ILLINOIS POLLUTION CONTROL BOARD
November 7, 1985

IN THE MATTER OF:	)	
	)	R84-4
ALGICIDE CHEMICALS, AMENDMENTS TO	)	(Consolidated)
35 ILL. ADM. CODE 602.103 AND 602.110	)	R84-19

PROPOSED RULE. FIRST NOTICE.
OPINION AND ORDER OF THE BOARD (by J. Marlin):

This matter comes before the Board upon the filing of separate proposals to amend 35 Ill. Adm. Code 602.103 by Applied Biochemists Inc. (Applied) on December 14, 1983 (R 84-4) and by Carus Chemical Company Inc. (Carus) on May 23, 1984 (R 84-19). Applied amended its proposal on January 10, 1984. Both proposals were consolidated for hearing by Hearing Officer Order on June 8, 1984 after Board discussion. Merit hearings were held in Springfield, Illinois on July 24, 1984 and in Chicago, Illinois on July 31, 1984. The Illinois Department of Energy and Natural Resources on November 27, 1984 found that an economic impact study was not necessary and stated that "[t]he cost of making a formal study is economically unreasonable in relation to the value of the study to the Board in determining the adverse economic impact of the regulation." (November 27, 1984 Negative Declaration). The Economic Technical Advisory Committee concurred in this finding on January 23, 1985. A supplemental hearing called by the Board to address informational deficiencies was held May 20, 1985 in DeKalb, Illinois. The participants submitted additional information after hearing. The Agency comments were received on October 7, 1985.

The current algicide permit section 602.103 allows the use of only copper sulfate in treating algae problems in bodies of water used as public water supplies. The petitioners request that the regulations be modified to allow the use of other products for this purpose. Applied's original proposal would amend the section to include all algicides registered with the USEPA for use in potable water. Its amended proposal narrowed that scope to include only copper sulfate, copper carbonate (malachite), copper monoethanolamine and copper triethanolamine compounds. Applied's two copper ethanolamine products are liquid Cutrine-Plus and granulated Cutrine-Plus. These are registered with the USEPA pursuant to the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA, 7 U.S.C. §136 et seq., 1982) for use in bodies of water that are potable water supply sources. (Reg. No's 8959-10AA and 8959-12AA). They are also registered with the Illinois Department of Agriculture (as of December 28, 1983; Applied Exhibit 20) pursuant to the Illinois Pesticide Act (IPA) Ill. Rev. Stat. 1985, ch. 5, par. 801 et seq. These are chelated

copper compounds which use ethanolamine complexes to keep otherwise insoluble copper carbonate in solution (JR. 30, 31)[1]. This results in a rather uniform copper concentration throughout the water (App. Exhs. 16, 9, 13, 14). The liquid form contains nine percent elemental copper (0.909 lbs./gal Cu). The granulated form contains 3.7 percent active copper material (App. Exh. 14, JR. 15).

Carus' proposal would amend section 602.103 to include its two potassium permanganate products, Cairox Technical and Cairox FF. These are registered with the USEPA (Reg. No.'s 8429-6, 8429-7) under FIFRA and with the Illinois Department of Agriculture (as of November 9, 1983; Carus Exhs. C,D) for use in potable water treatment systems. Under this registration, they may not be used in open bodies of water. Cairox Technical contains 98 percent potassium permanganate and two percent inert ingredients while Cairox FF contains 95.6 percent potassium permanganate and 4.4 percent inert ingredients, which includes a food-grade additive (Exhs. A,B,C; JR. 38).

The record does not support the proposal to amend sections 602.103 and 602.110 to encompass those potable water supply algicides registered with the USEPA for use in Illinois. In order to incorporate algicides registered with the USEPA pursuant to 40 C.F.R. Part 162 (1984), the Board is statutorily mandated to have on file a list of those chemicals. (Ill. Rev. Stat. 1985, ch. 127, par. 1006.02, 35 Ill. Adm. Code 100.385). The Board attempted to obtain the list of algicides approved for use in potable water supplies from the USEPA. It was not possible to secure a complete listing. Board exhibits 1, 2, 5, 6, 7, and 8 as well as the Hearing Officer Report of March 1, 1985 document the difficulties encountered during the attempt. The USEPA has been mandated by Congress to review all algicides currently registered with it and to reregister those that merit reregistration based on the latest scientific data [7 U.S.C. 136a(g) (P.L. 95-396 eff. 9-30-1978)].

The USEPA has not yet been able to complete this task. There is no evidence in the record to show that the products of Carus and Applied have been reregistered (See Carus Exh. A, B p.1; App. Exh. 1). Based on the record before it, the Board declines to incorporate all potable water supply algicides registered with the USEPA. It will, however, incorporate individual chemical compounds where the record contains sufficient information to justify such action.

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[1] JR. refers to the transcript of the July 1984 hearings which is consecutively paginated. MR. refers to the May 1985 hearing transcript.

Potassium Permanganate

Potassium permanganate is currently used at water treatment plants to treat drinking water at the raw water intake. It is a strong oxidizing agent which degrades in water in less than a minute (MR. 129). The principal degradation product is manganese dioxide which is highly insoluble and biologically inert (MR. 107).

The labels for Cairox FF and Cairox Technical state that they are for use in potable water treatment systems to be applied only by trained water treatment plant operators or persons under their direct supervision (Carus, Exh. C). Mammalian and aquatic toxicity studies were performed (Carus Exh. E). Acute oral (rat) and dermal (rabbit) toxicity studies show that the Carus products are corrosive to skin (Carus Exh. E). The lethal concentration of Cairox Technical in fifty percent of the bluegill sunfish (Lepomis machrochirus) exposed in a 96 hour static exposure study was determined to be 2.7 mg/l (Carus Exh. E, Summary). The LC50 for Cairox FF was 3.6 mg/l. The LC50 (48 hr.) for the macroinvertebrate Daphnia magna was 84 mg/l Technical Grade with no effect at 56 mg/l. An LC50 (96 hr.) value for the green algae Selenastrum capricornutum Printz was 210 mg/l Technical Grade with no effect below 100 mg/l. Id.

Carus would like to expand the use of potassium permanganate to include its application to public surface water supply sources. The current USEPA registration allows its use only in water treatment systems (MR. 121). Even if the Board approves Carus' request, the Company will need a Federal label change before the product can be used in water supply reservoirs. Carus intends to pursue this matter with the USEPA. Carus submitted a paper by Dr. Jerome Carr entitled "Integrated Iron and Nitrogen Control for Lake Restoration" which is now made Carus Exhibit F. Dr. Carr studied the use of potassium permanganate as an algicide in Morses Pond, a 102 acre pond in Massachusetts. The study showed a reduction in the amount of iron in the pond available for macrophytic uptake after application of potassium permanganate which in turn limited the amount of algae present (Carus Exh. F).

Potassium permanganate has been successfully used as an algicide in water treatment plants when it is applied continuously. In open water, treatment will be infrequent and the product concentration will be tailored to the chemistry of the receiving water (MR. 135). The immediate effect of the treatment is largely limited to the upper portion of the water column in the area behind the applicator's boat. Given this situation, the potential for widespread harm to the aquatic fauna in a lake is remote.

The Board finds that potassium permanganate is suitable for use as an algicide in public water supplies. In so finding, the Board notes that this compound must also be approved by the USEPA

for this purpose prior to such use. The Board further finds pursuant to Section 27(b) of the Act that the allowance of potassium permanganate as a public water supply algicide will have no adverse economic impact on the people of this State and will in fact foster competition between approved public water supply algicides.

Copper Carbonate (Malachite)

Applied, while proposing copper carbonate as an algicide, provided no information on it. The Agency in its comments stated that because malachite is "insoluble with a solubility factor of 1×10^{-34} and because it does not possess any algicidal properties, it should not be included in the list of acceptable algicides." (Ag. Comments, October 4, 1985). Because of the lack of any data supporting the inclusion of malachite, the Board will not include it as a public water supply algicide.

Copper Monoethanolamine/Triethanolamine

Both products of Applied contain copper in the form of mixed copper-ethanolamine complexes. Some of the breakdown products of Cutrine-Plus include diethanolamine, monoethanolamine, ammonia, acetic acid, hydroxyacetic acid, glyoxal, glyoxylic acid, oxalic acid, formaldehyde gas and formic acid. Cutrine-Plus is a slight skin irritant and is moderately toxic if swallowed. It is less corrosive than copper sulfate.

Toxicological data show Cutrine-Plus to be "[g]enerally nontoxic to fish and wildlife at recommended dosages," although "trout. . . and certain other sensitive fish species may be adversely affected in very soft water (below 50 ppm of $CaCo_3$)." (App. Exh. 13). Toxicity data for the bluegill sunfish and for the fathead minnow (Pimephales promelas) appear in Exhibits 11 and 17 while data on oral dose, single skin penetration, single inhalation, primary skin irritation and eye injury from animal studies appear in Applied Exhibit 12.

At 45 Fed. Reg. 53478 (August 12, 1980), the USEPA mentions that it was concerned with the presence of 2.1 ppm of N-nitrosodiethanolamine in an original Applied formulation "since 80 percent of known N-nitrosoamine compounds have been shown to be carcinogenic in a variety of species." (App. Exh. 7). The formulation was revised by Applied and now contains less than 1/ppm of N-nitrosodiethanolamine which represents a risk level acceptable to the USEPA. Id.

Prior to the May 20 hearing, the Board raised the question of the possible mutagenicity and carcinogenicity of triethanolamine (TREA). A scientific paper on that topic by Hoshino and Tanooka was placed in the record (Board Exh. 4). The researchers reported that mice fed on a diet including TREA developed tumors and that TREA in combination with sodium nitrite caused mutations in bacteria.

The Board retained Dr. William Hallenbeck, who has done research involving animal toxicology and human health effects to evaluate the Tanooka paper. He pointed out that the controls used in the test made it impossible to conclude with certainty that TREA caused the tumors. He also stated that, "a stable and direct, but unidentified, mutagen was found under test conditions which approached normal physiological parameters" (MR. 16 and 17). In answer to a question he replied, "...my overall conclusion about TREA is that at this point you could only go so far as to characterize it as a potential animal carcinogen and, therefore, a potential human carcinogen" (MR. 26). Regarding mutagenicity he pointed out that the Tanooka paper reported a four to five-fold increase in mutagenicity for the combination of TREA and sodium nitrite over sodium nitrite alone. He also stated that sodium nitrite is common in the human diet (MR. 56 and 57).

In response to the Tanooka paper, Applied presented two letters critical of the paper and entered a paper by Inone et. al. which considered the mutagenicity of TREA (Applied Exh. 25). This study found no evidence that TREA by itself was mutagenic. It also suggested further study to determine the exact cause of the tumors reported by Tanooka.

Applied's Exhibit 9 which was introduced at the July 24, 1984 hearing stated:

> In an effort to find any and all available references on chronic data on monoethanolamine and triethanolamine APPLIED BIOCHEMISTS, INC. contacted the environmental and toxicology branches of the ethanolamine manufacturers and suppliers, DOW CHEMICAL, UNION CARBIDE, OLIN CORPORATION, TEXACO INC. and its subsidiary JEFFERSON CHEMICAL. Based on our efforts, there apparently is no chronic data on ethanolamines. However, these contacts yielded significant information and insight into ethanolamines, their biodegradation and toxicology.

No mention was made of the Tanooka paper or the Inone paper which were published in 1978 and 1982 respectively. Applied's representative said at hearing that Applied was not informed of the Tanooka paper by the TREA manufacturers and first learned of it in the hearing officer order. He also indicated that the information had not been supplied to the USEPA during the Federal registration process (MR. 69).

Applied Exhibit 10 lists the expected concentration of TREA in treated water as between 0.48 ppm and 2.4 ppm (see MR. 75 for correction). Applied gave no data as to how long TREA persisted in the body of water after treatment and in what concentration (MR. 66).

The USEPA approved Cutrine and Cutrine-Plus for use in public water supplies and the Illinois EPA has recommended that they be approved in Illinois. The Board notes that Federal approval was based largely upon information supplied by Applied, who in turn relied on data provided by TREA suppliers. The Applied products have not yet been reregistered by the USEPA.

The Tanooka paper indicates that TREA is a possible carcinogen. The controls in that study were inadequate to determine whether TREA or TREA in combination with the heated diet, or some other combination of factors caused the reported tumors. Applied's rebuttal of the Tanooka paper failed to dispel the concerns raised. The questions raised can best be addressed by an experiment with proper controls. Regarding mutagenicity, there is reason to believe that TREA in conjunction with sodium nitrite (which is common in the diet) has mutagenic properties. In the absence of additional substantive data, the Board believes it is unwise to place this chemical in water supplies which are consumed by the public. The Board has no reason to conclude that the use of Applied's products containing TREA pose a threat in other bodies of water.

The Board finds that Applied has failed to demonstrate that TREA can be applied to public water supplies without posing a threat to the public health. Pursuant to Section 27(b) of the Act, Applied's data indicate that its product is competitive with the approved algicide (JR. 90-99). However, given the uncertainty over potential public health impacts of the product, the Board cannot find that approving Applied's petition will not have an overall adverse economic impact.

The Agency has suggested deleting the phrase "supervising the application of the algicide" from current Section 602.110. No reason for deleting the phrase was provided. The Board believes that the phrase is helpful and declines to delete it in the absence of a justification for doing so.

ORDER

The Board hereby directs the Clerk to cause first notice publication of 35 Ill. Adm. Code 602.103 and 602.110 as amended in the Illinois Register:

TITLE 35: ENVIRONMENTAL PROTECTION
SUBTITLE F: PUBLIC WATER SUPPLIES
CHAPTER I: POLLUTION CONTROL BOARD

PART 602
PERMITS

Section 602.103 Algicide Permits

No algicide shall be applied to any stream, reservoir, lake, pond, or other body of water used as a public water supply source

without an Algicide Permit issued by the Agency. Copper sulphfate ~~is~~ and potassium permanganate are the only algicides which may be used in public water supplies. Permits issued under this Section will be valid for public water supply sources only.

Section 602.110 Algicide Permit Applications

a. All applications for algicide permits shall contain:

   1. the name and certificate number of the certified operator supervising the application of the algicide,

   2. a statement describing the extent of the algae problem, history of any past algae problems, and algicide treatments, and a description of any fish kills which have resulted from treatments in the past; and

   3. adequate information to support exceeding the limits as stated in 35 Ill. Adm. Code 302: Water Quality Standards.

b. After any algicide permit is issued, and before the permit expires by its stated terms, if there is any major change either in the operation of the public water supply, or in algae growth, which affects the use of ~~copper sulfate~~ the algicide as outlined in the permit, the public water supply shall submit an application for modification of its permit. This application shall contain all of the information required by this subsection (b) and subsection (a) above.

c. Any algicide permit issued under this Section shall exempt permittee from obtaining an aquatic pesticide permit as provided in 35 Ill. Adm. Code 652.601.

IT IS SO ORDERED.

I, Dorothy M. Gunn, Clerk of the Illinois Pollution Control Board, hereby certify that the above Opinion and Order was adopted on the 7th day of November, 1985 by a vote of 7-0.

Dorothy M. Gunn
Dorothy M. Gunn, Clerk
Illinois Pollution Control Board