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OPERATING INSTRUCTIONS

BEP ESTERS OF 2,4-D AND 2,4,5-T ACIDS

1. Operating instructions for BEP-D and BEP-T are the same, only the charges differ.
2. BEP is the abbreviation used for butoxy ethoxy propanol.
3. CLEANLINESS - BEP esters MUST be kept free from CONTAMINATION by other esters and other alcohols. This includes isopropyl, butyl, PEG, etc.

   CASE I - If the previous batch run were a BEP-D or a BEP-T, no cleaning is necessary.

   CASE II - If ANOTHER LOW VOLATILE were the last batch run, then washing the esterifier out with water is good enough.

   CASE III - If an isopropyl or butyl ester were the last run, then the esterifier, ALL LINES, etc., must be thoroughly cleaned in the following manner:

   a. Wash out esterifier with water, preferably hot water.

   b. Drain the separator and reflux leg completely into a drum (this alcohol can be put into one of the holders for re-use). Blow any alcohol or benzol out of the receiver.

   c. Add about 200 gallons of water to the esterifier and put on water distillation. Reflux for about one-half hour, then cool and drain the esterifier, the separator, and the reflux leg.

   d. The esterifier is ready to be charged.

   e. To clean the receiver fill with water to the top, then drain.

   f. The foreman will see to the various piping changes needed.

4. Benzol for use in BEP esterifications must be obtained directly from Tank #105. Do NOT use benzol from Tank #118.

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5. Care must be taken NOT to get any alcohol into the esterifier.

6. Charges:

BEP-D

	Large Batch	Small Batch
BEP	2800 lbs. or 358 gals.	1994 lbs. or 255 gals.
2,4-D Acid	3150 lbs. (dry)	2240 lbs. (dry)

BEP-T

BEP	2480 lbs. or 317 gals.	1720 lbs. or 220 gals.
2,4,5-T Acid	3220 lbs. (dry)	2230 lbs. (dry)

NOTE: The above weights of 2,4-D and 2,4,5-T acids are dry weights. These weights must be corrected to the equivalent weight of "wet" acid by DIVIDING by the weight fraction of "real" acid present. These figures will be supplied by the foreman; if he does not give a figure assume 10% moisture for 2,4-D acid (0.90 fraction real acid) and 20% moisture for 2,4,5-T acid (0.80 fraction real acid).

7. When charged to the make up tank or the esterifier heat to 90°C. with agitation. While agitating take a sample and have the engineer run an acid value (see calculation sheet) and adjust the batch.

8. When the batch has been adjusted cool to 80°C. or below and add 100 gallons of fresh benzol (from Tank #105 ONLY) or recovered benzol (from BEP batch ONLY).

9. Fill separator with water. Put esterifier on water distillation.

10. During water distillation, check frequently to make sure only water is coming out of the adjustable drip leg. (Catch several drops from the drip leg in a test tube half full of water, benzol will float on top, while water will dissolve). If benzol is being lost out of the

drip leg raise the drip leg until benzol stops coming off, then wait until some water collects on the bottom of the separator (to reform the water seal) before re-lowering the drip leg. Sometimes it is necessary to add some water to the separator to reform the seal.

11. The esterification temperature during water distillation should be kept below 135°C. If the temperature rises above 135°C., cool down to below 80°C. and add 50 gallons of benzol.

12. When water stops coming off the drip leg try lowering the drip leg to remove more water:

    a. If water does not come off at a STEADY RATE after lowering the drip leg take a sample of the batch for an acid value.

    b. If benzol starts to come out of the drip leg follow the procedure outlined in Paragraph (10) above, and then take a sample of the batch for an acid value.

    Then:

    a. If the acid value is 12 or less the batch may be put on benzol distillation (See Paragraph 14).

    b. If the acid value is over 12 but less than 18 allow the batch to react for another two hours and have another acid value taken; if the acid value has gone down at least one unit allow the batch to react until the acid value reaches 12 or until it no longer goes down (Then follow the procedure in (c) below).

    c. With an acid value over 18 cool the batch down, add 1 quart of sulfuric acid, and put the batch back on water distillation. Follow this procedure too for an A.V. over 12 which does not decrease after following Paragraph (b) above.

13. If, after adding 1 quart of sulfuric and reacting, no water comes off have the acid value checked again. If the acid value has not decreased, cool the batch down and add BEP in the following quantities:

General Equation - gals. of BEP = $\frac{(A.V.-10)(W)}{(7.82)(R)}$, where W = total wt. of batch

R = 254 for 2,4-D

219.5 for 2,4,5-T

7.82 = lbs./gal. for BEP

		Gallons of BEP	
BEP-D	large	(3.02)(A.V.-10)	Simplified Equations
	small	(2.0)(A.V.-10)	
BEP-T	large	(3.50)(A.V.-10)	
	small	(2.4)(A.V.-10)	

Then put back on water distillation.

NOTE: It is important to avoid adding too much sulfuric acid as an excess of sulfuric acid will blacken and may even carbonize a batch of BEP ester. More than one quart of sulfuric acid should NOT be added without first consulting the foreman.

It is equally important to avoid excessive "cooking" time on a BEP ester. A batch that has not finished off within a time consistent with other BEP esters should be brought to the attention of the foreman.

14. When the A.V. (acid value) is 12 or less the batch is ready for benzol distillation. Cool down to about 80 to 90°C. Turn the vacuum on slowly (to avoid pulling ester over) and allow it to build up (minimum acceptable vacuum is 20", but try to get it as high as possible). Bring the temperature to 145°C. and hold it there for one-half hour. Sample and have the engineer run an acid value and specific gravity. Cool the batch to 90°C.

The following are the MINIMUM acceptable specifications for a finished batch. To pass with any other specifications, obtain permission from the foreman first.

	Specific Gravity	Acid Value
BEP-D	1.172 or higher	15.0 or less
BEP-T	1.220 or higher	13.0 or less.

15. If the acid value is too high add BEP, according to the formula given in Paragraph 13, 100 gallons of benzol and put back on water distillation.

If the specific gravity is too low add additional acid (2,4-D or 2,4,5-T according to the batch) according to the formula given below, 100 gallons of benzol and return to water distillation.

The general formula for adjusting a BEP batch which finishes with a low specific gravity is as follows:

a. $X = \frac{A - S.G.}{A - 0.938}$

b. lbs. of acid to add $= \frac{(V)(X)(7.82)(\overline{M})}{(197)\ (a)}$

where X is the volume fraction of free (that is, unreacted) BEP.

A is the average specific gravity of a finished batch:

for BEP-D A = 1.18

for BEP-T A = 1.23

S.G. is the specific gravity at 20°C. (of the low specific gravity batch of ester).

V is the total volume of the batch in gallons.

7.82 is the density of BEP in pounds per gallon.

$\overline{M}$ is the molecular weight of the acid:

for 2,4-D = 221

for 2,4,5-T = 255.5

197 is the average molecular weight of BEP plus 5% excess or

$$\frac{(188)(1.05)}{a}$$

a is the weight fraction of real acid assumed for 2,4-D to be 0.90 and for 2,4,5-T to be 0.80 (unless otherwise noted by the foreman).

This formula can be simplified by making the assumption that the volume of the batch, the molecular weight of BEP, and the weight fraction of acid are constant.

Then: BEP-D

large batch lbs. of wet 2,4-D acid = 22,400 (1.18 - S.G.)

small batch lbs. of wet 2,4-D acid = 13,500 (1.18 - S.G.)

BEP-T

large batch lbs. of wet 2,4,5-T acid = 24,300 (1.23 - S.G.)

small batch lbs. of wet 2,4,5-T acid = 16,900 (1.23 - S.G.)

16. When a batch has finished, cool to 100°C. or less, take a sample for the laboratory, and blow to the appropriate warehouse storage tank. Measure and record the number of inches of BEP ester blown to the storage tank, on the esterifier sheet.

CALCULATIONS FOR BEP ESTERS

1. Run all acid values (A.V.) to the first change of color with bromthymol blue indicator.
2. Adjusting loadings.

Stir sample well before putting in weighing beaker to get the water thoroughly distributed throughout the mixture. Weigh out a 1-2 gram sample and dissolve in about 100 to 150 ml of isopropyl alcohol.

Add about 10 ml of tap water (Failure to do this will cause the dissolved acid to form a gelatinous precipitate. If this happens you can still add the water afterwards and redissolve the precipitate). Titrate using 0.5N caustic soda solution.

$$\text{A.V.} = \frac{(\text{Factor})(\text{mls})}{\text{Wt. of sample, grams}}$$

NOTE: Factor is (Normality)(56.1) where 56.1 is the molecular weight of KOH.

To calculate the theoretical A.V. (which the above titrated A.V. must equal for the batch to be correctly loaded):

$$\text{Theoretical A.V.} = \left(\frac{M_1}{\frac{M_1}{a} + M_2}\right) R$$

where M_1 = molecular weight of the acid = 221.0 for 2,4-D
= 255.5 for 2,4,5-T

M_2 = molecular weight, plus 5% of BEP = 197

R = a factor obtained by dividing 56,100 by M_1
= 254.0 for 2,4-D
= 219.5 for 2,4,5-T

a = weight fraction of acid (This will vary according to the amount of moisture, free phenol, sulfuric acid, and sodium sulfate present; however, for plant acid, unless otherwise notified, use 0.90 for 2,4-D and 0.80 for 2,4,5-T).

3. To adjust a batch:

CASE I A.V. titrated is greater than the theoretical.

$$\text{Gals. of BEP to add (overcharged on acid)} = \frac{(\text{A.V. titrated} - \text{A.V. theoretical})(W)(197)}{(R)(M_1)(7.82)}$$

where R and M_1 have been defined above.

W = total batch weight, lbs.

CASE II - A.V. titrated is less than the theoretical A.V. (under-charged on acid)

lbs. of acid to add = $\frac{(\text{A.V. theoretical} - \text{A.V. titrated})(W)}{(R)(a)}$

where W,R, and a have been previously defined.

If certain assumptions are made these formulae may be simplified. If we assume 6000 lbs. as W for a large batch and 4000 lbs. as W for a small batch and a as 0.90 for 2,4-D and 0.80 for 2,4,5-T then for EVERY UNIT ABOVE OR BELOW THE THEORETICAL:

BEP-D

	large batch	small batch
Case I.		
Gals. of BEP to add	2.7	1.8
Case II.		
Lbs. of wet 2,4-D to add	26.2	17.5

BEP-T

Case I.		
Gals. of BEP to add	2.7	1.8
Case II.		
Lbs. of wet 2,4,5-T to add	34.2	22.8

4. Final A.V. is titrated with 0.1N caustic soda solution.