APPENDIX A

PROPOSED FEDERAL SPECIFICATION

HERBICIDE, Formulations of the Salts and Esters of 2,4-DICHLOROPHENOXYACETIC ACID (2,4-D)

1. SCOPE AND CLASSIFICATION

1.1. Scope. 2,4-Dichlorophenoxyacetic acid (2,4-D) is an organic acid relatively insoluble in water or oil. It is normally compounded before being used as an herbicide. 2,4-D is a selective herbicide. When applied as a post-emergence spray it will kill many broadleaved weeds and woody plants, with little or no injury to many grasses, sedges, and other monocotyledonous plants. However, when used as a pre-emergence spray or as a foliage spray on seedlings, 2,4-D can also be used to control many annual grasses. This specification covers three general types of 2,4-D.

1.2. Classification. Formulations of 2,4-D covered by this specification shall be of three general types as specified:

Type I: Dry powder sodium salt forms, which are the least toxic to plants per pound of 2,4-D acid equivalent.

Type II: Liquid amine salt forms, which are intermediate in toxicity to plants per pound of 2,4-D acid equivalent.

Type III: Liquid ester forms, which are the most toxic forms of 2,4-D to plants per pound of 2,4-D acid equivalent, including:

Class 1. Volatile alkyl esters of 2,4-D; and
Class 2. Low-volatile esters.

2. APPLICABLE SPECIFICATIONS, OTHER PUBLICATIONS, AND DRAWINGS

2.1. Specifications. There are no other Federal specifications, publications, or drawings applicable to this specification.

3. REQUIREMENTS

3.1. Type I. The dry powder form shall consist of sodium salt of 2,4-dichlorophenoxyacetic acid monohydrate and such modifying and conditioning agents as are needed. The formulated compound shall contain a minimum of 80 percent 2,4-dichlorophenoxyacetic acid as determined in 4.2.1. The product shall be soluble in soft or hard water (600 ppm calcium carbonate) at the concentrations specified in the directions for use, nonfoaming, and contain no ingredients which will inhibit the application of the material at the concentrations normally used for weed control. The price per pound of 2,4-D acid equivalent contained per pound of bulk will be a factor in evaluating bids and making the award.

3.2. Type II. The liquid amine salt form of 2,4-dichlorophenoxyacetic acid shall contain a minimum of 4 lb of 2,4-D acid per gallon of formulation at 68 F, as determined in 4.2.2. The amine in this formulation shall be either the alkyl or

alkanolamine or mixtures of those types. The product shall be soluble in hard or soft water at the concentrations specified in the directions for use, nonfoaming, disperse easily, making a solution that contains no ingredients which will inhibit the application of the material at the concentrations normally used for weed control. The product shall contain no ingredients which will coagulate with water. The material shall contain sequestering agents which facilitate its application in hard or soft water. The price per pound of 2,4-D acid equivalent contained in each gallon of preparation will be a factor in evaluating bids and in making the award.

3.3. Type III. The liquid ester forms of 2,4-dichlorophenoxyacetic acid.

3.3.1. Class 1. The volatile esters of 2,4-dichlorophenoxyacetic acid. The alkyl liquid esters of 2,4-D shall contain a minimum of 2 lb of 2,4-D acid per gallon of formulation as determined in 4.2.3. The esters in this class shall belong to the alkyl group such as methyl, ethyl, propyl, isopropyl, butyl, amyl, and pentyl, or mixtures of these alkyl esters. The formulation shall be a clear solution readily miscible with oil and emulsifiable when mixed with water. It shall contain the necessary solvents, carrying and emulsifying agents, such that the emulsion formed requires a minimum of agitation to maintain intimate mixture with the diluent during the mixing and application period. The oil carrier for the formulation shall be of such gravity and viscosity, not detracting from the killing power of the active ingredients, to offer maximum penetration and spread of the spray solution. The price per pound of 2,4-D acid equivalent contained in each gallon of concentrate will be a factor in evaluating bids and in making the award.

3.3.2. Class 2. The low-volatile esters. These include the glycol, polyglycol and their ether ester derivatives of 2,4-D, as well as other heavy molecular weight esters of 2,4-D that are known to be low-volatile. The low-volatile esters of 2,4-D shall contain a minimum of 4 lb of 2,4-D acid per gallon of formulation at 68 F, as determined in 4.2.3. This class shall not include esters of the lower alkyl group such as methyl, ethyl, propyl, isopropyl, butyl, amyl, and pentyl, or mixtures of these alkyl esters. The formulation shall be readily miscible with oil and emulsifiable with water. The product shall be a clear solution, foaming, and shall include the necessary solvents, carrying and emulsifying agents, such that the emulsion formed requires a minimum of agitation to maintain intimate mixture with the diluent during the mixing and application period.

The oil carrier for the formulation shall be of such gravity and viscosity, not detracting from the killing power of the active ingredients, to offer maximum penetration and spread of the spray solution. When tested for volatility as described in 4.2.4, the product shall have an average response of less than 4.0. The price per pound of 2,4-D acid equivalent contained in each gallon of concentrate will be a factor in evaluating bids and in making the award.

3.4. Workmanship. The finished products shall be clean and uniform, and free from any defects which might impair their utility.

4. SAMPLING, INSPECTION AND TEST PROCEDURES

4.1. Sampling and inspection shall be as specified in the contract or order.

4.2. Tests.

4.2.1. 2,4-Dichlorophenoxyacetic acid content in sodium salt of 2,4-dichlorophenoxyacetic acid monohydrate. Dissolve a sample equivalent to about 1 gram of 2,4-D acid or 1.20 to 1.25 gram of the sodium salt in 50 ml of water, transfer to a 250-ml separatory funnel. Neutralize if necessary with 10 percent H_2SO_4, and add 10 ml in excess. Extract the aqueous phase twice with 75-ml portions of ether.

Wash the combined ether extracts free from mineral acid with three portions of water exactly 10 ml each. Avoid slight emulsification by excessive shaking. Filter the ether solution through a funnel containing a small piece of cotton previously saturated with ether into a 400-ml beaker, rinsing the separatory funnel with ether. Add 25 ml of water, a few boiling chips, and evaporate off the ether layer on a steam bath until approximately 25 ml of ether remains. Remove the beaker from the steam bath and evaporate off the remaining portion of ether at room temperature by means of a current of air. Dissolve the aqueous mixture in 100 ml of neutral ethyl alcohol and titrate with 0.1 N NaOH using 1 ml of indicators* (1g in 100 ml of alcohol).

Each milliliter of 0.1 N NaOH is equivalent to 0.02210 g of 2,4-dichlorophenoxyacetic acid or 0.02610 g of sodium dichlorophenoxyacetate.

Ref: "Methods of Analysis, A.O.A.C.," 8th Ed., p. 75, par. 5.133 (c).

4.2.2. 2,4-Dichlorophenoxyacetic acid content in amine salts of 2,4-dichlorophenoxyacetic acid. Transfer a sample equivalent (or a suitable aliquot of a sample diluted with water) to about 1 gram of 2,4-D acid to a 250-ml separatory funnel. Dilute to 50 ml of water and proceed as directed in 4.2.1. Calculate the percent 2,4-D acid found to the specific amine present in the sample.

4.2.3. Esters of 2,4-dichlorophenoxyacetic acid by determination of total chlorine. Weigh and mix 1.5 gram of boric anhydride (Eastman Kodak Co., Cat. No. 2685 or equivalent), 1.0 gram finely powdered potassium nitrate, and 0.4 gram finely powdered sucrose. Transfer approximately one-fourth of this mixture to a 42-ml Parr bomb electric ignition type, and add from a small weighing buret about 0.25 to 0.30 gram of sample containing from 0.030 to 0.034 gram of chlorine. (When a sample larger than 0.30 g is required, 2.5 g of boric anhydride should be used. In no cases should a sample larger than 0.6 g be taken.) Mix well with a thin stirring rod. Add the remainder of the boric anhydride, potassium nitrate, and sucrose mixture in small portions, and thoroughly mix after each addition. Measure 15 g of calorimetric-grade sodium peroxide in a standard measuring dipper, add a small portion to the contents of the bomb, and stir. Add the balance of sodium peroxide and thoroughly mix by stirring with the rod. Withdraw the rod and brush free of adhering particles. Quickly cut or break off the lower $1\frac{1}{2}$ inches of the stirring rod and imbed it in the fusion mixture. Sprinkle on the top of the fusion mixture a small quantity of finely ground sucrose. Prepare the head by heating the fuse wire momentarily in a flame and immersing it into a small quantity of sucrose. One milligram of the substance is sufficient to start the combustion. Assemble the bomb and ignite in the usual manner with a satisfactory shield between the operator and apparatus.

Place about 100 ml of distilled water in a 600-ml beaker and heat nearly to boiling. After cooling of the bomb, dismantle it and dip the cover in the hot water to dissolve any of the fusion which may be adhering to its under side. Wash cover with a fine jet of distilled water, catching the washings in the beaker. With a pair of tongs lay the fusion cup on its side in the same beaker of hot water, covering it immediately with a watch glass. After the fused material has been dissolved, remove the cup and rinse with hot water, cool the solution, add several drops of phenolphthalein indicator, neutralize with concentrated nitric acid, and add 5 ml in excess. From this point, the chlorine may be determined by electrometric titration or by the Volhard procedure as directed in the "Methods of Analysis, A.O.A.C.," 8th Ed., p. 80, par. 5.153 (a) (c).

*Either phenolphthalein or thymolphthalein may be used in the titration, provided the one selected is used in the standardization of the sodium hydroxide.

Note 1. The combination of materials used in a sodium peroxide bomb has explosive properties if wrongly handled, and the operator should remain fully aware at all times of the precautions that must be observed and the steps which must be taken to avoid damages to the apparatus and possibly personal injury. It is suggested that the instructions and precautions given in the "Parr Manual Number 121 - Peroxide Bomb Apparatus and Methods," Parr Instrument Co., Moline, Ill., be observed.

Note 2. A flame-fired bomb may be used in place of the electric-ignition type, but in case of dispute the electric-ignition type will govern.

4.2.4. Volatility Test - Relative Vapor Activity. The vapor activity test is conducted with gastight cellophane cases approximately $3\frac{1}{2}$ by $3\frac{1}{2}$ by 16 inches in size. Young rapidly-growing pinto bean plants about 4 inches in height are used as test plants. A single bean plant growing in a 3-inch pot is placed in each cellophane case just prior to testing the ester.

Two milligrams of acid equivalent as the ester are dissolved in 10 ml of 95 percent ethyl alcohol and a Whatman No. 1 filter paper (9-cm diameter) is thoroughly moistened by dipping in the solution. (Do not re-use the container used in this impregnation.) The alcohol is then allowed to evaporate, and the filter paper impregnated with the ester is inserted into the cellophane case containing the bean plant and fastened to the inside of the case 6 inches above the leaves of the test plant. The open end of the case is then sealed.

The case containing the test plant and treated filter paper is then placed in a dark room for a period of 24 hours. The temperature range of the room should be 80 to 90 F. Control plants are also sealed in separate cases. The experimental design is a randomized block with three replications, and each test is repeated three times. The evaluations shall be made following an exposure period of 24 hours.

Observations of the effect of the vapors on test plants should take into consideration whether or not the plant is slightly, moderately or severely injured, including such symptoms as degree of stem curvature, terminal bud inhibition, and degree of leaf curl. The relative vapor activity of an ester can be numerically designated as follows: 0, no visible effect; 1,2,3, slight injury, plant usually recovered with little or no reduction in growth, slight epinasty present, stem curvature slight; 4,5,6, moderate injury, plant usually recovered, moderate epinasty, moderate terminal bud inhibition and moderate stem curvature present; 7,8,9, severe injury, plant usually does not recover, pronounced epinasty, together with pronounced stem curvature; 10, plant killed.

Chemically pure 2,4-D acid and the butyl ester of 2,4-D are used as standards. The 2,4-D acid under most conditions is rated 0, whereas the butyl ester has a high vapor activity with a rating of 9.0. Esters receiving the following ratings would be classed as follows:

0	No vapor activity
1,2,3	Very low vapor activity
4,5,6	Low to moderate vapor activity
7,8,9	High vapor activity
10	Very high vapor activity

Esters must receive a vapor activity rating of less than 4 to be designated low-volatile.

5. PREPARATION FOR DELIVERY

5.1. Packaging. Unless otherwise specified, commercial packages are acceptable under this specification. The containers used shall neither affect nor be affected by their contents.

5.2. Packing. Unless otherwise specified, the subject commodity shall be packed in substantial commercial containers of the size and kind commonly used for the purpose, so constructed as to insure acceptance and safe delivery by common or other carriers, at the lowest rate, to the point of delivery called for in the contract or purchase order.

5.3. Marking. Unless otherwise specified, each container of 2,4-D formulation shall be labeled with instructions for use and marked in compliance with The Federal Insecticide, Fungicide, and Rodenticide Act and other applicable existing Federal laws. Date of pack and lot number shall appear on the label. In addition, the cover shall have the stock number and item nomenclature embossed on top or the stock number and item nomenclature shall be embossed on a metal plate and wired securely to the individual container.

6. NOTES

6.1. Intended Use.

6.1.1. Type I. The monohydrate sodium salt dry powder form of 2,4-D is sparingly water soluble. It is especially adapted for lawns, cemeteries, and in other areas where desirable vegetation such as flowers and ornamentals is likely to be injured by spray drift or vapors. The dry powder sodium salt in water solution is useful on easy-to-kill weeds. The main disadvantage of the powder form of 2,4-D is that it is not as effective as either the amine salts or esters of 2,4-D on hard-to-kill weeds or older weeds. Some nozzle clogging and other application difficulties are likely to result due to incomplete solution of the sodium salt when the dry powder form is applied at high rates with low-gallonage sprayers. The effectiveness of the sodium salt of 2,4-D is reduced when rains occur immediately following application. The sodium salt of 2,4-D is the least toxic form per pound of 2,4-D acid to plants as specified in Types I, II, or III.

6.1.2. Type II. The liquid amine forms of 2,4-D are highly soluble in water, making a relatively clear solution. They are quite stable and are effective for easy-to-kill or moderately easy-to-kill weeds. The amine salts of 2,4-D are much less volatile than the ester forms of 2,4-D and are somewhat better adapted for spraying for weed control near plants sensitive to 2,4-D. The liquid amine salt forms of 2,4-D are well adapted for spraying in lawns, turfed areas, and in tolerant field and horticultural crops for weed control. The amine salts of 2,4-D are not quite as effective on old, semiresistant weeds and woody species as are the esters. The amine salts of 2,4-D are more toxic to plants than the sodium salt of 2,4-D, but less toxic to plants than the esters of 2,4-D per pound of 2,4-D acid.

6.1.3. Type III. The liquid ester forms of 2,4-dichlorophenoxyacetic acid.

6.1.4. Class 1. The lower alkyl esters of 2,4-dichlorophenoxyacetic acid are comparatively volatile. When the lower alkyl esters of 2,4-D are used for weed control in tolerant field and horticultural crops they should be used at lower acid equivalent rates than either the sodium or amine salts of 2,4-D. The lower alkyl esters of 2,4-D are better adapted for the control of deep-rooted perennial weeds, harder-to-kill weeds, older semiresistant weeds, and woody species, than the sodium or amine salts of 2,4-D. The lower alkyl esters of 2,4-D should not be used in areas near sensitive crops such as cotton, grapes, tomatoes, and tobacco.

6.1.5. Class 2. The low-volatile esters of 2,4-D have the same intended use as the ester forms specified in Class 1. However, in areas where sensitive crops are grown, such as cotton, etc., if an ester form of 2,4-D is necessary, the esters specified in Class 2 should be used to reduce the hazard of volatility.

6.2. Ordering Data. Purchasers should specify type and class and should exercise any desired options offered herein.

6.3. Patent Notice. When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.