ILLINOIS POLLUTION CONTROL BOARD December 6, 1973

UNION OIL COMPANY OF CALIFORNIA CHICAGO REFINERY PETITIONER)))	
V.)) PCB)	72-447
ENVIRONMENTAL PROTECTION AGENCY RESPONDENT)))	

ARTHUR T. LENNON, ATTORNEY, in behalf of UNION OIL COMPANY DENNIS R. FIELDS, ASSISTANT ATTORNEY GENERAL, in behalf of the ENVIRONMENTAL PROTECTION AGENCY

OPINION AND ORDER OF THE BOARD (by Mr. Marder)

This action involves a variance request filed by Union Oil Company on November 6, 1972. Relief was sought from Rules 408, 1002 of Chapter 3 of the Water Pollution Regulations of Illinois and Rule 1.07-10 (c) of SWB-15. Variance would allow Petitioner to exceed the 0.025 mg/l standard as it applies to cyanide concentrations.

Union Oil Company of California owns and operates, in Lemont a major oil refinery. This refinery processes approximately 148,000 barrels of crude oil per day, and had a base cost of over two hundred and fifty million dollars.

The main units of this operation are cokers and fluid catalytic cracking (F.C.C.) units which are used to produce gasoline and other usable products from incoming crude oil. Both units raise the temperature of the incoming crude oil to about 900 degrees. This causes the high molecular weight substance to break down or "crack" to form the usable products. It is during this cracking that some of the resulting atoms form the cyanide ion. It has been found (R. 151) that much more cyanide is formed in the F.C.C. than in the coker units.

The products manufactured at the Chicago refinery range the entire gamut of hydrocarbons starting from the light gases (e.g., methane, ethane) to propane to gasoline. A large amount of both aliphatic and aromatic solvents are also manufactured. Heating oils of all grades (No. 2, 4, 6) as well as the residual tars used for asphalt are produced. Coke and sulphur are the other products produced.

As part of the variance petition, Petitioner included an Interim Report on Evaluation of Cyanide Problems at Union Oil Company of California's Chicago Refinery. This report outlined the potential sources and methods of cyanide removal. The Agency filed its original recommendation on December 22, 1972, in which it recommended a denial. On April 17, 1973, after the use of several discovery devices and meeting with the Petitioner, the Agency amended its recommendation. In its amended recommendation the Agency recommended a grant of variance subject to certain conditions. Hearings were held on June 4, 1973, in Romeoville, Illinois. At these hearings much technical information concerning the problems with cyanides was elicited. It is noted that the Respondent made no opening or closing statement at hearing and no witnesses were called at the hearing by the Respondent. The only evidence entered at the hearing by Respondent was the full text of its recommendation. This is particularly important in that Petitioner elicited testimony from a number of expert witnesses and all of this testimony was in essence unrebutted.

On October 18, 1973, the Board issued an order for more information. This order was an attempt to bring up to date the status of Petitioner's attempts to abate its cyanide levels. An updated second interim report was received and made part of the record.

Present Status of Petitioner's Effluent

The present regulation 1.07-10 (c) of SWB-15 will be replaced by Rule 408 (a) of Chapter 3: Water Pollution Regulations of Illinois on December 31, 1973. Both of these rules require an effluent concentration of no more than 0.025 mg/l of cyanide. The following is a table showing Petitioner's effluent loading:

	1972			1973		
January	0.149	mg/l	CN	0.258	mg/l	CN
February	0.135	н		0.190	11	
March	0.075	п		0.226	н	
April	0.074	н		0.167	n	
May	0.102	It		0.129	11	
June	0.225	11		0.045	11	
July	0.136	11		0.044	н	
August	0.097	11		0.078	н	
September	0.087	п		0.054	H	
October	0.075	11				
November	0.165	17				
December	0.251	11				

Although on the surface it would seem that the cyanide level has been decreasing, it is not clear as to whether this is due to better processing or different feed conditions. Petitioner has presented evidence (second interim report) that the generation of cyanide is highly dependent on the nitrogen loading on the crude oil feed. It is best for the Board not to take the position that the seeming downward trend of cyanide will continue without much additional work. Petitioner claims to be removing, during 1973, in excess of 95% of its incoming cyanide load. This reduction, however, is not enough to reach the 0.025 allowable limit as dramatized in the above table. It is alleged that notification of excessive cyanide levels was first brought to Petitioner's attention in May, 1971. Since then Petitioner alleges that all possible steps were initiated to try and solve the problem. Testimony (R. 5) was elicited that the Chicago refinery uses much less water than do others. As a result of this water conservation program, it is alleged that the cyanide problem is magnified due to the lack of inherent dilution effects found at other refineries of this type.

Analytical Problems Regarding Cyanide

Much testimony was offered regarding the difficulty in obtaining true and meaningful analytical data for cyanide at the low levels required to meet applicable standards. Petitioner is continuing to use the Federal Environmental Protection Agency publication, <u>Methods for</u> <u>Chemical Analysis of Water and Wastes 1971</u>, for its determination of total cyanide in its waste water. The Petitioner still does not have a method of determining the difference between simple and complex cyanide.

Alice Roketa (Manager of the Environmental Division of Arro Labs) testified (R. 74-78) that there are three basic sources which outline methods to determine cyanide: Standard Methods, Federal Book on Methods, and the ASTM method. These three sources generally use the same approach of distillation and titration or colorimetric determination. However, they do not distinguish between simple and complex cyanides.

Alfred Tenny (chemist, president of Tenco Hydro Aerosciences) testified (R. 116-120) that there is significant difficulty in getting accurate measurements at low levels of cyanide. As a chemist Mr. Tenny spent three years studying cyanides and alleges that at a level of 0.02 ppm. the error would be in the order of 30 to 50 percent. He alleges that the destruction of cyanide by catalysts and non-decomposition of the complex cyanides may be two reasons for errors. He also mentions that extremely good laboratory technique is required to obtain consistent results.

Dr. Fred Gurnham (President of Gurnham & Associates, Inc.) testified (R. 303-4) that he has been a member of the American Electroplaters Society and in charge of a project on analytical techniques for cyanide removal. Dr. Gurnham further testified that he does not think that 0.025 mg/l can be accurately measured. He further testified that if several laboratories were to test a standard 0.2 mg/l solution of cyanide the reports would be from 0.0 to 0.6 mg/l.

Free vs. Complex Cyanide

A great deal of testimony centered around the difference between

free versus complex cyanides. It is alleged that the problem of complex ions is one that has not been handled in the past and was not contemplated when the original water pollution regulations were adopted. The generally accepted method of cyanide removal is the alkaline chlorination process which has proven undesirable because of the possibility of toxic byproducts being formed by the interaction of ammonia, cyanide, and chlorine.

The abovementioned witnesses (Roketa, Tenny, Gurnham) all testified as to the differences between complex and simple cyanides. Witness Roketa testified that in her readings she has found that the complex (FE [iron]) cyanide is very much less toxic than is the simple (Na [sodium], H (hydrogen) cyanide. This is because the dissociation comes about by photodecomposition rather than by simple breakage of an ionic bond which is present in simple cyanide. Witness Tenny again covered the difference between co-ordinate and ionic bonding and reaffirmed the difficulty of obtaining a free cyanide radical in a complex or ferric cyanide. Mr. Gingham discussed the above again (R. 306) and further elaborated on the interaction of complex and simple cyanides when mixed in solution. He mentioned that a sodium iron cyanide is extremely stable and that very little if any iron is free (therefore very little free cyanide). This in the witness's opinion would reduce the toxicity of the complex to nil. He further stated that a standard first aid technique for cyanide poisoning is to drink an iron salt in hopes of complexing the free cyanide and thereby reducing toxicity.

Summary of Abatement Technology Tried

Petitioner has submitted a preliminary and second interim report on studies made to abate cyanide in its effluent stream. It is alleged that although these research projects are ongoing no satisfactory method has been found.

Testimony (R. 150) was entered that the source of cyanide generation has been located in the plant. Cyanide is alleged to be found as a byproduct in the cracking operations.

John Bernickes testified as to the status of all methods used in the plant to abate cyanide (R. 210-261). This information has been further updated in the second interim report submitted by Petitioner.

1. Carbon Adsorption: Two pilot plant studies were conducted by Petitioner, using the carbon adsorption method. The first pilot plant was operated under Calgon's guidance. This plant was run on a fairly high cyanide concentration stream. The summary of this effort was contained in Calgon's report to Petitioner. The essence of this report was that the tests were unsuccessful due to the presence of the stable ferrocyanide complex.

The second pilot plant was supervised by plant personnel. Preliminary jar tests were encouraging in that a carbon usage of 1.8#/1000 gal. of water would produce an effluent with negligible cyanide content. Pilot plant data showed that approximately 11.8 lbs. of carbon would be required to treat 1000 gal. of water. This extrapolates to 8,050 lbs. of carbon for each pound of cyanide removed. High velocity backwashing was used to strip adsorbed cyanide from the used carbon in an attempt to regenerate it. This technique had some effect. Attempts to catalytically oxidize adsorbed cyanide by the presence of oxygen and copper did not prove successful. No mention is made as to whether continuing studies are proposed as to this technique by Petitioner.

Reference (R. 172) was made to a total refinery treatment of cyanide by carbon adsorption in Marcus Hook, Pennsylvania. Petitioner makes no mention as to the results of this project in its interim report. This technology could be significant to Petitioner's problems and should be investigated fully in any further reports by Petitioner to the Agency.

2. <u>Chlorination:</u> Petitioner alleges that two programs involving chlorination were under study during the last year. Full-scale activated sludge chlorination and laboratory evaluation of alkaline chlorination were examined. From the data presented it would seem that chlorination has some merit as a cyanide reducing agent, but that little hope of achieving the 0.025 specifications can be offered by using present techniques. Tests involving the alkaline chlorination method proved unsuccessful.

Again Petitioner makes no reference as to whether it intends to further develop and explore this technology.

3. Incineration: This technique was deferred until such time as the volume of water can be reduced. The Board can agree that the use of 210 x 10^6 BTU/hr. for evaporation and incineration is excessive in light of the problem.

4. Polysulfide Injection: The technique of using polysulfide to convert cyanide to thyocyanide was explored. It is postulated that the thyocyanide radical will decrease the cyanide corrosion problem and reduce the formation of the ferrocyanide complex. It is unclear as to what the nature of the new product formed would be, and the problems as to its removal.

Petitioner plans a full-scale test run which started October 23, 1973. Results should be made available in any further reports to the Agency.

5. Precipitation: Attempts to form an insoluble cyanide complex have met with only moderate results. Petitioner has postponed the results of this mode of testing indefinitely.

Other processes either mentioned in testimony or alluded to in Petitioner's interim report include:

- A. A proprietary compound by Nalco
- B. Ozonation
- C. Wet oxidation
- D. Peroxide treatments

Mention is made of water reuse to bring the plant into compliance. Petitioner indicates a degree of confidence in this technique, although it stipulates its confidence with a number of assumptions. It is implied that this technique will be further explored.

From the above discussion it is clear that various methodologies are still under consideration. The summary has convinced the Board that Union Oil is pursuing a viable program in its attempts to abate its cyanide problem. It is also clear that Union Oil Company has not submitted a project completion date, because it is still unsure which technique will be satisfactory.

The nature of a project completion schedule is generally considered to include in its body an anticipated completion date. Under normal circumstances a variance would not be issued unless such a date is submitted. In Mt. Carmel Public Utilities vs. Environmental Protection Agency, PCB 71-15, the Board held:

> "As a matter of policy the Board does not favor the granting of variances without some definite assurance that the emissions will be controlled by available pollution control devices as soon as possible. Except for cases of 'no technology available' this Board must require that those who seek 'a shield against enforcement cases' (which is what a variance is) must have a definite program to control the emissions with existing control technology."

Implicit in this finding is the language used in Title VIII Section 33 (c) (iv) of the Environmental Protection Act. The language therein states that when the Board renders its decision in an enforcement action, one of the aspects to be considered is:

> "(IV) The technical practicability and economic reasonableness of reducing or eliminating the emissions, discharges or deposits resulting from such pollution source."

Although this language is under the enforcement section of the Environmental Protection Act, because a variance may be considered a "shield from enforcement action," it would also apply to variance determinations. The heavy weight of testimony entered has shown that the technology is not presently available to abate cyanide in a refinery stream. In this type of instance a good faith program of continuing research and development will be considered a viable alternate for a firm project completion date. It is emphasized that this program must be continuing. It is not enough to state that technology is not available. A Petitioner must attempt to develop, within its financial ability, a viable abatement technology. The Board feels that Union Oil is indeed pursuing this approach.

This method of granting a variance is not without precedent. In PCB 71-111, Sherwin Williams vs. Environmental Protection Agency, a variance was granted requiring a continuation of study regarding mercury abatement methods. The problem of cyanides in refinery streams is not unique to the Board. In Shell Oil v. Environmental Protection Agency, PCB 73-116, variance was denied, and in Clark Oil & Refining v. Environmental Protection Agency, PCB 73-238, variance was granted. The facts in both the above cases constituted the reasons for the divergent Board actions.

Hardship in Event of Denial: One of the primary preconditions for the grant of a variance is a showing of hardship if compliance is required. Union Oil Company alleges that the only alternate to variance would be the shutdown of the refinery. In addition to the enormous loss of revenue to Petitioner, this shutdown would necessitate the potential layoff of 650 refinery personnel.

At a time when energy resources are in short supply, the removal of significant quantities of petrochemical products would impose a significant hardship on the public in general.

Two witnesses were called on to testify as to Union Oil's social value in the community. Mr. Roy Hassert (Will County Chairman) testified (R. 18-21) that Union Oil Company is a major taxpayer to the township (approximately 3 million dollars a year). He further testified that DuPage Township relies on the tax money to operate the township. Mayor Maurice Berlinsky testified (R. 41) that Union Oil Company is a significant employer of families in the Joliet area.

Effect on Environment: The Agency has calculated that the increase of cyanide in the Sanitary and Ship Canal would be from 0.0255 mg/l to 0.0257 mg/l. This is an increase of .0002 ppm. Petitioner's figures show that during the 7-day 20-year low flow of the canal the increase of cyanide would be 0.0015 ppm. It is alleged that although this amount of cyanide can be mathematically calculated, it could not be analytically determined in a sample of canal water (R. 334). The opinion of Dr. Gingham was elicited (R. 335) as to the effect of such an increase on the canal. His response was that there would be none. The Agency in its recommendation also stated that it felt no significant harm to the canal would occur due to this increase in cyanide concentration.

As mentioned above this Petition for variance was submitted on November 6, 1972. At that time it was suggested that (R. 7) a one-year variance would be required to develop a solution to Petitioner's cyanide problem. The recently received (November 7, 1973) interim report shows that this goal has not been met. The Board in granting a oneyear variance from the date of its Order will in essence be allowing two years to develop a viable program (one year for litigation and a one-year variance). By doing so the Board must stress that every effort be made to abate this problem as soon as possible. In granting the variance the Board will apply some of the recommendations of the Agency. Progress reports will be required on a two-month rather than a one-month basis. This is in the hope that a significantly more detailed report can be submitted at each reporting date.

Analysis of Petitioner's effluent data shows that with rare exceptions a 0.20 mg/l cyanide level can be maintained. The variance will set this limit with provisions for brief excursions over this limit.

This Opinion constitutes the findings of fact and conclusions of law of the Board.

ORDER

IT IS THE ORDER of the Pollution Control Board that Petitioner be granted a variance from Rules 408 and 1002 of Chapter 3 and Rule 1.07-10 (c) of SWB-15 until December 6, 1974, subject to the following conditions:

- Petitioner's cyanide effluent concentration shall not exceed an average of 0.20 mg/l during the period of this variance.
- 2. At no time shall Petitioner's single month average be over 0.3 mg/l cyanide.
- 3. Petitioner shall utilize any methods it may find useful to keep its effluent at the lowest possible cyanide level.
- 4. Petitioner shall continue to diligently pursue its program of research and development in regards to cyanide reduction.
- 5. Petitioner shall submit to the Agency bi-monthly reports. Said reports shall include as a minimum:
 - A) Progress on all methods being pursued by Petitioner regarding cyanide reduction.
 - B) Future work anticipated on methods being pursued by Petitioner.
 - C) Any and all records of cyanide concentrations in Petitioner's effluent. At least one determination of cyanide shall be run per week.

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- D) What methods if any are being used to comply with (3) of this Order.
- 6. As soon as a technologically feasible program for cyanide reduction has been found, Petitioner shall commence on a compliance plan to implement this program.

IT IS SO ORDERED.

I, Christan L. Moffett, Cnerk of the Illinois Pollution Control Board, certify that the above Opinion and Order was adopted by the Board on the ______ day of _____, 1973, by a vote of ______ to ____.

Christen Maffett