D-7798 / LINURON SR 4-22-86

Releasable

Shaughnessy No.:035506

Date Out of EAB: APR 22 1986

Signature:

To: Ingrid Sunzenauer
Product Manager #
Registration Division (TS-767)

From: Emil Regelman, Supervisory Chemist
Review Section #3
Exposure Assessment Branch
Hazard Evaluation Division (TS-769)

Attached, please find the EAB review of...

Reg./File # :

Chemical Name: Linuron

Type Product : Herbicide

Product Name :

Company Name : DuPONT

Purpose : Response to Agency review of environmental fate data.

Date Received: 7/17/85

Date Completed: APR 22 1986

Monitoring Requested:

Monitoring Voluntarily Done:

Action Code(s): 827

EAB #(s) : 5769

TAIS Code: 40

Total Reviewing Time: 5.0 days

Deferrals to:

____ Ecological Effects Branch

____ Residue Chemistry Branch

____ Toxicology Branch

Manufacturing information deleted from page 8.

17 pages

Linuron

1.0 CHEMICAL:

Linuron [3-(3, 4-dichlorophenyl)-1-methoxy-1-methylurea]

2.0 Test Material:

1. Study 1: ^{14}C-phenyl(UL) labeled linuron formulated as Lorox Weed Killer wettable powder (50% active ingredient).

2. Study 2: ^{14}C-phenyl labeled linuron.

3. Study 3: ^{14}C-phenyl-(UL)-labeled linuron (98% radiochemically pure).

4. Study 4: ^{14}C-carbony-labeled linuron.

5. Study 5: ^{14}C-phenyl-(UL)-labeled linuron (98% radiochemically pure).

6. Study 6: ^{14}C-carbony-labeled linuron.

3.0 STUDY/ACTION TYPE: Response to registrant comments on our review of data submitted for Special Review.

4.0 STUDY IDENTIFICATION:

1. Hydrolysis of ^{14}C-phenyl (UL) labeled linuron. Joseph J. Dulka. E.I. duPont de Nemours and Company, Inc., Agricultural Chemicals Department, Research Division Experimental Station. Wilmington , DE 19898, Acc. No.255830. Document No. AMR-08-81.

2. Fate of ^{14}C-phenyl-labeled linuron in water exposed to sunlight. Jerry C-Y. Han E.I. duPont de Nemours and Company, Inc., Agricultural Chemicals Department, Research Division Experimental Station, Wilmington, DE. 19898. Acc. No.255830. Document No. AMR-20-80.

3. Microbial Degradation of ^{14}C-phenyl-labeled linuron in soil. Joseph J. Dulka, E.I. duPont de Nemours and company. Inc., Agricultural Chemicals Department, Research Division Experimental Station, Wilmington, DE. 19898. Acc. No. 25530. Document No. AMR-19-80.

4. Soil column adsorption studies with Lorox linuron weed killer. Robert L. Chrzanowski E.I. duPont de Nemours and Company. Inc., Agricultural Chemical Department, Research Division Experimental Station Wilmington, DE. 19898. Acc. No. 255830. Document No. AMR-276-84.

5. ^{14}C-phenyl-labeled linuron disappearance in the field at two locations Joseph J. Dulka E.I. duPont de Nemours and Company. Inc., Agricultural Chemicals Department, Research Division Experimental Station, Wilmington, DE. 19898. Acc. No. 255830. Document No. AMR-20-80.

6. The disappearance of ^{14}C-labeled linuron in soil I.J. Belasco E.I. du Pont de Nemours and Company. Inc., Agricultural Chemicals Department, Research Division Experimental Station. Wilmington, DE. 19898 Acc. No. 255830. Document No. AMR-277-84.

5.0 REVIEWED BY:

Arthur Schlosser
Chemist, Review Section 3
EAB/HED/OPP

Signature Arthur O. Schlosser

Date April 21, 1986

6.0 APPROVED BY:

Emil Regelman
Supervisory Chemist, Section 3
EAB/HED/OPP

Signature

Date APR 22 1986

7.0 CONCLUSIONS:

See discussion and response in section 10.

8.0 RECOMMENDATION:

The hydrolysis study, aqueous photolysis study and the column leaching study are not acceptable for meeting guideline requirements. See responses to comments in section 10. The two field dissipation studies cannot be accepted until it is demonstrated that the alternate protocol used will provide results similar to those from studies conducted according to guidelines recommendations. An estimate of the variability among three identically treated cylinders at a typical use site is needed along with comparative studies of new vs conventional protocols. See copy of attached memorandum dated October 28, 1985 from Mr. E. Regelman to Mr. Robert Taylor, Product Manager No. 25.

9.0 BACKGROUND:

Dupont submitted comments on data reviews previously made by the Agency. See Linuron Addendum Task 1 and Task 2 March 14, 1985.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

STUDY 1 - HYDROLYSIS OF ^{14}C-PHENY(UL) LABELED LINURON

COMMENT 1

- Test substances not in true solution in the 5 ppm studies

RESPONSE:

- Since the solubility of linuron in water is approximately 75 ppm, we believe the linuron was truly dissolved and not simply suspended. The suspended material noted in the report was apparently insoluble inerts from the formulation. The relatively good recovery of total radioactivity throughout each of the pH 5, 7 and 9 studies suggests the solution was homogeneous.

AGENCY RESPONSE:

We continue to question whether linuron was truly dissolved in the 5 ppm studies. The test material is referred to as a suspension several times in the text of the report, and on page four, reference is made to "agglomeration which resulted in a nonhomogeneous suspension". The claim that relatively good recovery of total radioactivity was achieved throughout each of the pH 9 studies is not corroborated by information given in Table II, page seven. Data in this table indicate that 19 to 27% of applied ^{14} activity is not accounted for in the buffered solutions while 50% is unaccounted for in the study with distilled water. These results are unacceptable and especially significant since it is claimed that the reaction containers were stoppered during the experiment.

COMMENT 2

- Analytical grade test substance was not used.

RESPONSE:

These hydrolysis studies were completed in 1979, prior to adoption of the current EPA Guidelines. At that particular time it was decided that the hydrolysis studies would be more meaningful if the radiolabeled test compound were formulated to more closely simulate a spray tank situation.

AGENCY RESPONSE:

While these hydrolysis studies were completed in 1979 they were only received by the Agency in 1984, two years after publication of the current EPA guidelines. Current guidelines should therefore govern the choice of test matierial. In addition, the use of formulated product for hydrolysis studies has never been recommended by the Agency in tentative guidelines issued before 1982. The recommended use of pure, unformulated test material to generate hydrolysis data is practical and in fact favors the

registrant in that testing of only one material is required. If the testing of formulated material were required multiple hydrolysis studies would have to be conducted for many pesticides to cover each of their formulations.

COMMENT 3

- The test was conducted at 20°C, not at 25°C.

RESPONSE:

- Once again, this study was conducted before the current guidelines were finalized. The fact that it differs from the recommended temperature by 5°C should not invalidate the study and the bottom-line results, i.e. linuron is relatively resistent to hydrolysis at pH 5, 7 and 9. The 0.1N HCl and 0.1N NaOH hydrolysis studies (Tables III and IV) were carried out at 25°C; linuron was very stable in 0.1N HCl throughtout the 30-day study.

AGENCY RESPONSE:

The fact that a hydrolysis study was conducted at 20°C rather than at 25± 1°C would not normally cause it to be judged invalid if the study is satisfactory in all other respects. This comment was made to bring this deviation from recommended procedure to the attention of registrant along with other deficiencies which combine to render a study invalid: inadequate material balance and insolubility of the test substance.

COMMENT 4

- The 5000 ppm test samples could not have been a true solution and exceeded the maximum recommended concentration of 250 ppm.

RESPONSE:

- We agree that the 5000 ppm samples were not true solutions. As noted on page 4 of the hydrolysis reports, linuron's aqueous solubility is approximately 75 ppm and this becomes the rate limiting variable when higher concentrations are used. This exaggerated concentration would not be required under current guidelines and should be considered as supplemental information only. The original intent of these 5000 ppm studies was to determine the rate of linuron hydrolysis in an aqueous suspension of the formulated product.

AGENCY RESPONSE:

We accept the registrant's response to our review comment.

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COMMENT 5

- The method of adjusting the pH was not reported.

RESPONSE:

- Commercially available buffer solutions were used to prepared the pH 5, 7 and 9 solutions.

AGENCY RESPONSE:

The buffers used in hydrolysis studies should be described and the concentrations given. The guidelines suggest caution in the use of high concentrations of buffers as catalysis effects may occur. See 161-1(c)(vii) and 161-1(d)(i).

COMMENT 6

No explanation was offered for the decrease in the [^{14}C] activity on day 7 only for the 5000 ppm treatment.

RESPONSE:

- The low recovery is probably due to poor sampling of the suspension.

AGENCH RESPONSE:

We accept the registrant's response to our comment.

DUPONT SUMMARY

Although these hydrolysis studies (conducted in 1979) do not rigidly adhere to all of the 1982 guidelines, we feel that the data are scientifically valid and believe they adequately address the major objectives of this study:

- o Linuron is stable to hydrolysis in aqueous solutions buffered at pH 5, 7 and 9 (at 20°C in the dark).

- o Hydrolysis products were identified as 3,4-dichloroaniline, desmethyl linuron, desmethoxy linuron and norlinuron. Repeating these studies at 25°C (instead of 20°C) and using the analytical grade test substance (instead of formulated linuron) would produce the same results.

AGENCY SUMMARY:

As stated in our response in comment 2 above, this hydrolysis study although conducted in 1979 was not submitted for review until 1984.

The guidelines were published 1982. It is obvious therefore that the registrant has had adequate notice of the Agency's recommended conditions and procedures for conducting this study. These include specification of test material, study temperature and information on pH adjustment as well as the need for a reasonable material balance. The deficiencies in material balance, the use of formulated material as test substance, and the questionable solubility of the test substance described under comment 1 above, render this study unacceptable.

STUDY 2

- FATE OF ^{14}C-PHENYL-LABELED LINURON IN WATER EXPOSED TO SUNLIGHT

COMMENT 1:

- No dark controls were provided to distinguish between photolysis and hydrolysis.

RESPONSE:

- Data from the hydrolysis study (See Study 1 above) showed linuron to be stable to hydrolysis for 30 days at pH 5,7 and 9. Thus, any degradation would have been due to photolysis or possibly microbial degradation.

AGENCY RESPONSE:

The hydrolysis study referred to (Study 1) has been found unacceptable (See Comments on this Study) and therefore cannot serve as a dark control for this photolysis study.

COMMENT 2

- Tests were conducted in nonsterile solutions and sediments with sufficient time (2 months) for extensive microbial degradation to occur.

RESPONSE:

- The photodegradation studies in Chesapeake Bay water (with and without sediment are beyond the current Guideline requirements for an aqueous photolysis study. The purpose for conducting these additional studies was to study the combined effect of photolysis, hydrolysis and microbial degradation under more realistic environmental conditions.

AGENCY RESPONSE:

We accept the registrant's response. This comment was made to point out the fact that processes other than photolysis may contribute to degradation in a given test system.

COMMENT 3

- The specific activity, purity and source of the [^{14}C] linuron was not specified and sediments and natural water were uncharacterized.

RESPONSE:

[redacted] It was converted to [phenyl-^{14}C(U)] linuron by Dr A. G. Jelinek at the Dupont Experimental Station (Wilmington, DE). The purified product has a specific activity of 23.5 uCi/mg and radiochemical purity >99%. As noted in the response to Comment 2, aqueous studies in natural water with and without sediment are not required under current Guidelines and, therefore, the lack of any characterization data concerning these samples should not invalidate the basis study.

AGENCY RESPONSE:

We accept the registrant's response to this comment.

Comment 4

- The tests conducted in distilled water were unbuffered and the pH was unspecified.

RESPONSE:

- The pH of our distilled water is typically in the range of 5-6. (Linuron is hydrolytically stable in this range.) Based on the composition of the identified photodegradation products and the very low concentrations of tests compound used in these studies, it is unlikely there would have been a significant change in pH.

AGENCY RESPONSE:

Photolysis studies should be conducted in buffered deionized or distilled water and the pH reported. See 161-2 (c)(2)(iv).

COMMENT 5

- The intensity of the sunlight, time of exposure and year, and other major variables affecting incident light were not provided.

RESPONSE

- The exposure portion of this study was conducted on the roof of the Agricultural Chemicals Department Building at the DuPont Experimental Station in Wilmintgon, DE in the Fall of 1977. Meterological data (e.g. mean sky cover and number of clear, partly cloudy and cloudy days) in Wilmington, DE during 1977 are included on page 2 of Attachment 1. The energy spectrum of natural sunlight in Wilmington DE, measured with a Li-Cor Model Li-1800 Spectroradiometer, is provided as Attachment 2.

AGENCY RESPONSE:

- The information submitted is very helpful, however the exact dates and duration of exposure must be reported also.

COMMENT 6

- The materials balance was inadequate; 22-58% of the radioactivity was not accounted for by 2 months after treatment.

RESPONSE:

- The radioactivity material balance in the distilled water solutions after 2 months irradiation (twice the recommended maximum exposure time) was 70-78% (Table 1 of report). This decrease is presumably due to photodegradation of the phenyl ring to one or more volatile products. Recoveries in the supplemental natural water studies, after two month irradiation, were lower (ranging from 42-55%); this may reflect losses of additional volatile metabolites resulting from microbial degradation.

AGENCY RESPONSE:

Materials balance data are considered inadequate. Table 1, page 23, indicates 70 and 78% recovery of ^{14}C at 2 months for the samples exposed in distilled water. Table 2 shows approximately 60% of applied ^{14}C recovered as linuron and other products. It appears therefore that the 10 to 18% of applied ^{14}C is not accounted for at 2 months. While the guidelines recommend only a 30 day exposure period they also call for four or more samples to be taken and chemically analyzed during exposure. In the study in question only one sample was taken during the recommended exposure time, and chemical identification of parent compound and degradation products was only made once at 2 months.

DUPONT SUMMARY:

- We believe the present report adequately answers the objectives of an aqueous photolysis study and should be judged scientifically valid.

- o Linuron undergoes photodegradation in aqueous solution at 20°C under natural lighting conditions with a first half-life greater than two months.

- o The major photodegradation products were unidentified polar compounds (which remained at the origin of the silica gel TLC plate; see Figure 1) and presumably low molecular weight volatile compounds resulting from degradation of the phenyl ring. Only 1-2% of the original radioactivity was identified as 3,4-dichlorophenylurea and 3(3,4-dichlorophenyl)-1-methylurea.

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AGENCY SUMMARY:

The aqueous photolysis study submitted is not acceptable because of the lack of dark control data, deficiences in materials balance and sampling schedule and in the analysis of degradation products. In addition the test pH should be reported and maintained as recommended in the guidelines and the exact dates of exposure must be reported.

STUDY 3

- MICROBIAL DEGRADATION OF ^{14}C-PHENYL-LABELED LINURON IN SOIL

DUPONT SUMMARY:

- This study was found acceptable and fulfills data requirements for aerobic soil metabolism.

AGENCY SUMMARY:

Study was judged scientifically valid and fulfills EPA Data Requirements.

STUDY 4

- SOIL COLUMN ADSORPTION STUDIES WITH LOROX LINURON WEED KILLER

COMMENT 1

- The purity of the test compound was not reported.

RESPONSE:

- The [carbonyl-^{14}C] linuron sample used in this study has a specific activity of 6.14 uCi/mg and radiochemical purity of 97%.

AGENCY RESPONSE:

We accept the reported specific activity and radiochemical purity of the test compound.

COMMENT 2

- The incubation temperature during the 30-day incubation period was not reported.

RESPONSE:

Linuron treated soils were aged in a greenhouse throughout the 30-day aging period. The minimum nighttime temperature was 68°F and the average daytime temperature was 75°F.

AGENCY RESPONSE:

- We accept the ~~the~~ reported temperature data.

COMMENT 3

- The radioactive residues were not characterized.

RESPONSE:

- Attachment 3 is a summary of the Day-28 data from laboratory biometer studies and the 1-Month data from the field soil dissipation studies. Most of the radiolabeled residues (other than linuron) were characterized as unextracted bound residues distributed throughout the various soil organic fractions; small percentages of desmethyl linuron, desmethoxy linuron and norlinuron were detected. Radiolabeled residues in the 30-day aged soils used for the soil column leaching studies would have a very similar composition.

AGENCY RESPONSE:

The purpose of the 'aged' leaching study is to define the vertical distribution of the test substance and its degradates. The guidelines recommend quantification of test substance and degradates in each 6 cm. segment of the soil column and in the eluate. This was not done. Qualitative information about the probable presence of soil degradates gained from other studies does not provide the needed data on the leaching of these compounds.

COMMENT 4

- Values of soil/water relationships (kd) were not determined.

RESPONSE:

- Kd values could not be calculated for any of these individual studies because <50% of the applied radioactivity was eluted from the soil columns in the first 20 inches of eluate.

AGENCY RESPONSE:

Kd values should be estimated from column leaching data if possible.

COMMENT 5

- The Flanagan soil reported to be a silt loam is a silty clay loam according to the USDA soil textural classification system.

RESPONSE:

- We agree.

STUDY 5

- ^{14}C-PHENYL-LABLED LINURON DISAPPEARANCE IN THE FIELD AT TWO LOCATIONS

COMMENT 1

- The test substance was not a typical end-use product.

RESPONSE:

- This is true. We have opted to use the raidolabeled test compound rather than the nonradiolabeled end-use product when conducting our field dissipation studies in contained cylinders. Averages of using the radiolabeled test compound for these studies are given on page 150 of Attachment 4. Formulation of very small amounts of radiolabeled end-use product can be extremely difficult, expensive and, in some cases, impossible.

AGENCY RESPONSE:

The effect of formulation on the dissipation of linuron in soil is unknown. Formulated product may dissipate at a different rate and even to different products than unformulated ^{14}C active ingredient. Therefore formulated product must be used as recommended by the guidelines unless side-by-side field studies indicate that no significant difference will occur.

COMMENT 2

- Results of linuron dissipation in soils confined to cylinders may not represent dissipation under actual use conditions.

RESPONSE:

- The stainless steel cylinder simply functions to isolate a column of soil and prevent lateral movement of radioactivity with aging time. The applied test compound is, in all other respects, exposed to the same environmental conditions as if applied over a much larger area.

AGENCY RESPONSE:

It has not been demonstrated that dissipation in the stainless steel cylinders will be similar to that in a recommended type of field study. Data on comparative studies are needed to show that this will occur.

COMMENT 3

- Complete meteorological and field test data such as air and soil temperatures, and depth of watertable were not reported.

RESPONSE:

- Rainfall data for both test locations are listed in Table IV of the report. Meteorological, precipitation and air temperature data for 1978 and 1979 at the Greater Wilmington Airport (located approximately 7 miles from Newark, DE test site) are given in Attachments 5 and 6. Recent soil temperature (highs and lows at depths of 2, 4 and 8 inches), air temperature and rainfall data from the Newark, DE test site (i.e. Stine Farm) are provided in Attachment 7. The uppermost water table is 6-10 feet below the soil surface. This shallow table, of water created by the impervious subsoil, cannot supply sufficient volumes of water for commercial use. The commercially usable water table (i.e. for irrigation, wells, residential use, etc.) exists beneath the bedrock level which extends from 60-100 feet below the soil surface.

AGENCY RESPONSE:

Response is acceptable.

COMMENT 4

- Recovery values and detection limits were not reported for the analytical methods used.

RESPONSE:

- Recovery values at each sampling interval are reported in Table II and III as "Total Recovery". Decreasing recoveries with aging time result from formation and evolution of volatile radiolabeled metabolites and/or from physical losses due to a heavy rain or wind storm. The detection limit, calculated as 2 times background radioactivity, is 0.01% (see Tables II and III of the report).

AGENCY RESPONSE:

Response is acceptable. However, in studies where non-radiolabeled test material is used recovery data and data on detection limits using 'spiked' soil samples will be required using 'cold' analytical methods.

COMMENT 5

- No precautions were taken to prevent runoff or splashing of the radio-labeled materials from the test cylinders.

RESPONSE:

- Typically about 1/2 to 1 inch of each cylinder is allowed to protrude above ground level and there is typically a small amount of soil compaction which lowers the soil level within the cylinder. These factors minimize losses during rainfall. Immediately after application, approximately 50-60 ml of water is added to each cylinder. This forms a more compact uniform

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soil surface and minimizes loss of tiny dirt particles which could occur under windy conditions.

AGENCY RESPONSE:

Response is acceptable.

STUDY 6

THE DISAPPEARANCE OF ^{14}C-LABELED LINURON IN SOIL

COMMENT 1

- The purity and specific activity of the test substance were not reported.

RESPONSE:

- The [carbonyl-^{14}C] linuron has radiochemical purity of 97% and a specific activity of 6.8 uCi/mg.

AGENCY RESPONSE:

Response is acceptable.

COMMENT 2

- The soil was not characterized.

RESPONSE

- The soil characterization data for keyport silt loam soil are listed below:

Sand	21%
Silt	62%
Clay	17%
Organic matter	2.8%
Nitrogen	0.97%
pH	6.4
Cation exchange capacity, mequiv/100 g	8.2

AGENCY RESPONSE:

Response is acceptable.

COMMENT 3

- Meteorological data were not reported.

RESPONSE:

- Meteorological data for 1976 and 1977 at the greater Wilmington Airport (located approximately 7 miles from the Newark DE test site) are included on the second page of Attachments 1 and 8.

AGENCY RESPONSE:

Response is acceptable.

COMMENT 4

- Field test data, such as soil and air temperatures, and depth of water table were not provided.

RESPONSE:

- Soil temperature data (highs and lows at depths of 2, 4 and 8 inches) at the Newark, DE test site are included in Attachment 7. Air temperature and precipitation data at the Greater Wilmington Airport (approximately 7 miles from the Newark, DE test site) during the course of this study are included in Attachments 1 and 8. The uppermost water table is 6-10 feet below the soil surface. This shallow table, created by the impervious subsoil, cannot supply sufficient volumes of water for commercial use. The commercially usable water table (i.e. for irrigation, wells, residential use, etc.) is beneath the bedrock level which extends from 60-100 below the soil surface.

AGENCY RESPONSE:

Response is acceptable.

COMMENT 5

- The test substance was not a typical end-use product.

RESPONSE:

- This is true. We have opted to use the radiolabel test compound, rather than the nonradiolabeled end-use product, when conducting field soil dissipation studies in confined cylinders. Advantages of using the radiolabeled test compound are noted on page 150 of Attachment 4. Formulation of small amounts of radiolabeled end use product can be extremely difficult, expensive and, in some cases, impossible.

AGENCY RESPONSE:

See our response to comment 1, Study 5.

COMMENT 6

- Results of linuron dissipation in soil confined to cylinders may not represent dissipation under actual use conditions.

RESPONSE

- The stainless steel cylinder simply functions to isolate a column of soil and prevent loss of radioactivity due to lateral movement of the radioactivity with aging time. The applied test compound is, in all other respects, exposed to the same environmental conditions as if it were applied over a much larger area.

AGENCY RESPONSE:

See response to comment 2, Study 5.

COMMENT 7

- Recovery values and detection limits were not reported for the analytical methods used.

RESPONSE:

- The recovery values, expressed as percent of original treatment, are listed in Table 1 of the report under "Total". The detection limit of total radioactivity was 0.1% of applied.

AGENCY RESPONSE:

See response to comment 4, Study 5.

COMMENT 8

- [^{14}C] Linuron residues were characterized only in the top 1-inch of the soil.

RESPONSE:

- Characterization of the residues in the top 1-inch section of soil accounted for 89-97% of the total radioactivity in each cylinder. Analysis of any other sections, none of which contained more than 3% of the total radioactivity, was not practical.

AGENCY RESPONSE:

Soil residues should be identified at the 0.01 ppm level if feasible at whatever depth they occur.

DUPONT SUMMARY:

- The results of this May 1976-May 1977 field dissipation study in Newark DE are consistent with the above May 1978-November 1979 study (i.e. study 5). We believe it provides sufficient information on the mobility, degradation and dissipation of linuron under environmental conditions. This soil cylinder approach using a radiolabeled test compound has been acceptable to the Agency in the past.

AGENCY SUMMARY:

- Data on comparative studies will be needed to show that the use of unformulated radiolabeled test material in steel cylinders will yield data on field dissipation that are substantially similar to that generated by recomended conventional methods. Data are also needed that will provide an estimate of the variability among three identically treated cylinders at a typical use site.

See the attached memo of Oct 28, 1985 on this subject from Emil Regelman EAB/HED to Robert Taylor Product Manager 15.

11. COMPLETION OF ONE-LINER: Not applicable

12. CBI APPENDIX: Comments on previously submitted CBI data are assumed to be CBI and should be treated as such.