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Effects of Water and Copper Complexes in Combination with Reward® Herbicide[1]

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ABSTRACT

An array of various copper algaecides and herbicides have been developed and are now marketed by several manufacturers for the aquatic vegetation control market. Reward® Landscape and Aquatic Herbicide (diquat dibromide) manufactured by Syngenta Crop Protection, Inc. (formerly Zeneca Ag Products), is often used in combination with a copper-based material to enhance algal or herbicidal activity against specific aquatic nuisance plant species. For subsurface applications, aquatic plant managers may utilize little water as a diluent with Reward to maximize the range of area that can be treated from one tank before re-filling. Isolated instances of chemical incompatibilities between Reward and some common aquatic copper herbicides have been reported. Syngenta conducted a compatibility trial evaluating Reward along with an updated formulation of Reward (termed Reward QIT = Reward Quality Improved Technology in this paper). The purpose of this study was to determine the compatibility of Reward concentrates in combination with eight different copper materials and compatibility in distilled water, hard water, alkaline and acidic water to indicate any compatibility problems. Results of this trial indicate all Reward and copper herbicides tested to be compatible in the various water types. Precipitate development in some concentrate mixtures without water demonstrate the importance of dilution of concentrates with water.

Key words: Diquat, copper, compatibility, dilution, precipitate.

INTRODUCTION

Aquatic applicators in the U.S. aquatic vegetation management market may commonly mix aquatic herbicides together in the spray tank in dilution with water, in some cases utilizing as little water as possible. For submersed vegetation control, water volume is not as critical for coverage as surface applications, so dilution concentrations in spray mixtures may vary greatly. Physical compatibility of herbicide mixtures may be adversely affected when mixed without a water diluent. Herbicides are usually diluted in water of differing qualities of hardness and/or acidity utilizing either city water, well water or water pulled directly from the water body to be treated. Zeneca introduced a new formulation of Reward Landscape and Aquatic Herbicide (Reward QIT), to replace the current formulation in June 2000. This study was initiated to investigate and compare the stability and compatibility of the two formulations of Reward (both containing 240 grams diquat cation per liter) and some primary copper-based herbicides used in the aquatics market, in acidic, basic, hard and distilled water, alone and when mixed as concentrates. The combinations of Reward and copper herbicides were tested as a worst-case indication of whether problems may occur when mixing with different volumes of water as a diluent. The manufacturer discourages the use of direct concentrate mixtures of Reward Landscape and Aquatic Herbicide with any herbicides or other pesticides without first diluting in water and only if the mixture has been tested for compatibility first.

MATERIALS AND METHODS

Products were mixed in 200 ml beakers, using magnetic stir bars rotating at 200 RPM. Mixture details are given in the data summary below. Mixtures were either of two concentrates (mixed together in the order shown), or of products diluted in water of different qualities. The different water

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types are defined as follows; distilled water—pH = 7.79, hard water—pH = 7.68 (349 ppm of calcium and magnesium ions), acidic water—pH 4.39 (derived by adding 1% w/w of Fisher pH 4.00 buffer to distilled water), and basic water—pH 9.40 (derived by adding 1% w/w of Fisher pH 10.00 buffer to distilled water). These water types are representative of the range of water that could exist in field conditions compared to distilled water as a standard.

Where products were diluted in water, the beaker was first half-filled with the respective water type, agitation begun, then the herbicide added at the ratio of one part product (herbicide) to five parts water, and the beaker topped off with the remaining required amount of water. Reward Landscape and Aquatic Herbicide, for field use, is commonly diluted with water to make a 0.25% to 2% solution. In this study 20 ml Reward was added to 50 ml water while agitating, and the mixture topped up to 120 ml of solution (20 ml Reward : 100 ml water). This equates to a one part Reward concentrate to five parts water (16.67% solution). For solid copper sulfate, this is equivalent to 0.453 kg copper sulfate in 3.81 liters of water. Concentrates were mixed together in the ratios shown in the paragraph below. Solid copper sulfate was added directly to the liquid concentrated tank-mix partner product. For concentrates of Reward mixed with concentrates of copper products in dilution with water, the total volume of the two concentrates equaled 20 ml, in the correct ratio of Reward : copper product with 100 ml of water.

Where products were mixed as concentrates, herbicides tested were Reward Landscape and Aquatic Herbicide, Reward Landscape and Aquatic Herbicide QIT (referenced as Reward QIT), Algae-Pro® (7% elemental copper from copper triethanolamine complex and solubilized copper), copper sulfate (copper sulfate pentahydrate 99%), Captain® (9.09% elemental copper from copper ethanolamine complexes), Clearigate® (3.825% elemental copper from copper monoethanolamine complex, copper triethanolamine complex and copper carbonate), Cutrine-Plus® (9% copper monoethanolamine complex, copper triethanolamine complex and copper carbonate), Komeen® (8% elemental copper from copper ethylenediamine complex and copper sulfate pentahydrate), K-Tea® (8% elemental copper from copper-triethanolamine complex), and Nautique® (9.1% elemental copper from copper ethylenediamine complex and copper triethanolamine complex)[4]. Mixture rates were extrapolated from the various herbicide labels based on what was determined to be a normal rate range for each material to be applied per surface acre. As such, on a liter volume basis, Reward and Reward QIT were mixed with the following copper products at the following rates; Algae-Pro 0.75 liters and 5 liters, with copper sulfate 0.309 kg and 0.9525 kg, with Captain 0.6 liters and 5 liters, with Clearigate 1 liters and 9 liters, with Cutrine-Plus 0.6 liters and 12 liters, with Komeen 1.5 liters and 10 liters, K-Tea 1 liter and 10 liters, and Nautique 5 liters and 10 liters. These ratios were calculated down to equate to a total 20 mL (Table 2) volume.

[4]REWARD® is a registered trademark of Syngenta Crop Protection, Inc., Komeen® and K-Tea® are trademarks of Griffin Corporation. Nautique®, Algae-Pro® and Captain® are trademarks of SePRO Corp.; Clearigate® and Cutrine-Plus® are trademarks of Applied Biochemists Inc.

Visual assessments were made during mixing, after one hour, six hours and two days. Mixtures were monitored for the following characteristics; dramatic color change, heat, gas production, and formation of a precipitate. If any of these changes occurred, the mixture was deemed as a "fail" with the reason for the failure noted based on the four characteristics outlined. If no, or very minor, changes occurred a "pass" to "medium" notation was made. In the case of a medium rating, only minor "clouding" of the mixture was apparent while agitation was maintained, and the mixture was deemed as able to be sprayed with conventional spray equipment.

When a failure was recorded, in the case of a precipitate forming, that mixture was then tested in dilution with the four water types to determine if the failure was avoidable by dilution with the 1:5 dilution of herbicide(s) to water. All tests were carried out at room temperature.

RESULTS AND DISCUSSION

All individual products diluted in the four water types resulted in passes. Therefore, Reward, Reward QIT, and all the copper products tested would be expected to be physically compatible with hard, basic, acidic and distilled water. pH changes of the mixture solutions were relatively minimal. One hundred and four total treatments were assessed at mixing (zero days) and up to two days after mixing. Noted in Table 2 are cases where a "fail" or "medium" resulted up to the two-day evaluation period.

At the two-day evaluation period, mixtures of concentrates of Clearigate, K-Tea, Cutrine-Plus, Nautique or Captain with Reward or Reward QIT, with no water diluent, resulted in failures (black precipitates). With the exception of Reward + Clearigate, all of these failures were the ratios where the lower rate of the copper product to Reward or Reward QIT were mixed. Reward QIT plus Nautique failed at the six hour rating in addition to the two day rating but only at the one part Reward QIT : five parts Nautique ratio. Copper sulfate mixed at the rate of 0.9525 kg/l of Reward concentrate resulted in a failure due to incomplete dissolution of the copper sulfate crystals, not a tank-mix incompatibility. Neither the high nor the low rate of copper sulfate crystals dissolved fully in the Reward QIT concentrate and therefore should be dissolved in water prior to use.

TABLE 1. THE PH VALUES OF TWO FORMULATIONS OF DIQUAT DIBROMIDE AND VARIOUS AQUATIC COPPER HERBICIDES. THESE VALUES SHOULD BE CONSIDERED WHEN CONSIDERING MIXTURES OF THE VARIOUS HERBICIDES.

Herbicide	pH (Units)
Reward	5.71
Reward QIT	4.26
Clearigate	9.98
Copper sulfate (dissolved as 0.119 kg/L distilled water)	4.23
K-Tea	9.37
Komeen	10.63
Cutrine-Plus	10.12
Nautique	13.08
Algae-Pro	7.16
Captain	9.78

TABLE 2. THE RESULTING pH RANGES AND INCOMPATIBILITIES OF VARIOUS AQUATIC HERBICIDES IN MIXTURES OVER TIME ARE PRESENTED BELOW. VISUAL ASSESSMENTS WERE BASED PASS = NO CHANGES OCCURRED, MEDIUM = SLIGHT CLOUDING OF MIXTURE OCCURRED, FAIL = THICK BLACK PRECIPITATE FORMED.

			Visual Assessment		
Herbicide(s)	pH	Rate(s)	1 hour	6 hours	2 days
Reward + Clearigate	8.41	10 ml 10 ml	pass	pass	fail
Reward QIT + Clearigate	9.18	10 ml 10 ml	pass	pass	medium
Reward + Clearigate	9.73	2 ml 18 ml	pass	pass	fail
Reward QIT + Clearigate	9.73	2 ml 18 ml	pass	pass	medium
Reward + K-Tea	9.07	10 ml 10 ml	pass	pass	fail
Reward + Cutrine-Plus	9.19	12.5 ml 7.5 ml	pass	pass	fail
Reward QIT + Cutrine-Plus	9.76	12.5 ml 7.5 ml	pass	pass	medium
Reward + Nautique	12.93	3.33 ml 16.67 ml	pass	pass	fail
Reward QIT Nautique	13.09	3.33 ml 16.67 ml	pass	fail	fail
Reward + Captain	9.14	7.5 ml 12 ml	pass	pass	fail
Reward QIT + Captain	9.52	7.5 ml 12 ml	pass	pass	fail

For the concentrate mixtures that failed (Table 2) without water diluent, these mixtures diluted with water resulted in passes to medium ratings up to the two day rating, except for Reward mixtures with Nautique in the one : five ratios at the two day ratings for all four water types. Reward QIT mixtures with Nautique at the same ratios and same water types as above resulted in medium ratings indicating that Reward QIT may be more compatible than Reward in combination with Nautique and water diluent.

The pH of the concentrated products (Table 1) may be important in determining whether a particular mixture might fail, but more importantly demonstrates the broad range of differences between relatively similar products. pH may affect the compatibility of different products as are other factors such as ion concentration within products, ratio of use rates of the concentrated products in the mixture, how well buffered the concentrates are, amount of water in the mixture and the chemistry involved in formulating the products, particularly the type of (chelated) copper complex used. The thick black precipitate that occurred in some of the Reward + copper concentrate mixtures is most likely due to copper ethanolamine complexes at high pH in the tank-mix solution. Some, but not all of the copper products containing the copper ethylenediamine complex appear to be stable at a high pH, when tank-mixed with Reward. Copper ethanolamine complexes appear to be stable at neutral pHs when tank mixed with diquat. The thick black precipitates found in tank-mix failures may be due to hydrolysis of diquat dibromide at high pH (Tomlin 1997, Stuzka and Dokoupilova 1990). The hydrolysis breakdown product is theorized to react with a component of the tank-mix solution to form an insoluble precipitate.

Reward + copper product incompatibilities may result from inadequate water diluent, insufficient agitation, and/or holding the tank mixture too long (past six hours). Concentrate compatibility problems may be overcome by using direct injection systems that keep concentrates separate until they enter the boom. This might be a viable option for applicators who are unsure of how long concentrated products will sit in their spray tanks after mixing. Factors such as unpredictable weather can greatly extend the length of time a mixture remains in a spray tank.

The data indicate that Reward QIT performs similarly to the standard formulation of Reward in regards to physical compatibility with copper herbicides and in various water types. The study was conducted to determine the importance of water volume as a diluent when mixing products as well as identifying specific incompatibilities and differences. Caution should be exercised when mixing any materials, and all label recommendations should be followed. Biological efficacy was not evaluated in this trial.

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