Journal of Bacteriology, Oct. 1997, pp. 6127-6132.

5. C. Mark Ott, Ph.D. and Duane L. Pierson, Ph.D., Microbial Monitoring and Disinfection aboard NASA Spacecraft, EASI, Wyle Laboratories, 1290 Hercules Drive, Houston, Texas 77058, NASA Johnson Space Center.

6. N. Simonetti, G. Simonetti, F. Bougnol, and M. Scalzo, Electrochemical Ag+ for Preservative Use, *Instituto di Microbiologia and Dipartmento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Facolita di Farmacia, Universita "La Sapienza,"* Rome Italy, Applied and Environmental Microbiology, Dec. 1992, pp. 3834-3836.

7. Moyaar T. Yayha, Susan M. Kutz, Lee K. Landeen, and Charles P. Gerba, Swimming Pool Disinfection, *An evaluation of the efficacy of copper:silver ions,* Journal of Environmental Health, Vol. 51, Number 5, May/June 1989, pp. 282-285.

8. Moyaar T. Yayha, Lee K. Landeen, Maria C. Messina, Susan M. Kutz, Richard Schulze, and Charles P. Gerba, Disinfection of bacteria in water systems by using electrolytically generated copper:silver and reduced levels of free chlorine, Department of Nutrition and Food Science and Department of Microbiology and Immunology, University of Arizona, Tucson, AZ 85721, Canadian Journal of Microbiology, Vol. 36, 1990, pp. 109-116.

9. William Welbes, Legend Technical Services, Inc., Testing to Evaluate Performance Frog Cartridge Used One Year, Tested 8-3-98, Frog cartridge identified as J. Steinberg pool Frog, one year old, Legend Project #98-2534

10. William Welbes, Legend Technical Services, Inc., Testing to Evaluate Performance With *E. coli,* Test 10-12-98, Legend Project #98-3987

11. William Welbes, Legend Technical Services, Inc., Testing to Evaluate Performance With *Pseudomonas,* Test 10-21-98, Legend Project #98-4375

12. Heather Bjornson, Microbiological Study with *E. coli* to Demonstrate the Efficacy of Silver Ions, chlorine, and their combination in killing *E. coli*, 04/02/02

## V COMMENTS ON THE SUBMITTED EFFICACY DATA DISCUSSION:

**Reference 12**

In this particular reference, King Techology, Inc. performed laboratory tests under conditions that differentiate between the efficacy of chlorine alone and chlorine plus silver in the killing of *E. coli.* Results indicated a 0.5 minute treatment with 0.4 ppm chlorine resulted in a 2.04 log reduction in the *E. coli*

level as compared to the untreated control. In contrast, treatment with a combination of 0.4 ppm chlorine plus 10 ppb silver resulted in a 2.64 log reduction. Although, the efficacy of the combined system passed guideline requirements for swimming pool disinfectants, there was no significant statistical difference when compared to free chlorine in the King Technology testing.

**References 3, 7, and 8**

Note the above references all use electrolytically generated copper with silver ions in evaluating chlorine compounds to the combination of copper:silver ions and free chlorine. In all instances the combination of copper:silver with free chlorine resulted in a much higher $\log_{10}$ reduction than just silver ions and free chlorine.

## VI BRIEF DESCRIPTION OF PROPOSED EUP:

The stated objective of the EUP is as follows: "The proposed study is intended to substantiate the disinfectant effectiveness of a combination product consisting of chlorine plus a proprietary silver release system, both intended for use in swimming pools. The amount of free available chlorine (FAC) that will be maintained in the water within each pool during the study will be between 0.4 and 1 ppm."

King Technology, Inc. is proposing the use of one residential in-ground pool of approximately 8,000 gallons and one above ground of approximately 12,000 gallons will be filled and operated with the test device (Frog Mineral Reservoir, containing the test substance, Frog Mineral formula). Two Frog Mineral Reservoirs randomly selected from a group of commercial reservoirs will be installed and used for a period of six months with each of two outdoor swimming pools, following label directions. Unused reservoirs will be retained. Water in each pool will be recirculated through the Frog Mineral Reservoir, which will release silver ions to the water through the pool return. The level of chlorine in each pool will be maintained by addition of sodium hypochlorite.

Each pool will be circulate at least 8 hours daily. Both pools will be maintained with the addition of pool additives representative to the usage in the study locale. An average of three human bathers will use the above ground, 12,000 gallon pool and an average of two human bathers will use the 8,000 gallon pool. Both pools will have a human bather load for at least one-half hour at a minimum of five days a week. A minimum of 144 samples will be collected during the six-month test period and undergo microbiological examination. A subset of this number will undergo physical and chemical analysis.

Microbiological examinations of the pool waters will be conducted regularly, following methods from Standard Methods for the Examination of Water and Wastewater, 18$^{th}$ Ed., and will include heterotrophic plate counts and

tests for the presence of *Enterococcus faecalis*, *Pseudomonas aeruginosa*, and *Escherichia coli*. Chemical and physical analyses of the pool waters will be conducted using approved EPA methodolgy.

Additional parameters to be measured on a daily basis: free chlorine, silver ions, pH, air temperature, pool water temperature, clarity/turbidity, bather load, and bacterial load. On a monthly basis the iron, copper, alkalinity, nitrogen ammonia, calcium hardness and chloride levels will be measured.

## VII COMMENTS ON EUP PROTOCOL:

In the EUP application, King Technology, Inc. proposes the use of one-residential 8,000 gallon in-ground pool and one 12,000 gallon above ground pool. Each pool will be circulated at least 8 hours daily with an average of two human bathers in the in-ground pool and three bathers in the above ground pool for six full months. A minimum of 144 samples will be collected during the six-month test period and undergo microbiological examination. A subset of this number will undergo physical and chemical analysis. Additional parameters will be measured on a daily basis: free chlorine, silver ions, pH, air temperature, pool water temperature, clarity/turbidity, bather load, and bacterial load. On a monthly basis the iron, copper, alkalinity, nitrogen ammonia, calcium hardness and chloride levels will be measured. The applicant's protocols incorporated all test parameters required for field testing of swimming pools and are acceptable for field testing. However, additional information must be submitted to the Agency. See comments under conclusions.

## VIII CONCLUSIONS:

In the submitted efficacy data discussion, laboratory tests that differentiate between the efficacy of chlorine alone and chlorine plus silver in the killing of *E. coli* indicated a 0.5 minute treatment with 0.4 ppm chlorine resulted in a 2.04 log reduction in the *E. coli* level as compared to the untreated control. In contrast, treatment with a combination of 0.4 ppm chlorine plus 10 ppb silver resulted in a 2.64 log reduction. Although, the efficacy of the combined system passed guideline requirements for swimming pool disinfectants, there was no significant statistical difference when compared to free chlorine in the King Technology testing. Exactly how the silver ions influence the microbial activity has not been shown. The silver ion has been investigated in terms of its activity against different microorganisms, however, with regard to the mechanism of action, silver is microbicidal only if it is in the ionic state. Since silver compounds ionize poorly, the synergistic effect needs to be explained to the Agency in more detail. The Agency will accept the application for the EUP at this time, however, the additional information listed above must be submitted.