



KEHE MSS
Box 99

SHELL DEVELOPMENT COMPANY

EMERYVILLE, CALIFORNIA

TELEPHONE OLYMPIC 3-2100

January 22, 1951

DR. ROBERT A. KEHOE
University of Cincinnati
The Kettering Laboratory
College of Medicine - Eden Avenue
Cincinnati 19, Ohio

Dear Dr. Kehoe:

Thank you very much for your letter of January 17, particularly your confidential reference to the situation regarding isopropyl alcohol manufacture. After some thought it would seem to me best if you would get in touch with our Dr. C. H. Hine, toxicologist. His address is also Shell Development Company, Emeryville, California.

Very truly yours,

A. J. Johnson
Vice President

January 17, 1951

Mr. A. J. Johnson
Shell Development Company
Emeryville, California

Dear Mr. Johnson:

Thanks for your letter of January 4 and for the sample of ethyl chloride bottoms forwarded in accordance with your letter.

With reference to the sample, we shall make certain observations by physical methods, with the idea of establishing what may be the nature of materials in the sample as demonstrated by spectrophotometric means. You will hear from us later on our findings. It may be that the results will be of sufficient interest that we might wish to pursue the subject further with you, but we shall leave that until there is something to report.

I should appreciate it very much if you would let me know who in your organization might be addressed concerning the hygienic problem which may arise in connection with the manufacture of isopropyl alcohol. There is a situation here which, to the best of my knowledge from hearsay, is of some interest to your company. I prefer to say nothing about it except in confidence to the right person, and therefore would appreciate it if you would let me know whether you should be addressed on this subject or whether I should get in touch with some other responsible person in your company. Thus far, any discussion which I have had on this subject has been with members of the management and of the medical staff in the United Kingdom.

Very truly yours,

Robert A. Kehoe, M. D.

RAK ef

C.C.: Mr. H. Fossett
Dr. A. Wesley Horton



SHELL DEVELOPMENT COMPANY

EMERYVILLE, CALIFORNIA

TELEPHONE OLYMPIC 3-2100

January 4, 1951

*File
Assoc. Ethyl
Cross file Shell Co. Cal.*

*Write to Shell
ack.
State what is being done
Raise question of copyright*

DR. R. A. KEHOE
Kettering Laboratory
Cincinnati, Ohio

Dear Dr. Kehoe:

Attached is a copy of a letter from the Associated Ethyl Company Limited to our affiliates in England regarding your interest in the heavy ends in the bottoms from ethyl chloride manufacture. In accordance with this letter, we are shipping to you today by Railway Express a one-liter sample of ethyl chloride bottoms produced in pilot plant operations here at Emeryville.

*Sample
rec'd
1/11/51
gine
to
Hore*

*Leaked slightly
thru cap.*

Very truly yours,

SHELL DEVELOPMENT COMPANY

A. J. Johnson

HAC:ec
Encl.

C
O
P
Y

THE ASSOCIATED ETHYL COMPANY LIMITED

NORTHWICH, CHESHIRE

Our Ref. MZF/4A

Date: 2.11.50

Dr M. A. Matthews,
The Shell Petroleum Company Ltd.,
Chemical Industry Management,
St Helen's Court
Great St Helen's
LONDON E.C. 3.

Dear Dr Matthews,

Ethyl Chloride Process

Recently we had a visit from Dr R. A. Kehoe who, as you probably know, is our organisation's Chief Medical Consultant. Dr Kehoe, of course, is aware of our general plans for increasing our "Ethyl" Fluid manufacturing capacity, and he mentioned to us a possibility that should be examined, that is the possible production in the ethyl chloride process of certain potentially dangerous polymers. I think, speaking very generally, that he was concerned essentially with aromatic materials possessing high boilingpoints of about 300°C or over.

From the data which you have so far made available to us, the bottoms would appear to have a composition essentially as follows:

Ethyl Chloride	9.9%
Isopropyl Chloride	1.7%
1.1 Dichloroethane	63.0%
2 Chlorobutane	2.1%
111 Trichloroethane	5.5%
1.2 Dichloroethane	17.3%
Heavy Ends	0.5%
	<u>100.0%</u>

Also present are traces of 2 methyl-butene, 2 dichloromethane, allyl chloride, 1 chloropropane, t-butyl chloride, chloroform and carbon tetrachloride.

The heavy ends from these bottoms then amount to about 5-lbs per hour, which appears to be a relatively negligible order of magnitude.

I would, however, like to ask you if there is any information available on the composition of the 0.5% of the heavy ends, from data which may be available from pilot plant operations. Furthermore, is it possible to give an operation on the probable performance of the full scale plant, in this respect. If by chance there should be any of these bottoms available in Emeryville I wonder if consideration could be given to letting Dr Kehoe have some of this material, in order that he might have it examined at the Kettering Laboratory in Cincinnati.

Yours very truly,

(Sgd) H. FOSSETT

hf/ecd

THE ASSOCIATED ETHYL COMPANY LIMITED NORTHWICH CHESHIRE

Telephone: NORTHWICH 3241/7.

Telegrams & Cables: ETHYLPORT, NORTHWICH.

Head Office:

ARTILLERY HOUSE,
ARTILLERY ROW,
LONDON, S.W.1.
ABBAY 3974.

OUR REF. HZF/5(1)

YOUR REF.

DATE

9th January 1951

CONFIDENTIAL

Dr. R. A. Kehoe,
University of Cincinnati,
The Kettering Laboratory of
Applied Physiology,
Eden Avenue,
Cincinnati,
Ohio, U.S.A.

Dear Bob,

Many thanks for your letter of the 2nd January, regarding the broad question of the production of undesirable heavy ends in the EC/DCE processes.

"Shell" of course, will be indulging in deliberate cracking, but we understand that so far as our feed stock is concerned, this will be collected from several sources throughout the refinery, and that they will not be undertaking pyrolysis with the sole object of making the ethane/ethylene feed. They will, however, be putting in a gas separation plant to prepare this feed stock.

From conversations I have had with the "Shell" people in Holland, they seem conversant with the potential hazards. There seems to be no doubt that the situation can be kept under a proper state of review from the time production commences.

I have to take this opportunity of thanking you for your cordial New Year wishes, which I heartily reciprocate.

Yours sincerely,

hf/ecd


(H. Fossett)

January 2, 1951

AIR MAIL

Mr. H. Fossett,
The Associated Ethyl Company Limited,
Northwich, Cheshire,
England.

Dear Hu:

Thanks for your letter of December 15 with further reference to the ethyl chloride/dichloroethane processes. This has given us as much information as we can make use of. I turned the information over to Doctor Horton who has little comment to make, but who feels that the possibility of trouble within your own plant is most unlikely, since you do not engage in cracking paraffin gases to olefins.

With respect to the problems that Shell will face, we are inclined to feel that there is the distinct possibility that aromatic compounds may be produced, and that opportunities for exposure to these might give rise to real risks. The extent of these risks is unpredictable, since we do not know just what is the carcinogenic material nor what concentration in the atmosphere is required to cause trouble. In short, then, exposure must be reduced to the absolute minimum. Therefore, the operation of the plant should be kept under close observation, and if opportunities present themselves for exposure of personnel to escaping vapors from various stages of the operation, every effort should be made to correct such defects in the processes. We are much more concerned here with the inhalation of carcinogenic materials, than we are with skin contact. On the other hand, the latter has to be thought of as well as in any situation in which there is an accumulation of high boiling aromatic compounds which may come in contact with the skin.

I agree with you that this matter can be left for further consideration after the plants are in actual operation. If we can be of any assistance at that time, we will certainly be glad to do so.

With kindest personal regards and with best wishes at this season of the year,

Sincerely yours,

RAK ef

Robert A. Kehoe, M. D.

Dictated but not read.

CONFIDENTIAL.

To Dr Horton
for return to me after meeting

THE ASSOCIATED ETHYL COMPANY LIMITED NORTHWICH CHESHIRE

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OUR REF. MZF/4(d)

YOUR REF.

DATE 15/12/50

Dr. R. A. Kehoe,
University of Cincinnati,
Kettering Laboratory of
Applied Physiology,
Eden Avenue,
CINCINNATI,
U.S.A.

Dear Dr. Kehoe,

I have to acknowledge receipt of your letter of the 6th December, regarding the possible production of undesirable heavy ends in our proposed ethyl chloride/dichloroethane processes. It is not clear from your letter whether you had by then received mine of the 2nd November.

I am afraid I can add very little to the information contained in that letter, at any rate at this stage, other than to advise you that Shell Development have made arrangements to have despatched to you one sample of the heavy ends which apparently is in existence from their pilot plant operations. I believe that the quantity is only in the order of a litre, so that it may be difficult to examine this satisfactorily, in view of the relatively small quantity (half percent) of the residual heavy ends which these bottoms contain.

With regard to your specific query as to whether the process involves the cracking of paraffin gases to olefins, I can say that this practice will not be involved specifically at our plant. We plan to receive from the Shell Refinery at Stanlow, two streams, one of which is ethane rich, the other being ethylene rich. The specified analysis of these two streams is as follows.

	<u>Ethane Rich Stream</u>	<u>Ethylene Rich Stream</u>
Methane % M	-	2.0
Ethylene "	9.5	90.0
Ethane "	90.0	7.5
Acetylene "	-	0.5
Propylene "	0.5	-
	<u>100.0</u>	<u>100.0</u>

December 6, 1950

Mr. H. Fossett,
The Associated Ethyl Company Limited,
Northwich, Cheshire,
England.

Dear Hu:

Following the dispatch of my letter of November 6 to you, Doctor Horton, on his return from one of his trips, came in to ask me some additional questions. Unfortunately I could not answer these and, therefore, it is necessary to pass them along to you.

In view of the fact that the production of isopropyl alcohol by more or less conventional methods has resulted in the creation of a definite hazard of cancer, on the part of persons who are exposed to vaporized materials which come from various stages of this process. Horton is still somewhat uncertain about the possibility of hazard in your plant operations. Obviously this same uncertainty extends to the operations in the Shell Company. Therefore, he was not altogether satisfied with my tentative opinion that you have nothing to fear. Incidentally the above information concerning isopropyl alcohol is somewhat confidential, and therefore I should not wish you to quote me in the matter, except in confidence to your own associates or perhaps to the Shell people. The question which Horton wished me to raise was whether or not you intend to engage in any cracking a paraffin gases to olefins. If you do engage in such cracking, there will be some end products to be considered, and the actual boiling point, or at least the initial boiling point of these residues, is no indication of their carcinogenic characteristics. Under these circumstances, and just so that I may not ask the wrong questions or get the wrong answers, I would suggest that it might be worth your while to send me, in confidence, if you wish, as complete a description as you have available of the procedures which you intend to use. Even the details will be important, and any tentative drawing of equipment would be useful. With this information at hand I think we can give you a satisfactory answer. I hate to be so persistent, but I want to be sure that I do not give you any false advice.

With kindest personal regards,

Sincerely yours,

Robert A. Kenoe, M. D.

RAK ef

November 6, 1950

Mr. H. Fossett,
The Associated Ethyl Company Limited,
Northwich, Cheshire,
England.

Dear Hu:

Thanks for your full letter of 2nd November on the "heavy ends"
of the product of the new ethyl chloride process.

I shall turn this information over to Doctor Horton of our staff,
but it is my tentative opinion that there is nothing to fear in
this situation. Unless Horton thinks otherwise, we shall drop the
matter, at least for the present.

Best regards,

Sincerely yours,

Robert A. Kehoe, M. D.

RAK ef

C.C.: Dr. A. Wesley Horton

THE ASSOCIATED ETHYL COMPANY LIMITED NORTHWICH CHESHIRE

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Head Office:

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ABBEY 3974.

OUR REF. MZF/4(a)

YOUR REF.

DATE

2nd November 1950

CONFIDENTIAL

Dr. R. A. Kehoe,
University of Cincinnati,
Kettering Laboratory of
Applied Physiology,
Eden Avenue,
CINCINNATI,
U.S.A.,

Dear Dr. Kehoe,

I am afraid I have delayed slightly my reply to your letter of the 5th October, on the subject of the possible quantity and quality of the heavy ends which will be produced in our new ethyl chloride process. I had hoped to try and get more factual information, but I do not believe that this will be really possible until the plant is in operation. We will then be able to, and we most certainly will, make a careful study of this aspect.

The best data that we have available at the moment is extracted from the process manual, and is given below. I have written to "Shell" to see whether there is any material off the pilot plant operations which might be made available to your laboratory for examination.

The process consists of the chlorination of ethane and the hydrochlorination of ethylene to produce crude ethyl chloride. This crude ethyl chloride is then redistilled and the high boiling fraction or bottoms discarded. The residue contains the heavy ends, and consists of the following substances in the proportions shown :

Ethyl Chloride	9.9%
Isopropyl Chloride	1.7%
1.1 Dichloroethane	63.0%
2 Chlorobutane	2.1%
111 Trichlorethane	5.5%
1.2 Dichloroethane	17.3%
Heavy Ends	0.5%
	100.0%

TO: Dr. R. A. Kehoe.....

- 2 -

DATE: 2nd November 1950.....

Also present are traces of 2 methyl-butene, 2 dichloromethane, allyl chloride, 1 chloropropane, t-butyl chloride, chloroform and carbon tetrachloride.

As previously stated, the quantity of heavy ends from the bottoms, mixed with the rest of the product is 5-lbs/hr. which is made up of benzene and substituted benzenes, paraffinic material, and chloropropenes.

It would appear that this bottom fraction leaves the fractionating column at a temperature of 210°F and a pressure of 38 p.s.i.g. fully liquid, and is cooled to 110°F . This means that the boiling point of the mixture at atmospheric pressure is of the order of 80 or 90°C , certainly not lower than 60°C .

Yours sincerely,

hf/ecd


(H. Fossett)