

PETRO-TEX CHEMICAL CORPORATION

P. O. BOX 2584
HOUSTON 1, TEXAS
July 20, 1956

1208 A

*Am.
Food*

Prof. Ing. Giulio Natta
Milano
Via Mario Pagano, 54
Milan, Italy

Dear Prof. Natta:

I am enclosing several copies of the picture we took when you were at the Petro-Tex plant. The names of the people are typed on the back.

We certainly enjoyed yours and Mrs. Natta's visit with us. We will look forward to seeing you the next time you come to this country. We will try to show you more of Texas and to find larger fish for Mrs. Natta to catch.

With best regards.

Very truly yours,

PETRO-TEX CHEMICAL CORPORATION

Gordon Cain
Gordon A. Cain
Vice President

GAC:ch

Enclosures

827A
July 25, 1956

*Am
Food*

Mr. Gordon A. Cain, Vice President
PETRO-TEX Chemical Corporation
P. O. Box 2584
HOUSTON 1, Texas

Dear Mr. Cain,

I thank you even so much for the photos we have sent to me. My visit in Houston has been very interesting and, at the same time very pleasant. My wife and I will never forget the kindness of you all and the wonderful time we spent in Texas.

We are very honoured to have ^{been} considered citizens of Texas and we are very grateful to you for the lovely present of the "horns" which will find a very honourable place in our home.

Many thanks also for the visit to the butadiene plant of your Company, which has been very interesting for me.

Please be so kind of thanking Mr. and Mrs. Mares and other people of Petro Tex we met in Houston.

We are longing to see you in Italy. Our best regards to Mrs. Cain and to you.

Very sincerely yours,

Giulio Natta

*Castello
Petro-TEX*

November 5, 1958

Dr. Gordon A. Cain
Vice President
PETRO-TEX Chem. Corp.,
Houston 1, Texas
P.O. Box 2584

1170/mb

Dear Dr. Cain,

Thank you for your letters dated October 20 and 31 and for the data related to the purification of butadiene and acetylene you have so kindly sent me.

Rosita and I were very glad to meet Lucia and you in Milan; only we regret that your visit had to be so short.

I do hope to have the pleasure of seeing you soon again in Italy or in the United States.

Cordially yours,

G. Natta

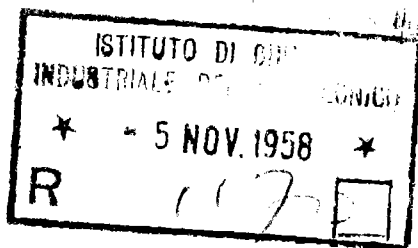


PETRO - TEX

C H E M I C A L C O R P O R A T I O N

HOUSTON 1, TEXAS • P.O. BOX 2584 • TEL. WALNUT 6-8871

October 31, 1958



Prof. Giulio Natta, Director
Istituto di Chimica Industriale del Politecnico
Piazza Leonardo da Vinci, 32
Milano, Italy

Dear Professor Natta:

Enclosed is a memorandum prepared by Dr. Welch, Director of Research of Petro-Tex, on the removal of acetylenes from butadiene. I hope that you will find this helpful.

Again Lucia and I want to thank you and Mrs. Natta for a very pleasant evening in Milan.

Sincerely,

Gordon Cain
Gordon A. Cain
Vice President

GAC:bh
Enc.

PETRO-TEX CHEMICAL CORPORATION
OFFICE CORRESPONDENCE
P. O. BOX 2584 HOUSTON 1, TEXAS

DATE: Oct. 24, 1958

TO: G. A. Cain
FROM: L. M. Welch
RE: DATA ON ACETYLENE REMOVAL FROM BUTADIENE FOR PROFESSOR NATTA

COPIES TO:

H. B. Johnson
J. J. King
J. R. Mares
J. H. Powell

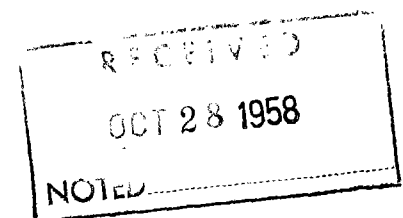
FILE:

In accordance with your recent request the attached memorandum by Dr. Johnson discloses our laboratory method of removing acetylenes from butadiene. We have discussed the contents of this memorandum with Hughes Powell in order to avoid premature disclosure of confidential information. We have in fact greatly modified the extent of this disclosure to Professor Natta at Mr. Powell's suggestion. As you may know, we have on file one application covering the treatment of butadiene with sodium dispersion.

I believe this information could be of some assistance to Professor Natta in his work. I cannot see that we are disclosing anything of great importance to Petro-Tex.

L. M. Welch

LMW:rs



PETRO-TEX CHEMICAL CORPORATION

P. O. BOX 2584
HOUSTON 1, TEXAS

ACETYLENE REMOVAL FROM BUTADIENE

October 24, 1958

Introduction

Small concentrations of ethylacetylene and vinylacetylene are produced in the dehydrogenation of butane and/or butenes. These acetylenes must be removed or reduced to a very low concentration in order to produce a polymerization-grade butadiene. A treatment with sodium dispersion is highly effective in removing vinylacetylene and partially effective in removing ethylacetylene. By proper control of reaction conditions the loss of butadiene may be held to a few percent.

Experimental

Sodium dispersion must be freshly prepared in order to have maximum activity, although a good dispersion will retain fair activity for several weeks. The laboratory Cowles Dissolver Unit (Cowles Dissolver Co., Cayuga, N. Y.) produces a sodium dispersion having particles in the 1-15 micron range. At 105°C 300 grams of sodium may be dispersed in 1000 ml xylene with the addition of ten grams oleic acid as a stabilizing agent. The dispersion is diluted with two parts of xylene before use.

The sodium dispersion is added at the top of a five-foot column one-inch in diameter filled with a butadiene pre-saturated solution of xylene. The sodium reacts with upward moving gaseous hydrocarbon fed in near the bottom of the column. The column is packed to a height of four feet with 1/8 inch glass helices which serve both to disperse the hydrocarbon in the suspending xylene and to slow the movement of the dispersed sodium in order to ensure its complete reaction before drawing off. Addition of sodium dispersion from a stirred, nitrogen blanketed addition funnel is controlled manually by a stopcock. The additions are made at regular intervals. Spent sodium is drawn off at the bottom of the column.

Hydrocarbon is fed at a controlled rate into the column and is collected in a receiver immersed in a dry-ice alcohol bath. Ice water is circulated through a spiral condenser placed between the column outlet and the receiver in order to prevent xylene from passing over with the light hydrocarbon.

Data on two typical runs are given in the following table:

<u>Reaction Conditions</u>	<u>Run A</u>	<u>Run B</u>
Temperature, °C	25	25
Rate of Hydrocarbon Flow - Std.Liters/Hour	36	36
Rate of Vinylacetylene Flow - Moles/Hour	0.0956	.00156
Rate of Sodium Addition, Ml/Hr.	15.9	0.91
Rate of Sodium Addition, Moles/Hour	0.0690	0.00397

Average Analyses of Effluent and Feed in Mol %

Run A:

	<u>Butene-1</u>	<u>Butene-2</u>	<u>Butadiene</u>	<u>Acetylenes</u>	
				<u>Ethyl</u>	<u>Vinyl</u>
Feed	0.00	64.82	27.54	1.69	5.95
Effluent	0.98	71.16	27.74	0.12	0.00

Run B:

Feed	0.09	18.92	80.73	0.086	0.095
Effluent	0.14	18.97	80.85	0.038	0.00

Discussion

The spent sodium is gray in color. The color intensity serves as a visual control on the scrubber performance. Older sodium dispersions are less active and tend to coalesce in the column. In most cases it is possible to hold the butadiene loss to ten percent or less.


Harlan B. Johnson

HBJ:rs

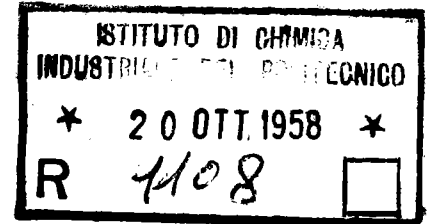


PETRO - TEX

C H E M I C A L C O R P O R A T I O N

HOUSTON 1, TEXAS • P.O. BOX 2584 • TEL. WALNUT 6-8871

October 17, 1958



Prof. Giulio Natta, Director
Istituto di Chimica Industriale del Politecnico
Piazza Leonardo da Vinci, 32
Milano, Italy

Dear Professor Natta:

Lucia and I arrived back in Texas last week. We had a very pleasant trip to southern France and Spain after we left you in Milan.

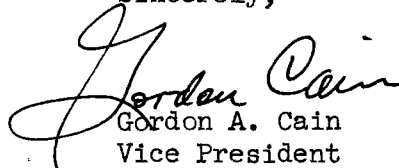
In our discussion in Milan you mentioned the importance of having a low acetylene content in the butadiene used for polymerization. I told you that our research department had done work on the removal of acetylenes from butadiene. Dr. Welch is preparing a summary of this. It will be finished in a few days and I will send it to you.

I also promised to send you a sample of the 3-methyl butene-1 that we have. However, on further checking we find that this material contains about 100 ppm of sulphur that is not removed by washing with caustic. We will be glad to send this to you but I would assume that this high sulphur content would make it undesirable for polymerization.

Phillips has high purity 3 methyl butene-1. We will be glad to get some of this and send it to you if you would like to have it. In the meantime we will start work on the removal of sulphur from our 3 methyl butene-1. If this is successful, we will let you know.

Both Lucia and I want to tell you how much we enjoyed seeing you and Mrs. Natta. The dinner we had with you was one of the high points of the trip.

Sincerely,


Gordon A. Cain
Vice President

GAC:bh



ISTITUTO DI CHIMICA INDUSTRIALE
DEL POLITECNICO
PIAZZA LEONARDO DA VINCI, 32 - MILANO

Rif. n. 1037/al

26 Settembre 1958

MILANO,

TELEF. { 292.125 - 292.126
292.105 - 106 - 107

Eng. Ing. Piero GIUSTINIANI
Administratore Delegato
Soc. Montecatini

S. d. S.

C. P. C.

Ing. G. Malibio
Ing. S. Larcher
Ing. G. Marullo
Ing. B. Orsini

Egregio Ingegnere,

Le comunico alcune notizie che ho avuto da Mr. Cain stamane, che ritengo possano interessare alcuni settori della Montecatini.

La Soc. PETROTEX, che ha un impianto per la produzione di butadiene di potenzialità di 200.000 t/anno (di cui però ne può collocare soltanto 160.000 t/anno), dispone di alcuni monomeri che possono presentare un certo interesse per noi :

Isotil-butene-1 : la Petrotex separa dalla frazione C_4 10 t/anno di isotil-butene-1 ad una purezza di 90%. Poiché il polimero isotattico del isotil-butene-1 è molto cristallino e fonde a circa 300°C, ritengo sia interessante studiarne la preparazione da monomeri tecnici, dato che noi ne abbiamo studiate soltanto la sua preparazione su scala di laboratorio. Inoltre può essere interessante studiarne meglio le proprietà tecnologiche ed eventualmente le possibilità di filatura. Mr. Cain ha promesso che ci invierà un campione di 1 litro per via aerea e successivamente per via normale una ventina di litri. Con il primo quantitativo cercheremo di mettere a punto la polimerizzazione del monomero tecnico. Con il secondo quantitativo, forse potrà fare qualche prova di filatura.

Butene-1 : la purezza del butene-1 di cui la Petrotex dispone è la seguente :

butene-1	47,6 %
butene-2	1,0 %
isobutene	0,8 %
n-butene	0,6 %
butadiene	meno di 0,1 %
acido	15 ppm
carbonili	-
Cl_2	-

✓

Il prezzo di vendita del monomero è di 6,25 \$/lb, ma tale prezzo potrebbe diminuire per fortissimi quantitativi. Esso però appare più alto di quello indicato per altre olefine che, purificate, sono valutate ai seguenti prezzi di vendita :

etilene : 4,8 \$ per lb.
propilene: 5 \$ " "

È interessante osservare che il butene della Petrotex è completamente esente da composti acetilenici.

butadiene : il butadiene tecnico viene prodotto dalla Petrotex alla seguente composizione :

butadiene	99 %
vinil-acetilene	100 ppm
carbonili	-
solfo	-
$C_2 +$	0,1 %

Mr. Cain consiglia come metodo per separare i composti acetilenici il trattamento con sodio metallico a temperatura ambiente. È però da tener presente che a temperature di 40°C o superiori il sodio può iniziare la polimerizzazione fortemente esotermica del butadiene puro.

isoprene : La Petrotex sta occupandosi della deidrogenazione dell'isopentene ad isoprene mt. Mr. Cain ritiene che l'isoprene, qualora venisse prodotto in impianti della potenzialità di 50.000 t/anno, costerà 1-2 \$/lb in più del butadiene di uguale purezza. Poiché il costo del butadiene è oggi 16 \$/lb, l'isoprene non dovrebbe costare più di 16 \$/lb. Con tale prezzo dell'isoprene la produzione del polioisoprene (Coral Rubber) è considerata economicamente possibile soltanto se il prezzo della gomma naturale è superiore a 30 \$/lb.

È da tener presente che il costo della gomma GRS è di soltanto 24 \$/lb.

isobutene : il prezzo di vendita a termi dell'isobutene è di 7-8 \$/lb, ma il prezzo dell'isobutene per usi interni può essere valutato a 5-6 \$ per lb. Esso risulta quindi superiore a quello dell'etilene e del propilene. Tenuto conto della più bassa temperatura di polimerizzazione dell'isobutilene e della necessità di impiegare solventi costosi, si deve ritenere che il costo di polimerizzazione dell'isobutilene risulterà sempre superiore a quello prevedibile in grandi impianti per la copolimerizzazione di etilene-propilene. Perciò i copolimeri C_2-C_3 , an-

(1)

che indipendentemente da certe loro migliori proprietà, dovrebbero
però presentare, dal punto di vista del costo di produzione,
maggiore interesse della gomma butile.

Cordiali saluti.

Fto: G. Natta

Am
August 1st 1958

Dr. Gordon A. Cain
Vice President
Petro-Tex Chem. Corp.,
Houston 1, Texas

Our ref. 919/mh

Dear Dr. Cain,

I have received your kind letter of July 29 and I am very glad to hear that Mrs. Cain and you are homing to Milan on September 24. Also I look forward to meet Mrs. and Mr. Ott, of whom I have not heard since I left the States.

I do not expect to attend the meeting of the Society of Chemistry and Industry in Liege next September.

Mrs. Natta and myself are looking forward to meet all of you in Milan and to recall the pleasant time you spent together in Houston two years ago.

Most cordially,

Yours sincerely,

G. Natta

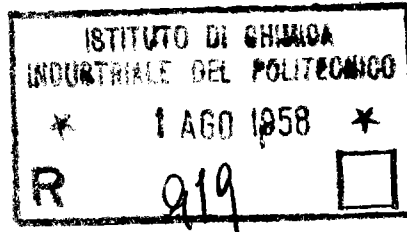


PETRO - TEX

C H E M I C A L C O R P O R A T I O N

HOUSTON 1, TEXAS • P. O. BOX 2584 • TEL. WALNUT 6-8871

July 29, 1958



Professor Giulio Natta, Director
Istituto di Chimica Industriale Del Politecnico
Piazza Leonardo da Vinci, 32
Milano, Italy

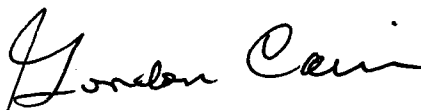
Dear Professor Natta:

Mrs. Cain and I expect to be in Milan from September 24 until the evening of the 26th. Dr. and Mrs. Ott are meeting us there and Dr. Ott may have already written you about our trip.

In any case, we are looking forward to seeing you and Mrs. Natta and hope that on at least one of those evenings you will be free to have dinner with us.

I expect to be in Liege for the meeting of the Society of Chemistry and Industry earlier in September. Possibly I will see you there.

Very truly yours,


Gordon A. Cain
Vice President

GAC:bh