E. I. du Pont de Nemours & Company
INCORPORATED
Wilmington, Delaware 19898

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File 20.0

December 18, 1980

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COMMENTS ON EPA'S NEW CHROMIUM STANDARD FOR EP TOXICITY

We support EPA's amended position which recognizes that hexavalent chromium is the toxic metal component in chromium-bearing wastes. We suggest that the toxicity package, put together for our case on K074, be included in the Company response as an assist to EPA in defending its new position from other commentators who may challenge the amended standard.

Secondly, our R&D Division (Frank Cappelleri at Newark) has reviewed EPA's proposed method for chromium (VI) analysis as described in amended Appendix A (Federal Register, 45, P. 72032-3, October 30, 1980). We conclude that the technique is impractical for the several reasons cited below and request that these comments be included in the Company response and a plea made for the adoption of the Du Pont method (attached).

1. Waste streams contain many reactive chemical species. Several would interfere with the reagents specified in the EPA method and cause it to yield erroneous results. Specifically:

- o inherent barium, calcium and strontium would precipitate as sulfates and thus interfere with the quantitative coprecipitation of lead sulfate and chromate which is the basis of the method.
- o surfactants such as amines, sulfonic acid derivatives and polyethyleneoxide derivatives would react with the lead sulfate reagent chelating lead and, thereby, preventing the quantitative coprecipitation of lead chromate and sulfate.

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- o the several oxidizing and reducing agents commonly contained in waste streams would interfere with the oxidation step.

2. The method proposes the use of Furnace Atomic Absorption Spectrometry, a new technique that is not readily available and on which the body of literature is not extensive. Thus, variable interpretations of results are possible which could lead to legal challenges. We feel the Agency should try to avoid such confrontations.

3. The method is very time- and effort-intensive. This would not only make it expensive to use but would allow for several sources of error to interfere with the generation of accurate and meaningful results.

Rather than just critique EPA's procedure, we believe Du Pont assist by suggesting a technique that is simple and reliable and which has been proven in plant practice on real-life waste streams. This procedure (attached) involves ion-exchange chromotography of the complex waste matrix on a chemically simple column to separate hexavalent chromium, followed by conventional atomic absorption spectrophotometric analysis for chromium VI in the eluate. At Newark where the method has been used on chromium-containing wastes, a detectability limit of 0.01 µg/cc (1 ppb) has been achieved consistant with a reproducability factor of ± 0.02 µg/cc (ppb) standard deviation.

K. D. DASTUR

KDD:slw
Att.

WASTE STREAM CHROMIUM VI ANALYSIS

I. SUBJECT Analysis of CrVI in waste water effluents.

II. DETERMINATION

Concentrations of CrVI are determined by atomic absorption spectroscopy after elution through a cation exchange column.

III. PRINCIPLE

By passing a solution over an ion exchange column of a sulfonic acid type that is in the acid form, CrIII is removed, allowing CrVI through. Results may be obtained with a $\pm$ .02 µgm/cc standard deviation determined first on known controls prepared from CrVI and CrIII standard solutions and then on waste water effluents where the method of standard additions was used.

IV. EQUIPMENT

1) 25 cc capacity ion exchange column containing a course fitted glass disc.

2) "REXYN" 101 resin (Fisher) (see figure 1)
It is an organic strong acid cation exchanger of a sulfonated polystyrene copolymer in the hydrogen form, medium porosity.

3) Boiling flash, 250cc flat bottom pyrex, equipped with a 24/40 ground glass joint (see figure 2).

4) Kjedlahl condenser with a 24/40 standard taper ground glass joint (see figure 2).

5) 1000 mg/L chromium atomic absorption standard.

6) Jarrell Ash Model 810 atomic absorption spectrophotometer.

V. COLUMN PREPARATION

One slurries a sufficient quantity of resin in a small beaker to load a 25 cc column half full. One then backwashes to eliminate any channeling that may occur, simultaneously stirring the column with a long rod, to insure uniformity throughout. Letting the column settle gently, one then takes care not to let it go dry at any time by adjusting the flow out of the column with a clamp. For complete generation of the acid column and to wash any impurities from the resin, one then passes 10 cc of a 1:5 dilution of concentrated sulfuric acid and distilled water through the column at about 1 cc/min, followed by a sufficient quantity of water to wash the column neutral. The column is disposed of routinely after five analyses to insure that there is no depletion of active sites. This method is used on treated waste where chromium concentrations are expected to be low. The column is now ready for operation.

VI. PROCEDURE

One pipettes 10cc of solution to be analyzed and that has been neutralized onto the aforementioned column. This is eluted at 3cc/min and collected in a 250cc boiling flask. Being careful not to let the column go dry at any time, one washes with distilled water at the same rate to 100cc total volume. The column effluent is then evaporated to 5cc by boiling on a hot plate using a Kjeldahl condenser. The flask and trap is then washed quantitatively into a 10cc volumeteric flask using distilled water sparingly. A trigger spray wash bottle is suitable for this. The resultant solution is stored in a linear polyethylene sealed container until analyzed to prevent glass adsorption of the chromium.

The sample is now run on an atomic absorption spectrophotometer for the determination of chromium concentration. A nitrous oxide-acetylene flame is used to avoid chemicals and/or matrix interferences with only slight reduction in sensitivity. The instrument is run in the concentration mode and standardized against prepared concentrations of chromium at 0.00, 0.10, 0.25, 0.50, 0.75 and 1.00 µgm/cc Cr. The instrument is operated at 3579A with a slit width of 4Å using a chromium hollow cathode lamp operating at 10 milliamps. Detection limit is .005 µg/cc. The nitrous oxide-acetylene gas mixtures are adjusted for maximum sensitivity.

Frank A. Cappelleri

FRANK A. CAPPELLERI

Ion Exchange Column

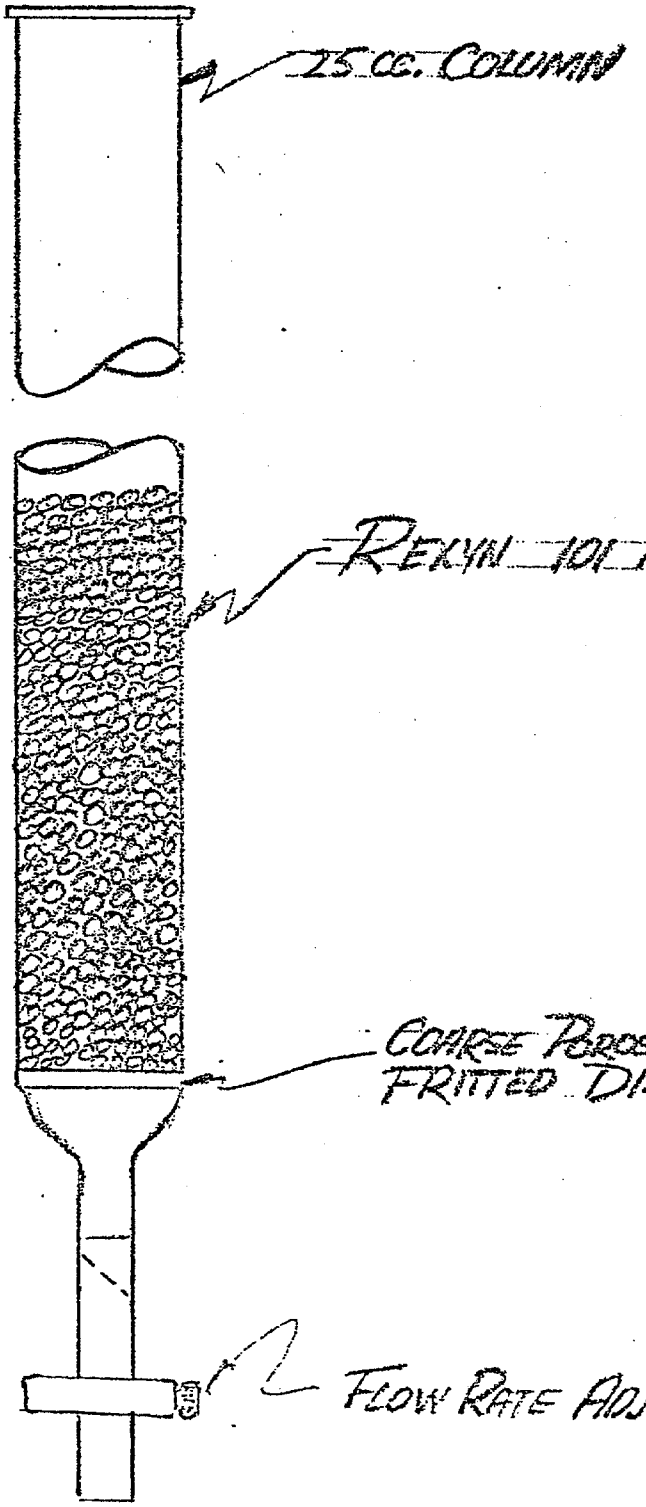

fig. 1

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EVAPORATION EQUIP.

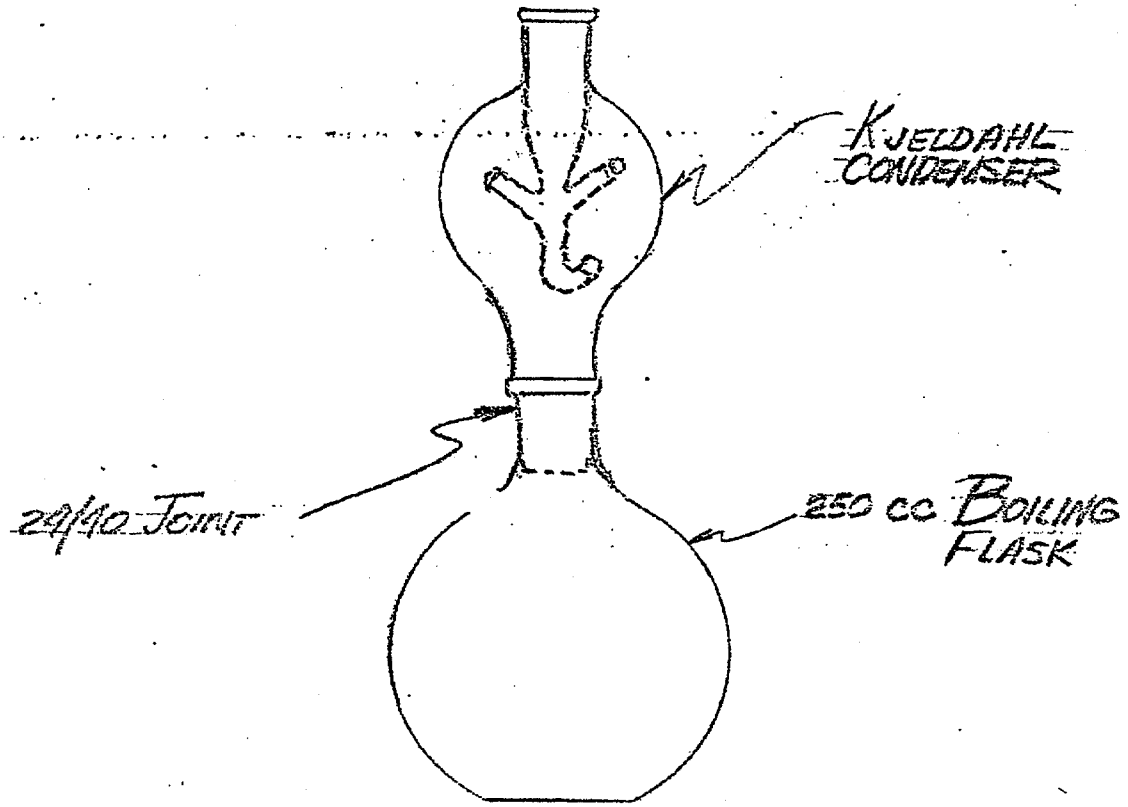

fig. 2