SINCLAIR RESEARCH, INC.
400 EAST SIBLEY BOULEVARD
HARVEY, ILLINOIS

July 13, 1962

U.S. Atomic Energy Commission (3)
Washington 25, D.C.

Attention: Isotopes Branch
Division of Licensing and Regulation

Gentlemen:

We hereby request issuance of a license to conduct tests with catalysts labeled with specific gamma emitters in fluid catalytic cracking units in refineries. This application is presented in the form required by Title 10, Part 30.24 (h), with some reference to Part 20 requirements where applicable. It is not clear to me whether this license comes under Part 20 or 30.24 (h) but, in any event, we trust that the information is presented completely enough for your evaluation.

(i) General Requirements of 30.23

(a) To the best of our knowledge these tests are "for a purpose authorized by the act".

(b) Complete descriptions of our radiation detection and measuring equipment are given in the applications for license 12-140-4. This equipment and associated facilities at Harvey are more than adequate to handle all phases of the catalyst labeling and to assay the tagged catalysts. Film badges, pocket dosimeters and portable survey meters (Juno and end window geiger counter) will be used by qualified personnel under my direction at the site of the test. Shipment of tagged catalyst to the test site will be made in a safe manner. We have no doubt that our equipment and facilities "are adequate to protect health and minimize danger to life and property".

(c) The tests will be conducted under my supervision. My experience is given in previous license applications. As consultants we have used and will use engineers specifically acquainted with fluid catalytic cracking units, both at Sinclair Research and in Sinclair Refining Company. Our record to date shows no problem with respect to protecting health "and minimizing danger to life and property" in either refinery experiments or in extensive laboratory experiments utilizing radioactive materials.

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(d) To the best of our knowledge we satisfy any special requirements contained in 30.24.

(ii) The tracer is to be contained on fluid cracking catalyst which consists of small particles of a high surface area material containing silica and alumina. In the tests considered, 5 to 10 lbs. of tagged catalyst is added to at least 1000 pounds of unlabeled catalyst. These catalysts are added to an operating refinery fluid catalytic cracking unit containing many tons of catalyst. The purpose of the work is to determine the length of time it takes for various portions of the labeled catalyst batch to appear in the catalyst fines discarded to the air by the fluid catalytic cracking unit. These appearance times are a function of the particular type of cracking unit under investigation and also of the particular type of catalyst added to the unit. The catalyst to be added to the unit can be added in the dry state or as a slurry in oil or water.

The tracers desired are Scandium-46 (85 day half life) and Zirconium 95 - Niobium 95 (Zr 95 - 63.3 day half life, Nb 95, 35 day half life). The total amount of either one of these tracers to be used is determined by the size of the unit into which it is to be injected.

An example of a small unit is the Sinclair Wood River Refinery fluid catalytic cracking unit. Inventory of catalyst in this unit is about 80 tons of fluid cracking catalyst. Stack loss to the atmosphere is about 2 tons per day. Air rate to the regenerator section from which the catalyst is lost from the unit is around 21,000 standard cubic feet per minute. This air leaves the unit at a temperature of around 600°C.

Based on data from others the added catalyst should be well mixed with the catalyst in the fluid unit in a time period of one to two hours.

In this example the amount of tracer to be used is 20 millicuries per test. Assuming perfect mixing then 2/80 of the catalyst inventory is lost per day. The total amount of catalyst in the unit is kept constant by the addition of 2 tons of fresh catalyst per day. The amount of radioactivity leaving the unit the first day then is 2/80 x 20 millicuries or 0.5 millicuries.

21,000 standard cubic feet per minute is 8.53×10^{11} ml/day of gas, which carries along the catalyst fines, leaving the stack per day. At a stack temperature of 600° the volume of air leaving the stack per day is 2.73×10^{12} ml/day.

The concentration of radioactivity measured at the point of leaving the stack the first day is then

$$\frac{0.5 \times 10^{3} \text{ microcuries/day}}{2.73 \times 10^{12} \text{ ml/day}} = 1.65 \times 10^{-10} \text{ uc/ml}$$

It is of interest to calculate the average concentration of radioactive material at the stack averaged over a time period of one year as is permissible

in Part 20. The concentration of radioactive material at any time in the fluid unit for a material of 85 day half life is equal to

$$Co\ e^{-(.05 + \frac{.693}{85})\ t} = Co\ e^{-.058t}$$

where Co is the concentration of tracer in the unit on the first day, t is time in days. The 0.05 term in the exponential accounts for dilutions in the unit due to the continuous addition and removal of 2 tons per day in a unit containing 80 tons of material (2/80). The second term accounts for radioactive decay.

The average value over a year is

$$\frac{Co \int_{o}^{365} e^{-.058t}\ dt}{365} = \frac{Co}{365\ (.058)} = .047\ Co$$

Therefore, the average concentration of radioactive material per year, leaving the stack at the point of leaving the stack is

$$(1.65 \times 10^{-10})(4.7 \times 10^{-2}) = 7.7 \times 10^{-12}\ \text{uc/ml}$$

This value is to be compared with the part 20 values for concentrations in air in unrestricted areas of 8×10^{-10} uc/ml for Scandium-46 and 1×10^{-9} uc/ml for Zirconium-95. It may readily be seen that we are well below these values.

What is desired in this license application is that we be allowed to use an amount of tracer so that the calculated radioactive concentration at the point of leaving the stack the first day, on the basis of perfect mixing be equal to the unrestricted area limits given above. The radioactive decay and mixing features insure that this is a very safe procedure.

The possibilities of hazard due to ingestion of the tagged catalyst are negligible. The maximum concentration of 0.5 millicuries in 2 tons corresponds to a concentration on the catalyst of one microcurie per four pounds of catalyst. In only 12 days it decreases to one microcurie per 8 pounds of catalyst. The ingestion of this amount of catalyst is impossible so that any credible amount of ingestion leads to body burdens very much below that allowed for continuous exposure.

The safety factors in this test are so great that even if on the first day there were as much as 5 times the amount of tracer leaving the unit as is calculated on the basis of perfect mixing there would still be no radiation hazard.

The concentration of radioactive material in the hydrocarbon products of the fluid cracking unit will be negligible since metallic elements of the two kinds considered do not leave the catalyst and enter the product.

The catalyst is labeled by impregnation from an aqueous solution. The catalyst is then dried and heated to a temperature sufficient to fix the tracer on to the catalyst, usually in the form of an oxide. This procedure follows standard catalyst preparation techniques and will be carried out at Sinclair Research, Inc. at Harvey, Illinois by qualified personnel. The amount of radioactivity added is determined by scintillation counting techniques in equipment we have available. A sample of the tagged catalyst is obtained and counted to insure that no errors have been made in regard to the amount of radioactivity used.

The tagged catalyst leaving the stack of the fluid catalytic cracking unit is continuously emitted with the actual amount and concentration of radioactive material per pound of catalyst decreasing very rapidly with time as is detailed above. If the license granted allows a concentration of 8×10^{-10} uc/ml for Scandium-46 and 1×10^{-9} uc/ml for Zr 95 in the effluent catalyst on the first day, calculated on the basis of perfect mixing, then we believe that no significant safety hazard exists.

(iii) The 30.73 limit for Scandium-46 is 4×10^{-4} uc/ml and for Zirconium (40) is 6×10^{-4} uc/ml. The bulk density of this catalyst is close to 0.7 gm/cc. On this basis the Scandium-46 limit corresponds to one microcurie per 3.7 pounds of catalyst and the Zirconium 95 limit to one microcurie per 2.5 pounds of catalyst. The 30.73 limit is not exceeded even for the first day for Scandium-46 and Zirconium-95.

The ingestion of an amount of catalyst likely to lead to a body burden of even one microcurie is however impossible on physical grounds since it is physically equivalent to the ingestion and retention in the body of four or more pounds of sand.

The high temperature calcining procedure by which the tracer is added to the catalyst, coupled with the high surface area of the catalyst and its chemical nature, makes the reconcentration of the byproduct material extremely unlikely.

There is some possibility of inhalation or ingestion of the byproduct material but as pointed out above the amount of catalyst that can be ingested is so small that the maximum conceivable body burden is extremely small.

The concentration of byproduct material in the liquid hydrocarbon products from the fluid catalytic cracking unit is negligible on chemical grounds.

Experience with similar tracer techniques by others in the past has shown that the effluent catalyst is widely dispersed which aids further in the safety of the operation.

The concentration is chosen on the basis of obtaining accurate data with respect to concentrations of tracer in the catalyst from the stacks and particularly in measurements on suitably sized fractions of the stack samples. Another consideration is to be able to obtain data over a reasonable time

period which helps to set the level of total activity desired to be used. To lower the concentrations significantly would invalidate some of the test data desired.

We would like a license to use this method at the following locations, all of which are on property of the Sinclair Refining Company:

Wood River, Illinois
East Chicago, Indiana
Marcus Hook, Pennsylvania
Houston, Texas
Sinclair, Wyoming

The first use of this test is contemplated for Wood River, Illinois.

We trust that the information presented above is sufficient for your evaluation purposes.

Yours very truly,

SINCLAIR RESEARCH, INC.

A. I. Snow

A. I. Snow, Chairman
Radioisotope Committee

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