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Author Kotchman, G.S., Jr.

Corporate Author Non-Explosive Munitions Division, Air Force Armament Laboratory, Air Force Systems Command, United States Air Force, Eglin AFB, Florida

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AFATL-TN-70-

FLUSHING TECHNIQUES FOR DEFOLIANT SPRAY TANKS

by

G. S. KOTCHMAR, Jr., 1st Lt, USAF
A. L. YOUNG, 1st Lt, USAF
N. A. HAMME

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NON-EXPLOSIVE MUNITIONS DIVISION
AIR FORCE ARMAMENT LABORATORY
AIR FORCE SYSTEMS COMMAND-UNITED STATES AIR FORCE
EGLIN AIR FORCE BASE, FLORIDA

ABSTRACT

In support of development of the F-4D/PAU-7B (modified TMU-28) defoliant spray tank, flushing techniques were develop for flushing and/or washing defoliant agents Orange, White or Blue from spray tanks and/or from aircraft surfaces in the event of contamination. In addition, a solvent technique was developed for dissolving the precipitates formed following the mixing of defoliant agents Orange or White with agent Blue.

GENERAL COMMENTS

The use of more than one defoliant agent in Southeast Asia (SEA) has resulted in compatibility problems between the agents. Remaining quantities of the defoliants Orange or White in the spray tank or in other parts of the spray system, if not properly removed, will form persistent precipitates with agent Blue. The need for a solvent system, applicable for use in the field, which will dissolve these precipitates, is of interest to defoliant operations. In addition the development of the F-4D/PAU-7B (modified TMU-28) defoliant spray tank for use with agents White and/or Blue has generated a requirement for techniques in flushing and/or washing defoliant agents from not only the spray tanks but also from the aircraft surface in the event of contamination.

A description of the three agents used in defoliant operations in SEA is given in Table 1. Further data on these agents can be obtained from a technical note by Young and Wolverton (5) or from a technical report by Darrow, Irish, and Minarik (4). Orange is readily soluble in fuel oils or other non-polar organic solvents, but insoluble in water. Agents Blue and White are soluble in water but insoluble in organic solvents and diesel fuel. None of the three agents are compatible with each other, more especially agents Orange and White with agent Blue. The liquid formulation of Blue was introduced to the SEA operations in 1965 (4). In a technical manual on the use of herbicides (1), dated 22 November 1966, agent White was first described for use in defoliant operations. In a "CAUTION" statement in this manual the compatibility of Blue

TABLE 1. Descriptions of the three military defoliants used in Southeast Asia with their military code, trade name, common name, and formulation.

Military Code	Trade Name	Common Name	Formulation
Orange	Brush Killer	2,4-D, 2,4,5-T	50-50 mixture of the 80% n-butyl esters of 2,4-D (2,4-dichlorophenoxyacetic acid), and 2,4,5-T (2,4,5-trichlorophenoxyacetic acid).
White	Tordon 101	2,4-D, picloram	10.2% of the triisopropanolamine salt of picloram (4-amino-3,5,6-trichloropicolinic acid), 39.6% of the triisopropanolamine salt of 2,4-D, and 50.2% inert ingredients (primarily triisopropanolamine).
Blue	Phytar 560 G	cacodylic acid, sodium cacodylate	4.7% cacodylic acid (dimethylarsinic acid), 26.4% sodium cacodylate (sodium dimethyl-arsinic acid), 3.4% sufactant, 5.5% sodium chloride, 0.5% antifoam agent, and 59.5% water.

(Phytar 560 G) with White (Tordon 101) was noted: "When Phytar 560 G and Tordon 101 are mixed a precipitate will form that will clog the spray system. Particular care will be exercised to remove residual Phytar by liberally flushing with water prior to filling aircraft tank with Tordon. Residual Tordon will be removed by the same means prior to filling with Phytar." No mention was made as to how to remove this precipitate if it occurred or of the compatibility of Orange with Blue.

Compatibility of Tordon 101 and Phytar 560 G was discussed by Buerge in a research memorandum of the Dow Chemical Company (3). Buerge noted that a white precipitate formed when the two formulations were mixed in a ratio of 1:19 or 19:1, Tordon 101 to Phytar 560 G, respectively. This precipitate was recognized as the sodium salt of 2,4-D which is only 4-5% soluble in water. Ingredients which were tried to prevent this precipitation from forming included kerosene, #2 fuel oil, heavy aromatic naphtha, polyglycol P-400, Polyglycol P-26-2 and each of the Dowanols. However, none of these chemicals prevented the precipitate from forming. Thus, Buerge concluded that the only way to prevent a precipitated from forming and to make the two formulations compatible was to dilute the formulation remaining in the spray tank with water. In considering the Model A/A 45Y-1 Defoliant Dispenser, Buerge stated: "If a minimum of 150 gallons of water is added to either formulation remaining in the tank and then the resulting mixture pumped or drained back down to 50 gallons, no precipitate will form when 950 gallons of the other formulation is added. If it is not desirable to pump or drain the mixture of water and formulation in the tank back down to 50 gallons, then 150 gallons of water can be added if Phytar 560 G is left in the tank, and then Tordon 101 can be added (to bring the total volume in the tank) to 1000 gallons. If Tordon 101 is left in the tank, however, approximately 500 gallons of water would have to be added before the Phytar 560 G is added to 1000 gallons to prevent a precipitate. Even then a little precipitate will form in this mixture after standing overnight." Furthermore, Buerge noted that to prevent the possibility of any precipitate forming in the lines when spraying is started, the remaining formulation in the tank should be diluted with water and pumped through the lines to clean the concentrated formulation out before the tanks are filled with a new formulation.

In a Dow Chemical Company research memorandum, Buerge (2) reported on the compatibility of Tordon 101 and Orange. Mixing of these two defoliants did not produce a precipitate. The only problem recognized with the mixing of Tordon 101 and Orange was a separation of the two on standing (with Tordon 101 on top) when the ratio of Orange to Tordon 101 was high and sufficient agitation was not present.

The need for solvent systems, applicable for use in the field, that will flush the spray tanks and systems efficiently is obvious. Improper flushing requires a solvent system to remove the formation of any precipitate. The efforts reported in this note were undertaken not to clearly identify the precipitates formed from the mixing of the defoliants, but rather to determine solvent systems and techniques which would meet the above requirements. Considerations were given to chemical availability in normal supply channels and to cost effectiveness.

LABORATORY RESULTS AND RECOMMENDATIONS

The precipitate formed when White and Blue are mixed has been identified as the sodium salt of 2,4-D.which is only 4-5% soluble in water (3). The precipitate formed when Orange and Blue are mixed may thus be the sodium salt of the n-butyl ester of 2,4-D or 2,4,5-T or a mixture of the two. The precipitates formed from mixing Orange or White with Blue appeared to be different as indicated by various solubility tests. To find a solvent system which would dissolve these precipitates, many solvents were tried. Solvents which were unsuccessful in dissolving both precipitates included chloroform, hexane, ethanol, keorsene, benzene, petroleum ether, carbon tetrachloride, toluene, butanol, methanol, and dilute hydrochloric acid. The precipitates were partially soluble in acetone, and Hot water with detergent broke up the precipitate formed from Orange and Blue.

A solvent system which will dissolve both precipitates is a 50% [redacted] (by volume) solution of N,N-dimethyl formamide (DMF) in water. With sufficient amounts of the solvent system in the tank (with scrubbing if possible), the precipitate should be removed. If difficulties should still persist, a higher concentration of DMF should be used. Purging the system with water will remove any remaining DMF. DMF has a boiling point of 153°C. (As with any organic solvent or fuel), the vapor can be harmful; thus, DMF should be kept away from heat and open flame. Contact with skin and clothing should also be minimized.

Solvent system recommendations for efficient flushing of individual defoliants (Orange, White, and Blue, respectively) were based on a residual content of 1 gallon in the F-4D/PAU-7B defoliant spray tank. Proper application of the recommendations should remove any precipitation problems.

The recommended flushing agent techniques are as follows:

a. To flush Orange from tank prior to the addition of Blue:

(1) Add approximately 5 gallons alcohol (methanol, denatured alcohol, or isopropyl alcohol). Mix. Flush as much as possible from tank. Note: flushing twice with alcohol using 2.5 gallons each time would get better results if flushing can be done easily.

(2) Add approximately 10 gallons water and mix. Flush milky solution from tank. Again add 10 gallons water and mix. Flush slightly cloudy solution from tank. If solution is still milky at this stage, repeat water flush third time.

(3) Add 2 gallons alcohol to tank, mix, and flush. Repeat adding 2 gallons alcohol, mix and flush. A check can be made at this stage by saving a small amount of the solution flushed out and adding to it a small amount of Blue. Mixture should be clear and tank should be ready for adding Blue.

b. To flush Blue from tank prior to the addition of Orange:

(1) Add approximately 5 gallons alcohol to tank. Mix and flush immediately so that residue does not settle out.

(2) Repeat adding 5 gallons alcohol, mix, and flush.

(3) Repeat adding 5 gallons alcohol, mix, and flush. Better cleaning can be obtained by flushing five times with 2 to 3 gallons of alcohol. Save small amount of final flush solution and add small amount of Orange. If the mixture remains clear, the tank is satisfactory for filling with Orange. If solution is cloudy, flush again until mixture of flush solution and Orange remains clear.

a. To flush White from the tank prior to the addition of Orange or Blue:

(1) Flush system with 5 gallons of detergent and water.

(2) After flushing thoroughly with water, add approximately 5 gallons of alcohol to tank, mix and flush.

(3) Save a small amount of flush solution and add small amount of Blue. If mixture remains clear, the tank is satisfactory for filling with Orange or Blue. If solution is cloudy, flush again until mixture of flush solution and Orange or Blue remains clear.

If a spray tank is only to be used with defoliants White and Blue, then the flushing recommendations would be as follows:

a. Assuming 1 gallon of WHITE is in the tank, a minimum of 10 gallons of water should be added. Flush this from the tank saving a small amount of the flush solution. To the small amount of the flush solution add a small amount of Blue, the defoliant to be used in the tank. Allow to set several minutes. If no semi-solid particles form, the tank is satisfactory for filling with Blue. If a precipitate forms, add more water to the tank and test a small amount of the flush solution with Blue to insure that the solution remains clear.

b. Assuming 1 gallon of Blue is in the tank, a minimum of 10 gallons of water should be added. Flush from the tank and test a small amount of the flush solution by adding a small amount of White. If no precipitate forms after setting for several minutes, the tank is satisfactory for filling with White. If a precipitate forms, repeat the flushing and test the flush solution until the solution shows no precipitate.

For all recommendations, the wash containing the diluted Orange, White, or Blue should, if possible, be diverted into pits or settling basins for incorporation into soil. It should not be directed into a stream or river.

LITERATURE CITED

1. Air Force, AFPS, SAMMA. 22 November 1966. Technical Manual-Use of Herbicides. T.O. 42C-1-17.

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4. Darrow, R. A., K. R. Irish, and C. E. Minarik. 1969. Herbicides used in Southeast Asia. Technical Report SAOQ-TR-69-11078, Plant Sciences Laboratories, Fort Detrick, Frederick, Maryland.

5. Young, A. L., and B. C. Wolverton. 1970. Military Herbicides and Insecticides. Technical Notes AFATL-TN-70-1, Air Force Armament Laboratory, Eglin Air Force Base, Florida.

Flushing Techniques for
Defoliant Spray Tanks

page 2
para/sent
1-3 - The need for a solvent system, capable of dissolving these precipitates and applicable for field use, is recognized by defoliant operational units.

page 4
2-4+5 combine to read:
Kerosene, #2 fuel oil, heavy aromatic naphtha, Polyglycol P-400, Polyglycol P-26-2 and each of the Dowanols failed to prevent the precipitate from forming.

page 5
3-3 delete "clearly"

page 6
1-4+5 delete sentence 4, change sentence 5 to read:
Solvents tested and shown to be incapable of dissolving both precipitates....

page 6

2-2 Introducing (more specific if possible) sufficient amounts of the the solvent system into the tank, followed by scrubbing if possible, should remove the precipitate.

2-3 - delete "should still"

page 7

a. (1)-4 Note: if flushing is easily accomplished, better results can be obtained by flushing twice using 2.5 gallons of alcohol each time.

a. (3)-3 4 Check for remaining Orange by adding a small amount of Blue to a portion of last solution flushed out. If mixture is clear, the tank is ready for adding Blues

b.(3)-2 Note: better cleaning...

1. I didn't quite understand the overall objective of this Tech Note. According to the title, it applies to flushing spray tanks in general. According to the abstracts, it was developed in support of the PAU-7B tank. In the ~~the~~ section on "General Comments", frequent reference is made to problems in flushing the A/A45Y-1 tank. Yet under "Recommendations", ~~a total of 9 gallons of alcohol are used to flush Orange, 15 gallons to flush Blue, 10 gallons to flush White~~, flushing procedures are given only for the PAU-7B tank. ~~E~~ Is this Tech Note ~~good~~ only ~~for~~ applicable to the PAU-7B tank? Or ~~can~~ does it ~~be used~~ also apply for other tanks? What if you have several tanks to clean at the same time? What if you wish to clean a large tank like the A/A45Y-1? I don't think ~~you scale~~ that the recommended quantities of solvent can be ~~sca~~ scaled up ~~by 50 times~~ a factor of 50 and still be cost efficient.

~~2. In the flushing procedure as given, can the alcohol~~

~~2. Page 9, the wash~~

~~2. What is the cost involved? What if the tanks were cleaned with water (Orange is just as insoluble in alcohol as in water) ~~and the recommended~~ pt as is presently prescribed ~~in the AF Manual~~ and the technique recommended here was restricted to cleaning a plugged tank after a "goof-up"?~~

2. On reading the report without prior initiation, one is prone to get the "precipitate-removal-with-DMF" mixed up with the flushing procedure. I recommend that the DMF procedures ~~should~~ be described in more detail (what is a "sufficient amount"? One gallon? Ten gallons? One liter? How long does it take to dissolve the precipitate? How often should the tank be flushed with water? etc. etc.) and placed in a separate chapter.

3. Physical and physiological dangers of DMF should be discussed in more detail. ~~For example~~ also, DMF should not "be kept away from heat and open flame" because "the vapor can be harmful". Probably because of ~~[illegible]~~ high volatility and flammability. (Is DMF really very flammable?)

4.

1. Description of Defoliants

BLUE is the code designation for a neutralized, liquid formulation containing cacodylic acid (dimethylarsinic acid) and its sodium salt. The BLUE currently in use is a liquid formulation produced by Ansul Company and is designated Phytar 560G. It contains a minimum of 21% sodium cacodylate with additional free cacodylic acid for a total dimethylarsinic acid equivalent of not less than 26% or 2.48 lb/gal. Phytar 560G contains 5% by volume of a surfactant plus 0.5% of an antifoam agent.

WHITE is the code designation for Tordon 101, a liquid formulation containing picloram (4-amino-3,5,6-trichloropicolinic acid) and 2,4-D in the form of triisopropanolamine salts. The composition of WHITE, based on weight of salt, is: picloram, 10.2%; 2,4-D, 39.6%. Based on weight of active ingredient or acid, the composition is: picloram, 5.7% or 0.54 lb/gal; 2,4-D, 21.2% or 2.0 lb/gal. The remainder consists of water, wetting agent, and other inert ingredients. Picloram or Tordon is a proprietary item produced by Dow Chemical Company.

2. Physical, Chemical, and Biological Properties

a. Physical State

BLUE (Phytar 560G) is a liquid formulation of cacodylic acid and its sodium salt. It is a reddish or brownish, free-flowing liquid.

WHITE (Tordon 101) is a dark brown, somewhat viscous liquid.

b. Solubility

BLUE is readily soluble in water and alcohol but insoluble in diesel fuel and oils.

WHITE is miscible in water but insoluble in diesel fuel and other oils. The triisopropanolamine forms of 2,4-D and picloram in WHITE are both readily soluble in water.

c. Volatility

BLUE is nonvolatile. Cacodylic acid and its salt have extremely low vapor pressures.

WHITE is considered nonvolatile. Picloram has a vapor pressure of 6.16 x 10^{-7} mm of Hg at 35 C.

WHITE, because of the low volatility of its active ingredients, has been suggested as a substitute for ORANGE for defoliation in areas adjacent to rubber plantations and sensitive broad-leaved crops. However, because of the high activity of the picloram component, extremely small amounts can damage sensitive species.

WHITE is stable and moderately resistant to ultraviolet radiation. Despite its water base, the formulation WHITE is flammable with a flash point of 35 C.

d. Corrosive Action

Corrosion tests with undiluted BLUE showed little or no effect on brass, copper, aluminum, and tin after an explsure of 1 month. Steel showed a rapid initial reaction and moderate corrosion with BLUE. Zinc was the least resistant metal, exhibiting a galvanic reaction in the cacodylate solution.

WHITE is noncorrosive on common metals and materials used in spray equipment.

e. Biological Properties

BLUE is a desiccant or contact herbicide and causes rapid browning of foliage. It shows relatively little translocation or movement within the plant. Foliage of broad-leaved vegetation affected by BLUE may abscise or shrivel and remain on the plant. Grasses may show rapid browning and death of top growth but regrowth of resistant perennial species may occur within 1 to 2 months. Defoliation of woody vegetation by BLUE shows short-term effect, with maximum effect at 2 to 6 weeks after treatment.

WHITE is a mixture of two systemic herbicides, picloram and 2,4-D. It is partially selective in its defoliant and herbicidal action on an array of plant species and is effective, principally, on woody and certain broad-leaved herbaceous plants. Both the picloram and 2,4-D components are relatively ineffective on grasses, bamboos, and other monocotyledonous plants. Forest areas defoliated with WHITE often show an immediate increase in these resistant plants.

Both picloram and 2,4-D are readily absorbed by the foliage. Picloram, apparently, is more easily absorbed by the root system than are 2,4-D and other phenoxy herbicides.

The picloram component of WHITE is more persistent in soils as compared with other chemicals such as ORANGE and BLUE. Microbial decomposition of picloram is limited and losses from soils occur principally by leaching and some photodecomposition. At rates used for defoliation it may persist in some soils for 1 year or more.

3. Storage

Herbicides are delivered in 55-gallon steel drums marked with an identifying color band. Drums may be stored in either a horizontal or vertical position. Under prolonged storage, stockpiles should be checked periodically to determine the condition of the containers and remove leakers or damage drums. BLUE and WHITE are stable chemicals with a storage life of several years. The chemicals may outlast the life of the metal containers under prolonged storage exposure to tropical heat, rain, and humidity.

4. Handling

BLUE may be handled safely with ordinary sanitary precautions in avoiding prolonged contact with skin or clothing. Cacodylic acid is readily absorbed through the skin; prolonged absorption may lead to a distinct garlic odor in the breath. Spillage should be avoided and removed by liberal flushing and rinsing with clear water.

Only ordinary precautions are recommended for handling WHITE, as for any common agricultural chemical. It may be mildly irritating to skin and eyes on prolonged contact. Contaminated clothing should be washed before reuse. Spillage on the skin should be rinsed with clear water.

BLUE should not be used in a spray system either following or preceding WHITE without thoroughly flushing the tank and system with water. A mixture of these two agents results in a precipitate consisting of the sodium salt of 2,4-D (a component of WHITE). If a change in agents is to be made, the tanks or spray system should be filled at least half full with clear water and the system exhausted of liquid before the new agent (BLUE or WHITE) is added.

5. Methods of Disposal

Loading and storage areas subject to chemical spillage may be partially decontaminated by repeated washing with ammonia water and flushing with clear water. Runoff water from such flushing operations should be diverted to settling basins or restricted areas not subject to overflow on cropland. Picloram in WHITE is persistent in spray equipment and containers or in soil, thus full decontamination of equipment or areas subject to spillage is extremely difficult. A vigorous regimen of soap and water, ammonia water, and clear water rinses and flushings is necessary. Equipment used for WHITE should not be used for other purposes such as fertilizing or applying insecticides.

Equipment used for application of BLUE should be thoroughly cleaned prior to storage or disuse. Several flushings of soapy or detergent water to which ammonia has been added may be used, followed by a clear rinse. For most spray systems a final rinse with diesel fuel may serve to prevent rust or sediment accumulation.

Excess spillage of BLUE in loading or storage areas should be removed by thorough washing with clear water and/or dilute ammonia. Runoff or wash water containing diluted BLUE should, if possible, be diverted into pits or settling basins for incorporation into soil. The chemical is rapidly adsorbed by soil and deactivated.

Used containers and residual chemical should be disposed of by burial whenever possible.

6. Toxicology

Cacodylic acid or dimethylarsinic acid, the active component of BLUE, contains arsenic in the innocuous pentavalent state rather than the toxic trivalent form. The acute oral toxicity (LD_{50}) of cacodylic acid in rats is 1,400 mg/kg for males and 1,280 mg/kg for females. For the formulation Phytar 560G or BLUE containing the acid and its sodium salt, the acute oral toxicity (LD_{50}) for rats is 2,600 mg/kg, a toxicity level lower than that of aspirin (1,750 mg/kg).

Cattle fed 24.5 mg/kg of cacodylic acid daily in a 60-day feeding test showed no arsenic in the milk and no storage of arsenic in the animal body on a cumulative basis.

In tests with fish, Gambusia, shiner, and largemouth black bass were able to withstand concentrations of cacodylic acid of at least 100 ppm for 72 hours, a rate equivalent to 270 lb of a chemical per acre-foot of water. It may, thus, be considered nontoxic to fish and animals.

When BLUE or cacodylic acid is applied directly to soil, the chemical is rapidly adsorbed and deactivated by the soil colloids so that new crops can be planted during the same growing season.

Toxicity data have been collected for the components 2,4-D and picloram and for the mixture WHITE. Picloram is extremely low in toxicity; the LD_{50} for acute oral toxicity in rats is 8,200 mg/kg; for sheep and cattle it is 488 to 650 mg/kg.

For Tordon 101, or WHITE, the acute oral LD_{50} for rats has been reported as 3,080 mg/kg; for sheep 2,000; and for cattle 3,163.

In a feeding test on cattle, 97.7% of the administered picloram was recovered unchanged in the urine; no picloram was detected in milk.

Median tolerance limits of fish to Tordon 101 ranged from 64 ppm for fathead minnow to 240 ppm for brook trout.

Toxicological studies conducted by Edgewood Arsenal and Dow Chemical Company indicate that a single direct exposure to a spray of WHITE, at prescribed rates, would not constitute a hazard to the skin or a systemic hazard by inhalation.

The chemical, picloram, is considered nontoxic and not hazardous to humans, animals, and fish.