FOREST SERVICE TECHNOLOGY & DEVELOPMENT PROJECT 2010-2012--*Testing Quaternary Ammonium Products (aquatic invasive species decontaminants) for Corrosive Effects to Fire Equipment*

Effects of the Quaternary Ammonium Disinfectant *Green Solutions High Dilution* (1.8%) on Metals and Non-Metallic Materials used in Fire Operations

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The study proposal:

In 2010, the Intermountain Region proposed that the Technical Center test the quaternary ammonium formulation G*reen Solutions High Dilution* (GSHD), a chemical commonly used to disinfect fire equipment, for possible corrosive effects on the metals that occur in tanks and fittings. Quat concentrations and exposure times recommended for aquatic invasive species decontamination would be used. Of particular importance would be metals used in aviation, such as internal helicopter tanks. In addition, we asked to test methods that, if quat compounds are used, would avoid corrosion, such as the efficacy of rinsing the equipment after exposure to these chemicals.
Testing this quaternary ammonium product for its potential for corrosion has obvious safety benefits, especially in gear used in aviation. If a protocol can be developed that would allow its safe use, quaternary ammonium could be utilized as an effective and inexpensive decontaminant for aquatic invasives, while at the same time avoiding costly damage to gear.

The Study

This experiment consisted of three tests, which are defined in Forest Service Specification 5100-304c for Long Term Retardant, Wildland Firefighting (2007), accessible at http://www.fs.fed.us/rm/fire/wfcs/documents/304c.pdf. Maximum allowable corrosion rates for this study are shown in Table 1.

Testing corrosive effects of GSHD on metals (uniform corrosion test)
The first test was the Forest Service's standard uniform corrosion test for fire chemicals which gives a corrosion rate of the metal/alloy expressed in mils per year. In this test, one coupon is fully immersed and a second is half immersed in the product and kept at 70°F for 90 days (Fig. 1). A third coupon is fully immersed and a fourth is half immersed in product and kept at 120°F for 90 days. There are three replicates for each of the four conditions, and the final corrosion rates are a result of the average of the three replicates. For corrosion testing, it was decided to use our standard metals and alloys. These are 2024 T-3 aluminum, 4130 steel, yellow brass, and Az31B magnesium. A 1.8% solution of the quaternary ammonium compound *Green Solutions High Dilution* (GSHD), a formulation shown to be effective against most aquatic invasive species encountered in fire operations, was tested.

Corrosion tests were not conducted on the quaternary ammonium compound concentrate because disinfection protocols will only expose metals and other materials to the diluted product, a 1.8% solution. In addition to the standard 90 day immersion into GSHD at 1.8% dilution, a complete set of

coupons (three replicates at each immersion and temperature) was also immersed for one day in GSHD at 1.8% dilution, then immersed in water for the remaining 89 days under the same conditions (full and partial immersions at 70°F and 120°F). This test was done to represent a tank being sterilized with GSHD and then filled with water. A third full set of coupons was immersed for one day in GSHD at 1.8% dilution, and then immersed in Phos-Chek WD881 foam mixed at 0.3% dilution for the remaining 89 days under the same conditions (full and partial immersions at 70°F and 120°F). This test was performed because previous tests have shown that foam solutions can be more corrosive when metals/alloys are exposed to other products first. The 0.3% dilution of Phos-Chek WD881 was chosen because it is the most common dilution used for helicopter operations. Results are shown in Table 2, along with results from a previous experiment where the same types of metals/alloys used in this study were exposed to evaluate tap water only. The maximum allowable corrosion rates for the metallic materials tested are shown in Table 1 under the "Mixed Products" section. All metallic materials tested for uniform corrosion were within specifications.

Testing corrosive effects of GSHD on non-metallic materials

The second test conducted determines the effects of the test solution, GSHD (1.8%), on non-metallic materials. Again, there are three replicates of each material, and their results are averaged. Standard materials include neoprene, polyvinyl chloride, fiber reinforced plastic, high density polyethylene, low density polyethylene, S 81733 (a sealant), and flexible cross-linked polyolefin. These materials are commonly found in aircraft and include sealants, gasket compounds, and tank liners. In addition to these seven materials, nine other non-metallic materials were tested. They include materials used in Bambi bucket construction and materials which line fire engine water tanks. All non-metallics are fully immersed into the solution at room temperature for 20 cycles. A cycle is comprised of the material being immersed for the evening and then being suspended to air dry during the day (Fig. 2).

Non-metallic testing indicates change in hardness as measured using a durometer, shores A and D (hardness scales), and change in volume measured in milliliters. When measuring hardness, shore A is used to measure softer materials like neoprene and shore D us used to measure harder materials like polyvinyl chloride. FS Specification 5100-304c states that there must be ≤ 10% decrease in hardness or ≤ 20% increase in hardness, and volume must not change by more than ±0.5ml on the final day of testing. Negative numbers in the "Hardness" column in Tables 3 and 4 indicate that the material softened whereas positive numbers show an increase in hardness. Negative numbers in the "Volume" column in Tables 3 and 4 indicate the material shrank, positive numbers indicate expansion. If any of the values fall outside of Forest Service parameters, a second measurement is taken 24 hours later. If values are still not within limits, the product fails. Results for standard test materials are shown in Table 3. Materials used and results of testing for the additional nine non-metallic materials are shown in Table 4. All non-metallic materials tested were within specifications.

*Testing for **intergranular corrosion** effects of GSHD on metals*

The third test measured intergranular corrosion in the metal coupons which went through the uniform corrosion process. In this test, one representative coupon from each of the four conditions described in the uniform corrosion process is sent in for intergranular corrosion analysis. The coupon is sliced and mounted, polished to a 0.3 micron alumna finish, etched, and examined under a 500 power microscope. No intergranular corrosion is permitted on the fourth polishing. As shown below in Table 5, no magnesium coupons showed intergranular corrosion. In contrast, 3 aluminum coupons showed intergranular corrosion all the way through the fourth polishing. Coupon A19908 was immersed in Green Solution High Dilution for one day at 70°F and then immersed in water for 89 days at 70°F. Coupons A19916 and A19918 were both immersed in Green Solution High Dilution for 1 day at 70°F and

then 89 days in the solution of 0.3% Phos-ChekWD881 at 70°F. All three coupons were partial immersions.

Results/Conclusions

For uniform corrosion and non-metallic materials tests, results for all materials fell within acceptable parameters according to FS specifications. Steel did have a slightly higher corrosion rate than the other metals (Table 2). Temperature was also a factor, with the 120° immersion having higher corrosion rates than the 70° immersions for steel. The non-metallic sealant S81733 was out of specification on the initial test day but then came into specification by the second day. Using the guidelines set forth by Forest Service Specification 5100-304c, *Green Solution High Dilution* (1.8%) would not pass the intergranular corrosion requirements for aluminum. This means GSHD would not be allowed to be used in fixed-tank helicopters, single-engine fixed-wing air tankers, or multi-engine fixed-wing air tankers. There are no intergranular corrosion requirements for helicopter buckets or ground based application equipment.

Table 1

Maximum Allowable Corrosion Rates (mils-per-year) for Wildland Fire Chemical Products (USFS Specification 5100-304c(2007)). Refer to the "Mixed Products" section (circled below) for the maximum allowable corrosion rates for this study

5100-304c – June 2007

Table 4. Maximum Allowable Corrosion Rates (mils-per-year) for Wildland Fire Chemical Products.[1]

	2024-T3 Aluminum				4130 Steel				Yellow Brass	Az31B Magnesium			
	Total		Partial		Total		Partial		Partial	Total		Partial	
Temperature: °F	70	120	70	120	70	120	70	120	120	70	120	70	120
	mils-per-year												
Concentrates													
Wet concentrates for fixed-tank helicopters	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Wet concentrates [2] except fixed-tank helicopters	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0				
Mixed Products													
Fixed-tank helicopters [3]	2.0	2.0	2.0	2.0	5.0	5.0	5.0	5.0	5.0	4.0	4.0	4.0	4.0
Fixed-wing air tankers [4]	2.0	2.0	2.0	2.0	5.0	5.0	5.0	5.0	5.0				
Helicopter bucket and [2] Ground-based application	2.0	2.0	2.0	2.0	5.0	5.0	5.0	5.0	5.0				

[1] All uniform corrosion rates shall be determined by 90-day weight loss tests. All uniform corrosion rates are the maximum allowable average of all replicates.

[2] Magnesium uniform corrosion tests shall be performed for performance information. Intergranular corrosion tests are not required on aluminum or magnesium.

[3] Intergranular corrosion tests shall be performed on aluminum and magnesium coupons; no intergranular corrosion is allowed.

[4] Intergranular corrosion tests shall be performed on aluminum coupons; no intergranular corrosion is allowed. Magnesium uniform corrosion tests shall be performed for performance information. Intergranular corrosion tests are not required on magnesium.

Table 2

Results of 90-Day Corrosion Test on Metals as Measured by Change in Mass. Four metals were immersed in the quaternary ammonium formulation *Green Solutions High Dilution* (1.8%) in four treatments: (1) GSHD for 90 days; (2) GSHD for one day, water for 89 days; (3) GSHD for one day, Phos Chek WD881(0.3%) foam for 89 days; and (4) tap water for 90 days.

	Quaternary Ammonia (mils/year)			
	2024 T-3 Aluminum	**4130 Steel**	**Yellow Brass**	**Az31B Magnesium**
70° Total	0.1	0.9	0.1	1.0
120° Total	0.1	1.3	0.1	2.4
70° Partial	0.1	0.7	0.1	1.1
120° Partial	< 0.1	2.2	0.0	1.5
	Quaternary Ammonia-->water (mils/year)			
70° Total	0.3	1.8	< 0.1	0.9
120° Total	0.7	2.6	< 0.1	0.8
70° Partial	0.2	1.1	< 0.1	0.7
120° Partial	0.4	1.6	< 0.1	0.7
	Quaternary Ammonia --> foam (mils/year)			
70° Total	0.3	0.6	0.2	1.5
120° Total	1.3	1.5	0.2	1.6
70° Partial	0.3	0.9	0.2	0.7
120° Partial	0.4	2.0	0.2	1.0
	Tap Water from Northern Forest Fire Lab			
70° Total	< 0.1	1.5	0.2	1.2
120° Total	< 0.1	1.7	< 0.1	0.7
70° Partial	0.1	1.4	0.1	1.0
120° Partial	< 0.1	1.4	< 0.1	0.6

Table 3

Results of effects of the quaternary ammonium formulation *Green Solutions High Dilution* (1.8%) on Standard Non-Metallic Materials as measured by change in Hardness and Volume. Standard materials commonly found in aircraft (e.g. sealants, gasket compounds, tank liners) include neoprene (NEO), polyvinyl chloride (PVC), fiber reinforced plastic (FRP), high density polyethylene (HDPE), low density polyethylene (LDPE), S 81733, and flexible cross-linked polyolefin (FPO). FS Specification 5100-304c states that there must be ≤ 10% decrease in hardness or ≤ 20% increase in hardness, and volume must not change by more than ±0.5ml. Negative "Hardness" values indicate that the material softened; positive values show an increase in hardness. Negative "Volume" values indicate the material shrank, positive values indicate expansion

	HARDNESS		AFTER 24 HOURS		VOLUME	
MATERIAL	CHANGE	AVERAGE	CHANGE	AVERAGE	CHANGE	AVERAGE
	Percent	Percent	Percent	Percent	(ml)	(ml)
NEO-	-2.3				0.0	
NEO-	-4.7	-3.8			0.0	0.0
NEO-	-4.5				0.1	
PVC-	1.3				0.0	
PVC-	0.0	0.4			0.2	0.1
PVC-	0.0				0.2	
FRP-	0.0				0.1	
FRP-	0.0	-0.7			0.1	0.1
FRP-	-2.1				0.1	
HDPE-	-2.9				0.0	
HDPE-	-2.9	-2.9			0.0	0.0
HDPE-	-2.9				0.0	
LDPE-	-5.6				0.0	
LDPE-	-5.6	-4.9			-0.1	0.0
LDPE-	-3.7				0.0	
S 81733-	-13.8		-5.2		0.0	
S 81733-	-17.2	-14.9	-5.2	-5.2	0.1	0.0
S 81733-	-13.8		-5.2		0.0	
FPO-	1.8				0.0	
FPO-	-1.8	-0.6			0.0	0.0
FPO-	-1.8				0.0	

Table 4

Results of effects of the quaternary ammonium formulation *Green Solutions High Dilution* (1.8%) for materials found in helicopter Bambi Buckets and fire engine water tanks as measured by change in Hardness and Volume. FS Specification 5100-304c states that there must be ≤ 10% decrease in hardness or ≤ 20% increase in hardness, and volume must not change by more than ±0.5ml. Negative "Hardness" values indicate that the material softened; positive values show an increase in hardness. Negative "Volume" values indicate the material shrank, positive values indicate expansion

	HARDNESS		VOLUME	
MATERIAL	CHANGE	AVERAGE	CHANGE	AVERAGE
	Percent	Percent	(ml)	(ml)
003949/RMP101,Sheet,HDPE, 1 " Bambi Bucket	-2.7		0.0	
	0.0	0.6	0.0	0.0
	4.5		0.0	
Clear Co-poly polypropylene Engine w ater tank sight w indow	-6.7		0.0	
	0.0	-4.0	0.0	0.0
	-5.5		0.0	
Black copoly polypropylene Engine w ater tank	-4.4		0.1	
	-5.8	-3.9	0.0	0.0
	-1.4		-0.1	
001137/ BAD134201 Strip, w eather, 0.060" -0.155" Grip 825-300, bulb, Bambi Bucket	-5.0		0.0	
	-2.5	-4.1	-0.1	0.0
	-4.9		0.0	
001828/ FWR0107, w asher, 7/32"x 1-1/2", 1/8" neo , Bambi Bucket	-5.8		0.0	
	-5.7	-7.2	-0.1	0.0
	-10.0		0.0	
003901/RMFS002, fabric, stedprene, 60"BLK stedfast, Bambi Bucket	5.9		0.0	
	6.0	5.9	-0.1	0.0
	5.9		0.0	
003854/ RMFU3026 fabric, OBU 26oz, 56"1Org 3026 OBU, Bambi Bucket	8.3		0.0	
	12.1	9.6	-0.1	0.0
	8.3		0.0	
003855/ RMFU 1936, Fabril, OBU, 36oz, 56", IORG 1936 ORB, Bambi Bucket	-5.4		0.0	
	-5.5	-5.5	0.0	0.0
	-5.6		0.0	
003857/ RMFU 6672, fabril, OBU, 72oz, 56" IORG 6672 ORB, bambi Bucket	0.0		0.0	
	-6.0	-1.3	0.0	0.0
	2.0		0.0	

Table 5

Results of intergranular corrosion attack of quaternary ammonium formulation *Green Solutions High Dilution* (1.8%) on representative aluminum and magnesium coupons. 'Test #' indicates the polishing event. Coupon A19908 was immersed in GSHD for one day at 70°F and then immersed in water for 89 days at 70°F. Coupons A19916 and A19918 were both immersed in GSHD for 1 day at 70°F and then 89 days in the solution of 0.3% Phos Chek WD881 at 70°F. All three coupons were partial immersions.

Coupon Number (Aluminum)	Intergranular Attack (Test #1)	Intergranular Attack (Test #2)	Intergranular Attack (Test #3)	Intergranular Attack (Test #4)	Coupon Number (Magnesium)	Intergranular Attack (Test #1)
A19887	ND	ND	ND	ND	L9948	ND
A19888	0.0046	0.0056	ND	ND	L9949	ND
A19890	0.0030	ND	ND	ND	L9950	ND
A19893	ND	ND	ND	ND	L9955	ND
A19898	ND	ND	ND	ND	L9960	ND
A19899	0.0040	ND	ND	ND	L9961	ND
A19901	0.0020	ND	ND	ND	L9962	ND
A19908	0.0070	0.0050	0.0050	0.0086	L9963	ND
A19915	ND	ND	ND	ND	L9972	ND
A19916	0.0030	0.0050	0.0050	0.0080	L9974	ND
A19917	ND	ND	ND	ND	L9981	ND
A19918	0.0030	0.0030	0.0024	0.0024	L9983	ND

* ND = no intergranular attack detected

Fig. 1

USFS Standard Uniform Corrosion Test for fire chemicals. In this test, coupon replicates are half immersed and fully immersed in product. Three replicates of half immersion and three replicates of full immersion are stored in an incubator for 90 days at 70°F. Similarly, three replicates of half immersion and three replicates of full immersion are also stored at 120°F for 90 days.

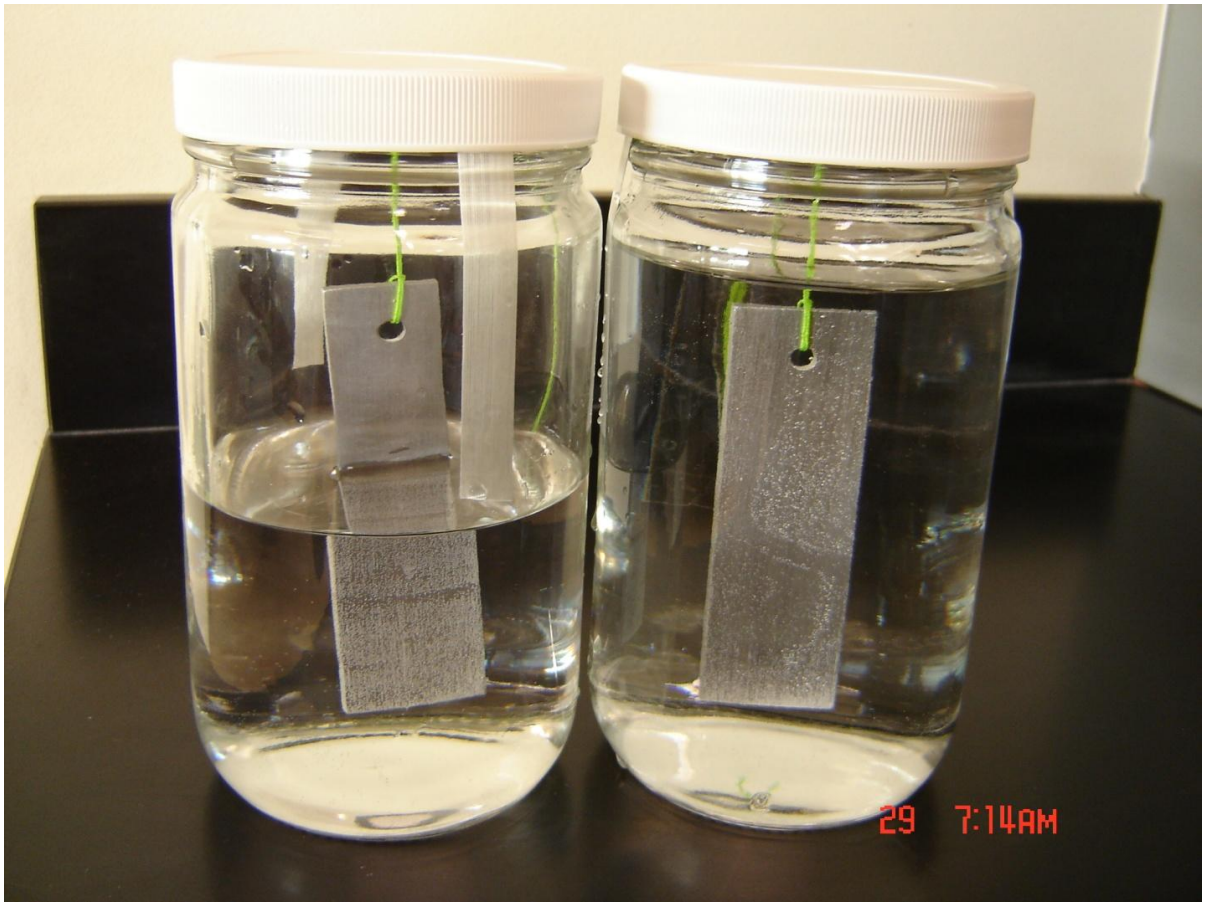

Fig. 2

Measuring effects of the quaternary ammonium formulation *Green Solution High Dilution* (1.8%) on non-metallic materials. All non-metallics are fully immersed into the solution at room temperature for 20 cycles. A cycle is comprised of the material being immersed for the evening and then being suspended to air dry during the day.