



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

OFFICE OF  
PREVENTION, PESTICIDES AND  
TOXIC SUBSTANCES

January 6, 2005

**SUBJECT:** Review of the King Technology Inc. Registration for the New  
Chemical, Silver Chloride, for its Use in Swimming Pools

**FROM:** Robert Quick, Chemist *Robert Q Quick*  
Risk Assessment and Science Support Branch  
Antimicrobials Division(7510C)

**TO:** Marshall Swindell, Product Manager Team 33  
Regulatory Management Branch I  
Antimicrobials Division(7510C)

**THRU:** Norm Cook, Chief *Norman Cook*  
Risk Assessment and Science Support Branch  
Antimicrobials Division(7510C)

**ID#:** 53735-King Technology Inc.

**DP BARCODE:** 307225

**DECISION#:** 335496

**PC CODE:** 072506

**CAS#:** 7783-90-6

**CHEMICAL NAME:** Silver Chloride

**MRID#:** None

## Introduction:

Technology Services Group Inc., on behalf of King Technology, Inc. has submitted a registration for the new chemical, silver chloride, for its use in swimming pools.

The package contains: 1) a letter from Technology Services Group Inc. dated May 6, 2004, from Mr. Erin Tesch to Mr. Marshall Swindell; 2) a letter from The EPA dated 3/9/04 from Mr. Marshall Swindell to Mr. Erin Tesch, Agent for King Technology Inc.; 3) a label for the product, Frog Mineral Reservoir; 4) literature for the Frog Mineral Reservoir Package [Cartridge System]; 5) literature for the Frog Mineral Reservoir Package [Skimmer Application]; and 6) literature for the Pool Frog Mineral Reservoir Patented Mineral Pool Sanitizer Instruction Manual.

## Background:

Silver chloride was first registered for use in 1974; however, there are no active registrations for the chemical. Silver chloride is being treated as a new chemical.

Our perusal of the internet, Google) shows a large number of sites that advertise the use of the "Frog Reservoir". The product is apparently already being sold before this proposed registration has been granted.

One advertisement from the internet for, "Rogers Pool & Patio" states, "Supplement the bacteria fighting job of the minerals by pouring a non chlorine oxidizer(Potassium Peroxymonosulfate) into your pool". This use for the peroxymonosulfate does not appear in the EPA OPPIN program. The EPA REFS program lists this chemical as an active registration for use in swimming pool water systems.

An MSDS from King Technology Inc. for the Pool Frog Mineral Reservoir lists the chemical family of the product as "Calcium Carbonate with Silver and Zinc compound". The meaning of this statement and its relationship with the product under review is unclear and should be explained by the registrant.

## Conclusions:

1. An MSDS from King Technology Inc. for the Pool Frog Mineral Reservoir lists the chemical family of the product as "Calcium Carbonate with Silver and Zinc compound". The meaning of this statement and its relationship with the product under review is unclear and should be explained by the registrant.

2. The label does not indicate what size of pool that can be treated with the Frog Mineral Reservoir. However, the Frog Mineral Reservoir Patented Mineral Pool Sanitizer Instruction Manual states the product purifies up to 30,000 gallons. The registrant should supply us with information explaining how the level of silver in pool water in various sized pools is controlled and how the desired level of silver in the pool water is maintained. Presumably the solubility of

silver and silver chloride which is expected to form in the swimming pool is the controlling factor.

3. It is unclear to us what the active ingredient in the pool water will be. It would seem that any silver ion that goes into solution in the pool water would immediately become silver chloride.

**The registrant should explain what the mechanism of action is for the efficacy of the Frog Mineral Reservoir containing silver chloride as the active ingredient.**

Is the active ingredient(s) silver and silver chloride?

4. The silver/silver chloride level in the treated pool water is likely governed by the solubility of silver/silver chloride in water. Both silver and silver chloride have very low solubility in water.

5. The registrant has submitted silver residue data from two pool studies, each conducted from June 2002 to January 2003. The analytical method used in the generation of the data is provided.

a. The analytical method used is entitled, "Determination of Dissolved Silver, Standard Methods Procedure 3113B. The reference is from *Standard Methods for the Examination of Water and Waste Water, 17<sup>th</sup> ed. (1989)*. No method validation data is provided from the registrant to show that the method provided adequate recoveries at the silver residue levels analyzed.

b. Assuming that the method was adequately validated, residue levels of silver in pool water did not exceed 0.028 ppm.

5. When RASSB stoichiometrically calculates the concentration of silver ion in the pool water based on the solubility of silver chloride in water, then the concentration of silver ion in the pool water would be on the order of 1.45 ppm or less. Because of the excess of chloride ion present in pool water, silver residues would be expected to be much lower than this level. The AD risk assessors should use the pool water residue data in their review.

#### Recommendations:

The residue chemistry considerations for this registration submission have not been adequately addressed. The registrant must respond to the residue chemistry questions raised in Conclusions 1 - 3 above.

#### Detailed Considerations

##### OPPTS GLN 1550 Chemical Identity

The active ingredient is silver chloride. CAS# 7783-90-6. The molecular weight is 143.3. Silver chloride is an inorganic chemical. The empirical formula is AgCl.

##### OPPTS GLN 860.1200 Proposed Use

The product proposed for use is Frog Mineral Reservoir. It is called a "Patented Mineral Pool Sanitizer" and "The Complete Low Chlorine Alternative". The label claims "50% to 80% reduction in chlorine when compared to the EPA recommendations of 1.0 to 3.0 ppm for standard chlorine treated pools".

The ingredient statement on the label claims the active ingredient as "silver(ionic, from 0.5% AgCl) - - .37%".

The label bears two sets of directions for use. One set is for use with chlorine Bac Pac EPA Reg. No. 53735-2[for cartridge system] and the second set are for use with an alternate source of chlorine using an EPA registered source of chlorine.

Before inserting the Frog Mineral Reservoir, the pool water is balanced to between pH 7.2 and 7.8 and total alkalinity between 60-120 ppm and the pool is shocked with a chlorine shock per the manufacturer's directions. Frog Minerals are said to be "approved for use with at least 0.25 ppm of chlorine". Then for the cartridge system:

1. Turn circulation pump off, turn control dial to Pac Removal setting, unscrew knob on side of Cyclor to drain water and remove cap from Cyclor.
2. Line up slot on the side of the Frog Mineral reservoir with the fin inside of the Cyclor and lower into the Cyclor.
3. If using the chlorine Bac Pac, inset into the center of this product according to the directions on its label then replace the cap and knob on the Cyclor and turn pump back on. Set the control dial on the Cyclor per the size of the pump run time of your pool according to the chart in the manual."

There are similar use directions for skimmer application.

The label does not indicate what size of pool that can be treated with the Frog Mineral Reservoir. However, the Frog Mineral Reservoir Patented Mineral Pool Sanitizer Instruction Manual states the product purifies up to 30,000 gallons. The registrant should supply us with information explaining how the level of silver in pool water in various sized pools is controlled and how the desired level of silver in the pool water is maintained.

After six months the Frog Mineral Reservoir must be discarded/replaced. The Reservoir cannot be reused once it is removed from the system. If the Reservoir, breaks while in the pool system, the raw materials must be vacuumed out.

#### **OPPTS GLN 860.1340 Nature of the Residue**

No information is provided on the nature of the residue that will result in swimming pool water from the use of the Frog Reservoir.

However, the Frog Reservoir contains silver chloride. Silver chloride is nearly insoluble in water.

The flow of pool water through the reservoir will presumably slowly dissolve a small amount of silver ion from the silver chloride in the frog. The residue resulting in water from the proposed use will be ionic silver. The silver will be present in the pool water passing through the pool water in very small amounts. Any dissolved ionic silver from the Frog Reservoir silver would be expected to react with chlorine which is also added to the pool water to again produce silver chloride.

It is unclear to us what the claimed active ingredient in the pool water will be. It would seem that any silver ion that goes into solution in the pool water would immediately become silver chloride again. **The registrant should explain what the mechanism of action is for the efficacy of the Frog Mineral Reservoir containing silver chloride as the active ingredient.**

Is the active ingredient(s) silver and silver chloride?

The silver/silver chloride level in the treated pool water may be governed by the solubility of silver/silver chloride in water. Both silver and silver chloride have very low solubility in water.

The EPA-approved chlorine source added to the water will also be present in the pool water as a residue. The chlorine source added to the pool can be determined as available chlorine.

#### **OPPTS GLN 860.1350 Analytical Method**

The analytical method used to generate silver pool residue data is entitled, "Determination of Dissolved Silver, Standard Methods Procedure 3113B. The reference is from *Standard Methods for the Examination of Water and Waste Water, 17<sup>th</sup> ed. (1989)*. No method validation data is provided for silver from the registrant to show that the method provided adequate recoveries at the silver residue levels analyzed.

**There are also Agency analytical methods for the determination of silver in water.**

The methods include:

OSWER Method 6010b: An Inductively Coupled Plasma-Atomic Absorption Spectrometry Method

OSWER Method 7760 A: An Atomic Absorption Method

**There are numerous analytical methods available for the determination of available chlorine in water.** These include test kits for the private home user.

#### **OPPTS GLN 860.1550 Residue Data**

The registrant has submitted silver residue data from two pools, each study conducted from June 2002 to January 2003. No method validation data are submitted. Assuming that the method was

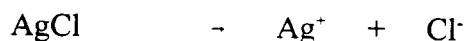
adequately validated by the registrant for use in his hands, residue levels of silver in pool water did not exceed 0.028 ppm.

It is unclear to us whether the silver residues resulting from the use of the Frog Mineral Reservoir in pool water are ionic silver or silver chloride. We have raised that question above under the Nature of the Residue section. The registrant should provide us with information to answer that question.

The Directions for Use on the label do not give any indication on the application rate for silver chloride from the Frog Reservoir. The silver/silver chloride level in the treated pool water may be governed by the solubility of silver/silver chloride in water. Both silver and silver chloride have very low solubility in water.

When RASSB stoichiometrically calculates the concentration of silver ion in the pool water based on the solubility of silver chloride in water, then:

The equilibrium constant for silver chloride in water is:



$$K_{sp} \text{ AgCl} = 1.8 \times 10^{-10} \text{ M}^2 \text{ (experimentally determined and found in the literature)}$$

where "sp" is the solubility product and "M" is the molarity of the solution.

Each ion of silver has an equal number of chloride ions in the water solution.

Then:  $K_{sp} = [\text{Ag}^+]^2 = \sqrt{1.8 \times 10^{-10} \text{ M}}$

$$[\text{Ag}^+] = 1.34 \times 10^{-5} \text{ M}$$

$$1.34 \times 10^{-5} \text{ mol } [\text{Ag}^+]/\text{L} \times 107.9 \text{ gm Ag/mol} = 0.00145 \text{ gm Ag/L}$$

or

$$1.45 \text{ mg/L(ppm)}$$

1.45 ppm is the concentration of silver ion expected in water from this calculation. However, because the pool water already contains  $\text{Cl}^-$  or  $\text{HClO}$  from the treatment of pool water from a pool chlorinating chemical, the concentration of free silver ion in the water would be expected to be much lower. The AD risk assessors should use the pool water residue data in their review. Maximum silver residues of silver in pool water based on the pool residue data do not exceed 0.028 ppm.