"MONTECATINI"
SOCIETÀ GENERALE PER L'INDUSTRIA MINERARIA E CHIMICA

AMMINISTRATORE DELEGATO

Cartella
U.C.C.

Telegrammi GABBRO MILANO
Telefono 6333
Telefoni interurbani
chiedere GABBRO MILANO
SEDE MILANO
Largo G. Donegani, 1-2

G/ra

1 APR. 1963
R 268

Milano, 30 marzo 1963

Caro Natta,

rispondo alla Sua del 28 marzo u. s. (256)

Per essere più tranquillo ho fatto scrivere dall' ing. Larcher - che ha già provveduto - all' Union Carbide per avere qualche ulteriore elemento oltre quelli contenuti nella lettera di accompagnamento del secrecy agreement.

Quando saremo in possesso di questa risposta riesamineremo da capo la questione e terremo conto di quanto Ella osserva a proposito delle nostre ricerche.

Intanto invito l' ing. Larcher, che legge la presente, ad esaminare con BREV la situazione brevettuale che riguarda l' uso del policondensante in atto a Terni. Poichè Ella dice che il sistema usato a Terni con il policondensante corrisponde, come principio generale, al sistema di Union Carbide, se il brevetto o i brevetti a suo tempo presi da Polymer riflettono anche il principio generale l' U.C.C. dovrebbe essere anticipata da noi o, meglio, da Polymer.

L' ing. Larcher, quindi, riferirà al più presto sull' argomento.

Cordiali saluti.

Preg.mo Signor
Prof. GIULIO NATTA
MILANO

Cartelle
U.C.C.

28 marzo 1963

Ing. P. Giustiniani
Amministratore Delegato
Soc. Montecatini
Sede

ns.rif.256/eg

P.c. Ingg. B. Orsoni
Ing. G. Ballabio

Caro Ingegnere,

ho esaminato le proposte della Union Carbide relative alla tintura del polipropilene che Lei mi ha dato in visione ieri.

Sono anch'io del parere che convenga accettare tali proposte dato che non ci impegnano in modo pericoloso.

Credo che convenga informare la Union Carbide che anche noi abbiamo già da tempo seguito gli stessi concetti preparando dei polimeri aventi composizione chimica definita più o meno compatibili con i polipropileni e che abbiamo già richiesto diversi brevetti sull'argomento.

L'impegno che richiede la Union Carbide al punto 5, dovrebbe limitarsi naturalmente alle notizie provenienti dalla Union Carbide ma non ai dati provenienti dalle nostre ricerche nel caso che le soluzioni proposte dalla Union Carbide corrispondano a polimeri già studiati dalla Montecatini.

Infatti, i concetti seguiti dalla Union Carbide corrispondono a quelli da noi seguiti con l'impiego della polivinilpiridina e di acrilati dialchil-amminoetanolo. In entrambi i casi si sono avute ottime proprietà tintoriali ma nel primo caso si sono avuti inconvenienti per la parziale decomposizione della polivinilpiridina durante la filatura a causa dell'alta temperatura. Nel secondo caso si è avuto qualche inconveniente per la reticolazione del polimero azotato che stiamo cercando di superare.

Anche il sistema usato a Terni col policondensato corrisponde come principio generale, al sistema della Union Carbide nel caso in cui il condensato presenti una composizione definita.

E' necessario che l'accordo con la Union Carbide non si impegni a limitare le nostre ricerche che riteniamo vicine a una soluzione soddisfacente.

Cordiali saluti.

G.NATTA

Cartelle UCC

UNION CARBIDE INTERNATIONAL COMPANY

DIVISION OF UNION CARBIDE CORPORATION

30 EAST FORTY-SECOND STREET, NEW YORK 17, N. Y., U. S. A.

CABLE ADDRESS: UNICARBIDE, NEW YORK

27 LUG 1959

R

Gentlemen:

Does your process include separation of entrained liquid from gas streams? If so, find out how you can get consistently better performance by using KARBATE Impervious Graphite Entrainment Separators - Type MV. They are dependable and give outstanding economies in removal of entrained liquids and solvent recovery.

Unusually simple in construction, Type MV units operate effectively over a wide range of gas flow rates, entrainment content, and liquid droplet sizes. They contain no moving parts and are non-clogging. KARBATE Entrainment Separators also offer virtually complete resistance to corrosion over temperature range from -40 deg. F. to 338 deg. F. (-40 deg. C. to 170 deg. C.). These units are compact and easy to install... furnished complete and ready for use. For more details on how you can benefit by using KARBATE Separators Type MV, write us for Catalog Section S-6900.

To further assist you, we shall be willing to place your name on our mailing list to receive technical data and new product information on KARBATE Products. Simply fill out the enclosed postcard and return to us.

Very truly yours,

UNION CARBIDE INTERNATIONAL COMPANY

W. C. Wilsey

W. C. Wilsey/rld

5/59

I nuovi Carbide!

10 Novembre 1958

Rif.n.1188/el

Egr.Ing. Piero GIUSTINIANI
Amministratore Delegato
Soc. Montecatini
Sede

Caro Ingegnere,

ricevo copia della lettera inviataLe dal Prof.Pino, relativa alla richiesta del Dr. Brown della Union Carbide di studiare la possibilità di sintesi di olefine partendo da CO e H_2.

Come Lei ricorderà ci eravamo già interessati della cosa una diecina di anni fa, ed allora si era considerato un processo Fischer modificato come metodo per produrre butilene come materia prima per la produzione di butadiene.

Il procedimento era risultato allora non economico, in quanto tale sintesi Fischer modificata produce una miscela di idrocarburi etilene, propilene, butene, penteni ed eseni, etc. ed anche in quelle condizioni in cui il pentene rappresenta il componente più abbondante si ha una notevole produzione di altre olefine.

Ritengo però che oggi, tenuto conto delle nuove possibilità di applicazione delle diverse olefine (polimerizzazione, ossosintesi, etc.) e della notevole purezza delle olefine ottenute per sintesi di CO e H_2 che elimina ogni problema di depurazione, convenga riesaminare il problema sia pure per ora soltanto in base ai dati della letteratura. Panso che un tale studio orientativo possa essere fatto facilmente dal SEPS.

Cordiali saluti.

G.Natta

"MONTECATINI"
SOCIETÀ GENERALE PER L'INDUSTRIA MINERARIA E CHIMICA

AMMINISTRATORE DELEGATO

8 NOV. 1958
P 1182

G/ra

Milano, 7 novembre 1958

Caro Natta,

il prof. Pino mi ha scritto di aver parlato con il dr. F.B. Brown del Research Department della Union Carbide Olefins Company.

Il laboratorio del dr. Brown ha un progetto di ricerca sulla sintesi di olefine partendo da ossido di carbonio, idrogeno ed eventualmente acetilene.

Ritiene cè se ne debba occupare anche noi ?

Cordiali saluti.

Preg.mo Signor
Prof. GIULIO NATTA
MILANO

ISTITUTO DI CHIMICA GENERALE
UNIVERSITÀ DI PISA
VIA RISORGIMENTO, 19 BIS - TELEF. 31-71

IL DIRETTORE

Pisa, 5 - 11 - 1958

6 NOV 1958

U.C.C.

Chiar.mo
Prof. Giulio Natta
Direttore dell'Istituto
di Chim. Industriale del Politecnico
Piazza L. da Vinci 32
<u>MILANO</u>

Egregio Professore,

Le invio copia di una lettera che ho spedito all'Ing. Giustiniani per informarlo della visita del dott. F.B. Brown a questo Istituto.

Mi ha alquanto sorpreso il fatto che la Union Carbide intenda studiare la possibilità di sintesi di olefine partendo da CO e H_2 ed eventualmente acetilene, campo nel quale dopo gli sviluppi della petrochimica sembrava non vi fosse molto da sperare.

Con i migliori saluti

P. Pino

Copia

ISTITUTO DI CHIMICA GENERALE
UNIVERSITÀ DI PISA
VIA RISORGIMENTO, 19 BIS - TELEF. 31-71

IL DIRETTORE

Pisa, 5-11-1958

Preg.mo Sig.
Ing. Piero Giustiniani
Amministratore Delegato
della Soc. Montecatini
Via F.Turati 18
MILANO

Egregio Ingegnere,

desidero informarLa che nella scorsa settimana ho avuto la visita del dott. F.B. Brown del Research Department della Union Carbide Olefins Company.

Il laboratorio del dott. Brown ha in programma un progetto di ricerca sulle possibilità di sintesi di olefine usando come materie prime ossido di carbonio, idrogeno ed eventualmente acetilene; desiderava sapere se il nostro Istituto era interessato a compiere ricerche in tale campo.

Naturalmente gli ho risposto che i nostri impegni attuali non ci consentivano di iniziare nuovi programmi di ricerca.

Poichè il dott. Brown non ha fatto alcun cenno alle poli olefine, mi sono ben guardato di entrare in argomento.

La prego di gradire i miei migliori saluti

(Prof. Piero Pino)

UCC

10 Luglio 1958

Rif.n.841/el

Al SETTORE PROGETTI E STUDI
Soc. "Montecatini
S e d e

Pnd

Campioni di tricloruro di titanio della U.C.C. :

con riferimento alla Vostra lettera dell'8 corrente, di cui Vi ringrazio, Vi prego di farmi avere i campioni di VCl_3 e VCl_2 dell'U.C.C., appena Vi perverranno.

Distinti saluti.

(Prof.G.Natta)

MONTECATINI
SOCIETÀ GENERALE PER L'INDUSTRIA MINERARIA E CHIMICA
ANONIMA - CAPITALE VERSATO L. 100.000.000.000

MILANO

SETTORE PROGETTI E STUDI

MILANO, 8 Luglio 1958

Si prega indirizzare a:
Please reply to:
Veuillez adresser à:
Postanschrift:
Montecatini-SEPS
Via Turati, 18
Milano (Italia)
Phone - Téléphone - Fernsprecher: 6333
Cables - Télégrammes - Drahtwort: GABBROPROGETTI - MILANO

9 LUG 958
R 841

Egr. Sig. Prof.
G. Natta
Direttore dell'Istituto
di Chimica Industriale
del Politecnico di Milano
Piazza Leonardo da Vinci, 32
Milano

Campioni di tricloruro di titanio della U.C.C.

Egregio Professore,

Le alleghiamo copia della lettera della U.C.C. relativa ai campioni di tricloruro di titanio di cui alla Sua richiesta del 23.5.58 indirizzata al nostro direttore Ing. Orsoni.

Distinti saluti.

"MONTECATINI"

Oggetto

Con riferimento alla Vs/ lettera del 8 c.m. Vi ringrazio ~~[illegible]~~
[illegible]
Vi prego di far avere i campioni di VCl_3 e VCl.
~~app~~ dell U.C.C. appena li riceverete
Distinti saluti

All.
Tw/pr

Cartelle
U.C.C.

MONTECATINI
Settore Progetti e Studi

Milano, 19 Giugno 1958.

ISTITUTO [illegible]
[illegible]
* 23 GIU 1958 *
R

Preg.mi Signori
✓ Prof. Natta,
Ing. De Varda.

Mr. Murphy della Union Carbide mi visiterà lunedí 14 Luglio.

Cordialmente :

Orsoni

Or/sl.

4 Settembre 1957

Egr. Ing. G. De Varda
Direttore BREV.

Rif.n.1493-94

Sede

Trattative con Union Carbide -"Verbal Disclosures - Written Disclosures"

Egregio Ingegnere,

con riferimento alle Sue lettere del 2 settembre, ritengo - come già Le ho accennato a voce - che non meriti di muovere delle contestazioni alla U.C.C., per quanto si riferisce alle Sue lettere del 14 e 17.6.57.

I migliori saluti.

(Prof.G.Natta)

MONTECATINI
Società Generale per l'Industria Mineraria e Chimica

Brevetti e Documentazione Tecnica

RP/ma

PROMEMORIA

Data, 2 Settembre, 1957

IN

3 SET 1957

R 1492

per il Signori Prof. NATTA
Ing. ORSONI
Ing. BALLABIO

e p.c. Ing. GIUSTINIANI

Oggetto: Trattative con Union Carbide - "Written Disclosures" -

Ci riferiamo alla lettera del 14/6/57 della Union Carbide in risposta alla ns/ dell'11/4 di cui Lei possiede copia.

Da un esame delle informazioni in essa contenute non sembra si debbano muovere alla U.C.C. contestazioni.

Le saremo grati se vorrà comunicarci con cortese sollecitudine il Suo punto di vista in merito, onde possiamo riscontrare al più presto la lettera della U.C.C.

Con i migliori saluti.

"BREVETTI E DOC. TECNICA"

MONTECATINI
Società Generale per l'Industria Mineraria e Chimica
Brevetti e Documentazione Tecnica

RP/ma

PROMEMORIA

Data, 2 Settembre, 1957

ISTITUTO DI [illegible]
INDU
3 SET 1957
R 1494

per il Signori Prof. NATTA
Ing. ORSONI
Ing. BALLABIO

e p.c. Ing. GIUSTINIANI

Oggetto: Trattative con Union Carbide-"Verbal Disclosures"

Ci riferiamo alla lettera del 17/6/57 della Union Carbide in risposta alla ns/ dell'11/4, di cui Lei possiede copia.

Da un esame delle informazioni in essa contenute non sembra si debbano muovere alla U.C.C. contestazioni.

Le saremo grati se vorrà comunicarci con cortese sollecitudine il Suo punto di vista in merito, onde possiamo riscontrare al più presto la lettera della U.C.C.

Con i migliori saluti.

"BREVETTI E DOC. TECNICA"

7

MONTECATINI
Società Generale per l'Industria Mineraria e Chimica
Brevetti e Documentazione Tecnica

47/mm

PROMEMORIA

ISTITUTO [illegible]
INDUSTRIALE
22 LUG 1957
R 1385

hp

Data, 19 luglio, 1957

per il Signor Ing. Piero GIUSTINIANI

e p.c. Ing. ORSONI
Prof. NATTA

Oggetto: Rapporti con UNION C.C.

Allego una lettera di Toulmin in merito alla recente crisi nei suoi rapporti con la Union, la quale aveva preso una opzione su un importante gruppo di brevetti della Commonwealth Engineering Company, controllata da Toulmin.

Toulmin mi aveva già fatto menzione in America di questo procedere scorretto della Union nei suoi confronti.

Ha tenuto duro e sembra averla spuntata con la Union in generale e con il suo amico (e ospite) Cornwell, che ora risulta essere anche Vice-Presidente della Linde, in particolare.

Con ossequio.

all/

H. A. Toulmin
(1858-1942)
H. A. Toulmin, Jr.
Herbert H. Brown
Daniel J. Hanlon, Jr.
Folsom E. Drummond
Edmund M. Jaskiewicz
William H. Pavitt, Jr.

Patent Solicitors
Melvin A. Crosby
P. D. Rohe

Toulmin & Toulmin
Attorneys at Law
Corporation and Patent Law
Dayton 2, Ohio

Dayton, Ohio
Toulmin Building
308 West First Street

Washington, D.C.
Pennsylvania Building

Springfield, Ohio
Ohio Fuel Gas Building

Brussels, Belgium
27 Rue de la Limite

Cable Address
Toulmin, Dayton
Toulmin, Washington

RICEVUTO IL
18 LUG. 1957
MONTECATINI - BREV

July 12, 1957

VIA AIR MAIL
CC Air Mail Two
Days Later

PERSONAL & CONFIDENTIAL

Dr. Guiseppe De Varda
Montecatini Brevetti
Via F. Turati 18
Milan, Italy

Dear Dr. De Varda:

You will recall that you asked me to find out from Union Carbide why it was that they did not give you an opportunity to enter into a contract with them in connection with the production of polyethylene in Italy, but instead gave it to your competitor, Edison.

The following is a copy of my wire to you reporting on this subject, which I later confirmed by a verbal discussion:

> REFERENCE UNION AGREEMENT YOUR ITALIAN COMPETITOR. MY FRIEND INVESTIGATED MATTER EXTENSIVELY AND REPORTED FOLLOWING. UNION IS ANXIOUS TO MAINTAIN AND EXPAND FRIENDLY RELATIONS WITH MONTECATINI. MURPHY HAD NOTHING TO DO WITH AGREEMENT YOUR COMPETITOR. AGREEMENT WAS NEGOTIATED BY UNION CARBIDE INTERNATIONAL CORPORATION ONE MONTH AGO. MY FRIEND AND HIS COMPANY UNION DEVELOPMENT NOT CONSULTED OR INVOLVED. SIMILAR CONTRACTS TO ITALIAN NEGOTIATED IN INDIA, BRAZIL, ENGLAND AND ELSEWHERE. FOLLOWING REMARKS PROBABLY

> EXPLAIN WHY YOU NOT INVITED INTO CONTRACT. YOUR U. S. STEEL CONTRACT SERIOUSLY AFFECTED THE OXYGEN PLANT PLANS OF LINDE COMPANY. YOUR ANNOUNCEMENT PURCHASE PLANT SITE WEST VIRGINIA ALSO PUT YOU IN CLASS COMPETITOR OF CARBIDE INVADING ITS MOST PROFITABLE MARKETS. ALL THIS MISUNDERSTANDING COULD BE ELIMINATED BY CORRECT PUBLIC RELATIONS PLANNING. WHAT WAS OUTCOME NEGOTIATIONS HILL AND KNOWLTON. UNFORTUNATE YOU WENT THEIR NEW YORK OFFICE. CLEVELAND OFFICE ONE I DEAL WITH. HAS ABLE MAN AND MUCH CHEAPER. HAVE PLAN CORRECT THE FOREGOING PROBLEMS WITH CARBIDE AND OTHER SIMILAR COMPANIES IF YOU DESIRE IT.

Apparently your competition in connection with U. S. Steel is hurting. Whenever a corporation of the size and prestige of Union Carbide begins to conduct its business on the basis of spite and bad temper because it lost an order, you can be sure that you are making progress in your own operations and you should be encouraged to continue your drive for business in the United States.

I would regard this as a most significant event and this petty operation by not giving you an opportunity is indicative of the progress you are making in the United States. People in the United States admire the "go getter", that is, a person or company that is very aggressive and gets results and beats out competition.

If you have a reputation of being tough competition, that you do not give any quarter and you do not ask for any, then you are on your way to being a successful factor in the United States economy.

There is an old saying that "you cannot make an omelet without breaking some eggs". When I start out to compete or get results in some commercial operation or even litigation, I do not worry about the retaliation or bad feelings of the other side. I go at them with both fists and try to beat them into submission.

I would regard the action of Union Carbide as a sign that you are making progress and a sign of weakness on their part.

Certainly it was not good business on the part of their management not to get competitive bids from you and your competitors in order to get the best deal possible in Italy.

Sometime soon I may have occasion to talk with the top management of Union Carbide and I am going to take the opportunity, if it presents itself, to indicate that I was surprised at their operating on such a petty basis instead of businessmen to get the best profit for the stockholders.

The attached statement of a matter in which I am dealing with them may be of some interest to you in showing how you have to deal with these very tough people.

The fact that Murphy broke down and cried in your office about the failure of the negotiations is just another indication of the fact that your operations are beginning to worry the management of Union Carbide, which is good news indeed. Let us give them a lot of worry and keep up this pressure because ultimately I think you will get a very good deal out of them, but they only understand force, as you will see from the attached statement of my experience.

I think it might be helpful, if I may suggest it, to present this letter to Dr. Giustiniani, for it will throw light on the policies to be followed in connection with the public relations program in the United States about which I have written him.

Yours faithfully,

H. A.

Encl. - statement

RICEVUTO IL:
18 LUG. 1957
MONTECATINI - BREV.

The undersigned owns The Commonwealth Engineering Company of Ohio. It has developed what is regarded by Union Carbide as one of the really great new developments in the processing of chemicals, foods and the like that are heat-sensitive without injuring the subject matter.

Four years ago, after a year of investigation without our knowledge, Mr. R. E. Cornwell, then Vice President of the Linde Company, entered into a contract with Commonwealth by which Linde would be given four years to try out the process. We turned over our million gallon pilot plant to them as the beginning of the operations.

Since then, they have spent some millions of dollars, built three multi-million gallon plants and are now getting ready to go on stream ultimately with a 22 million gallon plant. The process has been successful and the mechanism has turned out to be on a sound basis.

The four years is up on October 30, 1957. For the last year Mr. Cornwell has been trying to get me to agree to give him a two to four year extension for the acceptance of the final contract and his initial payments, which are due on October 30, 1957.

He has done everything he can to put pressure to bear upon me to give him the extension, all the way from threats and abuse to an offer of various considerations and has endeavored to put it on a friendship basis. It has been a rough experience. He has pulled no punches and has been about as disagreeable as a man can be.

I happen to be a veteran of a good many conflicts in peace and war, so I stood firm. I told him to take it or leave it, but that was the answer and he would have to either pay or abandon his multi-million dollar operation and we would place the matter elsewhere.

Several days ago I learned that he has decided to go forward and settle on October 30, 1957 paying his initial cash payment.

So that you can see the amount of money involved in this process, Cornwell predicts on behalf of Union Carbide that in one of the twelve industries in which this process is adaptable that he expects to pay over the next twenty years a royalty to Commonwealth of a million dollars a year as an average.

In other words, I had to gamble what is probably going to be a very large sum of money on standing firm, and apparently, it is going to pay rich dividends, because if I had shown weakness, he would have taken advantage of it.

In the foregoing story, there is a lesson for your good company. Here in the United States, you must be very firm in your position and very aggressive. It is the same policy that I have taken the liberty of recommending in connection with the Ziegler matter.

H. A. Toulmin

H. A. Toulmin
1858 1942
H. A. Toulmin Jr
Herbert H. Brown
Daniel J. Hanlon Jr
Folsom E. Drummond
Edmund M. Jaskiewicz
William H. Parett Jr

Patent Solicitors
Melvin A. Crosby
P. J. Peake

Toulmin & Toulmin
Attorneys at Law
Corporation and Patent Law
Dayton 2, Ohio

Dayton, Ohio
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308 West First Street

Washington, D.C.
Pennsylvania Building

Springfield, Ohio
Ohio Fuel Gas Building

Brussels, Belgium
27 Rue de la Limite

Cable Address
Toulmin, Dayton
Toulmin, Washington

ISTITUTO DI CHIMICA INDUSTRIALE POLITECNICO
21 MAG 1957
vie

May 15, 1957

UCC

RICEVUTO IL
2? MAG. 1957
MONTECATINI-BREV.

VIA AIR MAIL
Copy Boat Mail

Dr. Guiseppe de Varda
Montecatini Brevetti
Via F. Turati 18
Milan, Italy

Re: Union Carbide and Carbon Corp.

Dear Dr. de Varda:

This is to bring you up-to-date.

Mr. Cornwell has been promoted to President of Union Carbide Development Corporation. He had lunch with Mrs. Peake and myself in New York to discuss another matter. Nothing was said on either side, which I would interpret as meaning that your matter is still under serious consideration, per my letters of April 3, 6, and 9, 1957.

Mr. Cornwell is going to Washington to spend a day in discussing with Mrs. Peake another matter which he is interested in securing from Commonwealth. She has been carefully instructed to be non-committal and listen but not comment if he raises the issue.

Sincerely yours,

H A Toulmin Jr

Fotocopie per ing Giust
h Orsoni
prof Natta

MONTECATINI
Società Generale per l'Industria Mineraria e Chimica

Brevetti e Documentazione Tecnica

RP/ma

PROMEMORIA

ISTITUTO DI CHIMICA
INDUSTRIALE DEL POLITECNICO

1020 UCC

Data, 7 Maggio, 1957

per il Signor Ing. Bartolomeo ORSONI

e p.c. Ing. BALLABIO
Prof. NATTA

Oggetto: Disclosures verbali a Union Carbide - Vincolo segretezza -

Alleghiamo per conoscenza copia di una lettera inviataci il 30 aprile u.s. da Bakelite Co. per accusarci ricevimento della nostra comunicazione 15/3/57 con allegato elenco completo delle "Verbal Disclosures" fatte a suo tempo a Union, nonchè per comunicarci il loro accordo su quanto contenuto in detto elenco.

Con i migliori saluti.

"BREVETTI E DOC. TECNICA"

all/

TRADE MARKS
BAKELITE

BAKELITE COMPANY

A DIVISION OF UNION CARBIDE AND CARBON CORPORATION

UCC

230 GROVE STREET
BLOOMFIELD, N. J.

TRADE MARKS
VINYLITE

GENERAL OFFICES
30 EAST 42nd STREET
NEW YORK

April 30, 1957

Montecatini
Societa Generale per l'Industria
Mineraria e Chimica
Via Turati 18
Milan, Italy

4 MAG. 1957

Attention: Dr. G. de Varda, Chief Patent Counsel

Gentlemen:

This will acknowledge receipt on March 26, 1957, of your letter of March 15, 1957, and the Montecatini list, "Verbal Disclosures."

We have compared that list with the list submitted by Carbide with our letter of February 5, 1957 and find several, but relatively minor, differences between the two lists.

Our list contains the verbal disclosures as understood and so reported by our representatives at the time of their visit to Montecatini. Accordingly, we adhere to that list. We are, however, willing to acknowledge receipt as of March 26, 1957, of the differences in the disclosures as contained in the list which accompanied your letter of March 15, 1957.

Very truly yours,

UNION CARBIDE AND CARBON CORPORATION

By Frederick H Roberts

Pieroni p. f. archivio
copie a [illegible]
Prof Natta
a Ing Ballabio,
a Dr Ferrari

Prof Natta p.c.

UNION CARBIDE AND CARBON CORPORATION
30 EAST FORTY-SECOND STREET
NEW YORK 17, N. Y.

H. S. BUNN
EXECUTIVE VICE PRESIDENT

ISTITUTO DI CHIMICA
INDUSTRIALE DEL POLITECNICO
* 30 APR. 1957 *
R

rip

April 26, 1957

Ing. Piero Giustiniani
Managing Director of Montecatini
Societa General per l'Industria
Mineraria e Chimica
Via F. Turati, 18
Milan (134), Italy

Dear Ing. Giustiniani:

In the absence of Mr. Dial, I am writing to advise you that we have decided not to exercise our option for a polystyrene license under our agreement of November 26, 1956.

This decision, like our decision with respect to polypropylene, has been reached only after a thorough study by the members of our patent and research staffs.

As Mr. Dial told you in his letter of February 21, we still feel that as the patent picture clarifies an arrangement beneficial to both of us may be possible in the polyolefins field.

Sincerely yours,

H S Bunn

Howard S. Bunn

HSB:jg

MONTECATINI
Società Generale per l'Industria Mineraria e Chimica
Brevetti e Documentazione Tecnica

dV/ma

PROMEMORIA

ISTITUTO DI CHIMICA INDUSTRIALE DEL POLITECNICO
16 APR. 1957
R 871

Data, 15 Aprile, 1957

per il Signor Ing. Piero GIUSTINIANI

e p.c. Ing. ORSONI
Prof. NATTA

Oggetto: Contatti Toulmin-Union C.C. -

Trasmetto relazione Toulmin contatti avuti con Cornwell della U.C.C.

Significativo il retroscena Union. Decisione opzione polistirolo sarà probabilmente negativa come per polipropilene. Perdura però vivissimo interesse Union per entrambi.

Suppongo avremo controproposte che potremo respingere, accettare o preferibilmente tenere aperte in attesa eventuale nostro accordo du Pont.

L'azione condotta da Toulmin mi sembra abile e potrebbe anche risultare fruttuosa.

Con ossequio.

all/

H. A. Toulmin
1858-1942
H. A. Toulmin, Jr.
Herbert H. Brown
Daniel J. Hanlon, Jr.
Folsom E. Drummond
Edmund. A Jaskiewicz
William H. Pavitt, Jr.

Patent Solicitors
Melvin A. Crosby
P. D. Peake

Toulmin & Toulmin
Attorneys at Law
Corporation and Patent Law
Dayton 2, Ohio

Dayton, Ohio
Toulmin Building
308 West First Street

Washington, D.C.
Pennsylvania Building

Springfield, Ohio
Ohio Fuel Gas Building

Brussels, Belgium
27 Rue de la Limite

Cable Address
Toulmin, Dayton
Toulmin, Washington

April 3, 1957

AIR MAIL

CONFIDENTIAL

Montecatini Brevetti
Via F. Turati 18
Milano, Italy

Attn: Dr. Guiseppe De Varda

Re: Union Carbide

Dear Dr. De Varda:

This is in partial reply to your letter of March 12, 1957. I would like to defer the full reply until the following takes place.

After receiving your letter Mr. Cornwell called me from New York and asked me to have dinner with his wife and him next Wednesday evening April 4 in New York and then stated he wanted to discuss business with me on the following moring April 5. This should present the opportunity to sound him out delicately to see what the attitude of the company really is and to see if I can get an opportunity to make the statements that you wish me to make to him.

It may interest you to know that J. J. Murphy with whom you have been dealing is a fellow Vice President of the Union Carbide Development Corporation of which Mr. Cornwell is Senior Vice President. Therefore, undoubtedly (I have just received this information) Mr. Cornwell is fully conversant with the entire situation and I suspect is an active participant behind the scene as this corporation is the particular "brain child" of Mr. Dial.

Therefore, it seems that approaching Mr. Cornwell through the back door may lead us directly into the main house.

I do not know what will develop but you can be assured I will do the best for you, always keeping in mind that I must proceed with great caution, a course that I will follow. As Cornwell has followed with us in the Stepfreeze contract under which they have been operating and to which is attached a final contract that they must take or drop on November 30, 1957, and this method was quite agreeable to him, I think we are on sound ground now to sound him out without committing you as to such a contract in connection with your fibers and elastomers leaving the troublesome patent matter to future developments which will certainly have matured on or before the date when the final contract between Montecatini and Carbide would go into effect.

If I could get these general principles established in his mind I believe I will have done you a good service.

Cornwell likes to deal with us and when he does so he does not bring along any lawyers as he has full trust in me and knows I will not take advantage of him.

It is that good, sound businesslike basis I would like to see established on your behalf which I believe your management will find quite satisfactory.

I will advise you promptly what the outcome is.

Sincerely,

CC: Boat Mail

ISTITUTO DI CHIMICA
INDU[illegible]
15 APR. 1957
7 U.C.C.

REGISTERED

April 11th, 1957

UNION CARBIDE AND CARBON CORP.
Carbide and Carbon Building
30 East Forty-Second Street
NEW YORK, 17 (U.S.A.)
Attention: Mr. J.J. MURPHY, Director of Patent Affairs -

Our.ref. RP.ma

Gentlemen:

Re: Written disclosures

In your letter of February 19, 1957 you assert that the following information disclosed by Montecatini under Article III, Section 1 (b) of the Polypropylene Plastics Option and License Agreement and of the Polypropylene and Polystyrene Plastics Option and License Agreement, and in the answers to the questions in the First Enclosure to Corollary Letter No. 2 of said Polypropylene Agreement and in the First and Second Enclosures to Corollary Letter No. 2 of said Polypropylene and Polystyrene Agreement under Article III, Section 1 (d) of each of said Agreements, received and acknowledged by Union Carbide before January 1, 1957, was published or generally available to the public, or was already in the possession of Union Carbide before November 26, 1956, and is therefore excluded from the provisions of Article IV of said Agreements:

1. Method for the polymerization of propylene and for the purification of the polymer.
2. Intrinsic viscosity determination on Polypropylene.
3. Gas-Volumetric determination of the purity of organic aluminum compounds.
4. Chemical and physical analytical methods for $TiCl_3$.
5. Preparation of isotactic polystyrene and purification of polymer.
6. Preparation of isotactic, high molecular weight polystyrene and purification of polymer.
7. Viscosimetric determination of the molecular weight of isotactic polystyrene.
8. Laboratory preparation of $TiCl_3$.

./.

9. Quantitative X-ray determination of polypropylene crystallinity.
10. Crystal structure of isotactic polypropylene.
11. Polypropylene elastic modulus.
12. Mechanical properties of polypropylene extruded films.
13. Resistance of polypropylene to chemicals.
14. Physical properties of crude polypropylene of average molecular weight 100,000 to 200,000.
15 Rate of polypropylene crystallization.
16. Polypropylene stabilizers.
17. Time necessary to reach one-half of the maximum polystyrene crystallinity.
18. Rate of crystallization of polystyrene.
19. Effect of ultra-violet light upon the induction time of the oxidation reaction.
20. Effect of stabilizers upon the induction time of the oxidation reaction.
21. Influence of temperature upon the melt viscosity of polypropylenes having different molecular weights.
22. Comparison of the stabilization of polypropylene to Fertene.
23. Correlation between natural and accelerated aging.
24. Description of the accelerated apparatus.

The answers to the questions in the Enclosures to Corollary Letters No. 2 in each Agreement.

To the best of our knowledge the information disclosed in relation to points 5, 6, 16 above, referring to processing conditions, and points 9, 11, 12, 14, 15, 17, 18, 19, 20, 21, 22, 23, 24 referring to testing methods or to properties of the materials, and in the answers to the questions in the Enclosures to Corollary Letters No. 2, under points 7 and 9 for polypropylene and points 1, 3, 5, 6, 12 for polystyrene, had not been published before November 26, 1956.

./.

In accordance with the provisions of Article IV, Section 2 of each of said Agreements, we ask you therefore to kindly furnish us convincing evidence that the information relating to the above listed points was in the possession of Union Carbide before November 26, 1956.

Yours faithfully.

"MONTECATINI"
(F.to Ing.Orsoni-Ing.de Varda)

original by air mail registered
copy by air mail two days later

April 11th, 1957

U.C.C.

UNION CARBIDE AND CARBON CORP.
Carbide and Carbon Building
30 East Forty-Second Street
NEW YORK 17 (U.S.A.)

Attention: Mr. J.J. MURPHY, Director of Patent Affairs.

EP/ma

Gentlemen:

Re: Verbal disclosures

In your letter of February 21, 1957 you assert that the following information disclosed verbally to Union Carbide representatives during their visit to Montecatini under Article III, Section 1(c) of the Polypropylene Plastics Option and License Agreement and of the Polypropylene and Polystyrene Plastics Option and License Agreement and listed as "Miscellaneous Montecatini Verbal Disclosures", in the list attached to your letter of February 5, 1957, was published or generally available to the public, or was already in the possession of Union Carbide before November 26, 1956, and is therefore excluded from the provisions of Article IV of said Agreements:

Items as numbered on the list: "Miscellaneous Montecatini Verbal Disclosures" as follows: 1, 2, 3, 4, 5, 6, 7, 8, 10, 11, 12, 13, 15, 17, 18, 19, 20, 21, 22, 23, 24, 26, 28, 29, 30, 32, 33, 34, 35, 36, 38, 39, 40, 42 and 43.

To the best of our knowledge the information disclosed under points: 1, 3, 4, 5, 6, 7, 12, 18, 19, 20, 22, 23, 26, 28, 33, 38, 39, 40, 42, 43, as revised according to the list attached to our letter of March 15, 1957, had not been published before November 26, 1956.

In accordance with the provisions of Article IV, Section 2 of each of said Agreements, we ask you therefore to kindly furnish us convincing evidence that the information relating to the above listed points was in the possession of Union Carbide before November 26, 1956.

Yours faithfully.

"MONTECATINI"
(F.to Ing.Orsoni-Ing.de Varda)

original by air mail registered
copy by air mail two days later.

ISTITUTO DI CHIMICA
INDUSTRIALE DEL POLITECNICO
* 6 MAG 1957 *
R

copia p.c. Prof. NATTA

Milan, 4 April 1957

Dear Mr. Bunn,

I thank you for your kind letter of April 26th, by which you communicate to me the decisions of your Company with regard to polystyrene.

I do not doubt that your Company will have reached such decisions after a thorough study of the situation.

I too am of the opinion that the so cordial and friendly relationships already existing between U.C.C. and our Company could in future find other opportunities of mutual interests also in fields other than the polyolefins field.

With my best regards.

Yours sincerely,

(Ing. Piero Giustiniani)

Mr. Howard S. Bunn
Union Carbide and
Carbon Corporation
30 East Forty-Second Street
New York 17, N.Y.

MP/ma

April 2nd, 1957

INC
3 APR 1957
R UCC

UNION CARBIDE AND CARBON CORPORATION
Carbide and Carbon Building
30 East Forty-Second Street
NEW YORK 17 (U.S.A.)

Attention: Mr. J.J. MURPHY, Director of Patent Affairs

Gentlemen,

With your letter of February 18, 1957 you informed us that the information disclosed by Montecatini under Article III, Section 1(a) of the Polypropylene Plastics Option and License Agreement and of the Polystyrene Plastics Option and License Agreement, between Union Carbide and Carbon Corp. and Montecatini, was published or generally available to the public, or was already in possession of Union Carbide before November 26, 1956.

To the best of our knowledge the subject matter of the following Patent Applications had not been published anywhere before November 26, 1956:

United States	Patent	Application	Serial	No.	598,857
"	"	"	"	"	602,010
"	"	"	"	"	611,981
"	"	"	"	"	616,227
Italian	"	"		"	15,700/55
"	"	"		"	18,119/55
"	"	"		"	17,166/55
"	"	"		"	2,898/55

In accordance with the provisions of Article IV, Section 2 of each of said Agreements, we ask you therefore to kindly furnish us convincing evidence that the subject matter of the above listed Patent Applications was in the possession of Union Carbide before November 26, 1956.

Very truly yours

"MONTECATINI"

arch

original by air mail registered
CC: by air mail two days later

MONTECATINI
Società Generale per l'Industria Mineraria e Chimica

Brevetti e Documentazione Tecnica
dV/ma

PROMEMORIA

URGENTE

ISTITUTO DI CHIMICA
INDUSTRIALE DEL POLITECNICO
1 APR. 1957
R 744

Data, **30 Marzo, 1957**

Union Carb. Carbo.

per il Signor **Ing. Piero GIUSTINIANI**

e p.c. Ing. ORSONI
Prof. NATTA

Oggetto: Opzione Union licenza polistirolo - Contatti Toulmin-Cornwall -

Come da Sue istruzioni (e come da documentazione già in Suo possesso) abbiamo a suo tempo inviato a Toulmin:

a) copia della lettera di Murphy sui motivi per cui la Union non ha ritenuto di chiudere l'opzione polipropilene,

b) copia della nostra dettagliata risposta a Union,

c) lettera di istruzioni a Toulmin sulla linea da seguire nei suoi futuri contatti con Cornwall.

Allego ora fotocopia di due lettere in data 19 marzo pervenutemi da Toulmin.

Resto in attesa delle osservazioni Sue, dell'Ing. Orsoni e del Prof. Natta prima di rispondere.

Con ossequio.

G de Varda

all/

MONTECATINI
Società Generale per l'Industria Mineraria e Chimica
Brevetti e Documentazione Tecnica

EP/ma

PROMEMORIA

ISTITU
25 MAR 1957
R 711

Data, 22 Marzo, 1957

per il Signor Ing. Bartolomeo ORSONI

e p.c. Ing. BALLABIO
Prof. NATTA

Oggetto: Opzione Union - Vincolo Segretezza

Facciamo seguito alla ns/ del 25 febbraio con la quale La portavamo a conoscenza della lettera Union del 19/2/57 nella quale si asseriva essere U.C.C. alla data del 26/11/56 a conoscenza della maggior parte delle informazioni scritte contenute nei 24 documenti da noi consegnati a suo tempo a Union.

Poichè dobbiamo entro le prossime settimane prendere posizione in merito, La preghiamo di fornirci le eventuali informazioni in Suo possesso circa la effettiva disponibilità al pubblico delle singole informazioni in questione.

PregandoLa di gradire i nostri migliori saluti.

"BREVETTI E DOC. TECNICA"

MONTECATINI
Società Generale per l'Industria Mineraria e Chimica
Brevetti e Documentazione Tecnica
RP/ma

PROMEMORIA

ISTITUTO DI CHIMICA
INDU[illegible]NICO
* 25 MAR 1957 *
R 710 [illegible] Carlo

[illegible]

Data, 22 Marzo, 1957

per il Signor Ing. Bartolomeo ORSONI

e p.c. Ing. BALLABIO
Prof. NATTA

Oggetto: Opzione Union - Vincolo Segretezza

Facciamo seguito alla ns. del 25 febbraio con la quale portavamo a Sua conoscenza la lettera Union del 21/2/57 nella quale si asseriva essere U.C.C. alla data del 26/11/56 a conoscenza della maggior parte delle informazioni verbali da noi date ai loro rappresentanti.

Poichè dobbiamo entro le prossime settimane prendere posizione in merito, La preghiamo di fornirci le eventuali informazioni in Suo possesso circa la effettiva disponibilità al pubblico delle singole informazioni in questione.

Copia delle suddette informazioni corrette in base a quanto a suo tempo concordato e come trasmesse a Union C.C. Le è stata inviata il 15 m.c.

PregandoLa di gradire i nostri migliori saluti.

"BREVETTI E DOC. TECNICA"

DA Ing. de Varda

A Sig. Prof. G. Natta p.c.

Mod. UGEN 82

BREV
DIREZIONE
dV/RP/ma

March 15, 1957

arch.

ISTITUTO DI CHIMICA
INDUSTRIALE DEL POLITECNICO
20 MAR 1957
R

UNION CARBIDE AND CARBON CORP.
Carbide and Carbon Building
30 East Forty-Second Street
NEW YORK 17, N.Y. (U.S.A.)

Attention Mr. Frederick H. Roberts

Gentlemen:

Montecatini-Union Carbide and Carbon "Polypropylene and Polystyrene Plastics Option and License Agreements"

Referring to your letter of February 5 and to our of February 14th, 1957, we are now enclosing a list of the information which, according to our records, was verbally disclosed by Montecatini under the above agreements.

We will be grateful to you if you will kindly acknowledge receipt of the list returning to us the enclosed copy with your signature and inform us of whether you are in agreement with it.

Yours faithfully,

"MONTECATINI"

original by air mail with encls.
CC: by air mail two days later

MISCELLANEOUS MONTECATINI VERBAL DISCLOSURES

1. The per cent extractable in the polypropylene as made depends on the purity of the propylene, the purity of the titanium trichloride, and the temperature of polymerization. Product of greatest crystallinity is obtained when the propylene has been purified with aluminum alkyl prior to polymerization. The propylene should contain no more than 20 to 30 p.p.m. acetylene for the highest crystalline product possible. Allylene should be eliminated and there should be no other olefins for a very highly crystalline product.

2. Concerning catalyst yield. In their pilot plant process Montecatini obtained 150 to 200 gms. of polypropylene per gram of catalyst. In the laboratory they have obtained as high as 1000 gms. polymer per gram of catalyst, but this was by a process which in the present is not commercially employed.

3. The ultraviolet light stability of the crystalline polystyrene is very much like that of normal polystyrene. Montecatini feels that ultraviolet stabilization is not a problem with polystyrene.

4. Large particles of crystalline titanium trichloride will cleave in the course of propylene polymerization, that is, break down to an equilibrium size distribution, and consequently are satisfactory for the polymerization. Such large particles, however, increase the induction period.

5. Finely ground particles of $TiCl_3$ lead to a much more rapid initial polymerization rate. If the reaction heat is not sufficiently removed a higher percentage of amorphous product may be caused by the higher and uncontrollable polymerization temperature.

6. Montecatini does not usually grind titanium trichloride after preparation; they simply screen the material to remove large foreign bodies which may be present.

7. Montecatini has investigated the use of titanium dichloride in place of titanium trichloride. Titanium dichloride gives an equally crystalline product but Montecatini prefers the trichloride because the dichloride is much more difficult to prepare in a state of high purity and may contain titanium metal impurities which are difficult to remove from the product.

Initial ____________________ ./.

8. Apparently commercial styrene will not polymerize indefinitely like the pure propylene will. To help remove the polystyrene from the catalyst surface Montecatini uses benzene as a diluent in the polymerization.

9. Concerning polypropylene: After purification the polymer contain less than 0.01 by weight chlorine. The high molecular weight polymer contains no more chlorine than low weight polymer. Montecatini is not certain whether the chlorine is chemically bound or whether chlorinated compounds are mechanically occluded.

10. If the chlorine is not all washed out, HCl may be evolved upon pyrolysis. This is true of polymer purified according to Montecatini's written disclosure.

11. The majority of the polypropylene chains are terminated in a vinylidene type double bond.

12. Montecatini can stabilize against acid corrosion with conventional polyvinyl chloride stabilizers.

13. Concerning the preparation of the titanium trichloride, Montecatini showed Union their pilot plant operation at Ferrara. Mr. Negromanti described the process in some detail. (A corrected flow-sheet of the pilot plant is enclosed.)

14. The use of TiCl$_2$ instead of TiCl$_3$ leads in general to a lower rate of polymerization of propylene probably because of differences in surface areas.

15. The lattice constants of TiCl$_3$ and TiCl$_2$ are very close; this can allow the formation of solid solutions of the two compounds.

16. When using TiCl$_3$ after the polymerization has been carried to the point beyond the initial induction period, if it is stopped by removing monomer, it will start up again with no induction period and at the same rate as before.

17. The termination step in the propylene polymerization is principally due to either hydride ion transfer or to monomer transfer. Hydride ion transfer is favored at the higher temperatures.

Initial ____________

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18. Concerning the styrene polymerization, benzene of nitration grade is used as diluent. No other purification is necessary but is convenient when the water content is above 0.001 per cent.

19. Concerning mold corrosion with polypropylene, Montecatini have no experience with tests up to 100 hours. They have tried 10 hours continuous molding using a chromium-plated mold without corrosion occurring. Polyvinyl chloride stabilizers can be used to stop any corrosion which does occur. Good stabilizers are lead stearate, lead phosphite, and several epoxy stabilizers — at a concentration of 0.01 to 0.3 per cent.

20. Concerning stress endurance of polypropylene, the .91 to .92 density material resulting from the polymerization as revealed in the written disclosure does not break under 1000 continuous hours under a load of 3000 p.s.i.

21. The intrinsic viscosity-molecular weight relationship used by Montecatini for polypropylene is: $[\eta] = 1.18 \times 10^{-3} M^{0.63}$. The intrinsic viscosity is measured in tetralin at 125°C. This is the same formula that has been used for polyethylene by I.C.I.

22. It is possible to make fairly highly crystalline polystyrene directly to intermediate molecular weight levels by following the same procedure outlined in the written disclosure for high molecular weight polystyrene, using higher catalyst concentration. The molecular weight of the polystyrene which is first formed may be lower than the molecular weight obtained after several hours. After this initial period of time, however, the molecular weight remains practically constant with additional time.

23. Hydrogen can be used to lower the molecular weight of the polymers. Its use does not reduce the crystallinity of the polypropylene.
In the case of polystyrene the use of hydrogen is not as effectiv in lowering the molecular weight as in the case of polypropylene.

24. Thermal depolymerization may be used to reduce to any desired level the molecular weight of the highly crystalline, very high molecular weight polystyrene.

INITIAL ____________________

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25. Concerning the use of aluminum titanium alloy as a catalyst, the three-to-one aluminum-to-titanium ratio discussed in the patent application appears to be best. No explanation was given as to why such a ratio should be optimum. Such ratio corresponds, however, to a known intermetallic compound.

26. Montecatini prefers to use aluminum triethyl because it is easily prepared and gives a more crystalline polymer than the higher alkyl aluminums. They have never tried trimethyl aluminum at Ferrara. Aluminum tri-isobutyl is used as an intermediate in the preparation of the aluminum triethyl.

27. Montecatini claimed there was no change in the induction period in the polymerization of propylene in the case of polymerization promoted by $TiCl_3$, if the catalyst components are mixed, brought to the polymerization temperature below about 80°C, and then monomer is withheld for various periods of time.

28. The rate of polymerization of both styrene and propylene for a given volume of diluent decreases as the ratio of solid catalyst to diluent decreases. However, the molecular weight and the per cent crystallinity of both polypropylene and polystyrene are not largely affected by the catalyst-to-diluent ratio.

29. Calculated theoretical density of crystalline polypropylene is 0.936 g/cc.

30. Highly crystalline and highly oriented polypropylene shows less evident second order transition temperature, as determinated by dilatometric methods. This temperature, so determined, is only of significance for the amorphous form.

31. Catalyst activity changes during the induction period as the polymerization of propylene proceeds, and eventually levels out at a constant value, in the case of polymerization promoted by $TiCl_3$.

32. When large amount of catalyst are used in the polymerization to obtain lower molecular weight products, the molecular weight distribution in the product is probably very wide.

33. When aluminum triethyl is used with titanium trichloride as a catalyst component in a polymerization, an increase in temperature of the reaction over 100°C causes a decrease in molecular weight and at very high temperature a decrease in crystallinity.

INITIAL ____________________

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34. Concerning the preparation of amorphous polymers: The use of alkyl groups that are greater than four carbon atoms in length is desirable because the precipitate having catalytical effect so produced from $TiCl_4$ is generally more amorphous. The presence of long chain alkyl groups interferes with formation of a crystalline precipitate.

35. The viscosity molecular weight relationship for polyethylene:

$$[\eta] = 1.18 \times 10^{-3} M^{0.66}$$

has been used by Montecatini for polypropylene. It yields only conventional values. The viscosity is measured in tetralin at 135°C.

36. Concerning crystalline helices: The packaging volume of a right-handed helix is the same as with a left-handed helix for a given isotactic chain.

37. The use of very short reaction times is not a practical satisfactory means of producing low molecular weight, highly crystalline polystyrene.

38. The use of hydrogen to control the molecular weight of polystyrene is not as effective as it is with polypropylene.

39. High molecular weight, extracted polystyrene after molding and annealing is 45 to 60% crystalline. High molecular weight crystalline polystyrene after molding, at temperatures higher than 250°C, and quenching is not crystalline.

40. Concerning propylene polymerization: A metal alkyl containing an alkoxy group is a possible catalyst component but it is not as effective as triethyl aluminum.

41. Aging the $TiCl_3$ catalyst prepared according to the disclosure for ten to twenty hours at temperatures below 80°C does not alter its activity. Within the same temperature range, aging the catalyst in the absence of monomer does not change the induction period.

INITIAL ____________________

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42. The molecular weight and crystallinity of polypropylene are only slightly affected by the catalyst concentration. The reaction rate increases as the TiCl$_3$ quantity is increased, independently, within wide limits, from the concentration of the aluminum alkyl. As the temperature is increased over 100°C the molecular weight and crystallinity are lowered but the initial reaction rate increases. Using a catalyst on the basis of TiCl$_3$, crystallinity is not much affected by temperature below 80°C, decreases slightly from 80 to 100°C and decreases rapidly above 100°C.

43. For polypropylene, when a catalyst prepared from TiCl$_3$ obtained according to the disclosure is used at temperatures between 30 and 80°C, no variation in crystallinity with temperature is observed. An increase in catalyst concentration lowers the molecular weight.

Acknowledged receipt
on behalf of UNION CARBIDE AND CARBON CORPORATION

At ______________________________

on ______________________________

<u>BY AIR MAIL</u>

March 12, 1957

UNION CARBIDE AND CARBON CORP.
Carbide and Carbon Building
30 East Forty-Second Street
NEW YORK 17, N.Y.

GV/mm - 108/54

cc: Mr. Lucio LUCINI, President
Chemore Corporation
21 West Street
NEW YORK 6, N.Y.

Attention: Mr. John J. MURPHY
Director of Patent Affairs

Gentlemen:

We refer to Mr. Murphy's letter of February 28, 1957, addressed to Mr. [illegible].

We have noted that you have decided not to exercise your option for a polypropylene license under the terms of our agreement of November 26, 1956. We too hope that at some future time the conditions then prevailing will permit both our Companies to negotiate again an agreement in the field of polypropylene. We have also noticed that you are continuing your evaluation of Montecatini's polystyrene option.

We have read the "Memorandum re: Polypropylene", dated February 25, 1956, enclosed to said letter. We should like to briefly comment on the various statements contained therein as follows:

1 and 2. This fact had been duly weighed when proposing figures and provisions of the November 26, 1956 Agreement. If the patent situation had already been settled our offer would have been different

We are aware that possibly not all our claims in this field will be awarded to us. We are quite confident, however, that what patent protection we will finally get in the United States will be enough to prevent third parties from making our polypropylene products without a license from Montecatini.

3. In our opinion, interferences of some importance, if any, may in practice develop only with respect to the basic patent applications filed in 1954. The evidence <u>we</u> have

./.

in this connection is that there are only three firms besides Montecatini which can have some "prima facie" claim to enter the race, but we do not believe any of the three has a serious chance of success except perhaps in limited sections of the field. Anyway there are good prospects that important claims of ours will be allowed within 1957;

4. You will know that (as always happens in revolutionary developments) many people set out to invent patents or to re-invent inventions rather than patenting real inventions in this field. If we consider that Montecatini and Ziegler have filed in Italy well over 100 patent applications in the field of polyolefines your figure of 800 U.S. applications may even be low. Time will show however that only few of those applications will have controlling importance;

5. This does not seem to apply to the basic inventions on isotactic polymers, the non-obviousness of which, even to people familiar with the Ziegler catalysts and skilled in the art of polymerization, has been acknowledged by such authorities in the field as H.Mark, H.Tobolsky, C.Schildknecht, and, last not least, Ziegler himself.

6. In the future, if the then prevailing situation will warrant it in the interest of both our Companies, we shall be glad (though we are not bound any more to do so by our agreement with Professor Ziegler) to resume negotiations for a license to Carbide.

7 and 8. We have no difficulty in believing that Carbide can manufacture now polypropylenes by processes preferable to those patented by Montecatini in 1954 and 1955. We have obviously made, however, steps forward during 1956 and these early months of 1957. In fact, our Ferrara plant will go on stream next month and is expected to attain within a few months a capacity of 13,000,000 pounds per year. To the best of our knowledge Montecatini will therefore be the first Company in the world to manufacture polypropylene on a commercial scale. On the other hand it should not be forgotten that the Agreement of November 28, 1955 dealt primarily with patent problems.

9. In our opinion this statement is irrelevant. Even assuming that Professor Ziegler will have the "dominating position in the United States" this still does not enable a third party to manufacture polypropylene in the United States without being licensed under the patents that will be issued to us.

./.

As to your basic objection to the provisions of the Option and License Agreement signed by Carbide and Montecatini on November 26, 1956 we remark the following:

(1) We disagree about the alleged inadequacy of Article XIII of the Agreement. According to well-established principles in the civil-law countries, termination of an agreement must be based on the mutual consent of the parties or on valid reasons, such as nonperformance of contractual obligations.

(2) We have sought with the utmost care and study, and with the help of competent U.S. advisers, to draft an agreement which in all of its provisions is in accordance not only with the letter, but also with the spirit of the law of the U.S. and of the other countries affected by its working.
We have been authoritatively assured that we have succeeded in doing so.

(3) This evaluation is necessarily subjective. The terms which you attempt to compare are hardly homogeneous: and even if we are to try to weigh comparatively f.i. Ziegler's polyethylene process with Montecatini's polypropylene products, we must conclude that these inventions are both exceptionally good, but with a difference, i.e. that Ziegler's patent rights on polyethylene cover only one of the available processes for manufacturing a product already known. Furthermore, characteristics and commercial prospects of our polypropylene products are exceptionally bright.

Yours very truly.

"MONTECATINI"
(F.to Ing Orsoni - Ing de Varda)

original by air mail
CC: by air mail 2 days later

ISTITUTO DI CHIMICA
INDUSTRIALE DEL POLITECNICO
* 14 MAR 1957 *
R 608

BY AIR MAIL March 12, 1957

Mr. H.S. TOULMIN, Jr.
Toulmin Building
308 West First Street
DAYTON 2, OHIO (U.S.A.)

CONFIDENTIAL

GV/mm

Dear Mr. Toulmin,

1) I have received your several letters concerning policy and I have read with particular, keen interest the last one, dated March 5, 1957.

I have cabled to you immediately as follows:

> "Your interesting confidential March fifth received Stop Possibly wait our letter before further contacting your friend"

so as to prevent you, if possible, from meeting Mr.Cornwell before being sufficiently acquainted with the situation;

2) There have been lengthy and difficult negotiations between Montecatini and Union Carbide, extending for over eight months. The negotiations were even interrupted by Montecatini in August, 1956, and resumed after a while substantially at Carbide's urging. On November 26, 1956 two option and license agreements concerning polypropylene and polystyrene plastics were signed. The polypropylene option period expired on February 26 last; the polystyrene option period will expire on April 27, 1957 and is still open.

3) Union Carbide has decided not to exercise its option for the polypropylene license. We enclose copies of a letter (with enclosure) by Mr. Murphy, Director of Patent Affairs of Union Carbide, and of the reply we have sent him to-day;

4) We have replied to each of the several remarks contained in the enclosed Carbide's "Memorandum re: Polypropylene". We have attempted to be as objective as possible, letting the facts speak for themselves whenever we could, rather than expressing personal feelings or opinions.

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5) The beginning of the penultimate paragraph in Mr. Murphy's letter refers to a provision of a Montecatini-Ziegler Agreement, by which Montecatini undertook to grant licenses to five U.S. Companies which already enjoyed a privileged position, being Ziegler's licensees for the whole field of polyolefines (not only for polyethylene).

Since Carbide has not exercised the polypropylene option offered by Montecatini, we believe we have performed the above provision, and we express this view to Carbide.

6) Paragraph 9 of our letter to Mr. Murphy is intended to dispute Carbide's veiled hope that they will be able to manufacture polypropylene under the Ziegler patent rights only, which are already licensed to them.

7) I suppose Mr. Murphy has by now retired, or is going to retire shortly. He has been, with the assistance of a Carbide attorney, Mr. Lyon, the most prominent negotiator on Carbide's side. I feel he has never been in favor of entering the agreements, and that he has been persuaded to sign them under pressure from Carbide's management (possibly the President, Mr. Dial, or a group of younger executives).

8) On Montecatini's side the contracts have been negotiated under t the direct supervision of the management. Patent problems were dealt with by me and by my staff, while problems of a legal nature (with particular reference to the U.S. situation and to U.S. anti-trust laws) have been entrusted by Montecatini's legal Department and by our U.S. subsidiary Chemore Corp. to Chemore's counsel in New York. I add for your information that the Patent Department and the Legal Department of Montecatini work concurrently but independently from each other.

9) As indicated in paragraph 4, Carbide has not exercised its option on polypropylene plastics but has kept its option on polystyrene plastics open. Should you therefore meet Mr. Cornwell and have a chance of speaking with him about Montecatini licenses, I think that it would be preferable not to touch the subject of polypropylene plastics. May be you could however make encouraging suggestions as regards polystyrene plastics.

10) Finally, a personal observation, which you may possibly wish to convey to Mr. Cornwell as a thought of your own. The prospective developments of fibers and elastomers covered by our patents have a really outstanding interest. It would be surprising if Union would give up its chance to get a license under the polypropylene fibers. In fact, besides other considerations, Montecatini had undertaken, in a separate letter, to grant Carbide (in case Carbide exercised at least one of the

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two options on polypropylene and on polystyrene plastics provided for in the Nov. 26, 1956 Agreement) a license for the manufacture of polypropylene fibers within ranges of lump sum payments and royalties already agreed upon.

11) The Agreements signed on November 26, 1956 have been and are being kept secret by all parties concerned, also at the request of Carbide.

Yours very truly

(G. de Varda)

original by air mail
CC: by air mail two days later

MONTECATINI
Società Generale per l'Industria Mineraria e Chimica

Brevetti e Documentazione Tecnica

EP/ma

PROMEMORIA

Data, 28 Febbraio, 1957

[illegible] DI [illegible]
INDUSTR[illegible]
\- 4 MAR 1957
R 501 UCC

per il Signor Ing. ORSONI
Prof. NATTA
Ing. BALLABIO

e p.c. Sig. Ing. GIUSTINIANI

Oggetto: Opzione Union Carbide -
Conferma ns/ disclosures verbali -

Facciamo seguito alla ns/ lettera del 12 m.c. per inviare elenco delle disclosures verbali fatte a Union rivisto e corretto secondo quanto da Voi comunicatoci.

Vi preghiamo di voler cortesemente esaminare la nuova stesura prima dell'inoltro a Union facendoci eventualmente conoscere Vs/ eventuali ulteriori informazioni o varianti.

Con i migliori saluti.

"BREVETTI E DOC. TECNICA"

all/

MISCELLANEOUS MONTECATINI VERBAL DISCLOSURES

1. The per cent extractable in the polypropylene as made depends on the purity of the propylene, the purity of the titanium trichloride, and the temperature of polymerization. Product of greatest crystallinity is obtained when the propylene has been purified with aluminum alkyl prior to polymerization. The propylene should contain no more than 20 to 30 p.p.m. acetylene for the highest crystalline products possible. Allylene should be eliminated and there should be no other olefins for a very highly crystalline product.

2. Concerning catalyst yield. In their pilot plant process they obtained 150 to 200 gms. of polypropylene per gram of catalyst. In the laboratory they have obtained as high as 1000 gms. polymer per gram of catalyst, but this was by a process which in the present was not commercially employed.

3. The ultraviolet light stability of the crystalline polystyrene is very much like that of normal polystyrene. Montecatini feels that ultraviolet stabilization is not a problem with polystyrene.

4. Large particles of crystalline titanium trichloride will cleave in the course of propylene polymerization; that is, break down to an equilibrium size distribution, and consequently are satisfactory for the polymerization. Such large particles, however, increase the induction period.

5. Finely ground particles of $TiCl_3$ lead to a much more rapid initial polymerization rate. If the reaction heat is not sufficiently removed a higher percentage of amorphous product may be caused by the higher and uncontrollable polymerization temperature.

6. Montecatini does not usually grind titanium trichloride after preparation; they simply screen the material to remove large foreign bodies which may be present.

7. Montecatini has investigated the use of titanium dichloride in place of titanium trichloride. Titanium dichloride gives an equally crystalline product but Montecatini prefers the trichloride because the dichloride is much more difficult to prepare in a state of high purity and may contain titanium metal impurities which are difficult to remove from the product.

8. Apparently commercial styrene will not polymerize indefinitely like the pure propylene will. To help remove the polystyrene Montecatini uses benzene as a diluent in the polymerization.

9. Concerning polypropylene: After purification the polymer contain less than 0.01 by weight chlorine. The high molecular weight polymer contains no more chlorine than low weight polymer. Montecatini is not certain whether the chlorine is chemically bound or whether chlorinated compounds are mechanically occluded.

./.

10. If the chlorine is not all washed out, HCl may be evolved upon pyrolysis. This is true of polymer purified according to their written disclosure.

11. The majority of the polypropylene chains are terminated in a vinylidene type double bond.

12. They can stabilize against mold corrosion with conventional polyvinyl chloride stabilizers.

13. Concerning the preparation of the titanium trichloride, Montecatini showed us their pilot plant operation at Ferrara. Dr. Negromanti described the process in some detail. A flow-sheet of the pilot plant drawn from our understanding of the discussion is at the end of this list of disclosures. (A corrected flow-sheet is enclosed).

14. The use of $TiCl_2$ instead of $TiCl_3$ leads in general to a lower rate of polymerization of propylene probably because of differences in surface areas.

15. The lattice constants of $TiCl_2$ and $TiCl_3$ are very close; this can allow the formation of solid solutions of the two compounds.

16. When using $TiCl_3$ after the polymerization has been carried to the point beyond the initial induction period, if it is stopped by removing monomer, it will start up again with no induction period and at the same rate as before.

17. The termination step in the propylene polymerization is principally due to either hydride ion transfer or to monomer transfer. Hydride ion transfer is favored at the higher temperatures.

18. Concerning the styrene polymerization, benzene of nitration grade is used as diluent. No other purification is necessary but is convenient when the water content is above 0.001 per cent.

19. Concerning mold corrosion with polypropylene, they have no experience with tests up to 100 hours. They have tried 10 hours continuous molding using a chromium-plated mold without corrosion occurring. Polyvinyl chloride stabilizers can be used to stop any corrosion which does occur. Good stabilizers are lead stearate, lead phosphite, and several epoxy stabilizers -- at a concentration of 0.01 to 0.3 per cent.

20. Concerning stress endurance of polypropylene, the .91 to .92 density material resulting from the polymerization as revealed in the written disclosure does not break under 1000 continuous hours under a load of 2000 p.s.i.

21. The intrinsic viscosity-molecular weight relationship used by Montecatini for polypropylene is: $[\eta] = 1.18 \times 10^{-3} M^{0.65}$. The intrinsic viscosity is measured in tetralin at 135°C. This is the same formula that has been used for polyethylene by I.C.I.

22. It is possible to make fairly highly crystalline polystyrene directly to intermediate molecular weight levels by following the same procedure outlined in the written disclosure for high molecular weight polystyrene, using higher catalyst concentration. The molecular weight of the polystyrene which is first formed may be lower than the molecular weight obtained after several hours. After this initial period of time, however, the molecular weight remains practically constant with additional time.

23. Hydrogen can be used to lower the molecular weight of the polymers. Its use does not reduce the crystallinity of the polypropylene.
In the case of polystyrene the use of hydrogen is not as effective in lowering the molecular weight as in the case of polypropylene.

24. Thermal depolymerization may be used to reduce to any desired level the molecular weight of the highly crystalline, very high molecular weight polystyrene.

25. Concerning the use of aluminum titanium alloy as a catalyst, the three-to-one aluminum-to-titanium ratio discussed in the patent application appears to be best. No explanation was given as to why such a ratio should be optimum. Such ratio corresponds, however, to a known intermetallic compound.

26. Montecatini prefers to use aluminum triethyl because it is easily prepared and gives a more crystalline polymer than the higher alkyl aluminums. They have never tried trimethyl aluminum at Ferrara. Aluminum tri-isobutyl is used as an intermediate in the preparation of the aluminum triethyl.

27. Montecatini claimed there was no change in the induction period in the polymerization of propylene in the case of polymerization promoted by $TiCl_3$, if the catalyst components are mixed, brought to the polymerization temperature below about 80°C, and then monomer is withheld for various periods of time.

28. The rate of polymerization of both styrene and propylene for a given volume of diluent decreases as the ratio of solid catalyst to diluent decreases. However, the molecular weight and the per cent crystallinity of both polypropylene and polystyrene are not largely affected by the catalyst-to-diluent ratio.

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29. Calculated theoretical density of crystalline polypropylene is 0.936 g/cc.

30. Highly crystalline and highly oriented polypropylene shows less evident second order transition temperature, as determined by dilatometric methods. This temperature, so determined, is only of significance for the amorphous form.

31. Catalyst activity changes during the induction period as the polymerization of propylene proceeds, and eventually levels out at a constant value, in the case of polymerization promoted by $TiCl_3$.

32. When large amounts of catalyst are used in the polymerization to obtain lower molecular weight products, the molecular weight distribution in the product is probably very wide.

through a catalyst on the basis of $TiCl_3$

[illegible] $TiCl_3$

33. When aluminum triethyl is used as a catalyst component in a polymerization, an increase in temperature of the reaction over 100°C causes a decrease in molecular weight and at very high temperature a decrease in crystallinity.

34. Concerning the preparation of amorphous polymers: The use of alkyl groups that are greater than four carbon atoms in length is desirable because the precipitate having catalytical effect so produced from $TiCl_4$ is generally more amorphous. The presence of long chain alkyl groups interferes with formation of a crystalline precipitate.

35. The viscosity molecular weight relationship for polyethylene:

$$[\eta] = 1.18 \times 10^{-3} M^{0.65}$$

has been used by Montecatini for polypropylene. It yields only conventional values. The viscosity is measured in tetralin at 135°C.

36. Concerning crystalline helices: The packaging volume of a right-handed helix is the same as with a left-handed helix for a given isotactic chain.

37. The use of very short reaction times is not a practical satisfactory means of producing low molecular weight, highly crystalline polystyrene.

38. The use of hydrogen to control the molecular weight of polystyrene is not as effective as it is with polypropylene.

39. High molecular weight, extracted polystyrene after molding and annealing is 45 to 60% crystalline. High molecular weight crystalline polystyrene after molding, at temperatures higher than 250°C, and quenching is not crystalline.

./.

40. Concerning propylene polymerization: A metal alkyl containing an alkoxy group is a possible catalyst component but it is not as effective as triethyl aluminum.

41. Aging the $TiCl_3$ catalyst prepared according to the disclosure for ten to twenty hours at temperatures below 80°C does not alter its activity. Within the same temperature range, aging the catalyst in the absence of monomer does not change the induction period.

42. The molecular weight and crystallinity of polypropylene are only slightly affected by the catalyst concentration. The reaction rate increases as the $TiCl_3$ quantity is increased, independently, within wide limits, from the concentration of the aluminum alkyl. As the temperature is increased over 100°C the molecular weight and crystallinity are lowered but the initial reaction rate increases. Using a catalyst on the basis of $TiCl_3$, crystallinity is not much affected by temperature below 80°C, decreases slightly from 80 to 100°C and decreases rapidly above 100°C.

43. For polystyrene, when a catalyst prepared from $TiCl_3$ obtained according to the disclosure is used at temperatures between 30 and 80°C, no variation in crystallinity with temperature is observed. An increase in catalyst concentration lowers the molecular weight.

del SEPS -

UNION CARBIDE AND CARBON CORPORATION
Carbide and Carbon Building
30 EAST FORTY-SECOND STREET
NEW YORK 17

JOHN J. MURPHY
DIRECTOR OF PATENT AFFAIRS

CABLE ADDRESS
PATUNCARB NEW YORK

February 26, 1957

Dr. Bartolomeo Orsoni
Technical Director
Montecatini
Societa Generale per l'Industria
Mineraria e Chimica
Via F. Turati, 18
Milano (134), Italy

Dear Dr. Orsoni,

Last Thursday Mr. Dial wrote Dr. Giustiniani of our decision not to exercise our option for a polypropylene license under the terms of our agreement of November 26, 1956.

In line with Mr. Dial's letter I am enclosing a memorandum summarizing the most important aspects of the findings on which our decision was made.

Our respective evaluations of the patent rights as defined in the option agreement appear too far apart to warrant any probability of an agreement at this time.

I sincerely hope that some time in the future in pursuance of your obligations in our behalf with Professor Ziegler our respective companies can negotiate an agreement in the field of polypropylene. This I believe can happen only after the particular patent rights being considered have been more definitely evaluated by both parties, in which event terms and conditions commensurate with such evaluation should be more easily agreed upon.

We are continuing our studies of polystyrene and will advise you of our decision regarding our option in that matter in due course.

Very truly yours,

John J. Murphy

Enclosure
JJM/ep

cc: Mr. Lucio Lucini, President
Chemore Corporation
21 West Street
New York 6, New York

February 25, 1957

MEMORANDUM RE: POLYPROPYLENE

We have been making rather comprehensive studies of polyolefins in general and more recently polypropylene in particular. These studies have touched about every practical aspect of the problem that might have any effect on the overall technological and ecomonic picture. Listed below are the principal findings of the polypropylene study particularly with respect to the Montecatini license:

1. There is no assurance that Montecatini will obtain any very important patents in the polypropylene field.
2. It is now quite evident that Montecatini will not obtain all the important patents in the polypropylene field.
3. From evidence at hand there are patent applications owned or controlled by at least a dozen different concerns which will probably get into interference with Montecatini applications in the United States Patent Office. Undoubtedly it will be many years before any of these applications can issue, if indeed any of them does.
4. It is estimated that there are about 800 patent applications relating to polyolefins being prosecuted in the United States Patent Office at the present time. The ownership or control of these applications is spread over approximately 50 large industrial concerns.
5. Many apparent inventions in the field of polyolefins are findings which are quite obvious to those licensees of Ziegler skilled in the art of polymerization, so that it appears that patents in this field which actually issue will of necessity be quite narrow in scope to stand the test of validity.
6. It seems preferable to wait until Montecatini patents issue before we apply for any license thereunder in pursuance of Montecatini's agreement in our behalf with Professor Ziegler.
7. Analysis of the various samples of polypropylene submitted by Montecatini indicates that resins which have been produced by Carbide by processes preferable to those demonstrated by Montecatini are at least as good if not better from a commercial point of view.

8. As indicated by letters to Montecatini dated February 18, 19 and 21, practically all of the information furnished by Montecatini pursuant to the terms of the agreements was already known by Carbide. Therefore it appears unlikely that Montecatini will disclose to us something of technical value which is new and novel.

9. It appears quite certain that Professor Ziegler, under whose patent rights we have already been licensed, will have the dominating position in the United States.

Based on the above we consider the proposed terms and conditions of the Montecatini license out of proportion to the value of the licensed material. Listed below are our principal basic objections to the proposed license in light of the foregoing studies:

(1) The right of licensee to cancel is inadequate. 1?

(2) The licensee is denied its rights under the patent laws and general laws of the country in which the patents under which it is licensed are issued.

(3) The nonreimbursable amounts of the down-payment and the provisions relating to the payment of royalties are burdensome. (The licensed material is not as important as the licensed material in the Ziegler agreement and should not carry any provisions relating to the payment of royalties any more burdensome than those contained in the Ziegler agreement.)

1) La Montecatini non ha nulla in contrario a riprendere le trattative qualora i brevetti saranno concessi, ma non si impegna a farlo perchè nel frattempo può aver assunto altri impegni e, comunque, le condizioni possono essere diverse.

2) Riteniamo che i brevetti richiesti prima nel 1955 siano quelli fondamentali. Non è probabile che brevetti importanti chiesti negli U.S.A. non siano stati estesi in altri paesi. Dall'esame dei Brevetti concessi o richiesti in altri paesi, ci risulta che siano stati preparati o descritti prodotti corrispondenti al polipropilene isotattico precedentemente ai nostri brevetti.

3) Non riteniamo che vi sia dipendenza dai ns; brevetti Ziegler, almen nella forma in cui sono stati concessi in altri paesi, comunque tale dipendenza non autorizza i licenziatari di Ziegler a produrre il polipropilene con i procedimenti da noi brevettati.

4) Per quanto riguarda il punto 7), crediamo perfettamente che la Carbide nel 1957 sia capace di produrre dei polipropileni con processi preferibili a quelli brevettati dalla Montecatini nel 1954 e 1955. Anche noi, negli ultimi dieci mesi, abbiamo fatto dei notevoli progressi.
L'importante è se i processi od i prodotti Carbide non dipendenti o no da quelli Montecatini.

5) Non ci sorprende che i brevetti negli U.S.A. sulle poli-alfa-olefine siano 800. Solo quelli richiesti in Italia da Ziegler e dalla Montecatini superano i 100. Ciò conferma l'importanza del campo e quindi il valore dei primi brevetti.

MONTECATINI
Società Generale per l'Industria Mineraria e Chimica
Brevetti e Documentazione Tecnica

/ma

Data, **25 Febbraio, 1957**

PROMEMORIA

ISTITUTO DI CHIMICA
INDUSTR... ...ECNICO
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per il Signor 1 **Ing. ORSONI**
Ing. BALLABIO
Prof. NATTA

Oggetto: Opzione Union - Vincolo di segretezza -

Trasmettiamo per conoscenza copia di una lettera UNION Carbide data 19/2/57 nella quale Mr. Murphy sostiene che tutte le informazioni+ contenute nei 24 documenti, elencati nella suddetta lettera, da noi consegnati a suo tempo a Union, erano note, o disponibili al pubblico, oppure già in possesso di Union alla data del 26/11/56, e che quindi non ricadono sotto le disposizioni dell'Articolo IV (Secrecy).

Gli interessati sono pregati di voler cortesemente far controllare se a UNION sono state da noi "disclosed" soltanto le informazioni tecniche di cui ai suindicati 24 documenti oppure se ne sono state date altre non riportate da Mr. Murphy.

Con i migliori saluti.

"BREVETTI E DOC. TECNICA"

all/

+ scritte

UNION CARBIDE AND CARBON CORPORATION
UCC
30 EAST FORTY-SECOND STREET
NEW YORK 17, N.Y.

PATENT DEPARTMENT

CABLE ADDRESS
UNCARB NEWYORK

2 3 FEB 1957

Air Mail

February 19, 1957

Montecatini
Societa Generale per L'Industria Mineraria
e Chimica
Via Tursti 18
Milan, Italy

2 3 FEB. 1957
MONTECATINI - BREV.

Attn: Mr. G. deVarda
Chief Patent Counsel

Gentlemen:

In accordance with Article IV, Section 2(b) of the Polypropylene and Polystyrene Plastics Option and License Agreement and Article IV, Section 2(b) of the Polypropylene Plastics Option and License Agreement between Montecantini and Union Carbide and Carbon Corporation, Union Carbide asserts that the following information disclosed by Montecatini under Article III, Section 1(b) of each of said agreements, and in the answers to the questions in the First Enclosure to Corollary Letter No. 2 of said Polypropylene Agreement and in the First and Second Enclosures to Corollary Letter No. 2 of said Polypropylene and Polystyrene Agreement under Article III, Section 1(d) of each of said Agreements, received and acknowledged by Union Carbide before January 1, 1957, was published or generally available to the public, or was already in the possession of Union Carbide before November 26, 1956, and is therefore excluded from the provisions of Article IV of said Agreements:

1. Method for the polymerization of propylene and for the purification of the polymer.

2. Intrinsic viscosity determination on Polypropylene.

3. Gas-Volumetric determination of the purity of organic aluminum compounds.

4. Chemical and physical analytical methods for $TiCl_3$.

5. Preparation of isotactic polystyrene and purification of polymer.

6. Preparation of isotactic, high molecular weight polystyrene and purification of polymer.
7. Viscosimetric determination of the molecular weight of isotactic polystyrene.
8. Laboratory preparation of $TiCl_3$.
9. Quantitative X-ray determination of polypropylene crystallinity.
10. Crystal structure of isotactic polypropylene.
11. Polypropylene elastic modulus.
12. Mechanical properties of polypropylene extruded films.
13. Resistance of polypropylene to chemicals.
14. Physical properties of crude polypropylene of average molecular weight 100,000 to 200,000.
15. Rate of polypropylene crystallization.
16. Polypropylene stabilizers.
17. Time necessary to reach one-half of the maximum polystyrene crystallinity.
18. Rate of crystallization of polystyrene.
19. Effect of ultra-violet light upon the induction time of the oxidation reaction.
20. Effect of stabilizers upon the induction time of the oxidation reaction.
21. Influence of temperature upon the melt viscosity of polypropylenes having different molecular weights.
22. Comparison of the stabilization of polypropylene to Fertene.

23. Correlation between natural and accelerated aging.

24. Description of the accelerated apparatus.

The answers to the questions in the Enclosures to Corollary Letters No. 2 in each Agreement.

We are submitting a duplicate copy of this letter for your signature acknowledging receipt and for the return to us.

Very truly yours,

John J Murphy

Montecatini Societa Generale per L'Industria Mineraria e Chimica hereby acknowledges receipt of the above statement.

By______________________________

Dated____________________________

MONTECATINI
Società Generale per l'Industria Mineraria e Chimica

Brevetti e Documentazione Tecnica
/ma

Data, **25 Febbraio, 1957**

PROMEMORIA

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R 445 Ucc

per il Signor
1 Ing. ORSONI
Ing. BALLABIO
Prof. NATTA

Oggetto: Opzione UNION -
Vincolo Segretezza -

Facciamo seguito alla ns/ lettera del 12 m.c.
Alleghiamo per conoscenza copia di una lettera UNION datata 21 m.c. nella quale Mr. Murphy sostiene che tutte le informazioni verbali da noi date ai rappresentanti Union a suo tempo, e di cui ai numeri riportati nella suddetta lettera della lista intitolata "Miscellaneous Montecatini Verbal Disclosures" erano già note a Union alla data del 26/11/56.

Soltanto le informazioni di cui ai numeri: 9, 14, 16, 26, 27, 31, 37, e 41, esclusi da Mr. Murphy nella suddetta lista, ed eventuali altre "additional information" sembrerebbero essere state nuove per Union alla data della firma del contratto.

Con i migliori saluti.

"BREVETTI E DOC. TECNICA"

all/

UNION CARBIDE AND CARBON CORPORATION,
Carbide and Carbon Building
30 EAST FORTY-SECOND STREET
NEW YORK 17

JOHN J. MURPHY
DIRECTOR OF PATENT AFFAIRS

CABLE ADDRESS
PATUNCARB NEW YORK

February 21, 1957

25 FEB. 1957

Montecatini
Societa Generale per l'Industria
Mineraria e Chimica
Via Turati 18
Milan, Italy

Attention: Mr. G. de Varda, Chief Patent Counsel

Gentlemen:

In accordance with Article IV, Section 2(b) of the Polypropylene Plastics Option and License Agreement and Article IV, Section 2(b) of the Polypropylene and Polystyrene Plastics Option and License Agreement between Montecatini and Union Carbide and Carbon Corporation, Union Carbide asserts that the following information disclosed verbally to its representatives during their visit to Montecatini under Article III, Section 1(c) of each of said Agreements and listed as "Miscellaneous Montecatini Verbal Disclosures" in the list attached to our letter of February 5, 1957, was published or generally available to the public, or was already in the possession of Union Carbide before November 26, 1956, and is therefore excluded from the provisions of Article IV of said Agreements:

Items as numbered on the list "Miscellaneous Montecatini Verbal Disclosures" as follows: 1, 2, 3, 4, 5, 6, 7, 8, 10, 11, 12, 13, 15, 17, 18, 19, 20, 21, 22, 23, 24, 26, 28, 29, 30, 32, 33, 34, 35, 36, 38, 39, 40, 42, and 43.

quelle per loro
nuove soltanto
N° 9, 14, 16, 25,
27, 31, 37, 41
ed 'eventuale "additional"
information'

As we advised you in our letter of February 5th, to the best of our knowledge the list enclosed therewith was complete. In the event it is established that we received any additional verbal information we will advise you promptly whether that information was known to us at the time received.

We are submitting a duplicate copy of this letter for your signature acknowledging receipt and for return to us.

Very truly yours,

John J. Murphy

Montecatini Societa Generale per l'Industria Mineraria e Chimica hereby acknowledges receipt of the above statement.

MONTECATINI SOCIETA GENERALE PER L'INDUSTRIA MINERARIA E CHIMICA

By______________________________

Dated ______________________________

cc: Mr. Lucio Lucini, President
Chemore Corporation
21 West Street
New York 6, New York

JJM/ep

UNION CARBIDE AND CARBON CORPORATION
Carbide and Carbon Building
30 EAST FORTY-SECOND STREET
NEW YORK 17

JOHN J. MURPHY
DIRECTOR OF PATENT AFFAIRS

CABLE ADDRESS
PATUNCARB NEW YORK

February 21, 1957

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N

Montecatini
Societa Generale per l'Industria
Mineraria e Chimica
Via Turati 18
Milan, Italy

Attention: Mr. G. de Varda, Chief Patent Counsel

Gentlemen:

In accordance with Article IV, Section 2(b) of the Polypropylene Plastics Option and License Agreement and Article IV, Section 2(b) of the Polypropylene and Polystyrene Plastics Option and License Agreement between Montecatini and Union Carbide and Carbon Corporation, Union Carbide asserts that the following information disclosed verbally to its representatives during their visit to Montecatini under Article III, Section 1(c) of each of said Agreements and listed as "Miscellaneous Montecatini Verbal Disclosures" in the list attached to our letter of February 5, 1957, was published or generally available to the public, or was already in the possession of Union Carbide before November 26, 1956, and is therefore excluded from the provisions of Article IV of said Agreements:

Items as numbered on the list "Miscellaneous Montecatini Verbal Disclosures" as follows: 1, 2, 3, 4, 5, 6, 7, 8, 10, 11, 12, 13, 15, 17, 18, 19, 20, 21, 22, 23, 24, 26, 28, 29, 30, 32, 33, 34, 35, 36, 38, 39, 40, 42, and 43.

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N° 9, 14, 16, 25,
27, 31, 37, 41,
ed 'eventuale' addizionale
informazione

As we advised you in our letter of February 5th, to the best of our knowledge the list enclosed therewith was complete. In the event it is established that we received any additional verbal information we will advise you promptly whether that information was known to us at the time received.

We are submitting a duplicate copy of this letter for your signature acknowledging receipt and for return to us.

Very truly yours,

John J. Murphy

Montecatini Societa Generale per l'Industria Mineraria e Chimica hereby acknowledges receipt of the above statement.

MONTECATINI SOCIETA GENERALE PER L'INDUSTRIA
MINERARIA E CHIMICA

By ______________________________

Dated ___________________________

cc: Mr. Lucio Lucini, President
Chemore Corporation
21 West Street
New York 6, New York

JJM/ep

MONTECATINI
Società Generale per l'Industria Mineraria e Chimica
Brevetti e Documentazione Tecnica
dV/ma

PROMEMORIA

Data, 23 Febbraio, 1957

25 FEB 1957
432

per il Signor Ing. Bartolomeo ORSONI

e p.c. Prof. NATTA

Oggetto: Opzione Union C.C. - Impegno di segretezza -

La Union C.C. in base all'Art. IV "Impegno di Segretezza" ci invia l'allegata lettera concernente tutte le nostre domande di brevetto a lei comunicate in seguito alla firma dell'accordo di opzione del 26/11/56.

Delle 18 domande elencate, le prime 8, com pure la decima e la tredicesima erano effettivamente già note (almeno in gran parte) in seguito all'avvenuta pubblicazione dei corrispondenti brevetti in Belgio e in Italia. La nona domanda è uscita in Italia il 20/12/ dell'anno scorso. Le rimanenti 7 domande usciranno in Belgio e in Italia fra il marzo e il luglio dell'anno corrente.

Forse non è superfluo osservare che l'ultima domanda dell'elenco è stata da noi comunicata alla Union parecchio tempo dopo il 26 novembre, non essendo a tale data ancora trascorsi i dieci mesi dal deposito.

Allego per una migliore comprensione del meccanismo contrattuale l'Art. IV° del contratto.

La procedura seguita dalla Union è abbasta za regolare in quanto il giorno 26 di questo mese scadeva per Union la facoltà di svincolarsi dall'obbligo di segretezza per quanto riguarda le informazioni da noi avute in via confidenziale ma già note a Union.

A nostra volta abbiamo tre mesi di tempo per chiedere le prove della suddetta affermazione, il che ci converrà fare per le eventuali eccedenze fra i nostri depositi americani e i corrispondenti nostri brevetti pubblicati nel Belgio, rispettivamente in Italia.

Specialmente se Union non dovesse esercitare l'opzione sarà opportuno procedere ad un rigoroso confronto dei testi sia da parte BREV, sia da parte del Prof. Natta per accertare tutte le eventuali eccedenze, dando però presumibilmente per scontati anche i brevetti di prossima pubblicazione.

Quello che sorprende un po' nella lettera della Union è l'affermazione che già alla data del 26/11/56 Union conosceva il contenuto anche di quei nostri brevetti che non erano stati ancora pubblicati.

Con i migliori saluti.

all/

UNION CARBIDE AND CARBON CORPORATION
Carbide and Carbon Building
30 EAST FORTY-SECOND STREET
NEW YORK 17

JOHN J. MURPHY
DIRECTOR OF PATENT AFFAIRS

CABLE ADDRESS
PATENSCARB NEW YORK

RICEVUTO
22 FEB 1957

February 18, 1957

Montecatini
Societa Generale per l'Industria
Mineraria e Chimica
Via Turati 18
Milan, Italy

Attention: Mr. G. de Varda, Chief Patent Counsel

Gentlemen:

In accordance with Article IV, Section 2(b) of the Polypropylene and Polystyrene Plastics Option and License Agreement and Article IV, Section 2(b) of the Polypropylene Plastics Option and License Agreement between Montecatini and Union Carbide and Carbon Corporation, Union Carbide submits that the following information disclosed by Montecatini under Article III, Section 1(a) of each of said Agreements up to January 1, 1957, receipt of which has been acknowledged, was published or generally available to the public, or was already in the possession of Union Carbide before November 26, 1956 and is therefore excluded from the provisions of Article IV of each of said Agreements:

Canadian Patent Application Serial No.	686,992
United States Patent Application Serial No.	514,097
" " " " " "	514,098
" " " " " "	514,099
" " " " " "	514,068
" " " " " "	552,295
" " " " " "	550,164
" " " " " "	597,817
" " " " " "	598,857
" " " " " "	571,114
" " " " " "	602,010
" " " " " "	611,981
" " " " " "	611,788
" " " " " "	616,227
Italian Patent Application Serial No.	15700/55
" " " " "	18119/55
" " " " "	17166/55
" " " " "	2898/56

We are submitting a duplicate copy of this letter for your signature acknowledging receipt and for return to us.

Very truly yours,

John J. Murphy

JJM/ep

Montecatini Societa Generale per l'Industria Mineraria e Chimica hereby acknowledges receipt of the above statement.

Montecatini Societa Generale per l'Industria Mineraria e Chimica

By________________________________

Dated________________________________

Hercules polypropylene

laboratory data, both in Montecatini's own laboratories and in other laboratories where work is sponsored by Montecatini;

(c) arrange on Licensee's request for Licensee's representatives to inspect installations using the "Licensed Subject Matter" (not later however than December 31, 1957);

(d) make available to Licensee, if so requested, copies of any existing drawing and flow-sheets prepared by Montecatini for its own installations for the working of the "Licensed Subject Matter";

(e) discuss all aspects of the "Licensed Subject Matter" with Licensee's representatives.

The obligations under (b) (c) (d) and (e) shall be performed by Montecatini, insofar as they relate to the subject-matter of any applications of Article I, Section 1 (c), with a ten (10) months' delay from the first filing date of each said application.

Article IV : Secrecy

1. Licensee agrees that all unpublished technical information and the information under Article III, Section 2 (b) supplied to it by Montecatini under the provisions of this contract will be treated as confidential disclosures and shall be maintained in confidence and shall not be used without license from Montecatini up to June 30, 1967, provided that it is and to the extent that it remains un-published or generally unavailable to the public, and agrees to use its best efforts to prevent disclosure thereof to others by its executives, employees or represen-

[illegible]

tatives (even after their Agreement to work with Licensee is terminated) except:

(a) to suppliers of plant and equipment from whom a written undertaking shall have been obtained that they will treat all such information as secret and confidential and will use the same only for the purpose of supplying such plant and equipment to Licensee;

(b) to customers who purchase products in the "Licensed Field", limited only however to information of a technical sales service character and to the extent reasonably necessary in aid of sales and use of said products.

2. (a) It is understood that Licensee is at liberty to dispose of or to use any information, among that supplied to it by Montecatini under the provisions of said Agreement, of which Licensee was already in possession at the date of receipt of said Montecatini disclosures;

(b) To avail itself of such liberty Licensee shall promptly after receipt of the relevant Montecatini disclosure furnish to Montecatini a statement of the portion(s) thereof already in Licensee's possession at the said date and if so promptly requested by Montecatini, Licensee shall promptly furnish convincing evidence thereof;

(c) The term "promptly" whenever used in this Section shall mean a period not exceeding three months.

<u>Article V: Exercise of Option and License Grant</u>

1. Within two (2) months from the receipt by Licensee in the United States of the disclosure and materials provided for

387
U.C.C

19 Febbraio 1957

Egr.Sig.Ing. G. DE VARDA
Direttore Ufficio BREVETTI
Soc. " Montecatini "

Sede

e, p.c. Ing. B. ORSONI - Sede

Egregio Ingegnere,

ricevo ora copia della lettera indirizzata a Lei dall'Ing. Orsoni, relativa alla Opzione Union Carbide ed alla conferma delle disclosures verbali.

Per quanto riguarda le proposte di modifica del paragrafo n.5 del questionario Carbide, già le avevo considerato nella mia lettera del 15 u.s.

Per il n. 15 ricordo che si è parlato della cosa nel seguente modo :

"The lattices constantes of $TiCl_2$ and $TiCl_3$ are very close, and it can allow the formation of solid solutions between $TiCl_3$ and $TiCl_2$"

Per il n. 25 convengo con quanto l'Ing. Orsoni propone e penso che si possa aggiungere la seguente frase a tal paragrafo :

" .... but it is stated that it corresponds to the composition of a known intermetallic compound".

I migliori saluti.

(G.Natta)

Sede, 12 Febbraio 1957.

Preg. mo Signore
Ing. Giuseppe De Varda,
BREV.

- SEPS -
ARCHIVIO DIREZIONE

OPZIONE UNION CARBIDE.
Conferma nostra disclosures verbali.

Approvo gli argomenti elencati nella Nota "Miscellaneous Montecatini Verbal Disclosures", allegata alla lettera U. C. C. del 5 Febbraio, con le seguenti eccezioni e modifiche :

No. 5 : sostituirei il secondo periodo con la seguente dizione :
"This may be the cause of the higher ...."

No. 15: non ricordo questa affermazione;

No. 25: è vero che abbiamo ammesso di non conoscere il perchè il rapporto 3 a 1 dell'alluminio al titanio dà i migliori risultati; abbiamo peró aggiunto, il che non è riportato, che quel rapporto (il quale viene inteso come rapporto di pesi atomici), corrisponde a un composto inter-metallico.

Cordialmente :

f.to: Orsoni

Or/sl.

317
Brev.

15 Febbraio 1957

Egr. Sig. Ing. Piero Giustinian
Amministratore Delegato
Soc. " Montecatini "
Sede

e, p.c. Ing. G. De VARDA
Ing. B. ORSONI
Ing. [illegible]

Egregio Ingegnere,

ho esaminato accuratamente il questionario della "Union Carbide and Carbon" e convengo con l'interpretazione data dall'Ing. De Varda, ossia che l'Union Carbide and Carbon desidera avere una esatta delimitazione dei suoi impegni contrattuali, precisando quelle che sono le notizie avute da parte della Montecatini; poichè il questionario è stato redatto in modo da dare un significato leggermente diverso ai alcuni punti esaminati, ritengo utile precisarli meglio per evitare in futuro delle interpretazioni che possano essere sfavorevoli per la Montecatini.

Per tale ragione, penso che convenga inviare alla U.C.C. il questionario modificato come da copia qui acclusa.

I migliori saluti.

(Prof.G.Natta)

All.

COPIA PER SIG. PROF. NATTA

U.C.C

February 14, 1957

UNION CARBIDE and CARBON Corporation
Carbide and Carbon Building
30 East Forty - Second Street
NEW YORK 17, N.Y.
(U.S.A.)

Our ref. 188/54 - AMF/gi

Attention: Dr. Frederick E. Roberts

Gentlemen:

Montecatini-Union Carbide and Carbon Corporation "Polypropylene Plastics Option and License Agreement" and "Polypropylene and Polystyrene Plastics Option and License Agreement" dated November 26, 1956

We acknowledge the receipt of your letter of February 5, 1957, containing the informations verbally disclosed by Montecatini under the above Agreements.

We will certainly comply with your wish to have your list acknowledged, and have begun to carefully examine it. Since however some of our people who administered part of said information to Union are presently abroad, we cannot assure you that we will be through with our control by March 1, 1957, and we ask you therefore not to assume from our silence on that or any subsequent date that we approve of your list. We will however do our best to let you have our reply as soon as possible.

Very truly yours

"MONTECATINI"

(Ing Orsoni)

original by air mail
copy by air mail two days later

February 14, 1957

Mr. John J. MURPHY
Director of Patent Affairs
Union Carbide and Carbon Corporation
30 East 42nd Street
NEW YORK 17, N.Y.

Our ref. 105/54 - AMF/gl

Dear Mr. Murphy,

Montecatini - Union Carbide and Carbon "Polypropylene Plastics Option and License Agreement" - "Polypropylene and Polystyrene Plastics Option and License Agreement"

We refer to your letter of January 22, 1957 replying in part to our letter of January 14.

While in the said letter you agreed that the option period for polystyrene will end on April 27, 1957, we do not appear to have received a similar confirmation as to the end of the polypropylene option period. You will remember that there was a little discrepancy between your and our calculations of the starting date of the polypropylene option period, but that in our above-mentioned letter we told you that we were willing to prolong the period we had computed up to the end date proposed by you, i.e. February 26, 1957.

You would oblige by letting us have, for the sake of order, your formal confirmation that you agree on the above date.

With kind regards, we are

Very truly yours

"MONTECATINI"

(F.to Ing. Orsoni)

original by air mail
copy by air mail two days later

MONTECATINI
Società Generale per l'Industria Mineraria e Chimica

SETTORE IDROCARBURI

Data, 13.2.1957

ISTITUTO DI CHIMICA
INDUSTRIALE DEL POLITECNICO
* 14 FEB 1957 *
P 340

PROMEMORIA

per Egr. Sig. Ing. G. DE VARDA

Egr. Sig. Prof.G. NATTA
Egr. Sig. Ing. B. ORSONI

e p.c.Egr.Sig.Ing. P. GIUSTINIANI

Opzione U.C.C.

Riferimento Suo promemoria 12.2.1957.

Non si può dire che la lista contenga "all the informations" ma piuttosto un sommario di quanto è stato comunicato verbalmente.

A parte alcuni doppioni (n.12-19 ; n.21-35 ; n.23-38), sui punti n.2, 7, 11, 14, 20, 24, 29, 37, 41, Ferrara non ha esperienza e non ha dato le informazioni relative.

n.10 - E' un punto molto ambigue.

n.19 - Concentrazione stabilizzanti : deve intendersi compresa fra 0,01 e 0,3% ; a parte i sali di piombo, per i quali non si dispone di esperienza sufficiente, gli stabilizzanti epossidici vengono addizionati nella misura delle 0,25%.

n.34 - SEID non ha elementi per confermare l'interpretazione data, pur essendo d'accordo sull'impiego di Al-alchili superiori per la produzione di amorfo.

n.43 - Con $TiCl_3$ di normale produzione, un aumento di temperatura porta ad un aumento di amorfo. SEID non ha sperimentato il $TiCl_3$ puro.

Sullo schema dell'impianto $TiCl_3$, l'essiccatore dell'H_2 deve essere messo dopo il Deoxo (rame su pomice) ; manca un lavaggio a NaOH sul gas di ricircolo in coda a tutto il resto.

Distinti saluti.

Ing. G. Ballabio

co/

15 Febbraio 1957

Egr. Sig. Ing.Piero Giustiniani
Amministratore Delegato
Soc. " Montecatini "
<u>S e d e</u>

e, p.c. Ing. G. De VARDA
Ing. B. ORSONI
Ing. C. BALLARIO

Egregio Ingegnere,

ho esaminato accuratamente il questionario della "Union Carbide and Carbon" e convengo con l'interpretazione data dall'Ing. De Varda, ossia che l'Union Carbide and Carbon desidera avere una esatta delimitazione dei suoi impegni contrattuali, precisando quelle che sono le notizie avute da parte della Montecatini. Poichè il questionario è stato redatto in modo da dare un significato leggermente diverso ad alcuni punti esaminati, ritengo utile precisarli meglio per evitare in futuro dalle interpretazioni che possano essere sfavorevoli per la Montecatini.

Per tale ragione, penso che convenga inviare alla U.C.C. il questionario modificato come da copia qui acclusa.

I migliori saluti.

(Prof.G.Natta)

<u>All</u>.

MONTECATINI
Società Generale per l'Industria Mineraria e Chimica
Brevetti e Documentazione Tecnica

URGENTE

Data, **12 Febbraio, 1957**

dV/ma

PROMEMORIA

ISTITUTO DI CHIMICA
INDUSTRIALE DEL POLITECNICO
* 12 FEB 1957 *
R 317

Union carbide

per il Signori Ing. B. ORSONI
Prof. G. NATTA
Ing. G. BALLABIO

e p.c. Sig. Ing. P. GIUSTINIANI

Oggetto: Opzione Union Carbide - Conferma ns/ disclosures verbali -

Allego fotocopia di una lettera dalla Union che ci chiede di restituirle da noi firmata per conferma una lista di "disclosures" verbali da noi fattele dopo la firma del contratto di opzione, ossia dopo il 27 novembre 1956.

E' importante e si pregano perciò tutti i singoli interessati di far controllare accuratamente l'esattezza e la completezza di detta lista segnalandoci (all'attenzione del Dr. Pirani), possibilmente entro giovedì 14 m.c., le eventuali correzioni o aggiunte che bisogna apportare.

Con i migliori saluti.

G de Varda

Vi

all/

15 Febbraio 1957

Egr. Sig.Ing. Piero Giustiniani
Amministratore Delegato
Soc. " Montecatini"

Sede

e, p.c. Ing. G. DE VARDA
Ing. B. ORSONI
Ing. G. BALLABIO

Egregio Ingegnere,

ho esaminato accuratamente il questionario della "Union Carbide and Carbon" e convengo con l'interpretazione data dall' Ing. De Varda, ossia che l'Union Carbide and Carbon desidera avere una esatta delimitazione dei suoi impegni contrattuali, precisando quelle che sono le notizie avute da parte della Montecatini. Poichè il questionario è stato redatto in modo da dare un significato leggermente diverso ad alcuni punti esaminati, ritengo utile precisarli meglio per evitare in futuro delle interpretazioni che possano essere sfavorevoli per la Montecatini.

Per tale ragione, penso che convenga inviare alla U.C.C. il questionario modificato come da copia qui acclusa.

I migliori saluti.

(Prof.G.Natta)

All.

MISCELLANEOUS MONTECATINI VERBAL DISCLOSURES

1. The per cent extractable in the polypropylene as made depends on the purity of the propylene, the purity of the titanium triclhoride, and the temperature of polymerization. Product of greastest crystallinity is obtained when the propylene has been purified with aluminum alkyl prior to polymerization. The propylene should contain no more than 20 to 30p.p.m. acetylene for the highest crystalline product possible. Allylene should be eliminated and there should be no other olefins for a very highly crystalline product.	~~The per cent extractable in the pol propylene as made depends on the purity of the propylene, the purity and cristallinity of the titanium~~ ....
2. Concerning catalyst yield. In their pilot plant process they obtained 150 to 200 gms. of polypropylene per gram of catalyst. In the laboratory they have obtained as high as 1000 gms.polymer per gram of catalyst, but this was by a process which was not commercially feasible.	Concerning catalyst yield. In their pilot plant process they obtained 150 to 200 gms. of polypropylene per gram of catalyst. In the laboratory they have obtained as high as 1000 gms. polymer per gram of catalyst, but this was by a process which in the present was not commercially employed.
3. The ultraviolet light stability of the crystalline polystyrene is very much like that of normal polystyrene. Montecatini feels that ultraviolet stabilization is not a problem with polystyrene.	....
4. Large particles of crystalline titanium trichloride will cleave in the course of propylene polymerization; that is, break down to an equilibrium size distribution, and consequently are satisfactory for the polymerization.	....

./.

Such large particles, however, increase the induction period.	....
5. Extremely small particles of $TiCl_3$ lead to a much more rapid initial polymerization rate, and give a higher percentage of amorphous product. This may be caused by the higher and uncontrollable polymerization temperature.	Finely ground ~~Extremely small~~ particles of $TiCl_3$ lead to a much more rapid initial polymerization rate. If the reaction heat is not sufficiently removed a higher percentage of amorphous product may be caused by the higher and uncontrollable polymerization temperature.
6. Montecatini does not grind titanium trichloride after preparation; they simply screen the material to remove large foreign bodies which may be present.	Montecatini does not grind in the Ferrara pilot plant titanium trichloride ....
7. Montecatini has investigated the use of titanium dichloride in place of titanium trichloride. Titanium dichloride gives an equally crystalline product but Montecatini prefers the trichloride because the dichloride is much more difficult to prepare and may contain titanium metal impurities which are difficult to remove from the product.	Montecatini has investigated the use of titanium dichloride in place of titanium trichloride. Titanium dichloride gives an equally crystalline product but Montecatini prefers the trichloride because the dichloride may contain titanium metal impurities which are difficult to remove from the product. is much difficult to prepare in a state of high purity
8. Styrene will not polymerize indefinitely like the propylene will. Apparently the polystyrene has more difficulty falling off the surface of the catalyst. To help remove the polystyrene Montecatini uses benzene as a diluent in the polymerization.	Apparently commercial styrene will not polymerize indefinitely like the pure propylene will. To help remove the polystyrene Montecatini uses benzene as a diluent in the polymerization.
9. Concerning polypropylene: After purification the polymer contain less than 0.01 by weight chlorine. The high molecular weight polymer contains no more chlorine than low weight polymer. Montecatini is not certain whether the chlorine is	....

./.

	chemically bound or whether it is mechanically occluded.	chemically bound or whether chlorinated compounds are mechanically occluded.
10.	If the chlorine is not all washed out, HCl will be evolved upon pyrolysis. This is true of polymer purified according to their written disclosure.	If the chlorine is not all washed out, HCl may be evolved upon ....
11.	The majority of the polypropylene chains are terminated in a vinylidene type double bond.	....
12.	They can stabilize against mold corrosion with conventional polyvinyl chloride stabilizers.	....
13.	Concerning the preparation of the titanium trichloride, Montecatini showed us their pilot plant operation at Ferrara. Dr.Negromanti described the process in some detail. A flow sheet of the pilot plant drawn from our understanding of the discussion is at the end of this list of disclosures.	....
14.	The rate of polymerization of propylene with $TiCl_2$ is slower than with $TiCl_3$, but this is probably due to a difference in surface area.	The use of $TiCl_2$ (produced of $TiCl_3$) leads in general to a lower The rate of polymerization of propylene ~~with $TiCl_2$ is generally slower~~ .... probably
15.	$TiCl_2$ forms a solid solution with $TiCl_3$.	.... Vedi lettera del 19/2 a Assmi
16.	After the polymerization has been carried to the point beyond the initial induction period, if it is stopped by removing monomer, it will start up again with no induction period and at the same rate as before.	..... using $TiCl_3$

./.

17.	The termination step in the propylene and in the styrene polymerizations is due to either hydride ion transfer or to monomer transfer. Hydride ion transfer is favored at the higher temperatures.	The termination step in the propylene polymerization is principally due to ....
18.	Concerning the styrene polymerization, benzene of nitration grade is used as a dilumht. No other purification is necessary except when the water content is above 0.001 per cent.	Concerning the styrene polymerization, benzene of nitration grade is used as a diluent. No other purification is necessary but convenient when the water content is above 0.001 per cent.
19.	Concerning mold corrosion with polypropylene, they have no experience with tests up to 100 hours. They have tried 10 hours continuous molding using a chromium-plated mold without corrosion occurring. Polyvinyl chloride stabilizers can be used to stop any corrosion which does occur. The optimum stabilizers are lead stearate, lead phosphide, and several epoxy stabilizers —at a concentration of 0.01 to 0.02 per cent.	Concerning mold corrosion with polypropylene, they have no experience ..... Polyvinyl chloride stabilizers can be used to stop any corrosion which does occur. Good stabilizers are lead ....
20.	Concerning stress endurance of polypropylene, the .91 to .92 density material resulting from the polymerization as revealed in the written disclosure does not break under 1000 continuous hours under a load of 2000 p.si	.....
21.	The intrinsic viscosity-molecular weight relationship used by Montecatini for polypropylene is : $[\eta] = 1.18 \times 10^{-3} M^{0.65}$ The intrinsic viscosity is measured in tetralin at 135°C. This is the same formula that has been used for polyethylene by Ziegler.	.... This is the same formula that has been used for polyethylene by I.C.I.

./.

22.	It is possible to make fairly highly crystalline polystyrene directly to intermediate molecular weight levels by following the same procedure outlined in the written disclosure for high molecular weight polystyrene, but by stopping the reaction after only about one hour. A high catalyst concentration must also be used. Montecatini stated that the molecular weight of the polystyrene which is first formed is much lower than the molecular weight obtained after several hours. After this initial period of time, however, the molecular weight remains (practical) constant with additional time.	It is possible to make fairly highly crystalline polystyrehe directly to intermediate molecular weight levels by following the same procedure outlined in the written disclosure for high molecular weight polystyrene, using higher catalyst concentration. The molecular weight of the polystyrene which is first formed may be lower than the molecular ....
23.	Hydrogen ca-n be used to lower the molecular weight and does not reduce the of polystyrene, but it is not as effective as its use in lowering the molecular weight of polypropylene. ~~The~~ cristallinity i~~s not affected in either case.~~ In the case of polystyrene the use of Hydrogen is not so as effective, as the in lowering the molecular weight.	.... The cristallinity of polypropylene is not affected.
24.	Pyrolysis may be used to reduce to any desired level the molecular weight of the highly crystalline, very high molecular weight polystyrene.	Thermal depolymerization may be used ....
25.	Concerning the use of aluminum titanium alloy as a catalyst, the three-to-one aluminum-to-titanium ratio discussed in the patent application appears to be best. No explanation was given as to why such a ratio should be optimum.	....
26.	Montecatini prefers to use aluminum triethyl because it is easily prepared and gives a more crystalline polymer than the higher alkyl aluminums. They have never tried	....

./.

	trimethyl aluminum. Aluminum tri-isobutyl is used as an intermediate in the preparation of the aluminum triethyl.	trimethyl aluminum.in Ferrara plant. Aluminum tri-isobutyl is used an .....
27.	Montecatini claimed there was no change in the induction period in the polymerization of propylene if the catalyst components are mixed, brought to the polymerization temperature, and then monomer is withheld for various periods of time. better about 30'	Montecatini claimed there was no change in the induction period in the polymerization of propylene in the case of polymerization promoved by $TiCl_3$, if the catalyst components are mixed ....
28.	The rate of polymerization of both styrene and propylene decreases as the ratio of catalyst to diluent decreases. However, the molecular weight and the per cent crystallinity of both polypropylene and polystyrene are not affected by the catalyst-to-diluent ratio.	The rate of polymerization of both styrene and propylene for a given volume of diluent decreases as the ratio of solid catalyst to diluent decreases. However, the molecular weight and the per cent crystallinity of both polypropylene and polystyrene are not largely affected by the catalyst-to-diluent ratio.
29.	Calculated theoretical density of crystalline polypropylene is 0.936 g/cc.	....
30.	Highly crystalline and highly oriented polypropylene shows no second order transition temperature. This temperature is only of significance for the amorphous form.	Highly crystalline and highly oriented polypropylene shows less evident second order transition temperature, determined by dilatometric methods. This temperature,so determined, is only of significance ...
31.	Catalyst activity changes as the polymerization of propylene proceeds, and eventually levels out at a constant value.	Catalyst activity changes during the induction period as the polymerization of propylene proceeds, and eventually levels out at a constant value, in the case of polymerization promoved by $TiCl_3$.
32.	When large amounts of catalyst are used in the polymerization reaction to obtain low molecular weight product, the molecular weight distribution in the product is very wide.	When large amounts of catalyst are used in the polymerization to obtain lower molecular weight product, the molecular weight distribution in the product is probably very wide.

./.

33.	When aluminum triethyl is usdd as a catalyst component in a polymerization, an increase in temperature of the reaction causes a decrease in molecular weight and a decrease in crystallinity.	When aluminum triethyl is used as a catalyst component in a polymerization, an increase in temperature of the reaction over 100°C causes a decrease in molecular weight and at very high temperature a decrease in crystallinity.
34.	Concerning the preparation of amorphous polymers: The use of alkyl groups that are greater than four carbon atoms in length is desirable because the $TiCl_3$ precipitate so produced from $TiCl_4$ is more amorphous. The presence of long chain alkyl groups interferes with formation of crystalline ~~$TiCl_3$~~. precipitate	Concerning the preparation of amorphous polymers: The use of alkyl groups that are greater than four carbon atoms in length is desiderable becaeuse the precipitate having catalytical effect so produced from $TiCl_4$ is generally more amorphous. The presence of long ....
35.	The viscosity molecular weight relationship for polypropylene is : $[\eta] = 1.18 \times 10^{-3} M^{0.65}$ The viscosity is measured in tetralin at 135°C.	The viscosity molecular weight relationship for polyethylene is: $= 1.18 \times 10^{-3} M^{0.65}$ has been used by Montecatini for polypropylene. It yields only conventional values. The viscosity is measured in tetralin at 135°C
36.	Concerning crystalline helices : The internal packaging energy of a right-handed helix is the same as with a left-handed helix for a given all-dextro isotactic chain.	Concerning crystalline helices : The packaging volume of a right-handed helix is the same as with a left-handed helix for a given isotactic chain.
37.	To make highly crystalline, low molecular weight polystyrene by direct polymerization the same process used to make high molecular weight polystyrene is used except that shorter reaction times are necessary. It was stated that this is not a satisfactory means;of producing low molecular weight, highly crystalline polystyrene.	The use of very short reaction times is not a practical satisfactory means of producing low molecular weight, highly crystalline polystyrene.

./.

38.	The use of hydrogen to control the molecular weight of polystyrene is not effective as it is with polypropylene. The crystallinity of the product is not affected.	The use of hydrogen to control the molecular weight of polystyrene is not as effective as it is with polypropylene.
39.	High molecular weight, extracted polystyrene after molding and annealing is 65 to 70% crystalline. High molecular weight crystalline polystyrene after molding and quenching is not crystalline.	High molecular weight, extracted polystyrene after molding and annealing is 45 to 60% crystalline. High molecular weight crystalline polystyrene after molding, at temperature higher than 250°C, and quenching is not crystalline.
40.	Concerning propylene polymerization : A metal alkyl ~~xxxx~~ containing an alkoxy group is a catalyst but it is not as effective as triethyl alumimum	..... Prepared studying the [illegible]
41.	Aging the catalyst for ten to twenty hours does not alter its activity. Aging the catalyst in the absence of monomer does not change the induction period. below 80°	~~Twenty~~ Aging the ~~highly crystalline~~ $TiCl_3$ catalyst for ten....... below 80° independently from the concentration of $Al(Et)_3$ within very wide limits
42.	The molecular weight and crystallinitu of polypropylene are not affected by the catalyst concentration. The reaction rate increases and the yield decreases as the catalyst concentration is increased. As the temperature is increased the molecular weight, crystallinity and yield are lowered but the reaction rate increases. Crystallinity is not much affected by temperature below 75°C, decreases slightly from 75 to 100°C and decreases rapidly above 100°C.	The molecular weight and crystallinity of of polypropylene are only slightly affected by the catalyst concentration. The reaction rate increases as the $TiCl_3$ quantity is increased. As the temperature is increased over 100°C the molecular weight, crystallinity are lowered but the initial reaction rate increases. Using ~~$TiCl_3$~~ as catalyst, crystallinity is not much affected by temperature below 80°C, decreases slightly from 80 to 100°C and decreases rapidly above 100°C. on the base of $TiCl_3$

./.

prepared in $TiCl_4$, [illegible] the [illegible]

43.	For polystyrene when pure $TiCl_3$ is used, no variation in crystallinity with temperature is observed. An increase in catalyst concentration lowers the molecular weight.	For polystyrene when pure $TiCl_3$ is used, between 30 - 80°C, no variation in crystallinity with temperature is observed. An increase.. ~~weight~~........

MONTECATINI
Società Generale per l'Industria Mineraria e Chimica

Brevetti e Documentazione Tecnica

dV/ma

PROMEMORIA

URGENTE

ISTITUTO DI CHIMICA
INDUSTRIALE DEL POLITECNICO
11 FEB 1957
R 317

[illegible] Carbide

Data 7 Febbraio, 1957

M

per il Signor **Ing. Piero GIUSTINIANI**

e p.c. Ing. ORSONI
Prof. NATTA

Oggetto: Opzione UNION CARBIDE su nostro polipropilene -

Allego relazione Toulmin in data 24 Gennaio u.s. su un interessante colloquio avuto con Mr. Cornwall, Senior Vice-President della Union Carbide and Carbon Development Corp.

Particolarmente interessanti i giudizi espressi sul polietilene Ziegler e sul polipropilene in generale.

Anche le sue previsioni di "interferences" fra i trovati di ben 7 ditte concorrenti con la supposta esistenza di un "cavallo nero" che arrivando primo vincerebbe la gara, sono da considerarsi informazioni non del tutto trascurabili.

Tengasi presente che attualmente la Union dispone dei testi delle domande presentate a Washington sia nostre e di Ziegler, che della Phillips, che della I.C.I.

Anche se fosse vero che Cornwall "is indebted to the writer to do anything for him he can properly do" sono sempre molto scettico sul fatto che il famoso cavallo nero possa essere la Union.

Finora Toulmin non ha saputo nulla (almeno da parte nostra) in merito alla firma avvenuta il 27 Nov. u.s. del nostro contratto di opzione con la Union che, fra parentesi, scadrebbe il 26 m.c. anche se Murphy non ha mai voluto riconoscerci esplicitamente tale data.

Per queste ragioni Toulmin ignora pure l'impegno assuntosi dalla Union di riconoscerci la data di concepimento della ns/ invenzione in caso di future "interferences".

Allego infine un articolo critico abbastanza dettagliato e significativo sull'attuale politica di ricerca e di nuovi sviluppi seguita da Mr. Morse Dial e dai suoi collaboratori, articolo di "Fortune" del febbraio 1957 che forse non Le è stato ancora inviato dalla Chemore.

./.

MONTECATINI
Società Generale per l'Industria Mineraria e Chimica

Brevetti e Documentazione Tecnica

Data,

PROMEMORIA

per il Signor

.... pag.2)

C'è da domandarsi se in questo momento sia opportuno o no incaricare Toulmin di un ulteriore contatto con Cornwall per cercare di dissipare autorevolmente eventuali eccessive preoccupazioni di carattere brevettuale che potrebbero essere sorte in seguito ad una presa di posizione del Servizio Brevetti della Union di intonazione pessimista sulle prospettive future delle nostre domande di brevetto americane.

Con ossequio.

Gde Varda

all/

P.S. Since writing the foregoing letter I received information yesterday that is important for you to know. I had a guest at lunch, Mr. Gene Cornwall, Vice-President of Union Carbide and Carbon Development Corporation. Mr. Cornwall is the senior Vice-President of this new company that has been organized by Union Carbide to keep track of all new developments and to select those that are to be the foundation of new departments and new corporations for the future expansion of Union Carbide.

Mr. Cornwall, I understand, has been an active participant, either openly or secretly, in whatever negotiations you may have had with Union Carbide, if any, for licenses under the Natta inventions. He has also been concerned with the negotiations with Dr. Ziegler. Yesterday at lunch he volunteered the following information after some preliminary questions put to him that arose quite incidentally in another matter. He was discussing forthcoming new developments.

He made the following statements-

He said he thought there is going to be an interference with seven or eight corporate parties to the interference involving all the applications recently filed by leading companies in the polyethylene and polypropylene field. He stated he thought it was going to be quite a shock to these companies to find that there is a black horse who is going to appear with earlier dates than any of the present companies who have filed applications. I asked him who that was and he said he thought it was Du Pont and possibly Hercules.

Then he stated that low pressure polyethylene according to the Ziegler process is worthless in that it disintegrates after a period of time and that Ziegler is in trouble in Germany because piping and other articles made from his product are disintegrating, breaking, and proving useless. He indicated the same experience has been taking place among the Ziegler licensees in the United States.

I then asked him what about polypropylene. Here he was very enthusiastic and stated that this is an entirely different product and a very superior one. He said polypropylene is just the opposite of Ziegler's low pressure polyethylene. He went on to elaborate that statement.

Mr. Cornwall volunteered this information in the course of discussing some new developments in other fields, and mentioned it as an illustration of some points he was making as to the uncertainties of development work.

There was enough in his quite lengthy conversation to indicate that he was fully familiar with coming events and that he knew, through some grapevine source, that there would be an earlier (possibly Union Carbide) application that would be in interference and which was thought to ante-date competitive processes.

Phillips?

We are submitting this for what it may be worth but we thought it our duty to report it. It confirms our feeling set forth above, although we did not have this information at the time of dictating the above letter.

Let me add that I contributed no information to Mr. Cornwall, which I presume you will assume. I gathered the impression that Mr.Cornwall, who has been a friend of some years standing, was trying to give me some information he thought might be helpful so that I would take steps to protect you in any way I could. It was through Mr. Cornwall that Union Carbide took over, some four years ago, the "Step Freeze" process of Commonwealth Engineering Company and on which they are planning to spend many millions in commercialization so that he is indebted to the writer to do anything for him he can properly do. I therefore listened and am passing this on to you for that reason.

? [illegible] ?

The above also confirms and supports the position we have taken as to non-equivalency between ethylene and propylene in polymerization processes.

Very truly yours,

cc: Seamail

February 8, 1957

Mr. John J. MURPHY
Director of Patent Affairs
Union Carbide and Carbon Corp.
30 East 42nd Street,
NEW YORK 17, N.Y. (U.S.A.)

dV/RP/ma

Dear Mr. Murphy,

Re: Montecatini-Union Carbide "Polypropylene and Polystyrene Plastics Option and License Agreement"

Mr. Orsoni has brought to our attention your letter of January 29, 1957, in which you inquire about certain applications file by Montecatini in Italy in the field of polyolefines.

The patent and applications referred to are:

1) It.Patent 531,219, filed March 29, 1955.-
This patent, because of the particular type of catalyst disclosed, is not jointly owned by Prof.Ziegler, but is exclusively Montecatini's own. For this reason it was not included in the "Listed Patent Applications". According to paragraph No.4, Corollary Letter No. 2, attached to the above agreement, your Company, upon exercising the option will be entitled, however, to receive a non-exclusive license from Montecatini, without any down payment, on the same terms, including royalty rates, provided for in the Agreement, covering the lead-alkyl based catalysts and the use of them in the polymerization process whereby propylene or styrene may be transformed in the polymers, products and compositions of the kind referred to in Article I of the Agreement.

2) Patent Application No.11,522/55 - Filed in Italy - August 6, 1955.-
This refers to the polymerization of certain branched chain olefin with more than 4 carbon atoms and it was not listed because it doe not contain any claim referring to propylene or styrene containing copolymers.

3) Patent Application No.13,629/55 - Filed in Italy - Sept.26, 1955.-
This is our case U.73e. The correct filing date in Italy is not August 30 but Sept. 26, 1955. The corresponding U.S.A. Patent Application, S.No.611,981, filed Sept.25, 1956 is included in the list of United States Patent Applications in the option license agreement.

4) Patent Application No.16,950 - Filed in Italy - Dec. 1, 1955.-
This is a case similar to the one under 2) above and was not liste

./.

for the same reason.

We hope this will clarify the situation.

Yours very truly,

"N O R T E C A T I E F"

original by air mail
CC: by air mail two days later

697

Union Carbide
Carbon

20.11.1956

Egr.Ing.B.ORSONI
Direttore SEPS
Soc. Montecatini
Sede

Egregio Ingegnere

Le invio in duplice copia la risposta al questionario U.C.C. che abbiamo rielaborato oggi.

La pregherei di trasmetterne copia oltre che all'ing. Devarda, anche all'Ing.Ballabio ed al dott. Saccenti.

Per quanto riguarda il polistirolo poichè c'era oggi una riunione del Comitato N. 4 Polistirolo, si è discusso il problema anche coi partecipanti che sono d'accordo sulle risposte.

I migliori saluti.

G. NATTA

alleg.

2° ENCLOSURE TO COROLLARY LETTER No. 1

INFORMATION TO BE DISCLOSED UNDER ARTICLE XXI. 1(a)

QUESTIONNAIRE ON ISOTACTIC POLYSTYRENE FOR PLASTICS

✓ 1. How much polymer soluble in a solvent typical of the amorphous polymer is made along with the isotactic polymer?

✓ 2. Are purity requirements on monomer and diluent about the same as for other methods of styrene polymerization?

✓ 3. Which is the catalyst productivity?

✓ 4. Can catalyst residues be removed as easily and completely as is the case with the Ziegler polyethylene process?

[illegible] 5. Can the polymerization be controlled to produce polystyrenes having a wide range of molecular weights?

✓ 6. What is the foreseen maximum use temperature?

? — ✓ 7. At which temperature can the polymers be molded in injection machines or in extruders?

✓ 8. What general uses are foreseen?

? — ✓ 9. How do the mechanical properties differ from amorphous polystyrene?

✓ 10. What is the second order transition temperature?

✓ 11. How the isotactic polymer is different from the amorphous polystyrene in the gas and vapor transmission characteristics?

(12. How the isotactic polymer is different from the amorphous polystyrene to thermal and oxidative exposure? Are there known stabilizers? If so which are recommended?

? — 13. Can the isotactic polymer be used similarly to the common amorphous polystyrene?

✓ 14. What is the measured density and the probable theoretical crystalline density of isotactic polystyrene?

POLISTIROLO = QUESTIONARIO UNION CARBIDE =

20 novembre 1956

1) Il polimero solubile in metil-etil-chetone può essere inferiore al 5-10% a seconda del catalizzatore ed anche praticamente assente.

2) Il monomero deve avere le caratteristiche richieste per la produzione di polistirolo comune.

3) La produttività è bassa qualora si produce polimero isotattico a relativamente più basso peso molecolare e può salire sino ad oltre 30 g (oltre 100 g con metodi recenti) di polimero isotattico per grammo di catalizzatore complessivo quando si produce polimero a peso molecolare altissimo.

4) La depurazione del polimero dai residui di catalizzatore è altrettanto facile e completa come nel caso del polietilene Ziegler.

5) La regolazione del peso molecolare in fase polimerizzazione è possibile solo entro certi limiti variando le condizioni di polimerizzazione.

6) La temperatura massima di uso dipende dagli impieghi,(ad es. tra 150° (Vicat a 5 kg) e 200°.

7) Il polimero può essere lavorato a 260°/270°C nelle macchine a estrusione e nelle macchine ad iniezione.

8) Oggetti stampati, film e fibre.

9) Ecco alcune caratteristiche di confronto :

- Vicat (5 Kg.) - isotattico = 148/150°C
  amorfo = 90-100
- Rockwell - isotattico M = 95-100
  amorfo M = 70-80
- Modulo elastico a 20° - isotattico $4.6 \cdot 10^{10}$ dine/cm^2
  amorfo $3.7 \cdot 10^{10}$ " / "

10) La temperatura di transizione di secondo ordine è all'incirca eguale a quella del polistirolo comune.

11) E' prevedibile che i polimeri cristallini siano meno permeabili di quelli amorfi, ma non disponiamo di dati precisi.

12) Il polistirolo isotattico non mostra una sensibile instabilità al calore e alla luce, nè particolare tendenza all'ossidazione : pertanto non si è ravvisata finora la necessità di ricorrere a stabilizzanti.

13) Il polimero isotattico può essere usato sino a temperature superiori a quelle di massimo impiego del polimero comune ad es. nel campo tra 90-145° alle quali il polistirolo comune non può essere usato.

14) La densità è di 1.08 ; quella teorica dei cristalliti è di 1.12.

15) La chiarezza dipende dai trattamenti tecnici, meccanici ecc. e dalle dimensioni ed orientamenti dei cristalli.

POLISTIROLO = QUESTIONARIO UNION CARBIDE =

(Risposte SEID da sottoporre a Prof. Natta)

20 novembre 1956

1) Il polimero solubile in metiletilchetone è ~~dell'ordine del 6%.~~ [illegible] 5-10% [illegible]

2) Il monomero deve avere le caratteristiche richieste per la produzione di polistirolo comune.

3) La produttività ~~è di~~ 5 [illegible] gr. di polimero isotattico a [illegible] per grammo di catalizzatore complessivo. [illegible]

4) La depurazione del polimero dai residui di catalizzatore è altrettanto facile e completa come nel caso del polietilene Ziegler.

30 g (oltre 100 g con metodi recenti)

5) La regolazione del peso molecolare è possibile ~~entro~~ certi limiti ~~operando in presenza di idrogeno o~~ variando le condizioni di polimerizzazione.

6) Si ~~prevede non si debbano superare i 300°C.~~ [illegible] 228 [illegible]

7) Il polimero può essere lavorato a 260°/270°C nelle macchine a estrusione e ~~a~~ nelle macchine ad iniezione.

Vicat a 5 Kg

8) Oggetti stampati, film e fibre.

9) Ecco alcune caratteristiche di confronto :

- Vicat (5 Kg.) - isotattico = 148/150°C
  amorfo = ~~103/110°C~~ 90-100
- Rokwell - isotattico M = ~~97~~ 95-100
  amorfo M = 70 - 80
- Modulo elastico [illegible] 3.6 · 10^10 [illegible]
  3.7 · 10^10 [illegible]

10) La temperatura di transizione di secondo ordine è ~~simile~~ uguale a quella del polistirolo comune.

11) ~~Non disponiamo ancora~~ di ~~determinazioni attendibili.~~
I polimeri cristallini [illegible]

./.

12) Il polistirolo isotattico non mostra una sensibile instabilità al calore e alla luce, nè particolare tendenza all'ossidazione : pertanto non si è ravvisata finora la necessità di ricorrere a stabilizzanti.

nella temperatura superiore [illegible]

13) Il polimero isotattico può essere usato ~~come il~~ polimero comune. [illegible] nel campo 90-145.
alle quali il polistirolo [illegible] può essere usato

[illegible] massima temp. del

14) La densità è di 1.08 ; quella teorica dei cristalliti è di 1.12.

15) I pezzi stampati con adatta tecnica possono essere trasparenti come quelli ottenuti da polistirolo comune.

Del polistirolo [illegible] la [illegible] [illegible] temperatura, mancanza [illegible] e [illegible] ed [illegible] e delle ~~[illegible]~~ dimensioni [illegible] dei cristalli. [illegible]

Ottenuti film trasparenti.

1° ENCLOSURE TO COROLLARY LETTER No. 2

INFORMATION TO BE DISCLOSED UNDER ARTICLE III, 1(d)

QUESTIONNAIRE ON ISOTACTIC POLYPROPYLENE FOR PLASTICS

1. How much polymer soluble in boiling heptane is made along with the isotactic polymer?

2. What is the density of the isotactic polymer?

3. Can the polymerization be directed to produce high molecular weight amorphous polymer without formation of crystalline parts easily recognizable by X-ray examination?

4. Is the clarity of molded articles comparable to that of molded articles of polyethylene?

5. Can the isotactic polymer be stabilized so that it is satisfactory for certain outdoor uses?

6. Are purity requirements on monomer and diluent about the same as for Ziegler ethylene polymerization?

7. How does the catalyst productivity compare with that of the Ziegler polyethylene process?

8. Can catalyst residues be removed as easily and as completely as is the case with Ziegler polyethylene process?

9. Can the polymerization be controlled to produced a wide range of molecular weight polypropylenes?

POLIPROPILENE - QUESTIONARIO UNIUN CARBIDE -

20 Novembre 1956.

1) Assieme al polimero isotattico si forma dal 5 al 20% di polimero estraibile in eptano bollente a seconda della purezza dei prodotti impiegati.

2) La densità del polipropilene dopo estrazione con eptano è di 0,915-0,920.

3) E' possibile ottenere direttamente dalla polimerizzazione del solo propilene un prodotto contenente meno del 10% di residuo all'estrazione con n-eptano bollente (parzialmente cristallino).

4) Gli articoli stampati in polipropilene sono in generale più trasparenti di quelli di polietilene. E' possibile ottenere film trasparenti (paragonabili al cellophan).

5) Il polipropilene può essere stabilizzato fino ad avere un comportamento simile a quello del polietilene stabilizzato per usi all'aperto.

6) Le caratteristiche di purezza del propilene e del solvente devono essere analoghe a quelle richieste per polimerizzare l'etilene secondo Ziegler.

7) Per 1 gr. di catalizzatore totale (somma dei due componenti) si possono ottenere agevolmente 150/170 gr. di polimero; in buone condizioni di purezza del propilene e del solvente si può arrivare a sorpassare i 200 gr. per grammo.

8) I residui del catalizzatore possono essere rimossi facilmente e completamente come nel caso del polietilene Ziegler.

9) Si può regolare agevolmente il peso molecolare da circa 30.000 fino a circa 300.000.

POLIPROPILENE = QUESTIONARIO UNION CARBIDE =

(Risposte SEID da sottoporre al Prof. Natta)

20 Novembre 1956.

1) Assieme al polimero isotattico si forma dal ~~10~~ 5 al 20% di polimero ~~solubile~~ estraibile in eptano bollente, a seconda della purezza dei reattivi e solventi impiegati.

2) La densità del polipropilene dopo estrazione con eptano è di ~~0,92~~. 0,915 - 0,920.

È possibile ottenere direttamente dalla polimerizzazione del propilene [illegible]

3) ~~Non è mai stata tentata la produzione di polimero amorfo privo di polimero isotattico~~, e 10% di residuo all'estrazione un prodotto [illegible] meno che cristallino con normal eptano bollente (parzialmente [illegible]) in generale [illegible]

4) Gli articoli stampati in polipropilene sono ~~traslucidi~~ ~~come~~ quelli di polietilene. È possibile ottenere [illegible] trasparente (specialmente [illegible])

5) Il polipropilene può essere stabilizzato fino ad avere un comportamento ~~uguale~~ simile a quello del polietilene stabilizzato per usi all'aperto.

6) Le caratteristiche di purezza del propilene e del solvente devono essere analoghe a quelle richieste per polimerizzare l'etilene secondo Ziegler.

7) Per 1 gr. di catalizzatore totale (somma dei due componenti) si possono ottenere agevolmente 150/170 gr. di polimero; in buone condizioni di purezza del propilene e del solvente si può arrivare a sorpassare i 200 gr. per grammo.

8) I residui del catalizzatore possono essere rimossi facilmente e completamente come nel caso del polietilene Ziegler.

9) Si può regolare agevolmente il peso molecolare da circa 30.000 fino a circa 300.000.

Milano, 12 Ottobre 1956.

STATO DELLE TRATTATIVE PER GLI ISOTATTICI NEGLI STATI UNITI.

1. U.C.C.

U.C.C. aspetta i testi italiani e inglesi dei due contratti, per dichiarare il suo accordo.
Occorre definire la procedura per la firma e comunicarla a U.C.C.
Subito dopo la firma, U.C.C. darà luogo al pagamento, dopo ricevuto il quale, Montecatini comincerà le informazioni previste.
U.C.C. si propone di mandare in Italia un gruppo di tre o quattro persone, tre delle quali saranno :

Dr. Roberts, chimico, Director of Research, Bakelite Corp.;
Dr. Reading, fisico-chimico, strutturista, specializzato nelle relazioni fra struttura e proprietà dei polimeri;
Mr. Davison, bachelor degree of chem. engineering.

Dagli accenni che mi ha fatto il dr. Law, Vice President e capo delle ricerche della Bakelite e della Carb. and Carb. Chemical Div. (le due branche di U.C.C. che fanno produzioni chimiche), sembra che U.C.C. abbia finora prodotto essenzialmente polietilene a bassa pressione, con qualche lavoro anche nel campo del polipropilene.
Sono sempre molto interessati alle fibre di polipropilene e a quelle di polistirolo; ho detto che ció si potrà considerare più tardi.

2. DU PONT.

Dopo che ho richiamati e confrontati i precedenti del recente accordo con Ziegler, e l'offerta Du Pont per l'acqua ossigenata, non ha insistito sulla pretesa elevatezza del compenso chiesto da noi .
Piuttosto, Du Pont non vorrebbe assolutamente che Montecatini avesse la facoltà di trasferire i suoi eventuali brevetti passati e futuri americani ed esteri ai propri sub-licenziatari; sarebbe disposta a considerare una formola più restrittiva, per esempio limitando alla sola Montecatini senza diritto di sub-licenziare. Ho risposto che una formola più restrittiva si puó considerare.
Inoltre, non vuole essere costretta a prendere il know-how; riconosce che Montecatini ha fatto del lavoro, ma sente di avere una posizione per il lavoro già fatto e per quello futuro. Risposta : l'acquisto del know-how non è obbligatorio; ció non puó peró cambiare la valutazione che ne abbiamo fatto.
Per le eventuali interferenze, vorrebbe che in caso di sua dimostrata superiorità noi pagassimo; ho risposto che questa era la questione che appariva meno facile da risolvere, ma che noi potevamo considerare ogni soluzione che ci offrisse sufficiente protezione.

3. U.S. RUBBER.

Ha adattato il testo del contratto per quanto riguarda la Subject Matter alla ultima controproposta che avrebbe fatto l'ing. Giustiniani, cioè :

comprendere :	escludere :
(1) making polymers,	(1) shaping elastomers,
(2) curing,	(2) gum plastics,
(3) mixing and compounding elastomers.	(3) shaping plastic articles.

In questo nuovo testo le modifiche sono messe in evidenza rispetto al testo precedente, a noi noto. Queste modifiche sono importanti per l'Art. VII - Most Favored Licensee. U.S. Rubber è disposta a considerare nostre controproposte a questo riguardo.
U.S. Rubber vorrebbe procedere al più presto alla firma dell'accordo, possibilmente senza mandare una missione a Milano per altre discussioni; se peró ció è necessario, è disposta a farlo immediatamente. Occorre comunicare a U.S. Rubber le nostre reazioni al testo proposto, di cui ho dato una copia all'ing. De Varda.

4. FOOD MACHINERY CHEMICAL CO.

Nel primo incontro (4. X) ho sgombrato il campo dalla presunzione che occorresse una loro collaborazione particolarmente intensa per portare il nostro procedimento per il polibutene allo stesso grado di sviluppo per es. di quello del polipropilene; per conseguenza, un eventuale rapporto fra FMC e noi a questo proposito doveva seguire le linee di quello che avevamo proposto : opzione, seguita eventualmente da licenza in piena regola, che fra l'altro regolasse anche l'uso degli eventuali ritrovati di FMC.
Nel secondo incontro (9. X), mi hanno consegnato le unite proposte, che pur accettando la nostra procedura contengono notevoli diversioni. Ho detto che non possiamo allontanarci molto da certi schemi e proporzioni, per ovvie ragioni. Inoltre :

1) Opzione. Non riteniamo necessaria nessuna ricerca per parte nostra; noi daremo informazioni sufficienti perchè una Direzione efficiente e sperimentata come quella di FMC possa prendere una decisione. Se, data la particolare struttura della Società, due mesi non fossero assolutamente sufficienti per prendere una decisione dopo essere venuti in possesso delle nostre informazioni, noi potremmo considerare un periodo un po' più lungo, come due mesi e mezzo.

2) Le nostre condizioni erano per una licenza completamente non esclusiva.

3) La clausola della nazione più favorita deve essere limitata al polibutene.

4) D'accordo per considerare successivamente licenze per elastomeri e per fibre.

5) Per l'uso delle diolefine occorre fare un contratto a parte.

6) Idem per i buteni sostituiti.

7) Si puó considerare, purchè con sufficienti cautele.

8) Il funzionamento di un impianto di laboratorio e la fornitura di campioni saranno fatti prima dell'inizio del periodo di opzione, ma dopo il primo pagamento.

5. NOTA.

Tutte queste Ditte sono interessate a concludere un accordo con noi; U.S. Rubber a farlo rapidamente.

Prima di tutto, dobbiamo regolare i tempi per poter smaltire uno per volta gli impegni contrattuali che ci verrebbero. E' probabile che il gruppo U.C.C. arrivi in Italia ai primi di Novembre, e che ci darà da fare per 2 ÷ 3 settimane.

E' inoltre necessario preoccuparci di ben proporzionare i compensi dei diversi contratti; vi puó essere qualche difficoltà se dovessimo dare a FMC una licenza sui copolimeri di butadiene, a causa dei diversi compensi chiesti a FMC per il polibutene (1,350 M$) e a U.S. Rubber per i polibutadini (0,600 M$).

no

L'organizzazione americana è lenta a capire e decidere, ma rapidissima nell'eseguire. Occorre perció aspettarsi che una volta firmato un contratto, le situazioni cui ci troveremo di fronte siano del tutto diverse a quelle incontrate in questa fase di trattative.

Or/sl.

MONTECATINI
Società Generale per l'Industria Mineraria e Chimica

AMMINISTRATORE DELEGATO

PROMEMORIA

G/fp

ISTITUTO DI C[illegible]
INDUSTRIALE DEL [illegible]ICO
10 OTT. 1956
R 313

Data, 9 ottobre 1956

per il Signor
ing. BALLABIO
ing. ORSONI
dr. SACCENTI
prof. NATTA

Per quanto ne siate già a conoscenza, desidero ricordarVi che gli elementi da fornire alla Union Carbide durante il periodo di opzione sono quelli indicati nei seguenti paragrafi dell' "Option and license agreement" :

a) disclose to Licensee the specifications (but not the claims) of all the "Listed Licensed Applications" ;

b) send to Licensee a brief written description of the preferred techniques, apparatus and processes used or recommended by Montecatini for the preparation of polypropylene according to the patent applications referred to in clause a) of this Article ;

c) insure the performance in Italy in the presence of Licensee's representatives, of Montecatini's laboratory processes for the production of polypropylene ;

d) send to Licensee small samples of polypropylene obtained by Montecatini in the Licensed Field, so as to enable Licensee to make a preliminary technical and economic evaluation and patent study of the portion of the "Licensed Subject Matters" set forth in Article I, Section 4 (a).

Sono al corrente che per l'esame di tali elementi Vi siete già riuniti una prima ed una seconda volta : sabato prossimo 13 ottobre, al ritorno del Prof. Natta da Hüls, ci riuniremo ancora per stabilire definitivamente il "modus procedendi" da seguire nel dar corso ai nostri impegni con UCC .

Cordiali saluti.

ISTITUTO DI CHIMICA
INDUSTRIALE DEL POLITECNICO
* - 5 OTT. 1956 *
R

Crespi

POLIMERI ISOTATTICI

Riunione del 5 Ottobre 1956

Presenti:

Prof.	Natta
Ing.	Ballabio
Ing.	De Varda
Ing.	Greco
Ing.	Tredici

Si è letto il programma di massima per la comunicazione da fare alla U.C.C. in data 8 Giugno 1956, preparato dall'Ing. Orsoni.

BREV e SEID hanno dichiarato di avere pronta la documentazione da consegnare al ricevimento della missione.

Per quanto riguarda il campione è stato stabilito che, oltre al campione di 5 kg di polipropilene all'85% di estratto eptanico, verrà consegnato anche un piccolo campione di polipropilene praticamente isotattico al 100%, ottenuto mediante estrazione con trielina dal primo.

Eventualmente sarà dato anche un piccolo terzo campione di polipropilene isotattico al 90-92%, ottenuto per diretta polimerizzazione in condizioni particolari. Il Prof. Natta ritiene di aver individuato dette condizioni, che saranno ripetute sperimentalmente a Ferrara nei prossimi giorni.

Per quanto riguarda i campioni di polistirolo, oltre al campione di 5 kg al 90% circa di isotatticità, verrà consegnato anche un piccolo campione di polistirolo isotattico al 100%, ottenuto anche questo mediante estrazione con solventi.

SEID preparerà l'elenco delle prove di laboratorio che saranno effettuate a Ferrara e per le quali già è predisposta la apparecchiatura relativa.

In linea di massima dette sperimentazioni consisteranno in:

- produzione di polipropilene all'85% di estratto eptanico, peso molecolare circa 80.000;

./.

Ing. [illegible]

Oggetto **Alluminio trietile**

Egregio Ingegnere

Le confermo che le analisi fino effettuate al Politecnico avevano portato ad un ~~[illegible]~~ maggiore tenore di polimero di amorfo nel caso ~~adatto~~ non del polipropilene ~~[illegible]~~

usando il [illegible] / nel caso del polistirolo.

(con il trietil [illegible] [illegible])

Per quanto riguarda la produzione di Al trietile ~~[illegible]~~ Le confermo che ritengo anche io che la ~~[illegible]~~ ~~[illegible]~~ preparazione da Al-triisobutile rappresenti la soluzione ~~[illegible]~~ migliore.

Se Lei ci fornisse del triisobutile a Ferrara, data l'urgenza del problema, ~~[illegible]~~ per ~~[illegible]~~ [illegible] del D. Ferrara che si è [illegible] [illegible] [illegible] dello [illegible] degli alluminio alchili.

Poichè il problema di ridurre il tenore di amorfo è di importanza [illegible] ritengo che anche [illegible] si potesse ridurre la [illegible] a parità di [illegible], ciò non di meno si debba prefissare l'impiego dell'alluminio trietile per la produzione di polipropilene isotattico

alquanto [illegible] differenti

D [illegible] [illegible]

- produzione di polipropilene all'85% di estratto eptanico, peso molecolare circa 150.000;

- eventualmente preparazione di polipropilene al 90-92%, se le prove che saranno effettuate a Ferrara per la produzione di tale polimero secondo indicazioni del Prof.Natta risulteranno favorevoli;

- produzione di polistirolo a peso molecolare 500.000 al 90% circa di isotatticità.

Tf/amc.

6 Ottobre 1956

Sgr.Ing.B.Bellabio, Direttor
S.E.I.D. - Soc.Montecatini
Milano - Via F.Turati 18

p.c. Ing.G. de Varda
Dr. Greco
Ing.F.Tredici

Oggetto: Programma di preparazione di polipropilene a Ferrara per la
Union Carbide & Carbon.

Con riferimento alla riunione del 5 c.m., Vi confermo che il D
Mazzanti potrà andare a Ferrara martedì sera e potrà fermarsi se è neces
rio 2-3 giorni per esaminare con il Laboratorio di Ferrara la produzione
polipropilene a più elevato tenore di polimero isotattico (possibilmente
non meno del 90 %).

In base ai nostri risultati di laboratorio, le vie che consent
di aumentare il tenore di polimero isotattico sono le seguenti:

1) Materie prime molto pure.
2) Pretrattamento del $TiCl_3$ a freddo con alluminio alchile a concentraz
   ne relativamente alta (soluzione al 20-30 % circa).
3) Effettuare le polimerizzazioni in presenza di poco solvente (evitando
   con fortissima agitazione i pericoli di surriscaldamento locali).
4) polimerizzazione a temperature attorno a 70°C con velocità relativame
   bassa (pressione propilene non superiore a 3-5 At).
5) Tempo di polimerizzazione piuttosto lungo in modo da poter realizzare
   massima resa per unità di solvente e di catalizzatore.
6) Impiego di $TiCl_3$ altamente cristallino (non macinato). E' verosimile
   una asportazione delle parti più suddivise (mediante decantazione do
   trattamento con alluminio-alchile) sia utile.

Contemporaneamente si è deciso di ripetere a Milano alcune pr
per confermare nostri precedenti risultati orientativi.

Per quanto riguarda la produzione di polimero cristallino per estrazion
poichè l'etilesano fornisce risultati superiori alla trielina ed all'ep
Vi proporrei di usare in mancanza di etilesano dell'etilesene, che prob
mente presenterà proprietà solventi anche superiori all'etilesano. L'et
sene è ottenibile dall'alcool etilesilico.

./.

Il Dottor Mazzanti potrà anche indicare i dati per una prova d produzione di polipropilene prevalentemente amorfo (circa il 90 % di amo poichè io penso che convenga indicare alla Union i casi limiti dei tipi polipropilene.

In occasione della sua visita a Ferrara gradirei che il Dottor Mazzanti potesse discutere con i chimici di Ferrara sui risultati ottenu nella prove di copolimerizzazione etilene-propilene, campo del quale Mazzanti si è molto occupato.

Sono prossime le date di estensione negli U.S.A. dei brevetti copolimeri e sul polietilene ad alta cristallinità da $TiCl_3$ ed eventualm te potrà essere inserito qualche esempio delle prove effettuate su scal maggiore.

I migliori saluti.

G. Natta

Copia per Sig.Prof. NATTA

Carbide
Carbon

ordinario

148

18/9/56

PATUNCARB FOR LYON
NEW YORK

Since I understand from letter September 13 that special meetings of officers and directors are necessary for Union to reach its final decision on our final proposals please cable earliest possible date such meetings could be completed Stop Then we will advise you by cable according to our possibilities

ORSONI

Ing. B. ORSONI

ISTITUTO RICERCHE
"POLYMER" = TERNI

Terni, 12 settembre 1956

301/SU.33

/pz===

RISPOSTE AL QUESTIONARIO DELLA CARBIDE

===

Riportiamo nella presente nota le risposte aggiornate al questionario della "Carbide", modificate a seguito degli ulteriori risultati conseguiti nel nostro lavoro di ricerca.

D. 1) Fino a che punto il filo multibava di polipropilene è stato stabilizzato contro le perdite di tenacità alla luce del sole?

R. Nessuno degli stabilizzanti provati ha avuto efficacia. Solo con l'aggiunta di 1-2% di carbon black il tempo di dimezzamento della tenacità del filo multibava (bave ca. 4 denari) diviene 2,5-3 volte maggiore del filo tal quale.

D. 2) Quant'è per es. la caduta di tenacità alla luce del sole o ai raggi dell'arco elettrico, rispetto a quella del Nylon 66 e del Terilene?

R. Tempo di dimezzamento della tenacità alla luce solare ed agli agenti atmosferici per filati di polipropilene, Nylon, Terilene e seta (in giorni)

Filo	Inverno	Primavera	Estate
- Polipropilene lucido	92'	29	13-17
- Polipropilene opacizzato (1% TiO_2)	—	24	—
- Nylon lucido	168	75	60
- Nylon opacizzato (40/13)	90	32	24
- Terilene I.C.I. opaco	210	86	45
- Seta	—	19	19

Nota: E' opportuno segnalare che, dopo aver raggiunto il "dimezzamento", la caduta di tenacità dei fili di polipropilene e nailon opacizzato prosegue linearmente fino a zero, mentre quella degli altri fili prosegue più blandamente, con andamento presso a poco iperbolico.

D. 3) Fino a che valori è stato stabilizzato il filo multibava di polipropilene contro la caduta di tenacità in aria ad alte temperature (sopra 25°C)?

R. A 128°C: dopo ca. 120 ore il filo stabilizzato manteneva il 95% della tenacità iniziale, il filo non stabilizzato era fragile dopo 2-3 ore.

A 90°C: dopo ca. 400 ore il filo stabilizzato manteneva ca. il 95% della tenacità iniziale, mentre il filo non stabilizzato era fragile dopo ca. 50 ore.

Nota: A 50°C il filo non stabilizzato conserva una tenacità quasi inalterata dopo 500 ore.

A 35°C: Il filo non stabilizzato mantiene una tenacità quasi inalterata dopo 700 ore.

Non è stato quindi finora possibile valutare l'azione degli stabilizzanti a 35°C ed a 50°C.

D. 4) Quali stabilizzanti sono stati trovati efficaci nel prevenire il deterioramento delle fibre di polipropilene al calore ed alla luce?

R. Per la luce l'unico stabilizzante relativamente efficace è il carbon-black; al calore il Nonox EXN I.C.I. (ingiallisce i fili) e lo Santowhite Crystals Monsanto: quest'ultimo lasciava il filo bianco anche dopo il trattamento a caldo (120 ore a 128°C ± 2) ma con lucentezza diminuita.

Facciamo osservare che aumentando il titolo delle bave da ca. 4 a ca. 500 denari, il tempo di dimezzamento della tenacità del filo al calore risulta raddoppiato (prova a 128°C). Aumentando il titolo delle bave da ca. 4 a ca. 550 denari, il tempo di dimezzamento della tenacità all'U.V. aumenta di ca. 3 volte.

D. 5) Possono il filo o il fiocco di polipropilene trovare usi importanti nelle applicazioni tessili malgrado il loro basso punto di rammollimento?

R. Noi riteniamo che il punto di rammollimento del polip lene pur essendo inferiore a quelli del Nylon e del Perlon, non debba impedire l'impiego della fibra di polipropilene nei campi di applicazione tessile del Nylon e del Perlon per i quali è esclusa la possibilità di trattamento con ferro caldo.

Facciamo rilevare che il fissaggio della torsione in vapore viene normalmente eseguito a 135°C senza alcun fenomeno di impaccamento o apparente deterioramento della fibra .

Facciamo rilevare inoltre che fibre a base di cloruro di polivinile e suoi copolimeri hanno punto di rammollimento nettamente più basso delle fibre di polipropilene. Riteniamo che riuscendo a realizzare costi di produzione molto bassi tenendo presenti anche le elevate caratteristiche meccaniche, si possa prevedere l'ingresso della fibra di polipropilene nei campi di impiego delle fibre poliamidiche, notevolmente più costose.

D. 6) Quali applicazioni tessili sono state provate e trovate interessanti?

R. **Fiocco:** Tessuti per arredamento
Coperte
Calzetteria, puro e misto
Maglieria intima (allo studio)
Drapperia e laneria in misto con lana

Filo continuo:

- Calze per uomo
- Calze per uomo con filo elasticizzato (tipo filanca)
- Maglieria intima femminile (allo studio)
- Tessuti per arredamento (broccati, damascati, ecc.)
- Tessuti per arredamento con filo monobava.

D. 7) Quali applicazioni industriali sono state cercate e trovate interessanti?

R. <u>Filo continuo</u>: Funi realizzate con filo multibava e con filo monobava 200-300 denari; sacchi e tele da imballaggio; reti da pesca; filo monobava per pesca e tennis.

<u>Fiocco</u>: Tele da filtro; sacchi e tele da imballaggio.

<u>Nota</u>: Facciamo rilevare che pressuposto essenziale alla fabbricazione é l'economicitá del filato di polipropilene, particolarmente nel campo delle applicazioni industriali.

D. 8) Vi sono altre importanti deficienze del filato di polipropilene oltre al basso punto di rammollimento ed alla ossidabilità che ridurrebbero il suo uso nelle applicazioni tessili ed industriali?

R. Si: scarsa resistenza alla trielina e difficile tingibilità.

La scarsa resistenza ad alcuni solventi organici, in particolare alla trielina provoca, nelle condizioni del processo di lavatura a secco una retrazione sensibile dei filati di polipropilene. La trielina estrae inoltre i coloranti all'acetato che sono gli unici che in qualche modo tingono la fibra tal quale. Comunque il fenomeno della retrazione dei filati di polipropilene in trielina sembra dipendere esclusivamente dalla presenza di polimero non isotattico; riuscendo ad avere fibre costituite da polimero assolutamente isotattico, la resistenza alla trielina potrebbe risultare buona. Abbiamo uno studio in corso.

La tenacità dei filati trattati con trielina non varia sensibilmente (10% di diminuzione), mentre più sensibile è la variazione dell'allungamento. Sono in corso prove per la misura delle variazioni nelle caratteristiche elastiche.

La tingibilità dei filati di polipropilene tal quale è pressochè nulla: le tinte che si ottengono con coloranti all'acetato non hanno resistenza alla trielina nè alla luce ed al lavaggio a caldo. Buona risultati si hanno invece col processo di tintura in massa che fornisce buone tinte solide ad umido e resistenti alla luce. Buoni risultati tintoriali si hanno pure modificando il polimero con aggiunte di sostanze di varia natura.

D. 9) Può un filo di polipropilene per usi tessili (100-200 denari) con bave da 2÷6 denari, essere filato e stirato ad alte velocità di produzione (500-1000 metri/min)?

R. Abbiamo raggiunto qualche volta velocità di filatura di 900 metri/minuto, pur preferendo attualmente macchine con velocità intorno ai 500 metri/minuto. Nello stiro la velocità massima da noi finora conseguita è 100 metri/minuto: tuttavia quest'ultima deficienza diventa trascurabile nel campo del fiocco, considerate le elevate portate di produzione.

D. 10) Quali proprietà fisiche ha un filo ottenuto a velocità commercialmente accettabili? (lista delle proprietà fisiche - tenacità, resistenza all'abrasione e comportamento al creep).

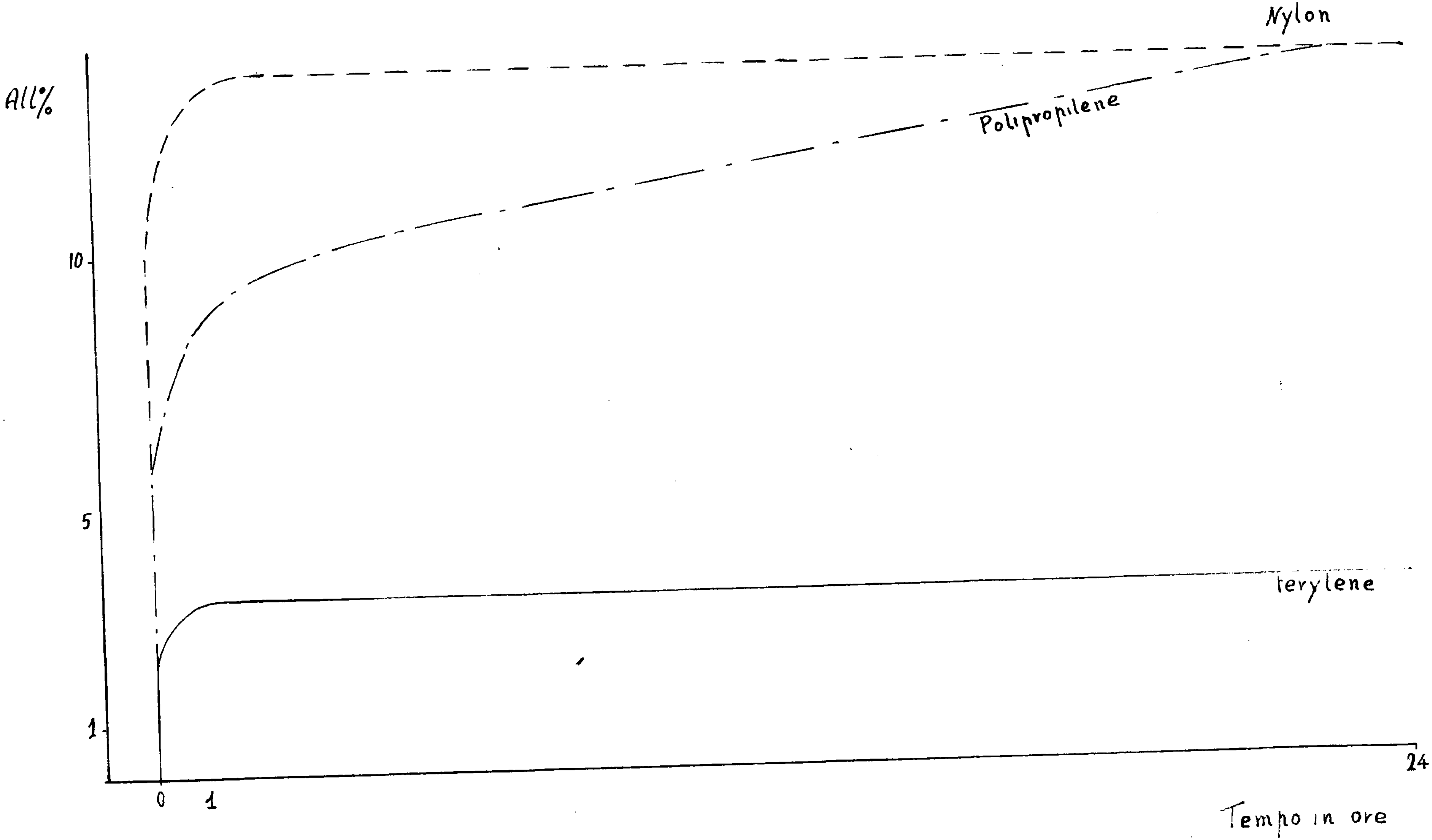
R.

- Tenacità a 20°C e 65% R.H.	5-6 g/den
- Allungamento (nelle stesse condiz.)	18-30 %

(Tenacità ed allungamento a 20°C in acqua non differiscono dai valori a 20°C in aria).

- Loop tenacity	90% della tenacità precede
- Retrazione in acqua bollente	0,5-3 %
- " in aria a 100°C	ca. 2%
- " " " " 130°C	" 10%

La resistenza all'abrasione è intermedia tra quella del Nylon e quella del Dacron.


All%
10
5
1
0
1
24
Tempo in ore
Nylon
Polipropilene
terylene

Per quanto riguarda il comportamento al creep delle fibre di polipropilene, distinguiamo la deformazione immediata da quella successiva. La deformazione immediata della nostra fibra è maggiore di quella del Terylene e minore di quella del Nylon; a parità di carico esse stanno fra loro approssimativamente come 1:2:3. Venendo ora alla deformazione successiva, abbiamo che mentre la deformazione di Terylene e Nylon rimane con il tempo approssimativamente uguale a quella istantanea, quella della fibra di polipropilene aumenta progressivamente con il tempo. A causa della predetta deformazione successiva, la deformazione totale del polipropilene, inizialmente inferiore a quella del Nylon, diventa dello stesso ordine di grandezza dopo ca. 24 ore. Riportiamo in diagramma l'andamento del fenomeno.

D. 11) E' riportato che il filo di polipropilene può essere tinto: possono ottenersi tinte intense ed un bel nero, senza ricorrere alla tintura sotto pressione?

R. Il nostro filato di polipropilene non si tinge nè in processi sotto pressione nè a pressione ordinaria, anche in presenza di rigonfianti; le tinture con coloranti all'acetato, come dicevamo, non sono da prendere in considerazione.
Buoni risultati, come riportiamo al punto 8), si sono avuti con la tintura in massa con la quale è possibile conseguire anche un bel nero pieno con un'aggiunta percentuale di colorante che per altri colori fornisce solo una tinta media.

D. 12) Possono ottenersi tinture uniformi (senza macchie e barrature) con manufatti di polipropilene preparati da filo continuo?

R. No.

D. 13) Vi è tendenza del filo di polipropilene a fibrillare oppure ad abradarsi durante i procedimenti di tessitura e maglieria?

R. No. Finora quest'inconveniente non si è mai verificato.

D. 14) Quale temperatura di filatura può tollerare il polipropilene prima di depolimerizzare?

R. Alle temperature utili per la filatura il polipropilene depolimerizza in maniera più o meno spinta in funzione del peso molecolare, del tempo di trattamento e dell'ambiente in cui si opera (azoto, aria, ecc.). Per noi il problema della depolimerizzazione del fuso alla temperatura di filatura non è preoccupante in quanto, anche verificandosi, noi riusciamo a controllarlo agevolmente.

D. 15) Se è necessario filare in atmosfera di azoto per prevenire l'ossidazione, qual'è l'indice di fusione per produrre fibre, secondo il "I.C.I. grader Test G" a 190°C?

R. Noi non ci basiamo sull'indice di fusione (I.C.I. grader Tests) ma sulla viscosità intrinseca misurata in trielina a 135°C. Il valore ottimo è ca. 1.

D. 16) E' stato necessario includere un:lubrificante nella polimerizzazione per favorire alte velocità di filatura?

R. No. Abbiamo tuttavia osservato che l'aggiunta di qualche unità percentuale di varie sostanse (p.es. il Wingstay, impiegato come stabilizzante termico) agevola sensibilmente la filatura, favorendo elevate velocità.

Copia per Sig Prof. Natta

[illegible] DI CHIMICA
INDUSTRI[illegible] POLITECN[illegible]
[illegible] 1956
17

AIR MAIL SPECIAL DELIVERY

September 7, 1956

Prof.

Mr. John J. MURPHY
Director of Patent Affairs
Union Carbide and Carbon Corp.
30 East Forty-Second Street
NEW YORK 17, U.S.A.

Re: Polypropylene negotiations

We acknowledge receipt of your cable dated August 6, reading as follows:

> "Greatly surprised at cable dated August fourth received from you today with all points but one agreed upon stop Apparently our last cable was not clear am sending details on this matter immediately"

as well as of your letter dated August 7, which has been received when our Offices were closed down for a fortnight due to the yearly vacation period.

With our cable dated August 3, reading as follows:

> Replying your cable August second stop Provided new supplementary letter contains following provisions stop First Montecatini has exclusive right but subject to technical arbitration to evaluate existence of dominating claims which have to be taken care of second Montecatini alone is entitled to conduct negotiations with the owner of dominating claims and Union shall give Montecatini all possible assistance in such negotiations if and when requested comma we accept requested deletion in contract or by supplementary letter of words quote 50% of unquote in Article XVIII dominating patents page 30 line 7 stop Please cable your final answer within August third
>
> Orsoni"

we had also accepted your request to be entitled to credit against Montecatini not 50% but 100% of the royalties, that should have been paid by you to third parties, owners of patents, if any, dominating processes licensed to Union by Montecatini. Such concession which was the last of a long series, was to be regarded as a final grant from our part and subject to the condition that Montecatini, as it was taking upon itself 100% of the burden, would be entitled to conduct by itself all the negotiations for obtaining a license from such third parties.

It was obviously understood that relevant licence agreements, if any, executed by Union with third parties, before 1956 (Montecatini-Union negotiations started on January 1956) were to be considered a binding engagement for Union and therefore no longer subject to said limitation, except for the evaluation of the existence or not of dominating claims.

In fact, even in our cable dated August 1, reading as follows:

> "Your cable July thirtyfirst stop due our other engagement cannot extend deadline for completion of matters you raise beyond August third stop We understand your philosophy but we confirm first dash Article XVI dash validity of patents cannot accept proposed insertion Section 2 first line page 29 stop Accept however insertion after written words quote which claims unquote quote are applicable to the licensed field and unquote semicolon cannot accept sixth and fifth line from the bottom deletion words quote either Article XII or unquote but accept insertion quote Sections one and two unquote after quote Article XIII unquote stop Second dash for reasons already stated at length cannot accept deletion of words quote 50% of unquote stop Third dash we are agreeable proposed revision letter number 2 comma paragraph 5 (A) stop Fourth dash in order to protect your interests and your obligations under other licenses could accept only very slight changes of Article IV dash secrecy and Article XVIII dash dominating patents provided they do not contradict our views known to you semicolon please cable drafts Stop Please consider this cable as final stop We are awaiting your final answer by cable stop Should you decide to accept we may agree on how to execute the agreement in order to offset the vacation period Ursoni"

./.

we accepted to take into account such obligations of yours, if any.

On the contrary, your cable dated August 3 (see attached copy) suggested substantial modifications to articles IV (Secrecy) and XVIII (Dominating Patents). These modifications were meant to protect not only Union's obligations under the license agreements entered into between Union and third parties before 1956, obligatio that Union intends obviously to fulfill, but also future agreements between Union and third parties, the latter being in contradiction with what we had proposed in our two cables dated August 1 and 3.

We have therefore concluded that of our final counter-proposal made on August 3, you had accepted only the increase of the percentage of Montecatini's liabilities (for royalties, if any, to be paid by Union to third parties and creditable against royalties due by Union to Montecatini) but not the enhanced guarantees for Montecatini's protection to which our Company had conditioned its final grant.

Since you had not accepted our counter-proposals within August 3 (this was the deadline previously fixed) we have sent you on August 4 a cable informing you that we wanted to recover our freedom from any previous engagement.

______ 0 ______

Re-examining the negotiations between our two Companies, which took place during the first seven months of 1956, we are quite agreeable to attest that you have done your best to remove most of the various divergencies which had arisen from the beginning between Montecatini and Union about the licence agreement.

We have noticed however that, in sustaining the legitimate interest of your Company, you were inclined to draw up the articles of the agreement in a way which would most likely have resulted in almost automatically widening possible future discrepancies between Union and Montecatini, such as may result during the life of agreements of this type, instead of using a language which would stimulate your Company to collaborate and to try to settle in a friendly way such future possible discrepancies.

./.

It is because of this particular attitude of yours, which : confirmed in our opinion also by the contents of your cable of August 3rd, that (we want to say it quite openly) we started worrying and, in order to do our best on our part to protect as much as possible the legitimate interests of our Company, became very cautious in accepting your continuous requests for new modifications.

_______ o _______

Having stated this, we wish to inform you that we are willing to do our part in trying to remove misunderstandings which may unintentionally have arisen between us, and that we are willing to reopen our offer, which will stand until Sept. 20 next, as follows:

As to supplementary letter No. 2 we are willing to add a new paragraph 3 as suggested by you in your letter dated August 7 limited however only to agreements already entered into between you and third parties before 1956. In such specific cases as indicated by you a relevant disclosure shall however be provided for to be made and convincing evidence shall be furnished by Union to a neutral patent agent mutually trusted by the parties, who is bound to keep secrecy, and whose evaluation (on whether the controversial piece of information was already in possession of Union at the date of receipt of the corresponding Montecatini disclosure) shall be final and binding.

As to paragraph 14 of your letter dated August 7 (reported in your cable of August 3) the formula you proposed is, as we have already told you, in conflict with both meaning and wording of our cables dated August 1 and 3.

In order to be able to agree in principle upon the formula suggested by you, we see no other solution but to go back to a limitation of our contribution on royalties, if any, to be paid by Union to third parties owners of dominating patents, within a 50% ceiling, as we had previously suggested to you in our draft dated July 27, 1956. It does not seem in fact possible to find out another

./.

effective system to make the Union directly and efficaciously interested so that such supplementary royalties, if any, due to third parties, should not exceed minimum amounts and so as to avoid us being involved in actions which may not be strictly necessary.

Reference to dominating allowed claims of third parties should be however restricted only to Agreements executed by Union prior to 1956.

In said cases Union shall not however be required to furnish directly to Montecatini any evidence or make any disclosure which it may be prohibited from making by any such license agreements with said third parties owners of any such dominating claim. However Union shall furnish said evidence to an Arbitration Board (composed by a neutral patent agent and patent accountant) bound to secrecy and whose decision shall be final. In all other cases of dominating patents also Montecatini shall have the right, subject however to said technical [illegible], to evaluate the existence of dominating claims which have to be taken care of.

Finally, we wish also to underline that during the period of 7 months negotiations Montecatini has done its best and has honestly endeavoured to reach an effective agreement with Union.

In fact, records prove that all reasonable requests of Union have been accepted by us.

Montecatini had even gone further in accepting conditions which, according to the judgement of experts (including well-known U.S. experts) should not have been accepted by us: but that happened also because of your exceptional and consummate skill to negotiate, skill of which we had a convincing evidence up to your cable dated August 3.

We were however sure that an option and license agreement based on our draft dated July 27 modified according to our cable of August 1 and according to the present letter, constitutes a fair attempt to take into account the legitimate interests of both parties.

./.

The term of September 20, 1956, indicated above, is final. Your cable reply should therefore reach us within the said date, which in no case will be extended.

In case you should decide to enter said agreement, a good understanding would be established between our two Companies opening the door to a profitable and friendly collaboration, in the mutual interest of both parties.

Awaiting your final decision, we remain,

Yours faithfully,

"MONTECATINI"

(Ing [illegible])

encl.

original by air mail special delivery
confirmation copy two days later by air mail

COPY

CABLE OF UNION TO MONTECATINI DATED AUGUST 3, 1956.

Aug.3, 1956

GABBRO ORSONI MILANO

Replying your cable August third following are the drafts referred to in our exchange of cables August second prepared with consideration of the two provisions in your last cable as well as various provisions in our existing license agreement stop These drafts would be added as Paragraphs in letter number two as follows thirteen with reference to article four of the agreement it is understood and agreed that in the event any information supplied by Montecatini to Union under the agreement (1) has been previously disclosed to Union by another party comma Union comma in carrying out the provisions of section 2 of article four comma shall not be required to furnish any evidence which it is prohibited from disclosing under the terms of any agreement with such other party comma or (2) is subsequently disclosed to Union by another party comma Union shall not be restricted under the terms of this agreement from disposing of or using said information stop Fourteen with reference to article eighteen of the agreement it is understood and agreed that said article shall apply to claims of patents and to allowed claims of patent applications of third parties which dominate claims of any quote licensed applications unquote applicable to the quote licensed field unquote or patents issuing therefrom and shall apply to both existing and future license agreements with such third parties stop Montecatini and Union shall cooperate with one another in evaluating any dominant claim and in negotiating for future licenses with the owners of any dominant claims and shall give one another all possible assistance in regard thereto stop Union shall not however be required to furnish any evidence or make any disclosure which it may be prohibited from making under any existing agreements with the owners of any such dominating claims stop Negotiations for future licenses with the owners of dominating patents will be made by Montecatini or Union whichever in each particular case is most likely to obtain the most favorable terms stop In the interest of time suggest you prepare the contracts in final form to cover both polypropylene and polystyrene and submit for our approval stop Your prompt and courteous cooperation greatly appreciated - MURPHY

Domande

25.5.1956

Polipropilene plastici - Questionario Union

SCHEDULE C

INFORMATION TO BE DISCLOSED UNDER ARTICLE III.1(d)

1. How much polymer solubile in boiling heptane is made along with the isotactic polymer?
2. What is the density of the isotactic polymer?
3. Can the polymerization be directed to produce high molecular weight amorphous polymer without the isotactic polymer?
4. Is the clarity of molded articles comparable to that of molded articles of polystyrene or polymethylmethacrylate?
5. Can the isotactic polymer be stabilized so that it is satisfactory for outdoor use?
6. Do the best stabilizers hurt color or clarity of molded articles?
7. Are purity requirements on monomer and diluent about the same as for Ziegler ethylene polymerization?
8. How does the catalyst productivity compare with that of the Ziegler Polyethylene process?
9. Can catalyst residues be removed as easily and as completely as is the case with Ziegler polyethylene process?
10. Can the polymerization be controlled to produce any desired molecular weight polypropylene?

Risposte.

POLIPROPILENE QUESTIONARIO UNION

(Bozza da sottoporre al Chiar.mo Prof.Natta)

1) Assieme al polimero isotattico si forma dal 10 al 20% di polimero solubile in eptano bollente.

2) La densità del polipropilene dopo estrazione con eptano è di 0,92.

3) Non è mai stata tentata la produzione di polimero amorfo privo di polimero isotattico.

4) Gli articoli stampati in polipropilene sono traslucidi come quelli di polietilene.

5) Il polipropilene può essere stabilizzato fino ad avere un comportamento uguale a quello del polietilene stabilizzato per usi all'aperto.

6) I migliori stabilizzanti imbruniscono leggermente il prodotto.

7) Le caratteristiche di purezza del propilene e del solvente devono essere analoghe a quelle richieste per polimerizzare l'etilene secondo Ziegler.

8) Per 1 gr di catalizzatore totale (somma dei due componenti) si possono ottenere agevolmente 150/170 gr di polimero; in buone condizioni di purezza del propilene e del solvente si può arrivare a sorpassare i 200 gr per grammo.

9) I residui del catalizzatore possono essere rimossi facilmente e completamente come nel caso del polietilene Ziegler.

10) Si può regolare agevolmente il peso molecolare da circa 30.000 fino a circa 300.000 .

18/6/56

Telegramma - Questionario Union car. su polimeri.

COPIA

UCC

(ricevuto copia 25/5/56)

Domande.

22/V/56 LT JJ MURPHY FRANKFURTER HOF
FRANKFURT

ISOTACTIC POLYBUTENE-1 FOR PLASTICS 1 HOW MUCH POLYMER SOLUBLE
IN BOILING HEPTANE IS MADE ALONG WITH THE ISOTACTIC POLYMER ? 2 CA
THE POLYMERIZATION BE DIRECTWD TO PRODUCE HIGH MOLECULAR WEIGHT
AMORPHOUS POLYMER WITHOUT THE ISOTACTIC POLYMER 3 WHAT IS KNOWN
ABOUT MOLECULAR WEIGHT DISTRIBUTION 4 HOW DOES CLARITY OF THE
MOLDED ARTICLES COMPARE TO THAT OF MOLDED ARTICLES OF POLYSTYRENE
POLYMETHYLMETHACRYLATE AND POLYPROPYLENE 5 CAN THE ISOTACTIC POLY
BE STABILIZED SO THAT IT IS SATISFACTORY FOR OUTDOOR USE 6 DO THE
BEST STABILIZERS HURT COLOR OR CLARITY OF MOLDED ARTICLES 7 ARE
PURITY REQUIREMENTS ON MONOMER AND DILUENT ABOUT THE SAME AS FOR
ZIEGLER ETHYLENE POLYMERIZATION 8 HOW DOES THE CATALYST PRODUCTIV
COMPARE WITH THAT OF THE ZIEGLER POLYETHYLENE PROCESS 9 CAN CATALY
RESIDUES BE REMOVED AS EASILY AND COMPLETELY AS IS THE CASE WITH TH
ZIEGLER POLYETHYLENE PROCESS 10 CAN THE POLYMERIZATION BE CONTROL
ED TO PRODUCE ANY DESIRED MOLECULAR WEIGHT POLYBUTENE 1 WHAT
APPARENT ADVANTAGES DOES POLYBUTENE HAVE OVER ZIEGLER POLYETHYLENE
E.G. STRESS RUPTURE 12 IN WHAT RESPECTS IS THE POLYBUTENE INFERIO
TO ZIEGLER POLYETHYLENE 13 IS POLYBUTENE MORE STABLE TO OXIDATION
THAN POLYPROPYLENE IF SO WHY 14 WHAT USES DO YOU FORESEE FOR
POLYBUTENE? 15 WHAT IS THE MEASURED DENSITY AND THEORETICAL
CRYSTALLITE DENSITY OF ISOTACTIC POLYBUTENE 16 WHAT IS THE MAXIMU
STIFFNESS AT ROOM TEMPERATURE WHICH CAN BE OBTAINED FROM POLYBUTEN
(USE ZIEGLER POLYETHYLENE AS A BASIS OF COMPARISON.) 17 IS POLYBUT
BRITTLE AT LOW TEMPERATURE IF SO AT WHAT TEMPERATURE 18 WHATCOPOL
ARE THERE OF INTEREST AND WHAT SPECIAL PROPERTIES DO THEY HAVE
19 WHAT SIZE SAMPLES CAN WE OBTAIN FOR EVALUATION AT LEAST ONE HUN
DRED POUNDS WOULD BE MOST DESIRABLE BUT EVEN A FEW POUNDS WOULD BE
USEFUL ONE HUNDRED GRAMS OR SO WOULD BE HELPFUL FOR LABORATORY
EXAMINATIONS ISOTACTIC POLYSTYRENE FOR PLASTICS 1 HOW MUCH POLYMER
SOLUBLE IN BOILING HEPTANE IS MADE ALONG WITH THE ISOTACTIC POLYME

2 ARE PURITY REQUIREMENTS ON MONOMER AND DILUENT ABOUT THE SAME AS FOR ZIEGLER ETHYLENE POLYMERIZATION 3 HOW DOES THE CATALYST PRODUCTIVITY COMPARE WITH THAT OF THE ZIEGLER POLYETHYLENE PROCESS 4 CAN CATALYST RESIDUES BE REMOVED AS EASILY AND COMPLETELY AS IS THE CASE WITH THE ZIEGLER POLYETHYLENE PROCESS 5 CAN THE POLYMERIZAT BE CONTROLLED TO PRODUCE ANY DESIRED MOLECULAR WEIGHT POLYSTYRENE XX 6 WHAT IS THE MAXIMUM USE TEMPERATURE 7 CAN THE POLYMER BE MOLDED IN CURRENTLY AVAILABEE INJECTION MACHINES OR EXTRUDED IN AVAILABLE EXTRUDERS 8 WHAT MAIN USES ARE FORESEEN 9 HOW DO THE MECHANICAL PROPERTIES DIFFER FROM AMORPHOUS POLYSTYRENE 10 WHAT IS THE SECOND ORDER TRANSITION TEMPERATURE 11 WHAT ARE THE GAS AND VAPOR TRANSMISSION CHARACTER ISTICS 12 HOW STABLE TO THERMAL AND OXIDATIVE EXPOSURE IS THE PRODUCT ARE THER KNOWN STABILIZERS IF SO WHICH ARE RECOMMENDED 13 CAN THE ISOTACTIC POLYMER BE STABILIZED SO THAT IS SATISFACTORY FOR OUTDOOR USE 14 DO THE BEST STABILIZERS HURT COLOR OR CLARITY OF MOLDED ARTICLE 15 WHAT IS THE MEASURED DENSITY AND THE THEORETICAL CRYSTALLITE DENSITY OF ISOTACTIC POLYSTYRENE 16 HOW DOES CLARITY OF THE MOLDED ARTICLES COMPARE WITH THAT OF MOLDED ARTICLES OF AMORPHOUS POLYSTYRENE OR POLYMETHYL METHACRYLATE 17 WHAT COPOLYMERS ARE THERE OF INTEREST WHAT SPECIAL PROPERTIES DO THEY HAVE 18 WHAT SIZE SAMPLES CAN WE OBTAIN FOR EVALUATION AT LEAST ONE HUNDRED POUNDS WOULD BE MOST DESIRABLE BUT EVEN A FEW POUNDS WOULD BE USEFUL ONE HUNDRED GRAMS OR SO WOULD BE HELPFUL FOR LABORATORY EXAMINATIONS .

BUTILENE-1,

RISPOSTE AL QUESTIONARIO DELLA "UNION CARBIDE AND CARBON" RIGUARDANTE IL POLIBUTENE-1 ISOTATTICO

(Per alcune risposte riguardanti le proprietà meccaniche e le applicazioni di questo prodotto rimandiamo al Laboratorio Applicazioni Resine di Castellanza, il quale si è occupato di studiare il polibutene da tale punto di vista).

Risposte, Novara.

- - - - -

1) Quanto polimero solubile in n-eptano viene prodotto insieme con il polimero isotattico ?	Il polibutene-1 è completamente solubile in n-eptano; per separare approssimativamente la parte isotattica da quella atattica si usano perciò altri solventi: ad es. l'etere etilico. La parte insolubile in etere è in grande prevalenza isotattica e raggiunge il 70-80 del totale.
2) Può la polimerizzazione essere diretta ad ottenere polimero amorfo ad alto peso molecolare senza polimero isotattico ?	Impiegando opportuni catalizzatori si riesce a far sì che la parte amorfa del polimero abbia elevato peso molecolare (da 20.000 a 100.000). Non si è riusciti finora ad ottenere direttamente polimeri completamente amorfi, ma usando particolari accorgimenti si riesce a ridurre la parte isotattica a circa il 20% (determinata röntgenograficamente).
3) Cosa si conosce intorno alla distribuzione dei pesi molecolari ?	Lo studio della distribuzione dei pesi molecolari nel polibutilene- è ancora in corso. Esso è complicato dalla presenza di due tipi d polimero (isotattico e atattico) oltre che da catene miste (blocch di isotattico alternati a blocchi di atattico) aventi proprietà assai diverse.

	La frazione di polimeri a bassissimo peso molecolare (dell'ordine delle centinaia) ancora liquidi a temperatura ambiente varia tra lo 0,5% ed il 6% a seconda delle condizioni di polimerizzazione.
4) Com'è la trasparenza (clarity) degli articoli stampati paragonata a quella degli articoli stampati di polistirolo, polimetacrilato di metile e polipropilene ?	L.A.R. Castellanza
5) Può il polimero isotattico essere stabilizzato in modo che esso sia soddisfacente per usi all'aperto ?	L.A.R. Castellanza
6) I migliori stabilizzanti recano danno al colore o alla trasparenza (clarity) degli articoli stampati ?	L.A.R. Castellanza
7) I requisiti di purezza del monomero e i diluenti sono pressapoco gli stessi che per la polimerizzazione Ziegler dell'etilene ?	I requisiti di purezza dal punto di vista dell'umidità, dell'aria, di tracce di alcool, ecc., sono gli stessi che per il politene Ziegler. Diluenti inerti rispetto al catalizzatore possono essere sopportati anche in forti quantità per quanto naturalmente complichino la condotta del processo di polimerizzazione. La presenza di altre olefine polimerizzabili con lo stesso catalizzatore non impedisce la polimerizzazione, ma modifica le caratteristiche del polimero ottenuto.

8) Qual'è la produttività del catalizzatore paragonata con quella del processo per il polietilene Ziegler ?	E' più bassa: sinora si è raggiunta una produttività massima di 40-50 g di polibutene/gr di catalizzatore.
9) I residui del catalizzatore possono essere rimossi così facilmente e completamente come nel caso del processo per il polietilene Ziegler ?	Quasi altrettanto facilmente. Si ottengono nel polimero residui in ceneri dell'ordine del 0,1-0,2%.
10) Può la polimerizzazione essere controllata in modo da produrre polibutene di qualsiasi peso molecolare desiderato ?	Si, nel campo dei pesi molecolari ottenibili (da poche centinaia fino ad oltre 500.000).
11) Quali apparenti vantaggi ha il polibutene nei confronti del polietilene Ziegler, per esempio nella sollecitazione a rottura ?	L.A.R. Castellanza
12) Sotto quali aspetti il polibutene è inferiore al polietilene Ziegler ?	L.A.R. Castellanza
13) Il polibutene è più stabile all'ossidazione del propilene ? e se è così perché ?	L.A.R. Castellanza
14) Quali usi prevedete per il polibutene ?	LAR Castellanza

15) Qual'è la densità misurata e la densità teorica dei cristalliti del polibutene isotattico ?	L.A.R. Castellanza
16) Qual'è la massima rigidezza (stiffness) a temperatura ambiente che può essere ottenuta dal polibutene ? (usare il polietilene Ziegler come base di paragone).	L.A.R. Castellanza
17) E' il polibutene fragile a bassa temperatura? e se così a quale temperatura ?	L.A.R. Castellanza
18) Quali copolimeri presentano interesse e quali speciali proprietà essi hanno ?	I copolimeri del butene-1 sono ancora in fase di studio. Assai interessanti si presentano i copolimeri del butene-1 con l'etilene e con il propilene. Essi sono completamente amorfi e son dotati di notevoli proprietà el stiche.
19) Qual'è la quantità di prodotto che possiamo ottenere per valutarlo ? Un campione di un centinaio di libbre sarebbe il più desiderabile, ma anche poche libbre sarebbero utili; un campione di un centinaio di grammi sarebbe di aiuto per gli esami di laboratorio.	

Risposta.

LABORATORIO APPLICAZIONI RESINE

CASTELLANZA

18 Giugno 1956

[redacted]

Sezione Polimeri Isotattici

GG/pv

POLIBUTILENE ISOTATTICO

(4) 1) Gli articoli stampati in polibutilene isotattico sono translucidi quanto il polietilene e il polipropilene. Non sono quindi confrontabili con i materiali trasparenti, quali il polistirolo e il polimetacrilato di metile.

(5) 2) Sotto l'azione della luce solare diretta il polibutilene subisce una degradazione, che è rallentata ma non impedita dalla presenza di antiossidante.
La migliore protezione si raggiunge, analogamente a quanto si fa per il polietilene, con l'incorporamento di circa il 2% di carbon black.

(6) 6 3) E' ovvio che il carbon black rende opaco e nero il manufatto.
Tra gli antiossidanti usati contro l'azione termica vi sono alcuni che non hanno una sensibile influenza sul colore e sulla trasparenza.
E' sufficiente 0,1 - 0,2% di antiossidante per proteggere il polibutilene nella lavorazione ad alta temperatura.

(7) 4) Il polibutilene isotattico non è direttamente confrontabile con il polietilene Ziegler, in quanto i due materiali hanno un comportamento differente nella sollecitazione alla rottura.
La curva trazione-allungamento del polibutilene è tipica di un elastomero ed è caratterizzata da un basso modulo e da un elevato carico di rottura, mentre la curva del polietilene Ziegler è quella di materiale plastico rigido.
Come risulta dalle curve trazione-allungamento allegate nella relazione L.A.R. n° 7/56 Sezione Polimeri Isotattici del 22.5.56, nel polibutilene normale si ha un carico di snervamento di circa 60 kg/cm2 contro un carico di rottura di 200 kg/cm2. Questi valori salgono rispettivamente a circa 125 kg/cm2 e 360 kg/cm2 nel polibutilene arricchito in frazione cristallina.

Nel polietilene Ziegler il carico di snervamento e quello di rottura sono all'incirca nello stesso ordine (180 - 220 kg/cm2).

(12) 5) E' evidente da quanto detto in 4) che in confronto col polietilene Ziegler che è un materiale rigido, il polibutilene isotattico è inferiore nelle proprietà meccaniche (modulo di elasticità, rigidità flessionale, durezza) e nel punto di rammollimento Vicat.

Nella seguente tabella sono riportate le principali proprietà fisiche dei due polimeri.

		Polibutilene Isotattico	Polietilene Ziegler
- Carico rottura	kg/cm2	150 - 360	180 - 220
- Allungamento alla rottura	%	180 - 300	300 - 800
- Rigidità flessionale (stiffness)	kg/cm2	400 - 1600	4000 - 6000
- Punto rammollimento Vicat (1 kg di carico)	°C	92 - 120	115 - 127
- Punto di infragilimento (Brittle Point)	°C	da - 4 a - 20	- 65

Il polibutilene ha proprietà elettriche e chimiche (resistenza agli acidi, basi, di minerali e vegetali) pari a quello del polietilene Ziegler. A differenza di quest'ultimo resiste all'acido nitrico concentrato (94 %).

(13) 6) La stabilità alla ossidazione è pari o leggermente migliore a quella del polipropilene.

(14) 7) Col tipo arricchito in frazione cristallina:

a) film

b) rivestimenti isolanti per cavi elettrici

c) tubi flessibili

d) stampati ad iniezione

Col tipo normale:

a) foglie caricate per rivestimenti anticorrosivi e impermeabilizzanti

b) laminati con carta, alluminio, tessuti

c) modificazione di resine, cere paraffine, bitumi

(15) 8) Densità misurata = 0,915

Densità teorica = 0,960

9) Nel tipo normale la massima rigidità flessionale (stiffness) è circa 500 kg/cm2.

(16) Nel tipo arricchito in frazione cristallina si arriva a 1600 - 1700 kg/cm2.

Nel polietilene Ziegler la rigidità flessionale è 4000 - 6000 kg/cm2

(17) 10) Il punto di infragilimento (Brittle Point) varia da - 4 a - 20°C.

Bozza destinata al Prof. Natta per commento. Risposte -

QUESTIONARIO UNION CARBIDE AND CARBON

STIROLO.

1) Quanto polimero solubile in eptano bollente si forma assieme al polimero isotattico?

= Nella polimerizzazione dello stirolo secondo il brevetto U.63/b in solventi aromatici il 30% del polimero totale è estraibile con acetone bollente; l'estraibile con eptano è al massimo pari a quella dell'acetone.

2) I requisiti di purezza del monomero e del solvente sono simili a quelli necessari per la polimerizzazione dell'etilene secondo Ziegler?

= Le caratteristiche dello stirolo tecnico in commercio sono sufficienti; la purezza dei solventi deve essere all'incirca uguale a quella necessaria per la polimerizzazione dell'etilene.

3) La produttività (resa) del catalizzatore è paragonabile con quella del processo Ziegler di polimerizzazione dell'etilene?

= Operando secondo gli esempi del brevetto U.63/b,la produttività è di 5-8 gr di polimero isotattico per grammo di catalizzatore complessivo.

4) I residui del catalizzatore possono essere allontanati facilmente e completamente come nel caso della polimerizzazione dell'etilene Ziegler?

= La depurazione del polimero dai residui di catalizzatore è altrettanto facile e completa come nel caso del polietilene.

5) La polimerizzazione può essere controllata in modo da produrre qualsiasi peso molecolare si desideri?

= Nel brevetto U.63/b non è prevista la tecnica per la regolazione del peso molecolare .

./.

6) Qual'è la massima temperatura adoperabile?

ve

per usi

= Non è stato accertato un limite massimo di temperatura per la polimerizzazione.

7) Il polimero può essere stampato nelle comuni macchine ad iniezione?

= Per pesi molecolari elevati riteniamo che occorrano macchine speciali.

8) Quali sono i principali usi previsti?

= Fibre, film e oggetti stampati.

9) Come differiscono le proprietà meccaniche da quelle del polistirene e polistirolo amorfo?

= Non vi sono dati sul polimero isotattico puro in confronto con il polistirolo normale.

10) Qual'è la temperatura di transizione di second'ordine?

= La temperatura di transizione di second'ordine è simile a quella del polistirolo normale.

11) Quali sono le caratteristiche di permeabilità ai gas e vapor d'acqua?

= Non è stata determinata la permeabilità ai gas e vapori.

12) Qual'è la stabilità al calore e alla ossidazione del prodotto e vi sono stabilizzatori e quali sono?

13) Il polimero isotattico può essere stabilizzato in modo soddisfacente per esposizione all'aria aperta?

14) I migliori stabilizzatori rovinano il colore o la trasparenza negli articoli stampati?

= Il polistirolo isotattico non mostra una speciale instabilità al calore e alla luce nè particolare tendenza all'ossidazione; pertanto non si è ravvisata finora la necessità di ricorrere a stabilizzanti.

./.

15) Qual'è la densità misurata e quale la densità teorica dei cristalliti del polistirolo isotattico?

= Il peso specifico è di 1.08 a 20°; densità teorica dei cristalliti è di 1.12 .

16) La trasparenza degli articoli stampati è paragonabile a quella degli articoli stampati con polistirolo amorfo o con polimetil-metacrilato?

= I pezzi stampati con adatta tecnica possono essere trasparenti come quelli ottenuti da polistirolo normale.

17) Quali sono i copolimeri di qualche interesse e che speciali proprietà essi hanno?

= Nei brevetti in questione è solo accennata la possibilità di ottenere copolimeri con lo stirolo.

Le risposte al questionario della Carbide and Carbon per il polistirolo isotattico sono state redatte limitatamente al contenuto del brevetto U.63/b : non è stato quindi tenuto conto dei brevetti e delle conoscenze acquisite in seguito come la regolazione del peso molecolare con idrogeno o con catalizzatori speciali - e neppure dei procedimenti ad alta resa in polimero isotattico.

Volendo estendere le risposte allo stato attuale cioè includendo i brevetti U.92 (19/10/55), U.63/d (24/2/56), le risposte 1, 3, 5, verrebbero modificate come segue :

1) L'estraibile eptano può essere ridotto praticamente a zero.

3) In laboratorio si sono ottenute produttività fino a 100 gr per grammo e forse si potrà aumentare.

./.

5) La regolazione del peso molecolare è possibile entro certi limiti operando in presenza di idrogeno o variando le condizioni di lavoro (concentrazione di catalizzatore e di monomero, temperatura, rapporti reagenti catalitici) .

15 Giugno 1956

July 31, 1956

Mr. Augustus B. Kinzel, Vice Presiden
Research - Union Carbide and Carbon
30 East Forty-second Street
NEW YORK 17 - N.Y. - USA

Dear Mr. Kinzel,

I am very sorry that my busy trip through the States did not permit me to write to you before my coming back to Italy. I wish to thank you very much for [illegible] invitation and for the pleasant luncheon we had together.

I hope to have soon the pleasure to see you again in Italy or in the States.

With my best personal regards, I remain,

Truly yours,

Giulio Natta

Copia per Sig Prof G. Natta

(copia originale spedita a cu. Murphy 27.6.56

BY AIR MAIL-SPECIAL DELIVERY

May 31, 1956

Mr. John J. MURPHY
c/o Union Carbide & Carbon Corp.
30 East 42nd Street
NEW YORK, N.Y.
(U.S.A.)

dV/AMF/ms

Dear Mr. Murphy,

Re: Negotiations on polypropylene, polybutene-1 and polystyrene plastics -

As agreed in Milan on the 25th inst., we send you a draft definition of the "Licence Field" of the proposed Agreement between our two Companies, enlarged to include not only polypropylene but also polybutene-1 and polystyrene.+ You will notice that in the definition of "pool process" the words "purification of monomers" have been omitted, since no such operations have been claimed in any listed pool applications. Of course in giving the definition of the licensed field point 5/ /d has been maintained.

We also enclose a draft of a letter that could be sent to you to give you a licence for producing "authorised products" also if they have less than 2000 m.w.; and of another letter to confirm our willingness to give licences under each and all Montecatini U.S. and Canadian patents (if any) covering polymerization processes and catalysts that may be employed to produce the "authorised products".

Very truly yours,

"MONTECATINI"

encls.

original by air mail special delivery
copy by air mail two days later

+ This is the field that will be applied in case you decide for combinations A/4 or A/5 of our letter of yesterday.

February 5, 1957

Mr. John J. MURPHY
Director of Patent Affairs
Union Carbide and Carbon Corp.
30 East 42nd Street,
NEW YORK 17, N.Y. (U.S.A.)

dV/EP/ma

Dear Mr. Murphy,

Re: Montecatini-Union Carbide "Polypropylene and Polystyrene Plastics Option and License Agreement"

Dr. Orsoni has brought to our attention your letter of January 29, 1957, in which you inquire about certain applications filed by Montecatini in Italy in the field of polyolefines.

The patent and applications referred to are:

1) It.Patent [illegible], filed March [illegible], 1955.-
This patent, because of the particular type of catalyst disclosed, is not jointly owned by Prof.Ziegler, but is exclusively Montecatini's own. For this reason it was not included in the "Listed Patent Applications". According to paragraph No.4, Corollary Letter No. 2, attached to the above agreement, your Company, upon exercising the option will be entitled, however, to receive a non-exclusive license from Montecatini, without any down payment, on the same terms, including royalty rates, provided for in the Agreement, covering the lead-alkyl based catalysts and the use of them in the polymerization process whereby propylene or styrene may be transformed in the polymers, products and compositions of the kind referred to in Article I of the Agreement.

2) Patent Application No.11,[illegible]/55 - Filed in Italy - August 6, 1955.-
This refers to the polymerization of certain branched chain olefines with more than 4 carbon atoms and it was not listed because it does

May 31, 1956

Draft of a letter be sent by Montecatini to Union concerning licences under Montecatini's patented processes, if any, for the manufacture of products claimed in "Pool Applications".

Dear Sirs,

We refer to the enquiries that you have made in the course of the negotiations, and are pleased to inform you that in addition to the pool licence provided for in the Agreement between our Companies on plastics from .... polymers, we are ready to discuss with you an agreement to grant you a non-exclusive license, without any down payments but otherwise under the same conditions of the main pool licence agreement, under each and all Montecatini's U.S. and Canadian applications, if any, filed not later than December 31, 1956, and covering all polymerization processes and catalysts whereby said olefines may be transformed into authorised polymers, products and compositions claimed in "Pool applications" as defined in said agreement.

Very truly yours.

(MONTECATINI)

May 31, 1956

Draft of a letter to be sent by Montecatini to Union enlarging the licensed field to cover also polymers having molecular weight below 2000.

Dear Sirs,

With reference to the enquiries you have made in the course of the negotiations about the possibility of lowering the limit of 2000 for the molecular weight of the products considered under Article I, 4.(a) and 5,β/(a) and (b) of the Agreement between our Companies on plastics from ..... polymers, we are pleased to inform you that in partial derogation of the provisions of the said Article, we are ready to allow you without any down payment, but otherwise under the conditions of the said Agreement to produce, transform and use the products considered in Article I, 4, (a) and 5,β, (a) and (b) having a molecular weight below 2000; provided that said products and the process for obtaining and transforming them fall under at least one claim of the "Pool Applications" as defined in the said Agreement.

Very truly yours,

(MONTECATINI)

COPY

CABLE OF UNION TO MONTECATINI DATED AUGUST 3, 1956.

Aug.3, 1956

GABBRO ORSONI MILANO

Replying your cable August third following are the drafts referred to in our exchange of cables August second prepared with consideration of the two provisions in your last cable as well as various provisions in our existing license agreement stop These drafts would be added as Paragraphs in letter number two as follows thirteen with reference to article four of the agreement it is understood and agreed that in the event any information supplied by Montecatini to Union under the agreement (1) has been previously disclosed to Union by another party comma Union comma in carrying out the provisions of section 2 of article four comma shall not be required to furnish any evidence which it is prohibited from disclosing under the terms of any agreement with such other party comma or (2) is subsequently disclosed to Union by another party comma Union shall not be restricted under the terms of this agreement from disposing of or using said information stop Fourteen with reference to article eighteen of the agreement it is understood and agreed that said article shall apply to claims of patents and to allowed claims of patent applications of third parties which dominate claims of any quote licensed applications unquote applicable to the quote licensed field unquote or patents issuing therefrom and shall apply to both existing and future license agreements with such third parties stop Montecatini and Union shall cooperate with one another in evaluating any dominant claim and in negotiating for future licenses with the owners of any dominant claims and shall give one another all possible assistance in regard thereto stop Union shall not however be required to furnish any evidence or make any disclosure which it may be prohibited from making under any existing agreements with the owners of any such dominating claims stop Negotiations for future licenses with the owners of dominating patents will be made by Montecatini or Union whichever in each particular case is most likely to obtain the most favorable terms stop In the interest of time suggest you prepare the contracts in final form to cover both polypropylene and polystyrene and submit for our approval stop Your prompt and courteous cooperation greatly appreciated - MURPHY

MONTECATINI
Settore Progetti e Studi

Sede, 30 Luglio 1958.

RICHIESTA U.C.C.

Nel punto 1) della bozza di lettera presentataci in occasione delle ultime trattative a Milano da U.C.C., è chiesto se fra i polipropileni Montecatini vi sia almeno un tipo avente stiffness (la definizione di stiffness = che letteralmente significa rigidità o compattezza = è data nell'allegato C della detta lettera) di almeno 560 ÷ 700 kg/cm2, e un altro con almeno 1270 kg/cm2; inoltre, essi devono dare un allungamento inferiore al 10% dopo 1000 h continue a 60°C, con sollecitazioni rispettivamente di 70 e di 140 kg/cm2.

(Metodo a flessione)

Il tutto controllato su provini di 0,5x3,2x102 mm3, ritagliati da foglio calandrato.

Notasi che relativamente al punto 1) della lettera vi sono almeno tre deficienze di precisione :

(a) nella definizione di stiffness non si indica da quale carico iniziale si parte per incrementarlo del 10% al minuto.

(b) nella prova di allungamento per la durata di 1000 h a 60°C non si indica in quale atmosfera la prova debba essere fatta; si presume aria.

(c) nel definire le dimensioni del provino, non si indica in quale direzione esso debba essere tagliato rispetto alla direzione di laminazione del foglio; si presume parallelamente.

Nel rapporto del 26.VII di Castellanza non vi sono dati che possano essere rapportati alla stiffness. Sono indicati i risultati di prove di scorrimento a 60°C, e con carichi fino a 75 kg/cm2, ottenuti su un polipropilene 120/27, con durate fino a 250 h.

Con 75 kg/cm2, 60°C in aria, dopo 250 h, si ha un allungamento dell'8%; dall'estrapolazione delle curve risulta che per avere un allungamento inferiore al 10% dopo 1000 h, occorrerebbe applicare un carico inferiore a 50 kg/cm2. Siamo lontani dalle richieste U.C.C.

Per conseguenza, poichè le domande di U.C.C. sono indirizzo di ricerca di polimeri di alta rigidità, occorre

(a) selezionare qualità di polipropilene di peso molecolare elevato, e con minimo contenuto di polimeri amorfi;

(b) eseguire su queste le prove di stiffness e di scorrimento a caldo, avendo presenti i metodi e i risultati prospettati da U.C.C.

Or/sl.

Orsoni

MONTECATINI

SOCIETÀ GENERALE PER L'INDUSTRIA MINERARIA E CHIMICA
ANONIMA - CAPITALE VERSATO L. 84.000.000.000

MILANO

C. C. POSTALE: 3/3711
CAM. DI COMM.: 524
CASELLA POSTALE: 3596

TELEFONI: 6333 - 6334
TELEFONI INTERURBANI
CHIEDERE: GABBRO - MILANO
TELEGRAMMI: GABBROPROGETTI

SETTORE PROGETTI E STUDI

MILANO
VIA F. TURATI, 18

1189 A

19 Giugno 1956.

Preg.mo Signore
Prof. Giulio Natta
Istituto di Chimica Industriale
Politecnico di
Milano.

Pregiatissimo Professore,

rimetto i testi delle risposte che potremmo dare ai questionari predisposti da UCC sui tre polimeri.

1. Polipropilene.
   E' il questionario più facile e al quale è possibile rispondere in modo più completo.

2. Polibutilene-1.
   E' stato risposto in parte dall'Istituto Donegani, in parte da Castellanza. Alla domanda No. 13, di carattere in parte teorico, potrà rispondere più opportunamente Lei.

3. Polistirolo.
   Qui abbiamo dovuto essere generici nelle risposte ad alcune domande, tanto più che per ora dobbiamo evitare accenni al contenuto del Brevetto V.92 del 19.X.1955 (Regolazione del peso molecolare mediante idrogeno) e all'U.63 d del 24.II.1956 (Catalizzatori speciali). Ferrara sta lavorando per sperimentare un processo risultante dai due brevetti suddetti, allo scopo di confermare la possibilità di ottenere un polimero ad alto grado di isotassia e con pesi molecolari sufficientemente bassi.

Dal complesso delle risposte date, abbiamo ritenuto di poter affermare a UCC che noi, al momento voluto, risponderemo alle domande dei questionari. Naturalmente, per ora queste risposte restano riservatamente fra noi.

Coi migliori auguri e saluti :

Orsoni

All.
Or/sl.

MOD. SEPS 1 (A4) - 6000 - 3/56

Domande

25.5.1956

Polipropilene plastici - Questionario Union

SCHEDULE C

INFORMATION TO BE DISCLOSED UNDER ARTICLE III.1(d)

1. How much polymer solubile in boiling heptane is made along with the isotactic polymer?

2. What is the density of the isotactic polymer?

3. Can the polymerization be directed to produce high molecular weight amorphous polymer without the isotactic polymer?

4. Is the clarity of molded articles comparable to that of molded articles of polystyrene or polymethylmethacrylate?

5. Can the isotactic polymer be stabilized so that it is satisfactory for outdoor use?

6. Do the best stabilizers hurt color or clarity of molded articles?

7. Are purity requirements on monomer and diluent about the same as for Ziegler ethylene polymerization?

8. How does the catalyst productivity compare with that of the Ziegler Polyethylene process?

9. Can catalyst residues be removed as easily and as completely as is the case with Ziegler polyethylene process?

10. Can the polymerization be controlled to produce any desired molecular weight polypropylene?

Risposta.

POLIPROPILENE QUESTIONARIO UNION

(Bozza da sottoporre al Chiar.mo Prof.Natta)

1) Assieme al polimero isotattico si forma dal 10 al 20% di polimero solubile in eptano bollente.

2) La densità del polipropilene dopo estrazione con eptano è di 0,92.

3) Non è mai stata tentata la produzione di polimero amorfo privo di polimero isotattico.

4) Gli articoli stampati in polipropilene sono traslucidi come quelli di polietilene.

5) Il polipropilene può essere stabilizzato fino ad avere un comportamento uguale a quello del polietilene stabilizzato per usi all'aperto.

6) I migliori stabilizzanti imbruniscono leggermente il prodotto.

7) Le caratteristiche di purezza del propilene e del solvente devono essere analoghe a quelle richieste per polimerizzare l'etilene secondo Ziegler.

8) Per 1 gr di catalizzatore totale (somma dei due componenti) si possono ottenere agevolmente 150/170 gr di polimero; in buone condizioni di purezza del propilene e del solvente si può arrivare a sorpassare i 200 gr per grammo.

9) I residui del catalizzatore possono essere rimossi facilmente e completamente come nel caso del polietilene Ziegler.

10) Si può regolare agevolmente il peso molecolare da circa 30.000 fino a circa 300.000 .

18/6/56

Telegramma - Questionario Union sui 3 polimeri

COPIA

UCC

(ricevuto copia 25/5/56)

Domande.

22/V/56 LT JJ MURPHY FRANKFURTER HOF
FRANKFURT

ISOTACTIC POLYBUTENE-1 FOR PLASTICS 1 HOW MUCH POLYMER SOLUBLE IN BOILING HEPTANE IS MADE ALONG WITH THE ISOTACTIC POLYMER ? 2 CAN THE POLYMERIZATION BE DIRECTED TO PRODUCE HIGH MOLECULAR WEIGHT AMORPHOUS POLYMER WITHOUT THE ISOTACTIC POLYMER 3 WHAT IS KNOWN ABOUT MOLECULAR WEIGHT DISTRIBUTION 4 HOW DOES CLARITY OF THE MOLDED ARTICLES COMPARE TO THAT OF MOLDED ARTICLES OF POLYSTYRENE POLYMETHYLMETHACRYLATE AND POLYPROPYLENE 5 CAN THE ISOTACTIC POLYMER BE STABILIZED SO THAT IT IS SATISFACTORY FOR OUTDOOR USE 6 DO THE BEST STABILIZERS HURT COLOR OR CLARITY OF MOLDED ARTICLES 7 ARE PURITY REQUIREMENTS ON MONOMER AND DILUENT ABOUT THE SAME AS FOR ZIEGLER ETHYLENE POLYMERIZATION 8 HOW DOES THE CATALYST PRODUCTIVIT COMPARE WITH THAT OF THE ZIEGLER POLYETHYLENE PROCESS 9 CAN CATALYST RESIDUES BE REMOVED AS EASILY AND COMPLETELY AS IS THE CASE WITH THE ZIEGLER POLYETHYLENE PROCESS 10 CAN THE POLYMERIZATION BE CONTROLLED TO PRODUCE ANY DESIRED MOLECULAR WEIGHT POLYBUTENE 1 WHAT APPARENT ADVANTAGES DOES POLYBUTENE HAVE OVER ZIEGLER POLYETHYLENE E.G. STRESS RUPTURE 12 IN WHAT RESPECTS IS THE POLYBUTENE INFERIOR TO ZIEGLER POLYETHYLENE 13 IS POLYBUTENE MORE STABLE TO OXIDATION THAN POLYPROPYLENE IF SO WHY 14 WHAT USES DO YOU FORESEE FOR POLYBUTENE? 15 WHAT IS THE MEASURED DENSITY AND THEORETICAL CRYSTALLITE DENSITY OF ISOTACTIC POLYBUTENE 16 WHAT IS THE MAXIMUM STIFFNESS AT ROOM TEMPERATURE WHICH CAN BE OBTAINED FROM POLYBUTENE (USE ZIEGLER POLYETHYLENE AS A BASIS OF COMPARISON.) 17 IS POLYBUTENE BRITTLE AT LOW TEMPERATURE IF SO AT WHAT TEMPERATURE 18 WHATCOPOLYME ARE THERE OF INTEREST AND WHAT SPECIAL PROPERTIES DO THEY HAVE 19 WHAT SIZE SAMPLES CAN WE OBTAIN FOR EVALUATION AT LEAST ONE HUNDRED POUNDS WOULD BE MOST DESIRABLE BUT EVEN A FEW POUNDS WOULD BE USEFUL ONE HUNDRED GRAMS OR SO WOULD BE HELPFUL FOR LABORATORY EXAMINATIONS ISOTACTIC POLYSTYRENE FOR PLASTICS 1 HOW MUCH POLYMER SOLUBLE IN BOILING HEPTANE IS MADE ALONG WITH THE ISOTACTIC POLYMER

./

2 ARE PURITY REQUIREMENTS ON MONOMER AND DILUENT ABOUT THE SAME AS FOR ZIEGLER ETHYLENE POLYMERIZATION 3 HOW DOES THE CATALYST PRODUCTIVITY COMPARE WITH THAT OF THE ZIEGLER POLYETHYLENE PROCESS 4 CAN CATALYST RESIDUES BE REMOVED AS EASILY AND COMPLETELY AS IS THE CASE WITH THE ZIEGLER POLYETHYLENE PROCESS 5 CAN THE POLYMERIZATIC BE CONTROLLED TO PRODUCE ANY DESIRED MOLECULAR WEIGHT POLYSTYRENE 6 WHAT IS THE MAXIMUM USE TEMPERATURE 7 CAN THE POLYMER BE MOLDED IN CURRENTLY AVAILABEE INJECTION MACHINES OR EXTRUDED IN AVAILABLE EXTRUDERS 8 WHAT MAIN USES ARE FORESEEN 9 HOW DO THE MECHANICAL PROPERTIES DIFFER FROM AMORPHOUS POLYSTYRENE 10 WHAT IS THE SECOND ORDER TRANSITION TEMPERATURE 11 WHAT ARE THE GAS AND VAPOR TRANSMISSION CHARACTER ISTICS 12 HOW STABLE TO THERMAL AND OXIDATIVE EXPOSURE IS THE PRODUCT ARE THER KNOWN STABILIZERS IF SO WHICH ARE RECOMMENDED 13 CAN THE ISOTACTIC POLYMER BE STABILIZED SO THAT IS SATISFACTORY FOR OUTDOOR USE 14 DO THE BEST STABILIZERS HURT COLOR OR CLARITY OF MOLDED ARTICLE 15 WHAT IS THE MEASURED DENSITY AND THE THEORETICAL CRYSTALLITE DENSITY OF ISOTACTIC POLYSTYRENE 16 HOW DOES CLARITY OF THE MOLDED ARTICLES COMPARE WITH THAT OF MOLDED ARTICLES OF AMORPHOUS POLYSTYRENE OR POLYMETHYL METHACRYLATE 17 WHAT COPOLYMERS ARE THERE OF INTEREST WHAT SPECIAL PROPERTIES DO THEY HAVE 18 WHAT SIZE SAMPLES CAN WE OPTAIN FOR EVALUATION AT LEAST ONE HUNDRED POUNDS WOULD BE MOST DESIRABLE BUT EVEN A FEW POUNDS WOULD BE USEFUL ONE HUNDRED GRAMS OR SO WOULD BE HELPFUL FOR LABORATORY EXAMINATIONS .

BUTILENE-1,

RISPOSTE AL QUESTIONARIO DELLA "UNION CARBIDE AND CARBON"

RIGUARDANTE IL POLIBUTENE-1 ISOTATTICO

(Per alcune risposte riguardanti le proprietà meccaniche e le applicazioni di questo prodotto rimandiamo al Laboratorio Applicazioni Resine di Castellanza, il quale si è occupato di studiare il polibutene da tale punto di vista).

- - - - -

Risposte, Novara.

1) Quanto polimero solubile in n-eptano viene prodotto insieme con il polimero isotattico ?	Il polibutene-1 è completamente solubile in n-eptano; per separare approssimativamente la parte isotattica da quella atattica si usano perciò altri solventi: ad es. l'etere etilico. La parte insolubile in etere è in grande prevalenza isotattica e raggiunge il 70-80% del totale.
2) Può la polimerizzazione essere diretta ad ottenere polimero amorfo ad alto peso molecolare senza polimero isotattico ?	Impiegando opportuni catalizzatori si riesce a far sì che la parte amorfa del polimero abbia elevato peso molecolare (da 20.000 a 100.000). Non si è riusciti finora ad ottenere direttamente polimeri completamente amorfi, ma usando particolari accorgimenti si riesce a ridurre la parte isotattica a circa il 20% (determinata röntgenograficamente).
3) Cosa si conosce intorno alla distribuzione dei pesi molecolari ?	Lo studio della distribuzione dei pesi molecolari nel polibutilene-1 è ancora in corso. Esso è complicato dalla presenza di due tipi di polimero (isotattico e atattico) oltre che da catene miste (blocchi di isotattico alternati a blocchi di atattico) aventi proprietà assai diverse.

	La frazione di polimeri a bassissimo peso molecolare (dell'ordine delle centinaia) ancora liquidi a temperatura ambiente varia tra lo 0,5% ed il 6% a seconda delle condizioni di polimerizzazione.
4) Com'è la trasparenza (clarity) degli articoli stampati paragonata a quella degli articoli stampati di polistirolo, polimetacrilato di metile e polipropilene ?	L.A.R. Castellanza
5) Può il polimero isotattico essere stabilizzato in modo che esso sia soddisfacente per usi all'aperto ?	L.A.R. Castellanza
6) I migliori stabilizzanti recano danno al colore o alla trasparenza (clarity) degli articoli stampati ?	L.A.R. Castellanza
7) I requisiti di purezza del monomero e i diluenti sono pressapoco gli stessi che per la polimerizzazione Ziegler dell'etilene ?	I requisiti di purezza dal punto di vista dell'umidità, dell'aria, di tracce di alcool, ecc., sono gli stessi che per il politene Ziegler. Diluenti inerti rispetto al catalizzatore possono essere sopportati anche in forti quantità per quanto naturalmente complichino la condotta del processo di polimerizzazione. La presenza di altre olefine polimerizzabili con lo stesso catalizzatore non impedisce la polimerizzazione, ma modifica le caratteristiche del polimero ottenuto.

8) Qual'è la produttività del catalizzatore paragonata con quella del processo per il polietilene Ziegler ?	E' più bassa: sinora si è raggiunta una produttività massima di 40-50 gr di polibutene/gr di catalizzatore.
9) I residui del catalizzatore possono essere rimossi così facilmente e completamente come nel caso del processo per il polietilene Ziegler ?	Quasi altrettanto facilmente. Si ottengono nel polimero residui in ceneri dell'ordine del 0,1-0,2%.
10) Può la polimerizzazione essere controllata in modo da produrre polibutene di qualsiasi peso molecolare desiderato ?	Si, nel campo dei pesi molecolari ottenibili (da poche centinaia fino ad oltre 500.000).
11) Quali apparenti vantaggi ha il polibutene nei confronti del polietilene Ziegler, per esempio nella sollecitazione a rottura ?	L.A.R. Castellanza
12) Sotto quali aspetti il polibutene è inferiore al polietilene Ziegler ?	L.A.R. Castellanza
13) Il polibutene è più stabile all'ossidazione del propilene ? e se è così perché ?	L.A.R. Castellanza
14) Quali usi prevedete per il polibutene ?	LAR Castellanza

15) Qual'è la densità misurata e la densità teorica dei cristalliti del polibutene isotattico ?	L.A.R. Castellanza
16) Qual'è la massima rigidezza (stiffness) a temperatura ambiente che può essere ottenuta dal polibutene ? (usare il polietilene Ziegler come base di paragone).	L.A.R. Castellanza
17) E' il polibutene fragile a bassa temperatura? e se così a quale temperatura ?	L.A.R. Castellanza
18) Quali copolimeri presentano interesse e quali speciali proprietà essi hanno ?	I copolimeri del butene-1 sono ancora in fase di studio. Assai interessanti si presentano i copolimeri del butene-1 con l'etilene e con il propilene. Essi sono completamente amorfi e sono dotati di notevoli proprietà elastiche.
19) Qual'è la quantità di prodotto che possiamo ottenere per valutarlo ? Un campione di un centinaio di libbre sarebbe il più desiderabile, ma anche poche libbre sarebbero utili; un campione di un centinaio di grammi sarebbe di aiuto per gli esami di laboratorio.	

Risposta.

LABORATORIO APPLICAZIONI RESINE

CASTELLANZA

18 Giugno 1956

[redacted]

Sezione Polimeri Isotattici

GG/pv

POLIBUTILENE ISOTATTICO

(4) 1) Gli articoli stampati in polibutilene isotattico sono translucidi quanto il polietilene e il polipropilene. Non sono quindi confrontabili con i materiali trasparenti, quali il polistirolo e il polimetacrilato di metile.

(5) 2) Sotto l'azione della luce solare diretta il polibutilene subisce una degradazione, che è rallentata ma non impedita dalla presenza di antiossidante.
La migliore protezione si raggiunge, analogamente a quanto si fa per il polietilene, con l'incorporamento di circa il 2% di carbon black.

(6) 3) E' ovvio che il carbon black rende opaco e nero il manufatto.
Tra gli antiossidanti usati contro l'azione termica vi sono alcuni che non hanno una sensibile influenza sul colore e sulla trasparenza.
E' sufficiente 0,1 - 0,2% di antiossidante per proteggere il polibutilene nella lavorazione ad alta temperatura.

(7) 4) Il polibutilene isotattico non è direttamente confrontabile con il polietilene Ziegler, in quanto i due materiali hanno un comportamento differente nella sollecitazione alla rottura.
La curva trazione-allungamento del polibutilene è tipica di un elastomero ed è caratterizzata da un basso modulo e da un elevato carico di rottura, mentre la curva del polietilene Ziegler è quella di materiale plastico rigido.
Come risulta dalle curve trazione-allungamento allegate nella relazione L.A.R. n° 7/56 Sezione Polimeri Isotattici del 22.5.56, nel polibutilene normale si ha un carico di snervamento di circa 60 kg/cm2 contro un carico di rottura di 200 kg/cm2. Questi valori salgono rispettivamente a circa 125 kg/cm2 e 360 kg/cm2 nel polibutilene arricchito in frazione cristallina.

Nel polietilene Ziegler il carico di osservamento e quello di rottura sono all'incirca nello stesso ordine (180 - 220 kg/cm2).

(12) 5) E' evidente da quanto detto in 4) che in confronto col polietilene Ziegler che è un materiale rigido, il polibutilene isotattico è inferiore nelle proprietà meccaniche (mudulo di elasticità, rigidità flessionale, durezza) e nel punto di rammollimento Vicat.

Nella seguente tabella sono riportate le principali proprietà fisiche dei due polimeri.

		Polibutilene Isotattico	Polietilene Ziegler
- Carico rottura	kg/cm2	150 - 360	180 - 220
- Allungamento alla rottura	%	180 - 300	300 - 800
- Rigidità flessionale (stiffness)	kg/cm2	400 - 1600	4000 - 6000
- Punto rammollimento Vicat (1 kg di carico)	°C	92 - 120	115 - 127
- Punto di infragilimento (Brittle Point)	°C	da - 4 a - 20	- 65

Il polibutilene ha proprietà elettriche e chimiche (resistenza agli acidi, basi, di minerali e vegetali) pari a quello del polietilene Ziegler. A differenza di quest'ultimo resiste all'acido nitrico concentrato (94 %).

(13) 6) La stabilità alla ossidazione è pari o leggermente migliore a quella del polipropilene.

(14) 7) Col tipo arricchito in frazione cristallina:

a) film

b) rivestimenti isolanti per cavi elettrici

c) tubi flessibili

d) stampati ad iniezione

Col tipo normale:

a) foglie caricate per rivestimenti anticorrosivi e impermeabilizzanti

b) laminati con carta, alluminio, tessuti

c) modificazione di resine, cere paraffine, bitumi

(15) 8) Densità misurata = 0,915

Densità teorica = 0,960

9) Nel tipo normale la massima rigidità flessionale (stiffness) è circa 500 kg/cm2.

(16) Nel tipo arricchito in frazione cristallina si arriva a 1600 - 1700 kg/cm2.

Nel polietilene Ziegler la rigidità flessionale è 4000 - 6000 kg/cm2

(17) 10) Il punto di infragilimento (Brittle Point) varia da - 4 a - 20°C.

Bozza destinata al Prof. Natta per commento. Risposte -

QUESTIONARIO UNION CARBIDE AND CARBON

STIROLO.

1) Quanto polimero solubile in eptano bollente si forma assieme al polimero isotattico?

? = Nella polimerizzazione dello stirolo secondo il brevetto U.63/b in solventi aromatici il 30% del polimero totale è estraibile con acetone bollente; l'estraibile con eptano è al massimo pari a quella dell'acetone.

2) I requisiti di purezza del monomero e del solvente sono simili a quelli necessari per la polimerizzazione dell'etilene secondo Ziegler?

= Le caratteristiche dello stirolo tecnico in commercio sono sufficienti; la purezza dei solventi deve essere all'incirca uguale a quella necessaria per la polimerizzazione dell'etilene.

3) La produttività (resa) del catalizzatore è paragonabile con quella del processo Ziegler di polimerizzazione dell'etilene?

= Operando secondo gli esempi del brevetto U.63/b, la produttività è di 5-8 gr di polimero isotattico per grammo di catalizzatore complessivo.

4) I residui del catalizzatore possono essere allontanati facilmente e completamente come nel caso della polimerizzazione dell'etilene Ziegler?

= La depurazione del polimero dai residui di catalizzatore è altrettanto facile e completa come nel caso del polietilene.

5) La polimerizzazione può essere controllata in modo da produrre qualsiasi peso molecolare si desideri?

= Nel brevetto U.63/b non è prevista la tecnica per la regolazione del peso molecolare.

./.

6) Qual'è la massima temperatura adoperabile?

per usi

= Non è stato accertato un limite massimo di temperatura per la polimerizzazione.

7) Il polimero può essere stampato nelle comuni macchine ad iniezione?

= Per pesi molecolari elevati riteniamo che occorrano macchine speciali.

8) Quali sono i principali usi previsti?

= Fibre, film e oggetti stampati.

9) Come differiscono le proprietà meccaniche da quelle del polistirene e polistirolo amorfo?

= Non vi sono dati sul polimero isotattico puro in confronto con il polistirolo normale.

10) Qual'è la temperatura di transizione di second'ordine?

= La temperatura di transizione di second'ordine è simile a quella del polistirolo normale.

11) Quali sono le caratteristiche di permeabilità ai gas e vapor d'acqua?

= Non è stata determinata la permeabilità ai gas e vapori.

12) Qual'è la stabilità al calore e alla ossidazione del prodotto e vi sono stabilizzatori e quali sono?

13) Il polimero isotattico può essere stabilizzato in modo soddisfacente per esposizione all'aria aperta?

14) I migliori stabilizzatori rovinano il colore o la trasparenza negli articoli stampati?

= Il polistirolo isotattico non mostra una speciale instabilità al calore e alla luce nè particolare tendenza all'ossidazione; pertanto non si è ravvisata finora la necessità di ricorrere a stabilizzanti.

./.

15) Qual'è la densità misurata e quale la densità teorica dei cristalliti del polistirolo isotattico?

= Il peso specifico è di 1.08 a 20°; densità teorica dei cristalliti è di 1.12 .

16) La trasparenza degli articoli stampati è paragonabile a quella degli articoli stampati con polistirolo amorfo o con polimetil-metacrilato?

(?)

= I pezzi stampati con adatta tecnica possono essere trasparenti come quelli ottenuti da polistirolo normale.

17) Quali sono i copolimeri di qualche interesse e che speciali proprietà essi hanno?

= Nei brevetti in questione è solo accennata la possibilità di ottenere copolimeri con lo stirolo.

Le risposte al questionario della Carbide and Carbon per il polistirolo isotattico sono state redatte limitatamente al contenuto del brevetto U.63/b : non è stato quindi tenuto conto dei brevetti e delle conoscenze acquisite in seguito come la regolazione del peso molecolare con idrogeno o con catalizzatori speciali - e neppure dei procedimenti ad alta resa in polimero isotattico.

Volendo estendere le risposte allo stato attuale cioè includendo i brevetti U.92 (19/10/55), U.63/d (24/2/56), le risposte 1, 3, 5, verrebbero modificate come segue :

1) L'estraibile eptano può essere ridotto praticamente a zero.

3) In laboratorio si sono ottenute produttività fino a 100 gr per grammo e forse si potrà aumentare.

./.

5) La regolazione del peso molecolare è possibile entro certi limiti operando in presenza di idrogeno o variando le condizioni di lavoro (concentrazione di catalizzatore e di monomero, temperatura, rapporti reagenti catalitici) .

15 Giugno 1956

UNION CARBIDE AND CARBON CORPORATION
30 EAST FORTY-SECOND STREET
NEW YORK 17, N. Y.

AUGUSTUS B. KINZEL
VICE PRESIDENT-RESEARCH

June 7, 1956

Dr. Giulio Natta
Hotel Pierre
Fifth Ave. & 61st Street
New York City, N. Y.

Dear Dr. Natta:

It would be a great pleasure if you could join me for lunch tomorrow, preferably at 12:30 but if some other time is more convenient to you, this can easily be arranged. Dr. Gillette has told me of his many interesting discussions with you and of course your fame is known to all of us. To this luncheon I am also inviting Directors of our Chemicals and Plastics Research Laboratories and Dr. Tschamler, now with Dr. Gillette, and a student of Prof. Mark. Of course I will be more than glad to have any associate that you may care to bring along. Many of us speak French so there should be no language difficulty.

I appreciate that your time is in great demand but do hope that you can meet with us before going to the Gordon Conference.

In view of the short time before tomorrow noon, would you please arrange to have word sent to my office as to whether you will be free to join us? That office is Room 1826 at the above address and that is where we would meet before going to lunch. I do hope you can come.

Sincerely,

Augustus Kinzel

ABK:CHN

Telephone: MU 7-8000

July 31, 1956

Mr. Augustus B. Kinzel, Vice President
Research - Union Carbide and Carbon
30 East Forty-second Street
NEW YORK 17 - N.Y. - USA

Dear Mr. Kinzel,

I am very sorry that my busy trip through the States did not permit me to write to you before my coming back to Italy. I wish to thank you very much for your kind invitation and for the pleasant luncheon we had together.

I hope to have soon the pleasure to see you again in Italy or in the States.

With my best personal regards, I remain,

Truly yours,

Giulio Natta

Copia per Sig. Prof. G. Natta

(copia originale spedita a sig. Murphy 24.6-56)

BY AIR MAIL-SPECIAL DELIVERY

May 31, 1956

Mr. John J. MURPHY
c/o Union Carbide & Carbon Corp.
30 East 42nd Street
NEW YORK, N.Y.
(U.S.A.)

dV/AMF/mm

Dear Mr. Murphy,

Re: Negotiations on polypropylene, polybutene-1 and polystyrene plastics -

As agreed in Milan on the 25th inst., we send you a draft definition of the "License Field" of the proposed Agreement between our two Companies, enlarged to include not only polypropylene but also polybutene-1 and polystyrene.+ You will notice that in the definition of "pool process" the words "purification of monomers" have been omitted, since no such operations have been claimed in any listed pool applications. Of course in giving the definition of the licensed field point 5/ /d has been maintained.

We also enclose a draft of a letter that could be sent to you to give you a licence for producing "authorised products" also if they have less than 2000 m.w.; and of another letter to confirm our willingness to give licences under each and all Montecatini U.S. and Canadian patents (if any) covering polymerisation processes and catalysts that may be employed to produce the "authorised products".

Very truly yours.

"MONTECATINI"

encls.

original by air mail special delivery
copy by air mail two days later

+ This is the field that will be applied in case you decide for combinations A/4 or A/5 of our letter of yesterday.

May 31, 1956

Draft of a letter be sent by Montecatini to Union concerning licences under Montecatini's patented processes, if any, for the manufacture of products claimed in "Pool Applications".

Dear Sirs,

We refer to the enquiries that you have made in the course of the negotiations, and are pleased to inform you that in addition to the pool lisence provided for in the Agreement between our Companies on plastics from .... polymers, we are ready to discuss with you an agreement to grant you a non-exclusive licence, without any down payments but otherwise under the same conditions of the main pool licence agreement, under each and all Montecatini's U.S, and Canadian applications, if any, filed not later than December 31, 1956, and covering all polymerization processes and catalysts whereby said olefines may be transformed into authorised polymers, products and compositions claimed in "Pool applications" as defined in said agreement.

Very truly yours.

(MONTECATINI)

May 31, 1956

Draft of a letter to be sent by Montecatini to Union enlarging the licensed field to cover also polymers having molecular weight below 2000.

Dear Sirs,

With reference to the enquiries you have made in the course of the negotiations about the possibility of lowering the limit of 2000 for the molecular weight of the products considered under Article I, 4.(a) and 5, β /(a) and (b) of the Agreement between our Companies on plastics from ..... polymers, we are pleased to inform you that in partical derogation of the provisions of the said Article, we are ready to allow you without any down payment, but otherwise under the conditions of the said Agreement to produce, transform and use the products considered in Article I, 4, (a) and 5, β, (a) and (b) having a molecular weight below 2000; provided that said products and the process for obtaining and transforming them fall under at least one claim of the "Pool Applications" as defined in the said Agreement.

Very truly yours.

(MONTECATINI)

May 31, 1956
~~May 29, 1956~~

LICENCE FIELD OF THE MONTECATINI-UNION POLYPROPYLENE, POLYBUTENE and POLYSTYRENE PLASTICS AGREEMENT.

4. The term "Pool Process" shall mean:

(a) any and all processes, disclosed by "Pool Applications" as listed in schedules A and B in which propylene, butene-1 and styrene are polymerized each by itself or each with one or both of the others, and/or with ethylene and/or with one or more other alifatic monoolefinic hydrocarbons in the presence of a catalyst and/or of a promoter to produce a product containing at least 50 mol% combined propylene or butene-1 or styrene, or at least 50 mol% of a combination of any two or of all of said three olefins and having a molecular weight above 2000, and shall mean any catalyst, and/or promoter disclosed by listed "Pool Applications" suitable for use in carrying out any of said disclosed processes, as well as any disclosed process or method of separating, purifying or stabilizing said products disclosed by listed "Pool applications". The "Pool Process" shall also include manufacture and preparation of said catalyst and/or promoters as disclosed by listed "Pool applications" whenever used for producing said products. The term "Pool Process" shall also include any products made by the practice of listed "Pool Applications" as defined and limited in this Agreement and any composition containing said products including resins and molding materials with the exclusion of elastomeric products and compositions. It shall also include foils, film, tapes,

./.

tubes, and similar articles made from any of said products or any of said compositions and the processes for their manufacture as disclosed by listed "Pool Applications"

(b) the term "Pool Process" shall also mean any claim of the "Pool Applications" as defined under 2, (c) provided that said claims are applicable to the "Licensed Field" as defined under paragraph 5/β

The term "Pool Process" will therefore not include textile fibres and elastomers as defined in section 8 and 9 of this article, their manufacture, and uses.

5) The term "Licensed Field" shall mean:

α - The "Pool Process" as defined under 4 (a),

β - Any process or processes whereby through the use of all catalysts and/or promoters, presenting metal alkyl linkages as disclosed by listed "Pool Applications" one may produce

(a) propylene, butene-1 and styrene polymers having molecular weight above 2000 and a linear structure with substantially no branchings longer than CH_3-, CH_3-CH_2- and C_6H_5- respectively

and/or

(b) mixed polymers of propylene, butene-1 and styrene with ethylene and/or with any other olefinic hydrocarbon $CH_2 = CHR$, R being a saturated aliphatic radical, said mixed polymers containing at least 50 mol% combined propylene or butene-1 or styrene, or at least 50 mol% of a combination of any two or of all said three olefins having a molecular weight above 2000 and a linear structure with substantially no branchings longer than CH_3, CH_3-CH_2 and C_6H_5 when no hydrocarbons higher than propylene or butene-1 or styrene respectively are present in the monomer mixture, and substantially no branchings longer than R, R being the saturated aliphatic radical with the highest number of carbon atoms present in the hydrocarbons constituting the monomer mixture.

The "Licensed Field" shall also include:

(c) all said catalysts and/or promoters suitable for use in the above defined processes and the processes used in their preparation, provided such catalysts and/or promoters are employed in the polymerization process as defined under 5/β

(d) processes for purifying the monomers provided such purified monomers are employed in the polymerization processes as defined under 5/β.

(e) any apparatus suitable for carrying out any of said processes as defined under 5/β

The "Licensed Field" shall also include:

(f) all polymer products for use in the plastic field as obtained by the processes defined under 5/β, as well as any process or method for separating, purifying and stabilizing said products,

(g) any composition for use in the plastic field made out of or containing such polymer products as defined under 5/β such as resins and molding materials (with the exclusion of elastomeric compositions, or compositions apt to be transformed into elastomeric products),

(h) articles made out of or containing such products and compositions, as defined under 5/β/f and 5/β/g, including films, foils, sheeting, tapes and other similar products

(i) any process and/or method for improving the characteristics of said products and compositions as defined in 5/β as well as improved processes for transforming them into films, sheeting, tapes and other similar articles.

./.

Therefore the processes of transforming the polymeric products and compositions into textile fibres and elastomeric products, fibers and elastomers themselves and their uses are in no case included in the "Licensed Field" of this Agreement.

Copia per il Signor Prof. G. NATTA

May 30, 1956

Mr. John MURPHY
c/o Union Carbide & Carbon Corp.
30 East 42nd Street
NEW YORK, N.Y.
(U.S.A.)

dV/AMF/ma

Dear Mr. Murphy,

re Negotiations on polypropylene, polybutene-1 and polystyrene plastics, and polypropylene fibers (105/54) -

While we are waiting to receive Mr. Lyon's letter, and we are already at work to meet the deadlines that we have agreed upon at Milan, we wish to write to you to sum up concisely the main terms under which we are offering Union the various alternative "packages" that have been discussed during our conversations:

A) Montecatini offers which will be valid until June 30, 1956 for the following combinations:

1) Pool licence under the polypropylene patents only, limited to the plastics field:

(a) Option payment:	\$75,000 (not creditable against future royalties)
Down payment:	\$1,000,000 (50% creditable against half of the running royalties),

or, alternatively

(b) Option payment:	as above
Down payment:	\$1,500,000 (100% creditable against half of the running royalties).

Running royalties: in both cases 5% on the net sales price of the polymer sold as such, or 3½% on the net sales price of shaped articles.

./.

2) Pool licence under the polypropylene and poly-butene-1 patents only, limited to the plastics field:

Option payment: $150,000 (not creditable)

Down payment: $1,500,000 or $2,250,000 respectively at the conditions stated under 1) (a) 1) (b)

Running royalties: as under 1).

3) Pool licence under the polypropylene and polystyrene patents only, limited to the plastics field.

Same terms as under 2).

4) Pool licence under the polypropylene, polybutene-1 and polystyrene patents, limited to the plastics field.

Option payment: $200,000 (not creditable)

Down payment: $2,000,000 or $3,000,000 respectively at the conditions stated under 1) (a) and 1) (b)

Running royalties: as under 1).

5) Pool licence for any of the foregoing combinations, plus Montecatini's know-how on polypropylene only:

$500,000 (not creditable) in addition to the payments provided for respectively under 1), or 2), or 3) or 4).

6) Pool licence under the polybutene-1 patents only, limited to the plastics field:

Option payment: $75,000 (not creditable)

Down payment: $750,000 (50% creditable against half of the running royalties) or alternatively $1,125,000 (100% creditable against half of the running royalties).

Running royalties: as under 1).

7) Pool licence under the polystyrene patents only, limited to the plastics field:

as under 6).

./.

8) Pool licence under the polybutene-1 and polystyrene patents, limited to the plastics field:

Option payment: $150,000 (not creditable)

Down payment: $1,500,000 or $2,250,000 respectively at the conditions stated under 6).

Running royalties: as under 1).

9) As to the pool and Montecatini patents covering the manufacture, starting from the monomer, of polypropylene fibers, we have undertaken to offer Union a licence when we are ready, i.e. presumably starting from October 1956, provided Union enters with us into an agreement for one at least of the above combinations.

Montecatini's terms will be kept within the following limits:

Down payment: not less than $1,000,000 nor more than $1,500,000 (50% creditable against 50% of the running royalties)

Running royalties (on the sales price of the fiber after the first reeling or other collecting operation after all the drawing operations): not less than 5% nor more than 7%,

and a reasonable option payment still to be fixed.

B) Duration of the option period:

1) Polypropylene:

As regards combination A) 1) and the polypropylene part only of the combinations A) 2), 3), 4) and 5), the option period in which Union may decide whether to execute or not a final Agreement will last two months starting from the date in which Union has received all the informations (limited to the polypropylene field) listed under Article III, 1, (a), (b), (c) and (d) of the Montecatini-Union Option Agreement.

The starting date of the said option period should be easily fixed with regard to the Montecatini activities provided for under III, 1, (a) (patent specifications) (b) (description of the preferred techniques) and (d) (samples).

As to the performance in the Montecatini laboratories of the processes for the polymerization of propylene, which is provided for under (c) in the same article, it will take place immediately on Union's request as soon as Montecatini has received the option payment. These experiments may be completed in about a week.

: May 30, 1956.

Anyway, for the sole purpose of determining the starting date of the option period, the obligations provided for under (c) will be considered as validly performed, as to the fifteenth day after the date of receipt by Montecatini of the option payment.

2) Poly-butene-1 and/or polystyrene.

As to combinations A) 6), 7) and 8), and the part concerning polybutene-1 and/or polystyrene in combinations A) 2), 3), 4) and 5), the option period within which Union may decide whether to execute or not a final Agreement will last four months starting from the date in which Union has received in the U.S. all the informations (limited however to the field of the said polymers) listed under Article III, 1, (a), (b), (c) and (d) of the Montecatini-Union Option Agreement.

Also in this case, there should arise no doubt as to the starting date of the option period as regards the obligations provided for under points (a), (b) and (d) of Article III, 1 of the said Agreement.

As regards however the performance in the Montecatini laboratories of the polymerization processes, which is provided for under point (c) of the same Article, it will take place immediately on Union's request, as soon as Montecatini has received the option payment. These experiments may be completed in about one week for either of the polymers, or in about two weeks for both.

Anyway, for the sole purpose of determining the starting date of the four months option period, the obligations provided for under (c) will be considered as validly performed as of the fifteenth day after the date of receipt by Montecatini of the option payment, as far as the combinations A) 6) or 7) or 8) are concerned: or as of the thirtieth day after receipt by Montecatini of the option payment in the cases stated under A) 2) or 3) or 4) or 5).

Sincerely yours

"MONTECATINI"
(Ing.Orsoni - Ing.de Varda)

original by air mail special delivery
copy by air mail two days later

dV/mm

30 Maggio 1956

Vit! Am
Pol. ost.

URGENTISSIMA

Ing. Piero GIUSTINIANI

e p.c. Ing. ORSONI
Prof. NATTA

Oggetto: Licenza Union isotattici -

Le trasmetto per cortese benestare bozza di una lettera per Mr. Murphy a cui sono allegate:

1) bozza di lettera aggiuntiva al contratto di opzione per quanto riguarda la licenza che noi siamo disposti a concedere sui polimeri di peso molecolare inferiore a 2000;

2) bozza di lettera circa la licenza sugli eventuali brevetti USA e Canadesi Montecatini che coprano processi per ottenere prodotti dell'accordo;

3) bozza della nuova definizione del "Licence Field" allargato per comprendervi anche il polistirolo e il poli-α-butene.

Con ossequio,

G de Varda

4 allegati

P.S. In base agli impegni presi con la Union questi documenti dovrebbero venire spediti entro domani.

P.S. In base agli impegni presi con la Union questi documenti dovrebbero venire spediti entro domani

BOZZA

May 30, 1956

Mr. John MURPHY
c/o Union Carbide & Carbon Corporation
30 East 42nd Street
NEW YORK, N.Y.
(U.S.A.)

Dear Mr. Murphy,

Re: Negotiations on polypropylene, polybutene-1 and polystyrene plastics, and polypropylene fibers (105/54) -

As agreed in Milan on the 25th inst., I send you a draft definition of the "Licensed Field" of the proposed Agreement between our two Companies, enlarged to include polybutene-1 and polystyrene.

I also enclose a draft of a letter that could be sent to you to give you a licence for producing "authorised products" also if they have less than 2000 m.w.; and of another letter to confirm our willingness to give licences under each and all Montecatini U.S. and Canadian patents (if any) covering polymerisation processes and catalysts that may be employed to produce the "authorised products".

Very truly yours.

Encls.

May 30, 1956

Draft of a letter to be sent by Montecatini to Union concerning licences under Montecatini's patented processes, if any, for the manufacture of products claimed in "Pool applications".

Dear Sirs,

We refer to the enquiries that you have made in the course of the negotiations, and are pleased to inform you that in addition to the pool licence provided for in the Agreement between our Companies on plastics from .... polymers, we are ready to discuss with you an agreement to grant you a non-exclusive licence (without any down payments but otherwise under the same conditions of the main pool licence agreement) under each and all Montecatini's U.S. and Canadian applications (if any), filed not later than January 1, 1960, and covering all polymerization processes and catalysts whereby said olefines may be transformed into authorised polymers, products and compositions claimed in "Pool applications".

Very truly yours.

May 30, 1956

Draft of a letter to be sent by Montecatini to Union enlarging the licensed field to cover also polymers having molecular weight below 2000.

Dear Sirs,

with reference to your enquiries about the possibility of lowering the limit of 2000 for the molecular weight of the products considered under Article I, 4.(a) and 5., β -(a) and (b) of the Agreement between our two Companies on plastics from .... polymers, we are pleased to inform you that in partial derogation of the provisions of the said Article, we are ready to allow you without any down payment, but otherwise under the conditions of the said Agreement to produce, transform and use the products considered in Article I, 4, (a) and 5, β, (a) and (b) having an average molecular weight below 2000; provided that said products and the process for obtaining and transforming them fall under at least one claim of the "Pool Applications" as defined in the said Agreement.

Very truly yours.

May 29, 1956

LICENCE FIELD OF THE MONTECATINI-UNION POLYPROPYLENE, POLYBUTENE and POLYSTYRENE PLASTICS AGREEMENT.

4. The term "Pool Process" shall mean:

(a) any and all processes, disclosed by "Pool Applications" as listed in schedules A and B in which propylene, butene-1 and styrene are polymerized each by itself or each with one or both of the others, and/or with ethylene and/or with one or more other alifatic monoolefinic hydrocarbons in the presence of a catalyst and/or of a promoter to produce a product containing at least 50 mol% combined propylene or butene-1 or styrene, or at least 50 mol% of a combination of any two or of all of said three olefins and having a molecular weight above 2000, and shall mean any catalyst, and/or promoter disclosed by listed "Pool Applications" suitable for use in carrying out any of said disclosed processes, as well as any disclosed process or method of separating, purifying or stabilizing said products disclosed by listed "Pool applications". The "Pool Process" shall also include ~~purification of monomers and~~ manufacture and preparation of said catalyst and/or promoters as disclosed by listed "Pool applications" whenever used for producing said products. The term "Pool Process" shall also include any products made by the practice of listed "Pool Applications" as defined and limited in this Agreement and any composition containing said products including resins and molding materials with the exclusion of elastomeric products and compositions. It shall also include foils, film, tapes,

./.

(any elastomer!)

tubes, and similar articles made from any of said products or any of said compositions and the processes for their manufacture as disclosed by listed "Pool Applications"

(b) the term "Pool Process" shall also mean any claim of the "Pool Applications" as defined under 2,(c) provided that said claims are applicable to the "Licensed Field" as defined under paragraph 5/β

The term "Pool Process" will therefore not include textile fibres and elastomers as defined in section 8 and 9 of this article, their manufacture, and uses.

5) The term "Licensed Field" shall mean:

α- The "Pool Process" as defined under 4 (a),

β- Any process or processes whereby through the use of all catalysts and/or promoters, presenting or forming metal alkyl linkages as disclosed by listed "Pool Applications" one may produce

no!

(a) propylene, butene-1 and styrene polymers having molecular weight above 2000 and a linear structure with substantially no branchings longer than CH_3-, CH_3-CH_2- and C_6H_5- respectively

and/or

lettera a parte!

~~metallorgan catalysators presenting metalalkyl linkages~~

(b) mixed polymers of propylene, butene-1 and styrene with ethylene and/or with any other olefinic hydrocarbon $CH_2 = CHR$, R being a saturated aliphatic radical, said mixed polymers containing at least 50 mol% combined propylene or butene-1 or styrene, or at least 50 mol% of a combination of any two or of all said three olefins, having a molecular weight above 2000 and a linear structure with substantially no branchings longer than CH_3, CH_3-CH_2 and C_6H_5 when no hydrocarbons higher than propylene or butene-1 or styrene respectively are present in the monomer mixture, and substantially no branchings longer than R, R being

No!

the saturated aliphatic radical with the highest number of carbon atoms present in the hydrocarbons constituting the monomer mixture.

The "Licensed Field" shall also include:

(c) all said catalysts and/or promoters suitable for use in the above defined processes and the processes used in their preparation, provided such catalysts and/or promoters are employed in the polymerization process as defined under 5/β

(d) processes for purifying the monomers provided such purified monomers are employed in the polymerization processes as defined under 5/β .

(e) any apparatus suitable for carrying out any of said processes as defined under 5/β

The "Licensed Field" shall also include:

(f) all polymer products for use in the plastic field as obtained by the processes defined under 5/β , as well as any process or method for separating, purifying and stabilizing said products,

(g) any composition for use in the plastic field made out of or containing such polymer products as defined under 5/β such as resins and molding materials (with the exclusion of elastomeric compositions, or compositions apt to be transformed into elastomeric products),

(h) articles made out of or containing such products and compositions, as defined under 5/β/f and 5/β/g, including films, foils, sheeting, tapes and other similar products

(i) any process and/or method for improving the characteristics of said products and compositions as defined in 5/β as well as improved processes for transforming them into films, sheeting, tapes and other similar articles.

./.

Therefore the processes of transforming the polymeric products and compositions into textile fibres and elastomeric products, fibers and elastomers themselves and their uses are in no case included in the "Licensed Field" of this Agreement.

MONTECATINI
Società Generale per l'Industria Mineraria e Chimica

Brevetti e Documentazione Tecnica

GV/ma

986 A

PROMEMORIA

Data, 28 Maggio, 1956

Am.

Union Carb. C

per il Signor Ing. Piero GIUSTINIANI

e p.c. Ing. ORSONI
Prof.NATTA

Oggetto: Trattative Union per licenza poli e fibre -

Allego una prima relazione sulle combinazioni, i pagamenti e le durate di opzione concordate con la Union.

E' in programma di inviare la versione inglese di questa relazione:

a) alla Union come conferma delle trattative svoltesi a Milano e delle condizioni concordate;

b) a Ziegler, a titolo informativo, togliendo però il punto 9) riguardante le fibre.

In attesa di Sue eventuali osservazioni e benestare, con ossequio.

GdeVarda

all/

26 Maggio, 1956

Ing. Piero GIUSTINIANI

e p.c. Ing. ORSONI.
Prof.NATTA

Oggetto: Trattative Union Carbide plastici di polipropilene, poli-alfa-butene e polistirolo, e fibre polipropilene

Nelle trattative svoltesi a Milano dal 14 al 17 e dal 23 al 25 maggio a.c. fra i Signori Murphy, Voorhees e Lyon per la Union Carbide e Giustiniani, Orsoni, Natta e de Varda per Montecatini, è stato convenuto quanto segue:

A) Offerte Montecatini valide fino al 30 giugno 1956 per una qualsiasi delle seguenti combinazioni:

1) Licenza pool per soli brevetti polipropilene, campo plastici:
Opzione $75,000.- (non recuperabile)
Down payment $1,000,000.- di cui 50% recuperabile con trattenute del 50% sulle royalties correnti;
oppure in alternativa: opzione come sopra - down payment di 1,500,000 dollari recuperabile al 100% con trattenute del 50% sulle royalties -
Royalties correnti in entrambi i casi 5% sul polimero venduto come tale, altrimenti 3½% sul prodotto formato.

2) Licenza pool per soli brevetti polipropilene + poli-1-butene: campo plastici:
Opzione $150,000 (non recuperabile)
Down payment di $1,500,000.-, rispettivamente $2,250,000.- alle condizioni sub 1).
Royalties correnti del 5% e del 3½%, come sub 1).

3) Licenza pool per soli brevetti polipropilene + polistirolo nel campo plastici -
Idem come sub 2).

4) Licenza pool per soli brevetti polipropilene + poli-1-butene + + polistirolo nel campo plastici:
Opzione: $200,000.- (non recuperabile) -
Down payment: $2,000,000.- rispettivamente $3,000,000.- alle condizioni sub 1).
Royalties correnti: 5% e 3½% come sub 1).

./.

5) Licenza su brevetti pool nel campo plastici per una delle 4 combinazioni precedenti con fornitura aggiuntiva know-how Montecatini per il solo polipropilene:
versamento di ulteriori $500,000.- (non recuperabili) in aggiunta a quanto precedentemente specificato sub 1), o sub 2), o sub 3), o sub 4).

6) Licenza sui brevetti pool nel campo plastici per il solo poli-1-butene:
Opzione: $75,000.- (non recuperabile)
Down payment: $750,000.- di cui il 50% recuperabile con deduzioni del 50% sulle royalties. In alternativa $1,125,000.- di cui 100% recuperabile con deduzioni del 50% sulle royalties.
Royalties correnti del 5% e del 3½% come sub 1).

7) Licenza per brevetti pool nel campo plastici per il solo polistirolo:
Idem come 6).

8) Licenza per brevetti pool nel campo plastici per il poli-1-butene + polistirolo:
Opzione: $150,000.- (non recuperabile)
Down payment: $1,500,000.- In alternativa $2,250,000.- alle condizioni sub 6).
Royalties correnti del 5% e del 3½%, come sub 1).

9) Per quanto riguarda i soli brevetti pool e Montecatini per arrivare dal monomero alle fibre in polipropilene, ci siamo impegnati di offrire una licenza alla Union quando saremo pronti, presumibilmente a partire dall'ottobre 1956, sempreché Union firmi con noi un accordo definitivo per almeno una delle 8 combinazioni precedenti.

Le pretese Montecatini saranno mantenute entro i seguenti limiti:
Down payment: non meno di un milione di dollari, non più di un milione e mezzo di dollari, recuperabili al 50% con deduzioni del 50% sulle royalties correnti
Royalties correnti sul valore commerciale della fibra (alla "first reeling operation after all the drawing operations") non meno del 5% e non più del 7%
ragionevole "option sum" ancora da determinarsi.

B) Termine dell'opzione:

1) Polipropilene

Per quanto riguarda la combinazione sub 1) e la sola parte polipropilene contenuta nelle combinazioni sub 2), 3), 4) e 5) del precedente capitolo A), il periodo di opzione (per decidere se firmare o meno un accordo definitivo) a disposizione della Union, scadrà due mesi dopo che saranno pervenute alla Union tutte le informazioni, limitatamente però al campo del polipropilene, elencate nell'articolo III/1/a),b),c) e d) del contratto di opzione Montecatini-Union.

Nessuna incertezza in merito all'eventuale data di inizio del periodo di opzione suddetto per quanto riguarda le prestazioni di cui ai punti a) (domande di brevetto), b) (descrizione delle tecniche preferite) e d) (campioni dei prodotti).

Per quanto riguarda invece le prove dimostrative sulla polimerizzazione nei laboratori Montecatini, previste al punto c) dello stesso articolo di contratto, esse avranno inizio subito dopo che Montecatini sarà entrata in possesso della "option sum" contrattuale, in qualsiasi giorno che ci verrà richiesto dalla Union, e potranno essere condotte a termine nel giro di una settimana.

Comunque, ai soli effetti dell'eventuale computo della scadenza dei due mesi di opzione, le prestazioni di cui al punto c) si intenderanno validamente ultimate al più tardi quindici giorni dopo la data di ricevimento da parte Montecatini della "option sum" contrattuale.

2) Poli-1-butene e/o polistirolo

Per quanto riguarda le combinazioni 6), 7) e 8) e la sola parte riguardante il poli-1-butene e/o il polistirolo nelle combinazioni 2), 3), 4) e 5) del precedente capitolo A), il periodo di opzione (per decidere se firmare o meno un accordo definitivo) a disposizione della Union scadrà 4 mesi dopo che saranno pervenute alla Union negli USA tutte le informazioni,(limitatamente però al campo dei suddetti polimeri), elencate nell'articolo III/1/a),b),c) e d) del contratto di opzione Montecatini-Union.

Nessuna incertezza in merito all'eventuale data di inizio del periodo di opzione suddetto per quanto riguarda le prestazioni di cui ai punti a), b) e d).

Per quanto riguarda invece le prove dimostrative sulla polimerizzazione nei laboratori Montecatini, previste al punto c) dello stesso articolo di contratto, esse avranno inizio subito dopo che Montecatini sarà entrata in possesso della "option sum" contrattuale, in qualsiasi giorno che ci verrà richiesto da Union, e potranno essere condotte a termine nel giro di una settimana per il solo poli-1-butene e per il solo polistirolo, e di due settimane per il poli-1-butene + polistirolo.

Comunque, ai soli effetti del computo della scadenza dei 4 mesi di opzione, le prestazioni di cui al punto c) si intenderanno validamente ultimate al più tardi entro 15 giorni dopo la data di ricevimento da parte Montecatini della "option sum" contrattuale per le combinazioni 6), o 7) o 8); invece nel caso delle combinazioni 2),o 3), o 4), o 5) le prestazioni di cui al punto c) si intenderanno validamente ultimate al più tardi 30 giorni dopo la data di ricevimento da parte Montecatini della relativa "option sum" contrattuale.

Con ossequio.

(G.dV.)

796 A

UNION CARBIDE AND CARBON CORPORATION
Carbide and Carbon Building
30 EAST FORTY-SECOND STREET
NEW YORK 17

JOHN J. MURPHY
DIRECTOR OF PATENT AFFAIRS

CABLE ADDRESS
PATUNCARB NEW YORK

May 3, 1956

Dr. Bartolomeo Orsoni
Technical Director
Montecatini
Via F. Turati, 18
Milan, Italy

Dear Dr. Orsoni:

The kind letter from Dott.Ing. G. de Varda and the enclosures thereto are at hand.

For your information, I am leaving for Europe immediately and arrangements have been made for our Mr. F. R. Lyon to meet me in Milano by May 14, at which time we will continue our discussions with respect to the entire subject matter of your Pool agreement with Professor Ziegler and the question of an exclusive license for fibers at least.

Looking forward to seeing you again and with kindest personal regards, I am

Sincerely yours,

John J. Murphy

JJM/ep

cc: Mr. Lucio Lucini

Rep. 942 A
15 Mont.

MONTECATINI
Settore Progetti e Studi

Sede, 25 Maggio 1956.

Preg.mi Signori

Prof. Natta,
Ing. Ballabio,
Ing. De Varda,
Ing. Marullo,
Dr. Saccenti.

Unisco estratto del testo concordato con la Union Carbide and Carbon riguardante le informazioni chè ci siamo impegnati a fornire alla Carbide se questa deciderà di prendere una opzione.

Le informazioni devono rigurdare il polipropilene isotattico, il polistirolo isotattico, il polialfabutilene isotattico.

A mio avviso, le informazioni riguardanti i diversi punti devono essere predisposte e fornite rispettivamente da :

Punto (a) . . . . BREV;

Punto (b) per il polipropilene e il polistirolo . . . . . SEID,
per il polialfabutilene . . . . ISTITUTO DONEGANI;

Punto (c) per il polipropilene e il polistirolo . . . . . LABORATORIO SEID,
ed eventualmente . . . . . LABORATORIO PROF. NATTA,
per il polialfabutilene . . . . ISTITUTO DONEGANI;

Punto (d) . . . . SERE.
(prima occorrerà definire i tipi e le qualità dei singoli campioni da mandare e poi provvedere alla loro spedizione).

Orsoni

Allegato.
Or/sl.

Milano, 25 Maggio 1956.

. . . .

Article III : Disclosure of informations.

1. Promptly upon receipt of the option payment of U.S. Dollars (......) as provided for in Article II, Montecatini shall :

(a) disclose to X all the "Pool applications" listed in Schedule A and of the Italian and German applications listed in Schedule B.

(b) send to X a brief written description of the preferred techniques, apparatus and processes used by Montecatini for the preparation of polypropilene according to the patent applications referred to in clause (a) of this Article;

(c) insure the performance in the presence of X's representatives of Montecatini's laboratory processes for the production of polypropylene;

(d) send to X small samples of polypropylene products obtained by Montecatini in the Licensed Field.

so as to enable X to make a preliminary technical and economic evaluation and patent study of the "Pool process" (Art. I, 4 (c)).

/sl.

Union Carbide Carbon

Am

JOHN J. MURPHY
30 EAST FORTY-SECOND STREET
NEW YORK

May 18, 1956.

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

Dear Prof. Natta,

Please accept my many thanks for the wonderful luncheon and many courtesies afforded to me by both you and Madam Natta during my recent visit to Milano.

I regret very much your being unable to visit with some of our people while in America. I should have written you last January confirming our understanding during my January visit to Milano.

Trusting I may be able to be of some service to you during your forthcoming visit and with kindest personal regards, I remain

Gratefully yours,

John J. Murphy

JJM/lg

UNION CARBIDE AND CARBON CORPORATION
Carbide and Carbon Building
30 EAST FORTY-SECOND STREET
NEW YORK 17

JOHN J. MURPHY
DIRECTOR OF PATENT AFFAIRS

CABLE ADDRESS
PATUNCARB NEW YORK

April 13, 1956

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

Dear Dr. Natta,

For your information, according to my present plans I expect to arrive in Milano on Sunday, May 13 and will be there Monday and Tuesday.

I will appreciate your advising me if you will still be in Milano and if so I will bring with me some samples of our new isotactic polypropylene fibers.

Looking forward to seeing you again and with kindest regards, I am

Sincerely yours,

John J. Murphy

JJM/ep

April 17, 1956

Dr. John J. Murphy
Director of Patent Affairs
Union Carbide and Carbon Corporation
30 East Forty-second Street
NEW YORK 17 =N.Y.=U.S.A.

Dear Dr. Murphy,

Referring to your kind letter of April 13, concerning your visit in Milan on May 13, I inform you that I think I shall be here on this date, but I cannot be sure, till now.

Hoping to have the pleasure to meet you again, with kindest regards, I am

Sincerely yours,

Giulio Natta

Union Carbide and Carbon

215 A

[illegible]

JOHN J. MURPHY
30 EAST FORTY-SECOND STREET
NEW YORK

February 1, 1956

Prof. Guilio NATTA
Instituto de Chimica Industriale
del POLITECNICO
Piazza Leonardo da Vinci, 32
MILANO, Italy

Dear Professor NATTA,

I wish to express my regret that I was unable to visit your laboratory while in Milano. I just had too many things to do that day before leaving the city and hope that you will accept my apologies.

I do however wish to express my appreciation and kindest respects to both you and Senora NATTA for the very lovely luncheon last Wednesday and certainly hope that when you both come to New York next June, I will be able to be of some service to you.

With kindest personal regards and best wishes to you both, I am,

Sincerely yours,

John J. Murphy

February 17, 1956

Mr. John J. Murphy
30 East Forty-second Street
NEW YORK, U.S.A.

Dear Mr. Murphy,

Many thanks for your kind letter of February 1.

I have been glad to make your acquaintance and I hope to have soon the opportunity to see you again in Italy or in U.S.A.

I thank you for the samples of polyethylene fibers you kindly gave to us: they showed a tenacity of 3 g/denier. We had already prepared fibers from our polyethylenes and they showed a tenacity of 5-6 g/denier. The Montecatini Co, hiwever, developed more the study of the polypropylene fibers, because they show greater elasticity and tenacity, and show also better dying properties. The phenomenon of creep, you pointed out, has been remarked also by us ib the old samples, but it is not appeared in the entirely isotactical products.

With kindest regards and best wishes also from Mrs. Natta, I am,

Very sincerely yours,

Giulio Natta

306

Prissone

UNION CARBIDE AND CARBON CORPORATION

UCC

30 EAST FORTY-SECOND STREET
NEW YORK 17, N.Y.

September 2, 1955

Dr. G. NATTA,
Instituto di Chimica Industriale,
Piazza Leonardo da Vinci, 32,
Milano, Italy.

Dear Dr. Natta :

I would first of all like to express again my pleasure to have had the opportunity to meet you on my last visit to Milan. Since then, I have taken the opportunity to further educate myself to your field of work, both through the excellent paper which you delivered in June at the Petroleum Congress, as well as through discussions of its import with Dr. Stirnemann and others.

On my last visit, you indicated that it might be possible at some later date to arrange for a discussion of experimental high-pressure techniques as practised in your laboratory. This has interested me very much and since I shall be in Milan on Monday September 12, I would like to enquire whether it would be convenient for you if I called at the Institute to see you. I expect to be free sometime during the early afternoon.

Please accept my apologies for such short notice and I hope that you will find it convenient.

Thanking you again, and with best regards to both yourself and Dr. Pino, I am

Gesellschaft Deutscher Chemiker

Very truly yours,

Carl E. Strick

Carl E. STRICK,
c/o European Research Associates,
95, rue Gatti de Gamond,
Brussels, Belgium.

La ringrazio, ma pur
[illegible] il giorno 12 settembre
a Milano

CES/LL

~~[illegible]~~ [illegible] Milano
~~[illegible]~~
~~[illegible]~~ Pino

Anche ed anche [illegible] [illegible]
[illegible] [illegible] [illegible] [illegible]
[illegible]

September 6, 1955

9.10

Mr. Carl E. Strick
c/o European Research Asoociates
95, rue Catti de Gamond
BRUSSELS, Belgium
Bruxelles

Dear Mr. Strick,

I received your kind letter of September 2, and I am very sorry but it is impossible for me to be in Milan on September 12, because of my previous engagement. Prof. Pino also will be absent, as he attend a congress of the Gesellschaft Deutscher Chemiker in Monaco, that will be held during that time.

I am very sorry. With my best regards, I am,

Very sincerely yours,

Giulio Natta

ESTERO

MOD. C. -

L'Amministrazione non assume alcuna responsabilità civile in conseguenza del servizio telegrafico.

MOD. 30 (Ediz. 1953)

INDICAZIONI D'URGENZA	Ricevuto il .... 19.... ore.... RICEVENTE Pel circuito N.	*Le ore si contano sul meridiano corrispondente al tempo medio dell'Europa Centrale.* *Nei telegrammi impressi a caratteri romani, il primo numero dopo il nome del luogo di origine rappresenta quello del telegramma, il secondo quello delle parole, gli altri la data e l'ora e i minuti della presentazione.*	Bollo dell'ufficio

Qualifica	DESTINAZIONE	PROVENIENZA	NUM.	PAROLE	DATA DELLA PRESENTAZIONE Giorno e mese	DATA DELLA PRESENTAZIONE Ore e minuti	Via e indicazioni eventuali d'ufficio

(1200804) Roma, 1953 - Istituto Poligr.

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STRICK UNION CARBIDE

UNION CARBIDE AND CARBON CORPORATION
UCC
30 EAST FORTY-SECOND STREET
NEW YORK 17, N.Y.

EXPRESS

April 13, 1955

Dr. G. NATTA,
Istituto di Chimica Industriale
del Politecnico,
Piazza Leonardo da Vinci, 32,
Milano (Italy)

Dear Dr. Natta :

Dr. R. H. Gillette, Director General of European Research Associates, has directed my attention to your letter of March 31, 1955, with the recommendation that I take advantage of the first opportunity I have to be in Milan to arrange for an appointment to meet you. By coincidence, according to my current schedule, I intend to visit Milan during the latter part of the fourth week in April, arriving in Milan on the afternoon of the 27. I would consequently like to confirm the fact that this date would also be convenient for you. Unless advised to the contrary, may I assume that it is agreeable and call your office on my arrival to establish a definite time ?

Since I am in Brussels at present and in close contact with the firm European Research Associates, S.A., if necessary, you may contact me in care of their address which appears below.

Thanking you for this consideration, I am,

Very truly yours,

Carl E. Strick

Carl E. STRICK,
c/o European Research Associates,
95, rue Gatti de Gamond,
Brussels, Belgium.

CES/LL

April 15, 1955

Mr. Carl E.Strick
c/o European Research Associate
95, rue Gatti de Gamond
BRUSSELS, Belgium

Dear Mr.Strick,

I received your letter of April 13, and I confirm you that the date of April 27 will be convenient for me. At your arrival, please call mu Institute (Telephon No.292.125 and 292.126) so that we may arrange an appointment.

Best regards,

Sincerely yours,

G.NATTA

MONTECATINI

METHOD FOR THE POLYMERIZATION OF PROPYLENE AND FOR THE PURIFICATION OF THE POLYMER.

This brief report describes the preferred technique for preparing isotactic polypropylene, when employing monomer and solvents of commercial purity.

Catalyst concentration in the solvent, Al/Ti molecular ratio, pressure, temperature and reaction time are chosen for best practical results in view of the commercial application.

As regards for instance the value of the Al/Ti molecular ratio it may be said that the results obtained with a 1:1 ratio are comparable to those obtained with the selected 2:1 ratio. The only difference is that with the selected ratio the results are normally reproducible , while with a 1:1 ratio a slight variation of other factors (especially the purity of the materials) is sufficient to prevent a complete reproducibility. The same holds for the catalyst concentration in the solvent; concentrations lower than 2.8 g/l can also be used (This figure indicates the sum of the two catalyst components). The results however are not very constant.

It should be noted finally that a polymerization time of 20 hours is selected because it has been shown that most of the polymer forms within this time at a commercially interesting rate (in these conditions a yield of 150-170 g of polymer for 1 g of total catalyst is obtained.

A higher output can be reached (250 g of polymer for 1 g catalyst) under different operating conditions, however with reaction times of 70-80 hours.

The selected operating conditions will be now described :

1. Raw materials and solvents.

(a) commercial n-heptane :

boiling range = 92.8° - 100.3 °C

n_D^{20} = 1.4049

S = 0.0013%

Bromine No = 0.13

H_2O < 0.001%

(b) propylene :

methane < 0.01%

ethylene $< 0.5\%$

ethane $< 3.0\%$

propylene = 88-93%

propane $< 5\%$

butene $< 0.2\%$

sulphur < 5 p.p.m.

acetylene < 25 p.p.m.

(c) commercial n- or i-butyl alcohol :

water content $< 1\%$

(d) commercial acetone :

water content $< 1\%$.

2. Catalysts.

(a) $TiCl_3$

$TiCl_4$ content absent

residue insoluble in methanol $< 0.2\%$

residue on a 850 mesh/sq. cm sieve absent

(analytical method : see enclosed description).

(b) $Al(C_2H_5)_3$

active Al content $> 85\%$

chlorine content $< 0.7\%$

(analytical methods : potentiometric and gas volumetric methods. See description enclosed).

3. Apparatus.

A 4 liter vertical steel autoclave, provided with a propeller type stirrer (400 r. p. m.) for crumbling the lumps of polymer which may form.

The autoclave is heated or cooled by means of a thermostated water jacket or an equivalent system.

Instruments for temperature control inside the autoclave and in the jacket.

A pressure gauge (0-10 ats) connected to the head of the autoclave.

A propylene cylinder, with pressure reducing valve, inserted in a manifold, to ensure a continuous feed of the monomer.

4. Polymerization.

50 ml heptane, 1.7 $TiCl_3$ weighed in a suitable glass vial and 2.5 g tryethyl aluminum ,measured with a g raduated syringe, are introduced, in an inert gas atmosphere, into a suitable glass flask.

The autoclave is heated and filled with an inert gas, then 1000 ml heptane, the catalyst, prepared as indicated, and additional solvent, up to a total of 1500 ml, are introduced.

The autoclave is then placed under vacuum and the gaseous monomer is fed, while stirring, at a temperature of 75 °C and under a pressure of 5 at.

This is continued for 20 hours; then the residual gases are vented.

5. Purification.

1500 ml butanol are introduced into the autoclave and the temperature is kept at 75 °C for 2 hours while stirring. The autoclave is then opened and the product is filtered under vacuum and washed twice with cold alcohol (1000 ml). The polymer is then repeatedly washed with acetone to completely remove the alcohol (total 2000 ml) filtered again and placed for 12 hours in a vacuum drier in a moderate nitrogen stream, at a temperature of 55-60 °C.

The described procedure is the preferred one for obtaining a polymer of a very low ash content. Products having about 0.2% ashes may be obtained using much simpler purification methods, employing no alcohols.

6. Results.

Dry polymer obtained g	703
Yield : g polymer/g catalyst	164
Percentage of purified polymer insoluble in boiling n-heptane	90
Intrinsic viscosity	3.42
Molecular weight	210.000
Ashes	0.01%.

7. Characteristics.

Brittle point = 0-4 °C

Penetration Test, Vicat 1 kg = 150 °C

Yield point = 270-290 kg/sq. cm

Tensile strength = 320-380 kg/sq. cm

Ultimate elongation % = 700-800

Bending modulus E = 8000-9000 kg/sq. cm

Rockwell hardness R = 85-87

Shore hardness D = 66-70.

PART A

Enclosure No. 1

Milano, November 28th, 1956.

MONTECATINI

INTRINSIC VISCOSITY DETERMINATION ON POLYPROPYLENE.

Viscometer : Desreux-Bishoff type (Bull.Soc. Chim. Belg. 59, 98-1950).

Solvent : Commercial tetrahydronaphthalene is distilled in a CO_2 stream and in the presence of 0.2% hydroquinone. After distilling the solvent is kept in an inert gas atmosphere.

Preparation of the solution : 0.02-0.1 g of finely divided polymer are weighed in the beaker supplied with the viscometer and 10 ml solvent are introduced through a pipette calibrated at room temperature. The beaker is placed in an oven at 150 °C and left there for one hour until the solution is completed. The beaker is inserted into the ground glass joint provided in the viscometer.

The viscometer is then placed in the thermostatic bath kept at 135 °C.

Efflux time determination : 10 minutes after the viscometer is introduced into the thermostat the efflux times are determined until a perfect reproducibility is reached. The solution is diluted with a suitable amount of solvent and the efflux times are determined again. The operation is repeated until 4 or 5 viscosity values are obtained at decreasing concentrations.

Relative viscosities are obtained by dividing the efflux times of the solutions (t_s) by the efflux time of the pure solvent ($t_\circ$).

$$\eta \text{ rel.} = t_s/t_\circ$$

Specific viscosities are calculated from relative viscosities.

$$\eta^{sp} = \eta^{rel} - 1$$

By plotting η sp/c versus c (c = g/100 ml solvent) and extrapolating for c= 0 the straight line which passes through the various points, the intrinsic viscosity $[\eta]$ (expressed.in 100 ml/g) is obtained.

PART A

Enclosure No. 3

Milano, November 28th,

MONTECATINI

CHEMICAL AND PHYSICAL ANALITYCAL METHODS FOR TITANIUM TRICHLORIDE

Chemical and physical analytical methods are described by means of which $TiCl_3$ can be determined with sufficient accuracy.

Some procedures are also illustrated for handling $TiCl_3$, in order to limit its deterioration as much as possible.

1. Analytical method.

The analytical method for testing $TiCl_3$ consists of the following operations :

(a) sampling,

(b) determination of tri-valent Titanium,

(c) determination of total Titanium,

(d) determination of total Chlorine.

A. Sampling.

In an atmosphere of dry and oxygen-free nitrogen the ground glass stopper of a 250 ml glass vessel, containing the $TiCl_3$ to be analyzed, is replaced with a suitable, perfectly dry rubber stopper provided with a glass tube bent at right angle, which is closed by a small rubber stopper (fig. 1). At the end of the glass tube a small think glass beaker (obtained from a test tube), about 5 cm high and with a diameter of 1.5 cm, is inserted, which has been previously weighed together with its 2 small stoppers. $TiCl_3$ is introduced into the small beaker by inclinating the $TiCl_3$ container and sligtly tapping on it, taking care that the substance does not adhere to the tube walls.

The small beaker is then removed and the hole of the stopper is quickly closed with the small rubber stopper; thereafter the whole is weighed again on the analytical balance.

The difference between the two weighings gives the amount of sample to be examined.

B. Determination of tri-valent titanium.

The beaker containing a 0.7 - 1.0 g sample, is placed in a 500 ml bottle of ordinary glass having thick walls, provided with a ground glass stopper and containing 150 ml of 1:2 hydrochloric acid, saturated with CO_2 (this is obtained by adding small pieces of dry ice) in order to remove the air.

The small beaker is broken by vigorously shaking the bottle and, after 40 minutes, the sample is titrated with a N/10 solution of ferric alum using ammonium sulphocyanide (10 ml of a 25% solution) as indicator, until the solution turns pink for the first time. During the titration it is convenient to add from time to time small pieces of solid CO_2.

$$\mathrm{Ti}^{+++}\% = \frac{\text{ml Alum Solution x alum factor x 0.479}}{\mathrm{TiCl_3}\text{ weighed}}$$

$$\mathrm{TiCl_3}\% = \mathrm{Ti}^{+++}\% \times 3.221$$

C. Determination of total titanium.

A sample of about 0.7 - 1.0 weighed in a beaker, as illustrated, is placed into a 500 ml thick walled flask containing 100 ml of 1:2 hydrochloric acid and 50 g of analytical grade granulated zinc. The small glass containing the sample is broken and the solution is boiled for 5 min. In order to avoid incidental sprays the flask is covered with a small funnel containing glass wool. Thereafter, 10 g zinc and 20 ml concentrated hydrochloric acid are added and the whole is left to rest for about 30 minutes.

After cooling, the solution is rapidly filtered through glass wool, washing first with diluted hydrochloric acid and then with water. The solution is titrated in CO_2 atmosphere with a ferric alum N/10 solution using ammonium sulphocyanide as indicator.

$$\text{Total Ti}\% = \frac{\text{ml Alum solution x alum factor x 0.479}}{\text{TiCl3 weighed}}$$

Deducting from the total titanium the tri-valent titanium found one obtains the tetra-valent titanium, corresponding to the $TiCl_4$ present in the sample.

$$\text{Total Ti} - \mathrm{Ti}^{+++} = \mathrm{Ti}^{++++}$$

$$\mathrm{TiCl_4}\% = \mathrm{Ti}^{++++} \times 3.691$$

The titer of the ferric alum solution used in the two determinations has been determined in the following way:

Exactly 20 ml of the solution to be titrated are introduced into a 300 ml flask, the free acid is neutralized with NaOH and air is removed by a stream of CO_2. Thereafter 5 ml of 10% hydrochloric acid and 5-6 g KJ are added. The flask is closed with a ground glass stopper, shaken and, after 20 min. rest at room temperature, titration is carried out with a thiosulphate N/10 solution in the presence of starch. When the blue color has disappeared, a CO_2 stream is passed through again. If the solution should turn blue again 2 g KJ are added and the titration is completed.

D. Total chlorine determination.

A sample of about 1.0 - 1.5 g weighed as illustrated, is placed in an ordinary 500 ml thick glass flask, provided with a ground glass stopper and containing 200 ml of 1:3 HNO_3. The small beaker is broken by vigorously shaking the flask, and the solution is left to itself, agitating from time to time, for an hour. The stopper is removed and carefully washed and the solution is brought exactly to 500 ml. 50 ml are withdrawn, added to 50 ml of N/10 $AgNO_3$ and brought to exactly 200 ml.

After 30 min. rest in the dark the solution is filtered on a dry filter. 100 ml are taken from the filtrate and titrated with an ammonium sulphocyanide N/10 solution, using ferric alum as indicator.

$$\text{Cl}\ \% = \frac{(50 - 2A) \times 10 \times 0.003547 \times 100}{TiCl_3 \text{ weighed}}$$

A = ml of N/10 NH_4SCN

In general, when $TiCl_3$ is dissolved, the presence is noted of a small residue, consisting of metallic Ti, which is insoluble in acid solutions. If the amount of residue is small, it does not alter notably the accuracy of the various determinations.

However, if the residue is appreciable, a determination of the residue must be carried out, proceeding according to B. and filtering the solution, 40 min. after the breakage of the beaker containing the $TiCl_3$ sample, through a dried weighed analytical filterpaper, and weighing again after drying in an oven until constant weight.

Care must taken that, during the filtration, the glass pieces of the broken beaker do not fall into the filter.

2. Method for screening $TiCl_3$.

A screen is prepared with a piece of glass tube, 5-6 cm of diameter, and about 20 cm long, fixing at one end of it a piece of stainless steel net with 850 meshes per square cm. The screen so obtained is introduced in a 250 ml glass into which about 100 ml n-heptane distilled on Na are subsequently poured.Using a suitable container (fig. 2), about 10 g $TiCl_3$ are weighed separately and then are introduced into the screen in a nitrogen atmosphere .

The container and the screen walls are washed with n-heptane contained in a suitable wash bottle. The screen is shaken for 10-15 min. while keeping it immersed in the liquid and moving it with strokes alternately parallel and perpendicular to the bottom of the glass. The screen is removed from the liquid and washed carefully inside and outside with n-heptane. The net must be examined for the presence of solid particles. If solid particles are present they can be quantitatively evaluated by immersing the screen (carefully washed with n-heptane to remove, especially from the outside, the $TiCl_3$ adhering to the screen) in CH_3OH for some hours. After washing the screen with CH_3OH, the Ti content of the methanol solution is determined with the usual methods and expressed in grams of $TiCl_3$ (1).

After this treatment, if a residue (2) of foreign substances remains on the screen, it can be weighed as such after drying it in a N_2 stream and transfering it from the screen into a weighing bottle.

$$\text{Residue \%} = \frac{1 + 2}{TiCl_3 \text{ weighed}} \times 100$$

3. Method for determining the methanol-insoluble residue in the $TiCl_3$.

Into a 500 ml , 2 necked flask, provided with a stirrer and a mercury valve and containing 100 ml analytical grade CH_3OH, about 8-10 g of exactly weighed $TiCl_3$ are introduced using the usual container (fig. 2). Further 100 ml CH_3OH are used to wash the container and to remove the last traces of $TiCl_3$. Before all these operations the flask must be carefully dried and filled with dry, oxygen-free nitrogen. The flask is kept under a slight pressure of nitrogen and the stirrer is started. After stirring for exactly 2 hours, the solution is filtered, if necessary, under a slight suction, on analytical filterpaper which has been previously dried at 100 °C and weighed. If the filtrate which passes through is not clear, the solution is filtered again . Finally the filter is washed with a small quantity of CH_3OH, dried in oven at 100 °C until constant weight is reached and weighed again. The residue is expressed in parts per 100 parts of $TiCl_3$ used.

4. Method for emptying containers and for sampling.

A. The containers in which TiCl3 is packed and delivered, are emptied into polythene bags, previously deaerated with dry and oxygen-free nitrogen. These bags are provided on one side with a 4-5 cm diameter stainless steel tube, closed by a rubber stopper.

The other side is bound tight to the container after unbolting and quickly removing the blank flange. When the material has been passed into the bag the container is removed and the mouth of the bag is rapidly closed by a suitable binding (fig. 3).

B. The rubber stopper is removed from the metal tube and TiCl is placed in previously prepared glass vessels, provided with a ground glass stopper, and which have been carefully dried and filled with dry nitrogen. During the operation a small quantity of nitrogen is continuously introduced into the glass vessel. When full, the glass vessel is closed with the glass stopper previously greased with a silicone grease.

The operation is continued in the same way until the bag is completely empty (fig. 4).

C. To withdraw from the glass vessels the amounts of $TiCl_3$ which must be used for the polymerization or as samples for analytical purposes (for this, 250 ml glass vessels with ground glass stopper are used), the glass stopper is quickly removed and replaced with a rubber stopper fitted with a glass tube of 2-3 cm diameter and a small tube for introducing nitrogen : both tubes are closed by rubber stoppers.

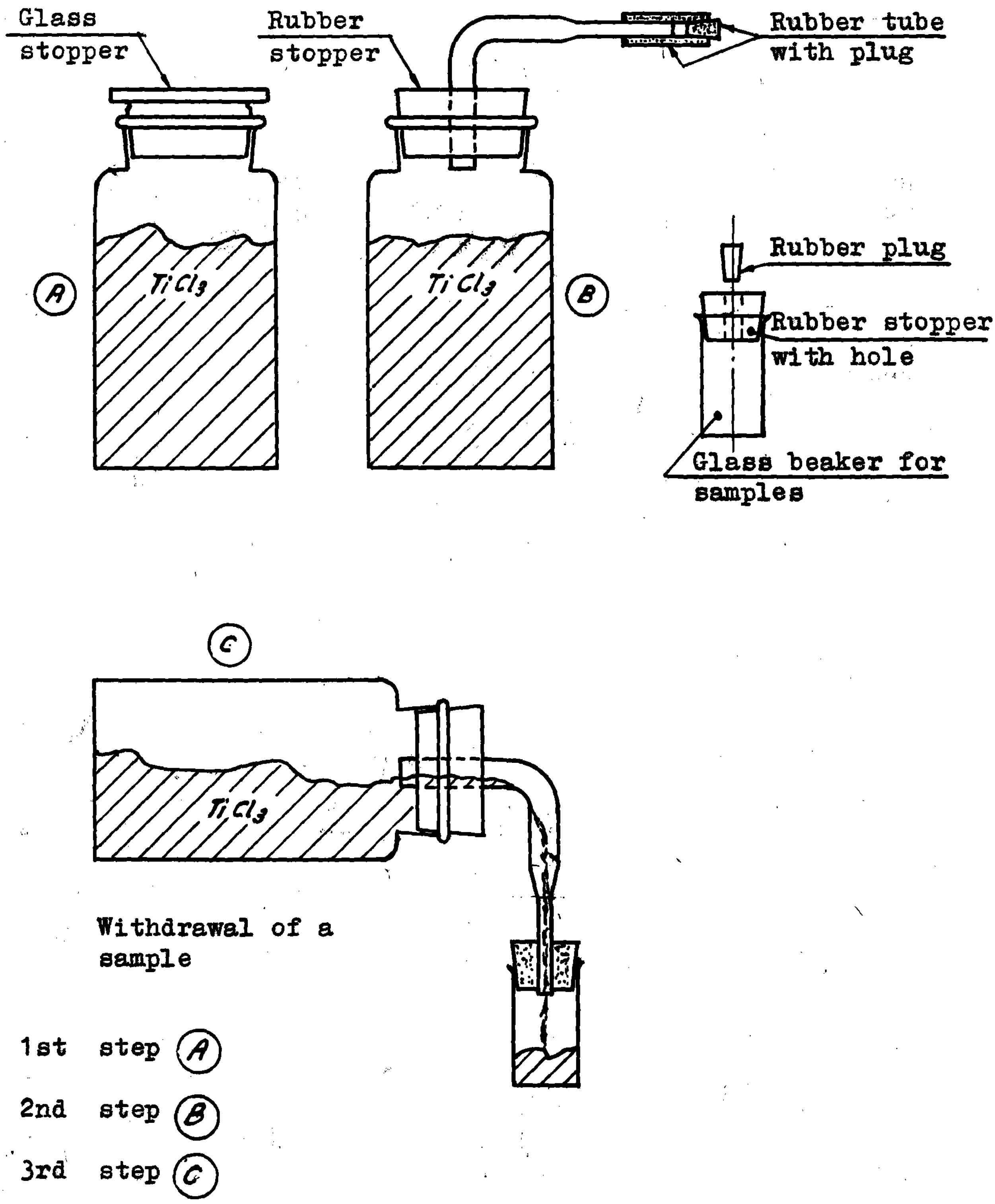
The small tube is connected with a dry nitrogen supply, the stopper on the big tube is removed and the glass jar is turned over introducing the large tube into the vessel in which the desired amount of $TiCl_3$ is weighed. $TiCl_3$ is introduced by tapping on the glass jar.

D. For withdrawing analitycal samples see the description of the method for the chemical analysis of $TiCl_3$.

Specifications for $TiCl_3$.

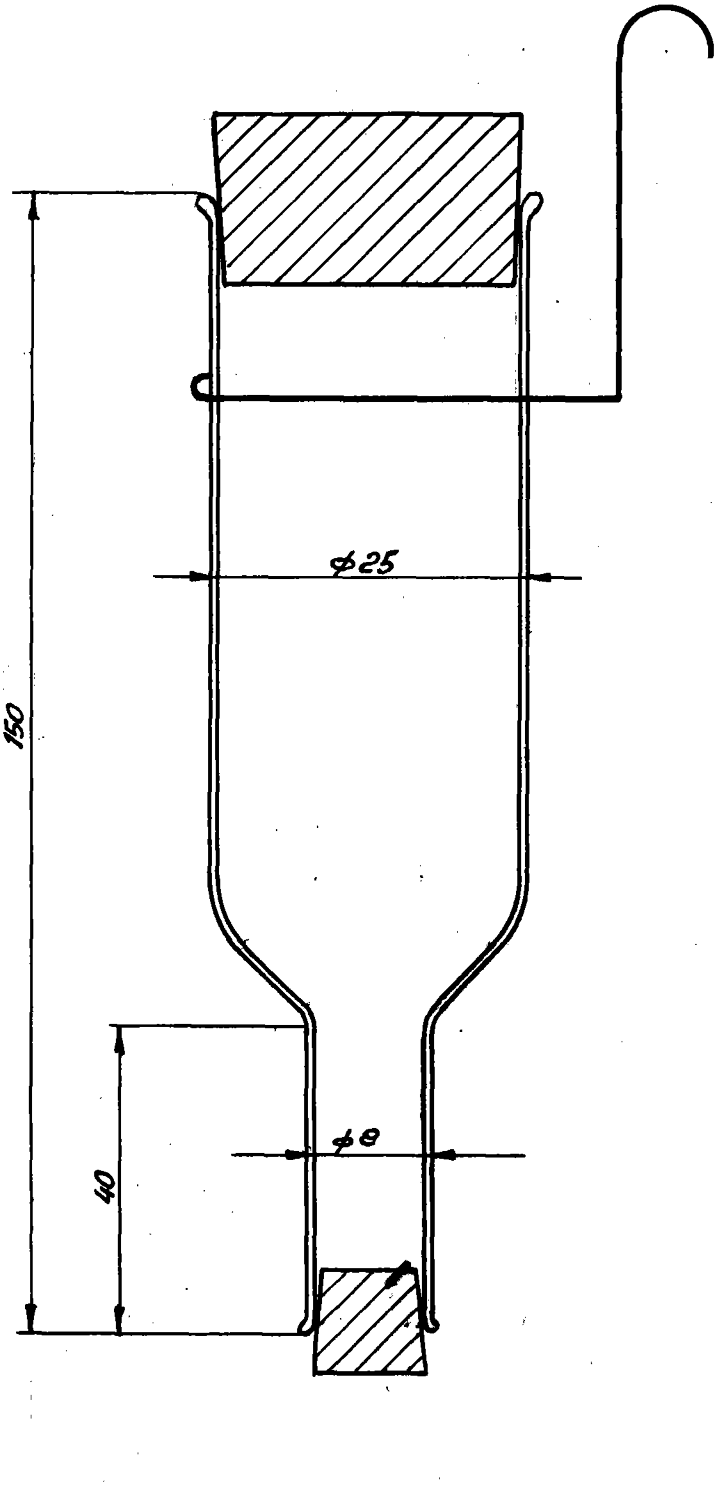
$TiCl_4$	absent
Residue in methanol	max 0.2%
Residue on the sieve (850 meshes/sq. cm)	absent.

FIG. 1



PROCEDURE FOR SAMPLING $TiCl_3$

FIG. 2



GLASS VESSEL FOR WEIGHING $TiCl_3$

FIG. 5

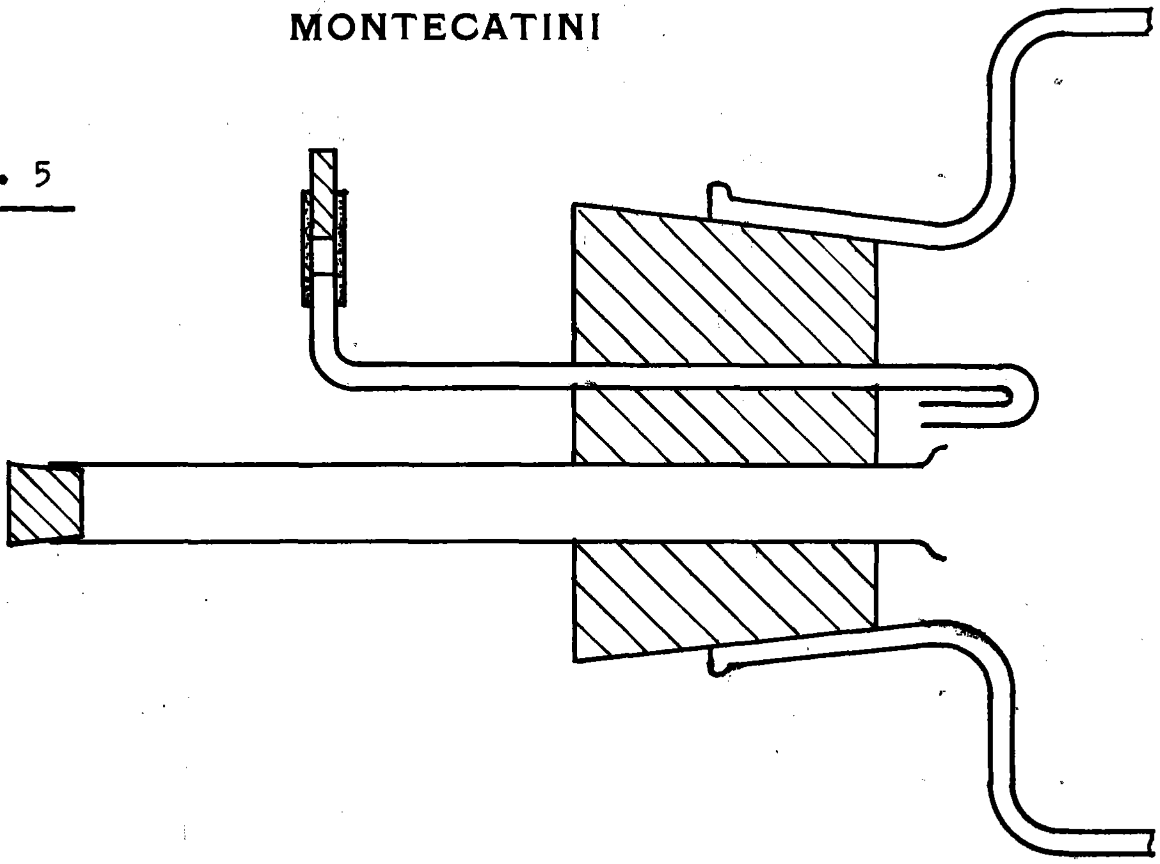


FIG. 3

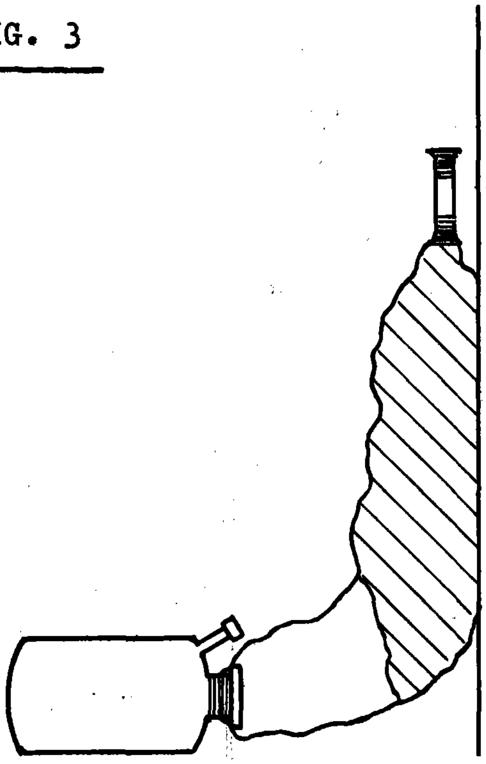
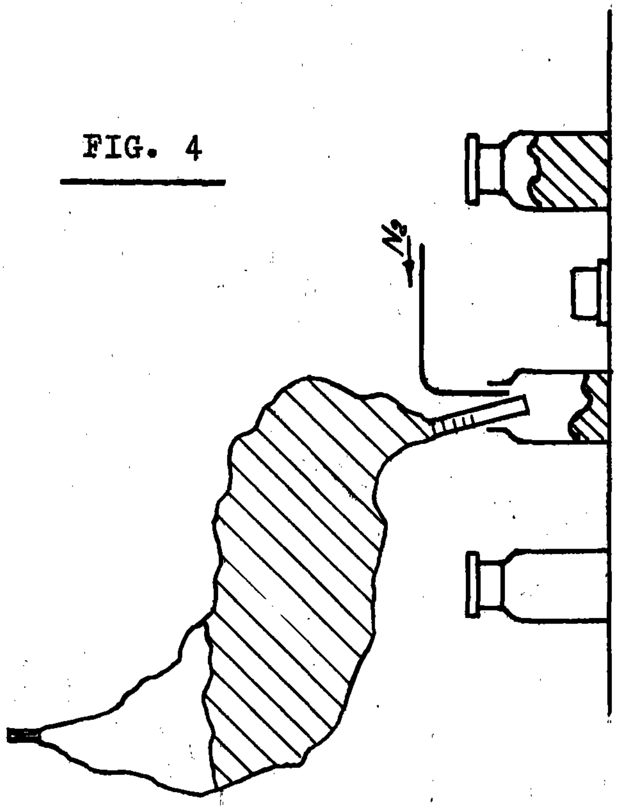


FIG. 4



PROCEDURE FOR WITHDRAWING $TiCl_3$

FROM METAL CONTAINERS AND GLASS JARS

PART B

ISOTACTIC POLYSTYRENE

Milano, November 28th, 1956.

PREPARATION OF ISOTACTIC POLYSTYRENE AND PURIFICATION OF THE POLYMER

Isotactic polystyrene is prepared by polymerizing styrene in solution in the presence of suitable catalysts which, in general, consist of organic aluminium compounds and transition metal halides. The method described has been selected in order to obtain a polymer having an average viscosimetric molecular weight of about 600,000 to 800,000.

The selected conditions are not absolute but allow the desired product to be obtained with a good reproducibility.

1. Raw materials and solvents.

(a) Styrene.

The average characteristics are as follows :

$$D^{20} = 0.9061$$

$$N_D^{20} = 1.5463$$

Purity as determined by the refractometric method = 99.6

Purity as determined by the cryoscopic method = 99.5 min.

Polymers = absent

Peroxides = 0.00032%

Aldehydes = 0.0083%

Phenylacetylene $<$ 0.01%

Stabilizers = none.

(b) Benzene.

Anhydrous, having a purity higher than 99.8% and being free of sulphur compounds (thiophene). Contains generally from C_6 to C_8 hydrocarbons impurities; particularly unsaturated hydrocarbons must be reduced to a minimum (bromine number less than 0.02).

A quick and efficient empirical method for determining the purity of the solvent consists in adding a few drops of $TiCl_4$: an intense orange colour must be obtained without any turbidity or precipitate.

2. Catalysts.

(a) $TiCl_4$.

The usually employed product has a $TiCl_4$ content higher than 99%. The usual yellow colour is attributed, rather than to the presence of iron, to partial decomposition of the $TiCl_4$ which, when freshly distilled in a nitrogen atmosphere (b.p. 135.8 °C at ordinary pressure), is practically colourless.

The analytical determinations, carried out according to the usual methods, are : Ti''', total Ti, chlorine, Fe.

(b) Triethyl-aluminium.

Triethyl-aluminium is prepared by dehalogenation of the monochloride with Na. It is diluted with benzene in a 1:1 ratio by weight, corresponding to a theoretical concentration of 435 g/l. The purity of the substance is determined on each batch by gas volumetric and potentiometric methods (see enclosed methods).

In general a triethyl-aluminium with a purity not lower than 85-86% based on total aluminium, and a Cl content corresponding to a monochloride content lower than 3% (0.7% Cl) can be used.

3. Apparatus.

The apparatus used for the experiments consists of :

1. A 4 litre steel autoclave, operating pressure 10 kg/sq. cm., max. operating temperature 150 °C, provided with :

   - A blade type stirrer rotating at about 350 r.p.m.
   - Thermometer pocket (with thermometric resistance, or thermometer)
   - Manometer (range 0-10 kg/sq. cm) with stop valve.

- 3 feeding tubes, with stop valves
- An insulated heating jacket, with fluid circulation, and thermometer pocket (with thermometric resistance or thermometer)
- Tight plug for fixing the feeding funnel on the head.

2. A glass feeding funnel, graduated from 0 to 500 ml, with cock. This is fixed at the moment of its use and is taken off after the charge is completed.

Before starting to charge, the autoclave is kept under a light positive nitrogen pressure. The nitrogen must be free from oxygen and humidity.

A suitable apparatus to purify the commercial N_2 must be provided.

4. Polymerization conditions.

The catalyst is prepared in the same autoclave used for the polymerization.

The typical conditions for the preparation of the catalyst are the following, starting with the autoclave already evacuated and washed with nitrogen :

400 ml of benzene are charged in the 500 ml drip-feed funnel mounted with a PVC tight joint in the hole on the head;

44 ml equal to 0.4 mols (75.8 g) of $TiCl_4$ will then be added and thereafter the volume increased to 500 ml with benzene. This will be poured into the autoclave and the funnel is washed with further 500 ml of benzene.

The stirrer is started and in the meantime 100 ml of benzene are charged into the funnel, adding a quantity of $AlEt_3$ solution containing 1.2 moles (= 137 g) of active substance.
(The total solvent introduced is about 1200 ml).

When the required temperature is obtained (70 °C), the pouring of the diluted triethyl into the autoclave will be started. The operation lasts 10-15 minutes in all. The temperature must be maintained around 70 °C.

Now, through the same funnel and stopping for the moment the stirrer, about 1800 ml = 1600 g of styrene will be added.

The funnel is quickly taken off, the hole closed with its plug, and the stirring is resumed. The required temperature is obtained almost immediately and must then be maintained at 70 ± 4 °C by convenient heating and cooling control.

The inner pressure rises and remains at 0.4 - 0.7 kg/sq. cm.

On the basis of the mentioned quantities, the polymerization conditions are the following :

Concentration of the polymer	60% vol.
Concentration of the catalyst	70 g/l.
Mol. ratio $AlEt_3/TiCl_4$	3.0
Temperature	70 °C
Time	7 hours.

At the end of the above mentioned time the reaction is stopped by introducing into the autoclave, under nitrogen pressure, about 400 ml of methanol in order to destroy the catalyst. Contemporaneously the heating is stopped and a rapid cooling with water circulation is carried out.

When about 45-50 °C will be obtained in the inside, the autoclave must be vented (because under pressure owing to the developed gases) and is then opened and the polymer discharged.

5. Purification of the polymer.

The mass discharged from the autoclave is dark brown because of the presence of the catalyst, and contains the isotactic polymers swollen by the solvent.

The purification is carried out in two different stages : washing with alcohol and extraction with solvents.

(a) Washing with alcohol.

Methyl alcohol is used normally. This operation is performed in order to remove the catalyst, the solvent and the residual monomer. The finer the particles of the polymer are and the easier and quicker this operation is. For this reason it is carried out in a normal paddle mixer. Usually washing 3 times is sufficient to obtain a polymer with a good degree of purity. During this operation it is convenient to limit the contact with the air, which oxidizes the products of decomposition of insoluble inorganic materials such as $Al(OH)_3$ and TiO_2 which increase the ash contents of the product.

(b) Extraction with solvents.

The extraction is carried out by treating the polymer with acetone or methyl-ethyl-ketone. The extraction is carried out in a conventional extraction apparatus. The product is finally dried in an oven at 80 °C in a stream of nitrogen.

The following table shows the average result of a typical operation :

Catalyst .

$Al(C_2H_5)_3$			$TiCl_4$			Al/Ti mols	T C°	Time
ml	g	mols	ml	g	mols			
159	137	1.2	44	75.8	0.4	3	70°	10-15'

Polymerization Conditions

Monomer				Solvent		catalyst g/l	T	Time
ml	g	mols	vol. %	ml	vol. %			
1800	1600	15.3	60	1200	40	71	70 °C	7 h

Amorphous		Isotactic					
acetone extract		polymer insoluble in acetone				polymer insoluble in MEK	
g	% of polymer	g	% of polymer	mol. weight	polymer soluble in MEK %	g	% on polymer
50	4.16	1150	95.84	650,000	2.1	1125	93.76

MONTECATINI

PART B

ISOTACTIC POLYSTYRENE

Preparation of high molecular weight polymer.

Milan, November 28th, 1956

PREPARATION OF ISOTACTIC HIGH MOLECULAR WEIGHT POLYSTYRENE AND PURIFICATION OF THE POLYMER.

Isotactic polystyrene is prepared by polymerizing styrene in the presence of suitable catalysts which consist, in general, of organic aluminum compounds and transition metal halides.

The method here described allows to obtain high conversions and a considerable productivity in terms of g of polymer per g of catalyst.

The data are to be considered as indicative; reproducibility is however rather satisfactory.

1) Raw materials and solvents.

(a) Styrene.

The average characteristics are as follows:

$$D_4^{20} = 0.9061$$

$$N_D^{20} = 1.5463$$

Purity as determined by the refractometric method	= 99.6%
Purity as determined by the cryoscopic method	= 99.5% min.
Polymers	= absent
Peroxides	= 0.00032%
Aldehydes	= 0.0083%
Phenylacetylene	less than 0.01%

(b) Benzene.

The employed benzene should be anhydrous, of a purity higher than 99.8% and should be free of sulphur compounds (thiophene) or unsaturated hydrocarbons (bromine number less than 0.02).

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Small amounts of aliphatic and aromatic C_6 to C_8 hydrocarbons are tolerated. Only a yellow-orange coloring, and no – turbidity or precipitate, should occur when adding a drop of titanium tetrachloride to the solvent.

2. Catalyst.

(a) $TiCl_3$.
Its purity must be higher than 99.6%, only very low contents of $TiCl_4$ and TiO_2 being tolerated.
Its color must be a deep violet (white spots indicate a deterioration of the product with formation of TiO_2); fineness must be such that no residue is left on a sieve of 5500 mesh.

(b) Triethyl aluminum.
Triethyl aluminum is prepared by dehalogenation of aluminum diethyl monochloride with sodium and is supplied in approximately 50% anhydrous benzene solution. The solution strenght is determined by gasvolumetry or by potentiometric titration. (See Part A Encl. N°2 for methods). The chlorine content must be below 0.7% (corresponding to about 3% monochloride).

3. Apparatus.
The apparatus consists of:

(a) A 4 litre steel autoclave, operating pressure 10 kg/sq. cm, max.operating temperature 150°C, provided with:

- A blade type stirrer rotating at about 350 r.p.m.
- Thermometer pocket (with thermoresistance, or thermometer)
- Manometer (range 0-10 kg/sq. cm) with stopcock
- 3 feed inlets, with valves
- an insulated heating jacket, for oil circulation, with thermometer pocket
- an opening on top, with plug.

(b) A glass dropping funnel, graduated to 500 ml, which is inserted at the moment of its use in the opening on top of the autoclave, by means of a short piece of P.V.C. tubing.

(c) A 100 ml glass flask, with ground glass stopper, a small glass tube with stopcock attached on one side and a nipple at the bottom.

(d) A 250 ml glass funnel, with stopcock, and a sharp flute mouth ending tube.

Before starting the operation the autoclave is completely deaerated and is kept under a small positive nitrogen pressure (the gas must be free of oxygen and humidity).

4) Charging the autoclave and polymerization.

The catalyst may be prepared separately, usually however it is convenient to prepare it in the same autoclave where the polymerization is performed .

$TiCl_3$ is weighed in the 100 ml flask, which is carefully dried; the bottom nipple carries a short piece of P. V. C. tubing with a screw clamp.

$TiCl_3$ is extracted from its container in a stream of nitrogen, arriving through the side tube of the 100 ml flask; the flask is then stoppered and the stopcock is closed.

29. 3 g are used, corresponding to 0. 19 mols.

The autoclave, previously deaerated and dried is under a slight nitrogen pressure. 200 ml benzene are measured in the 250 ml dropping funnel. The plug on top of the autoclave is removed and the nipple of the $TiCl_3$ containing flask is rapidly inserted into it: the flask is also kept under nitrogen. The screw clamp is opened and removed and, by means of the solvent, the $TiCl_3$ is transferred into the autoclave; the flask is then washed with more solvent. The plug is screwed on, the stirrer is started, and the inside temperature is brought to 80°C.

190 ml benzene are introduced in the 500 ml dropping funnel, which is inserted on one of the 3 feed inlets, and a volume of aluminum triethyl solution containing 0. 0634 mols $Al(C_2H_5)_3$(7. 23 g) is added to it.

The mixture is introduced in the autoclave, under stirring, in about 10 to 15 minutes. Once the addition is completed, 280 ml benzene and, finally, 1330 ml styrene (about 1200 g) are added in succession through the dropping funnel.

The time is noted and the reaction is continued for 18 hours, keeping the inside temperature at 80 ± 4°C.

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With the amounts indicated, the polymerization conditions are as follows:

Momoner concentration	66.7% by vol.
Catalyst concentration	18.2 g/l
Molar ratio $\frac{Al(C_2H_5)_3}{TiCl_3}$	0.33
Temperature	80°C
Duration	18 hours

At the end of this time 300 ml benzene are added and stirring is continued for one hour longer (the benzene addition is made in order to swell the polymer and make it more crumbly); then about 300 ml methanol are added, and the autoclave is cooled rapidly by circulating cold oil.

As soon as feasible, the gases deriving from the decomposition of the catalyst are vented, the autoclave is opened and the polymer is taken out.

5) Purification of the polymer

The polymer is purified with commercial methanol. To this end it is crumbled, soaked for some time in methanol, pulverized and then washed several times by decantation with methanol. After this treatment it appears as a grey powder with greenish-black spots.

If one does not want to treat the entire batch, this is filtered and dried on the filter as much as possible and weighed; then a weighed average sample (400 g) is filled into the extraction apparatus and extracted continuously with hot methanol for a convenient length of time.
Finally the purified polymer is washed on the filter with methanol and dried in an oven at about 80°C, in a nitrogen atmosphere until the weight is constant. From this weight the yield on the employed styrene is calculated.

Two average samples of the purified and dried polymer are extracted in a Kumagawa apparatus with acetone and with methyl-ethyl-ketone; on the dried M. E. K. residue the mol-wt. is determined. The extraction may obviously be carried out on larger amounts or on the

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totality of the polymer, using in succession the various solvents.

6. Summary of the operative conditions

(a) preparation of the catalyst

$TiCl_3$			$Al(C_2H_5)_3$			$Al(C_2H_5)_3$ / $TiCl_3$	Temperature	Duration
g	mol	ml solvent	mol	g	ml sol.	mol/mol	°C	minutes
29.3	0.19	200	0.063	7.2	190	0.330	80	10-15

(b) polymerization

Benzene		Styrene				Temp.	Duration
added ml	total ml	ml	g	mol	% vol.	°C	Hours
280	670	1330	1200	11.5	66.7	80	18

(c) Average results

Polystyrene: residue after extraction with M.E.K. 1080 g

Monomer conversion	90%
Yield g/g catalyst	29.6
Mol. wt. approximately	5.000.000
Intrinsic Viscosity	6.9

PART B

Enclosure No. 1

Milano, November 28th, 1956

VISCOSIMETRIC DETERMINATION OF THE MOLECULAR WEIGHT OF ISOTACTIC POLYSTYRENE.

Viscometer: Desreux - Bishoff type (Bull. Soc. Chim. Belg. 59, 38, 1950)

Solvent: The determination may be carried out either in tetralin at 100°C or in toluene at 30°C; the first method is suitable for polymers of rather high molecular weight or in general for polymers soluble only with difficulty. The second is successful only with isotactic polystyrenes showing a comparatively good solubility.

Commercial tetralin is distilled in a CO_2 stream and in the presence of 0.2% hydroquinone.
After distilling, the solvent is kept in an inert gas atmosphere.

Toluene must be of analytical grade, distilled and kept in a closed vessel.

Preparation of the solution: 0.01 a 0.03 g of finely divided polymer are weighed in the small beaker supplied with the viscometer and 10 ml solvent are introduced through a pipette calibrated at room temperature. When tetralin is used the beaker is placed in an oven at 150° and left there for 2 1/2 hours in order to dissolve the substance. The beaker is inserted into the ground glass joint provided in the viscometer. The viscometer is then placed in the thermostatic bath. When toluene is used the solution is obtained by shaking and moderate heating.

Efflux time determination: 10 minutes after the viscometer is placed into the thermostat, the efflux times are determined until a perfect reproducibility is reached. The solution is diluted with 10 ml solvent and the efflux times are determined again. Finally another 10 ml solvent is added and the determination is repeated. From these determinations the relative viscosities are obtained by dividing the efflux times of the solution (ts) by the efflux time of the pure solvent (t.).

$$\eta \text{ rel.} = \frac{ts}{t.}$$

From the relative viscosities the specific viscosities are calculated.

$$\eta_{sp} = \eta_{rel} - 1$$

By plotting η spec/c versus c(c= g/100 ml of solvent) and by extrapolation for c = 0 of the straight line that passes through the different points, the intrinsic viscosity $[\eta]$ is obtained, expressed in 100 ml/g.

Calculation of the molecular weight: from measurements in tetralin at 100°C the average viscosimetric molecular weight is obtained by the equation:

$$[\eta] = 0.94 \times 10^{-4}(\overline{M}_v)^{0.73}$$

From measurements in toluene at 30°C the average viscosimetric molecular weight is obtained by the equation:

$$[\eta] = 1.10 \times 10^{-4}(\overline{M}_v)^{0.725}$$

(Makromoleculare Chemie 20 , 37 - 1956).

NOTA B

POLISTIROLO ISOTATTICO

Copia n.5

PREPARATION OF ISOTACTIC POLYSTYRENE
AND PURIFICATION OF THE POLYMER

Isotactic polystyrene is prepared by polymerizing styrene in solution in the presence of suitable catalysts which, in general, consist of organic aluminium compounds and transition metal halides. The method described has been selected in order to obtain a polymer having a molecular weight of about 600,000.

The selected conditions are not absolute but allow the desired product to be obtained with a good reproducibility.

1 - **Raw materials and solvents**

a) Styrene

The average characteristics are as follows:

$$D^{20} = 0.9061$$

$$N^{20}_{D} = 1.5463$$

Purity as determined by the refractometric method = 99.6

Purity as determined by the cryoscopic method = 99.5 min.
Polymers = absent
Peroxides = 0.00032%
Aldehydes = 0.0083 %
Phenylacetylene 0.01%
Stabilizers = none

b) Benzene

Anhydrous, its purity higher than 99.8%. Must result free of sulphurized compounds (thiophene). Contains generally from C_6 to C_8 hydrocarbon impurities; particularly unsaturated hydrocarbons must be reduced to a minimum (bromine number less than 0.02).

A quick and efficient empirical method for determining the purity of the solvent consists in adding a few drops of $TiCl_4$: an intensive orange colour must be obtained without any turbidity or precipitate.

2 - **Catalysts**

a) $TiCl_4$

Its purity must be higher than 99%, only a very low concentration of $TiCl_3$ being tolerated. The usual yellow colour is attributed, rather than to the presence of iron, to partial decomposition of the $TiCl_4$ which, when freshly distilled in a nitrogen atmosphere (b.p. 135,8 °C at ordinary pressure) is practically colourless.

The analytical determinations, carried out according to the usual methods, are: Ti''', total Ti, chlorine, Fe.

b) Triethyl-aluminium

Triethyl-aluminium is prepared by dehalogenation of the monochloride with benzene in a 1:1 ratio by weight, corresponding to a theoretical concentration of 435 g/l. The purity of the substance is determined on each batch by the gas-volumetric method and the potentiometric (see enclosed methods).

In general a triethyl-aluminium with a purity not lower than 85-86%, based on a total aluminium, and a Cl content corresponding to a monochloride content lower than 3% (0.7% Cl), can be used.

3 - Apparatus

The apparatus used for the experiments consists of:

1)- A 4 litre steel autoclave, operating pressure 10 kg/sq.cm, max operating temperature 150 °C, provided with:

  - A blade type stirrer rotating at about 350 r.p.m.
  - Thermometer pocket (with heat resistance)
  - Manometer (range 0-10 kg/sq.sm) with stop salve
  - 3 feeding tubes, with stop salve
  - An insulated heating jacket, with fluid circulation, and thermometer pocket.
  - Tight plug for fixing the feeding funnel, on the head.

2) A glass feeding funnel, graduation from 0 to 500 ml, with tap. This is fixed at the moment of its use and is taken off after the charge is completed.

Before starting to charge, the autoclave is kept under a light positive nitrogen pressure. The nitrogen must be free from oxygen and humidity.

A suitable apparatus to purify the commercial N_2 must be provided.

4 - Polymerization conditions

The catalyst is prepared in the same autoclave used for the polymerization.

The typical conditions for the preparation of the catalyst are the following, starting with the autoclave already evacuated and washed with nitrogen:
400 ml of benzene are charged in the 500 ml drip-feed funnel mounted with a PVC tight joint in the hole on the head;

44 ml equal to 0.4 mols (75.8 g) of $TiCl_4$ will then be added and thereafter the volume increased to 500 ml with benzene. This will be poured into the autoclave and the funnel is washedwith further 500 ml of benzene.

The stirring is started and in the meantime 100 ml of benzene are charged into the funnel, adding a quantity of $AlEt_3$ solution containing 1.2 moles (= 137 g) of active substance.
(The total of the solvent introduced is about 1200 ml required).

When the required temperature is obtained (70°C), the pouring of the diluted triethyl into the autoclave will be started. The operation is lasting 10-15 minutes in all. The temperature must be maintained on 70°C.--

Now, through the same funnel and suspending for the moment the stirring, about 1800 ml = 1600 g of styrene will be added.

The funnel is quickly taken off, the hole closed with its plug, and the stirring is resumed. The required temperature is obtained almost immediately and must then be maintained on 70 ± 4°C by convenient heating and cooling control.

The inner pressure rises and remains on 0.4 - 0.7 kg/sq.cm.

On the basis of the mentioned quantities, the polymerization conditions are the following:

Concentration of the polymer	60% vol.
Concentration of the catalyst	70 g/l

Mol. ratio $AlEt_3/TiCl_4$	3.0
Temperature	70 °C
Time	7 hours.

At the end of the above mentioned time the reaction is stopped by introducing into the autoclave, under nitrogen pressure, about 400 ml of methanol in order to destroy the catalyst. Contemporaneously the heating is stopped and a rapid cooling with water circulation is carried out.

When about 45-50°C will be obtained in the inside, the autoclave must be vented (because under pressure owing to the developed gases) and is then opened and the polymer discharged.

5. Purification of the polymer

The mass discharged from the autoclave is dark brown because of the presence of the catalyst, and contains the isotactic polymers swollen by the solvent.
The purification is carried out in two different stages: washing with alcohol and extraction with solvents.

a) Washing with alcohol

Methyl alcohol is used normally. This operation is performed in order to remove the catalyst, the solvent and the residual monomer. The finer the particles of the polymer are and the easier and quicker this operation is. For this reason it is carried out in a normal paddle mixer. Usually washing 3 times is sufficient to obtain a polymer with a good degree of purity. During this operation it is convenient to limit the contact with the air, which oxidizes the products of decomposition of insoluble inorganic materials such as $Al(OH)_3$ and TiO_2, which increase the ash contents of the product.

b) Extraction with solvents

The extraction is carried out by treating the polymer with acetone or methyl-ethyl-ketone at the boiling point. In the first case the residual polymer is partially soluble in methyl-ethyl-ketone. The extraction is carried out ina conventional extraction apparatus. The product is finally dried in an oven at 80 °C in a stream of nitrogen.

The following table shows the average result of a typical operation:

Catalyst

$Al(C_2H_5)_3$			$TiCl_4$			Al/Ti	T	Time
ml	g	mols	ml	g	mols	mols	C°	
159	137	1.2	44	75.8	0.4	3	70°	10-15'

Polymerization Conditions

Monomer				Solvent		Catalyst g/l	T	Time
ml	g	mols	vol.%	ml	vol. %			
1800	1600	15,3	60	1200	40	71	70 °C	7 h

Product obtained

Amorphous		Isotactic					
acetone extract		polymer insoluble in acetone				polymer insoluble in MEK	
g	% of mon.	–	% of mon.	mol. weight	polymer soluble in MEK	g	% of monomer
50	3.1	1150	71.8	650.000	2.1	1125	70.5

RISERVATA

NOTA B

Allegato N°1

VISCOSIMETRIC DETERMINATION OF THE MOLECULAR WEIGHT OF ISOTACTIC POLYSTYRENE

Viscometer : Desreux - Bishoff type (Bull.Soc.Chim.Belg. 59 38 (1950)).

Solvent : The determination may be carried out either in tetralin at 100°C or in toluene at 30°C; the first method is suitable for polymers of rather high molecular weight which in general are soluble only with difficulty. The second is successful only with isotactic polystyrenes of relatively low molecular weight (lower than about 500.000).

Commercial tetralin is distilled under vacuum in a CO_2 stream and in the presence of 0.2% hydroquinone. After distilling, the solvent is kept in an inert gas atmosphere.

Toluene must be of analytical grade, distilled, and kept in a closed vessel.

Preparation of the solution : 0.01 - 0.03 of finely divided polymer are weighed in the small beaker supplied with the viscometer and 10 ml solvent are introduced through a pipette calibrated at room temperature. When tetralin is used the beaker is placed in an oven at 150° and left there for 2½ hours in order to dissolve the substance. The beaker is inserted into the ground glass joint provided in the viscometer, which is lubricated with a small amount of silicone grease. The viscometer is then placed in the thermostatic bath. When toluene is used the solution is obtained by shaking and moderate heating.

Efflux time determination : 15 minutes after the viscometer is placed into the thermostat, the efflux times are determined until a perfect reproducibility is reached. The solution is diluted with 10 ml solvent and the efflux times are determined again. Finally another 10 ml solvent are added and the determination is repeated. From these determinations the relative viscosities are obtained by dividind the efflux times of the solution (ts) by the efflux time of the pure solvent (t_0).

$$\eta \text{ rel.} = \frac{ts}{t_0}$$

From the relative viscosities the specific viscosities are calculated.

$$\eta \text{ sp} = \eta \text{ rel} - 1$$

By plotting η spec/c versus c (c = g/100 ml of solvent) and by extrapolation for c = 0 of the straight line that passes through the different points, the intrinsic viscosity $[\eta]$ is obtained, expressed in 100 ml/g.

Calculation of the molecular weight : from measurements in tetralin at 100°C the average viscosimetric molecular weight is obtained by the equation :

$$[\eta] = 0.94 \times 10^{-7} \, (\overline{M_v})^{0.73}$$

From measurements in toluene at 30°C the average viscosimetric molecular weight is obtained by the equation :

$$[\eta] = 1.10 \times 10^{-4} (\overline{M}_v)^{0.725}$$

(Makromoleculare Chemie <u>20</u> 37 - 1956)

MONTECATINI

LABORATORY PREPARATION OF $TiCl_3$

Milan, November 19, 1956

LABORATORY PREPARATION OF $TiCl_3$

Raw Materials

$TiCl_4$:

The titanium tetrachloride to be used must be distilled, colorless and free of impurities ($SiCl_4$, CO_2, $COCl_2$).

H_2 :

Hydrogen must be as pure as possible, preferably electrolytic.

Apparatus

In the attached scheme the apparatus required for the preparation of 15 - 20 g/h $TiCl_3$ is illustrated.

1) A H_2-cylinder.
2) A N_2-cylinder.
3) A 50 l-gasholder.
4) Mercury safety valve .
5) H_2-scrubber, consisting of an iron tube of 40 to 45 mm diameter, 1500 mm high, provided with a grate on the bottom and filled with reduced copper supported on pumice; heating is done by means of a 1.5 kw electric coil.
6) Water cooler, consisting of an iron coil of 9-12 mm diameter, 1 m long, welded directly to the lower part of apparatus 5) and connected to a trap 7) by means of a rubber stopper.
7) A trap consisting of a 1 liter-glass separatory funnel provided with a bottom discharge.
8) Regulating pyrometers.
9) 1 liter- Drechsel flask, empty.
10) 1 liter-Drechsel flask containing concentrated H_2SO_4.
11) A drier consisting of an iron tube of 40 to 45 mm diameter, 1000 mm high, filled with glass wool impregnated with P_2O_5.
12) Mercury gauge.
13) 14) Flowmeters containing vaseline oil as manometric liquid.
15) Thermocontrolled oil bath.
16) 2 liter-Drechsel flask, empty.
17) 2 liter-Drechsel flask containing $TiCl_4$.
18) 0.5 l-Drechsel flask as gas mixer.

19) Mercury thermometers.
20) Reactor: consisting of a stainless steel tube of 45-50 mm diameter, 1500 mm high, heated by a 3 kw electric coil and connected with apparatus No. 21 by means of a flange. The reactor must be very carefully insulated so as to avoid air drafts along the outside walls.
21) Stainless steel separator for $TiCl_3$ consisting of a cylindrical part, 300 mm in diameter and 200 mm high, and of a conical part, 200 mm high, provided with a bottom outlet and with a jacket for circulating water at 50 to 60 °C.
22) 2 liter-glass separatory funnel for collecting recovered condensed $TiCl_4$. The connection with apparatus 21 is obtained by means of rubber and stainless steel tubes of 30 to 35 mm diameter, with openings on top for inspecting the inside, provided with rubber stoppers.
23) Glass condenser with circulation of brine, with an inside tube of 20 to 25 mm diameter, 1 m high, connected by means of a ground joint.
24) Glass column for water scrubbing; inside diameter 35 mm, 2000 mm high, filled with Raschig rings.
25) H_2-burner.

For the connections, glass pipes, rubber stoppers and heavy rubber tubings are used. Screw clamps can be used on the rubber tubings (except for u).

Operating conditions

Flow rates:	H_2 at flowmeter 13)	95 Nl/h
	H_2 at flowmeter 14)	705 Nl/h
Temperature in column 5)		350 to 400 °C
Temperature of thermostatic bath 15)		80 °C
Temperature of the reactor		850 to 900 °C
Temperature of the water in the jacket of apparatus 21)		60 to 70 °C
Temperature of the brine in condenser 23)		- 20 °C

Operating procedure

1) The apparatus is swept with N_2 to remove air completely.
2) The tightness of the system is controlled.
3) N_2 is substituted with H_2
4) About 50 l/h H_2 are introduced through flowmeter 14) and heating of the copper column and of the reactor is started, controlling the temperature by means of the regulating pyrometers.

5) Thermostatic bath 15) is heated to the desired temperature.
6) Water and brine are circulated.
7) H_2 is introduced in the amount stated, controlling the flow-rates by means of flowmeters 13) and 14).

Once the apparatus is running the position of the stopcocks must be the following:

a) a, h, g, o: ..open
b) b, c, d, e, f, i, l, m, n, q : closed.

Stopping of the operation is done as follows:

1) Stopcock g is closed thus stopping the passage of H_2 through flowmeter 13).
2) Heating of reactor 20, of column 5) and of thermostat 15) is stopped.
3) Stopcock e and c are opened and a and o are closed.
4) The circulation of waters and brine is stopped.
5) Column 24) is swept with N_2 through stopcock 9).
6) The apparatus is kept under the pressure of a gasholder.

The position of the stopcocks must now be as follows:

a) c, e, h: open
b) a, b, d, f, g, i, l, m, n, o, q: closed.

Discharge of the product

The $TiCl_3$ obtained is collected in separator 21) as a very fine violet powder. It oxidizes at the air and can ignite, thus causing dangerous fires in the presence of H_2: it must be handled very carefully.

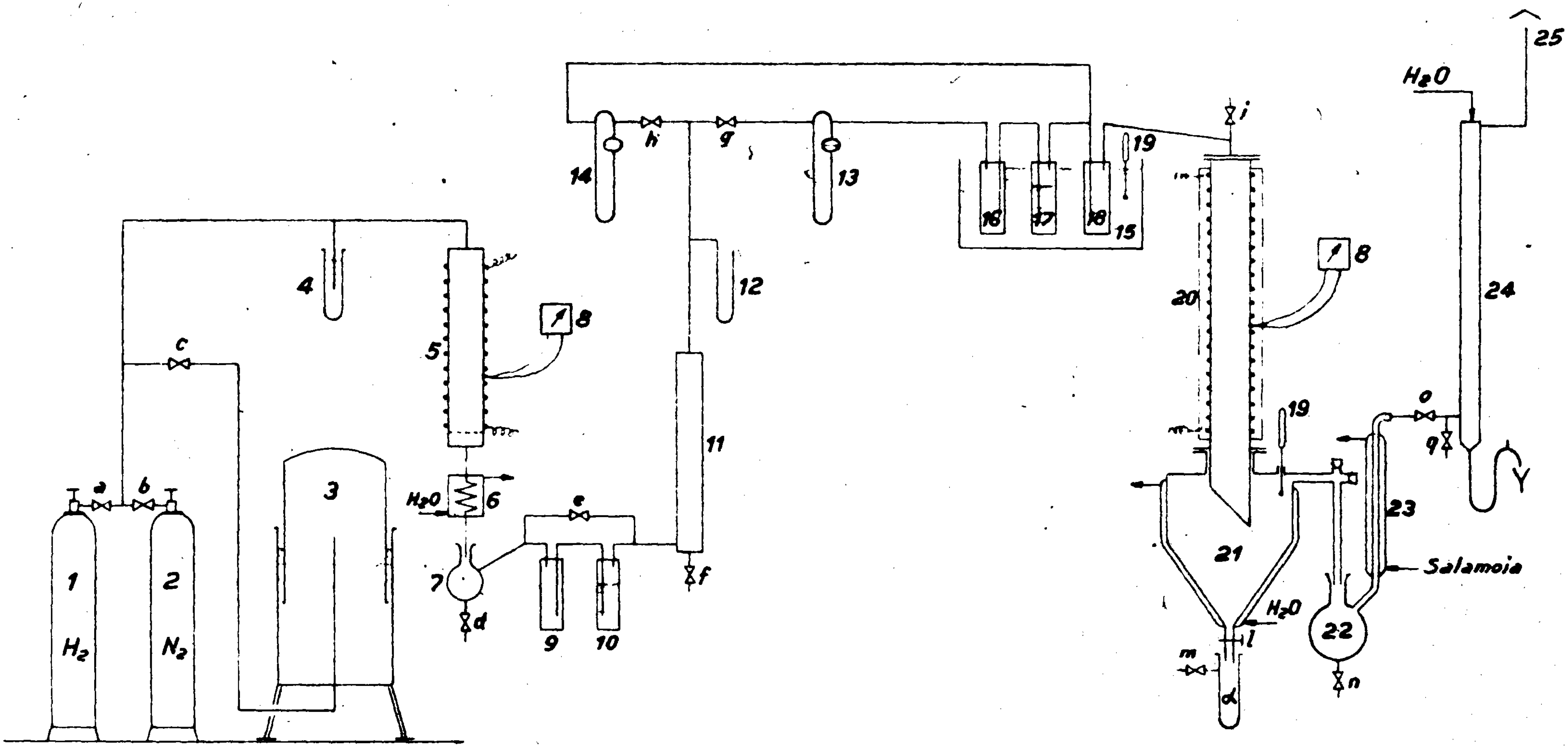
The discharge of the product is carried out through a rubber tubing of large diameter (40 mm) closed with screw clamp 1, connecting separator 21) with test tube α in which the product is collected.

Test tube α (40 mm diameter, 200 mm high) must be previously deaerated by sweeping it with oxygen-free nitrogen.
This is done through stopcock m, removing α slightly from the rubber tubing carrying clamp 1.

Once the discharge is completed, 1 is closed, α is removed from the rubber tubing and quickly closed with a rubber stopper .

NB:. The product may form aggregates in separator 21) so that tapping on it lightly may be necessary to facilitate the discharge.

Apparecchiatura per la preparazione di $TiCl_3$



MONTECATINI
SETTORE RESINE

Sezione Studi e Ricerche

CONSIDERAZIONI SUI DATI TECNICI CONTENUTI NELLA LETTERA "POLYPROPYLENE PLASTICS AGREEMENT" (UNION CARBIDE)

Milano, 9 agosto 1956.

Milano, 9 agosto 1956.

CONSIDERAZIONI SUI DATI TECNICI CONTENUTI NELLA LETTERA "POLYPROPYLENE PLASTICS AGREEMENT" (UNION CARBIDE)

Premessa

Le considerazioni contenute nella presente nota si riferiscono ai risultati ottenuti a Castellanza nelle prove di caratterizzazione dei quantitativi di polipropilene posti a nostra disposizione.

La quasi totalità dei prodotti da noi esaminati era di peso molecolare elevato. Per avere una fluidità tale da garantire una buona lavorabilità è stato per lo più necessario procedere ad una degradazione termica ossidativa per lavorazione su mescolatore a cilindri alla temperatura di 200÷220°C.

Detta precisazione, effettuata allo scopo di consentire una valutazione obiettiva di quanto verrà in seguito esposto, non dovrebbe però notevolmente influire sulla sostanza delle nostre considerazioni. Infatti i valori ottenuti sul materiale degradato dovrebbero risultare inferiori, ma non molto discosti, da quelli di materiali di pari grado ottenuti direttamente dalla polimerizzazione.

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Considerazioni sul punto 1

a. Viene richiesto che il grado dei due tipi di polipropilene presi in considerazione nella lettera, misurato con l'apparecchiatura e le condizioni standard per il polietilene (190°C, carico 2,1 kg), sia compreso fra 0,1 e 20 dg/min.

Assumendo il grado come indice di lavorabilità del materiale sarebbe, a nostro avviso, opportuno che la misura venisse effettuata ad una temperatura prossima a quella realmente adottata nelle lavorazioni del polipropilene. Abbiamo perciò scelto, per le nostre prove, la temperatura di 250°C mantenendo il carico di 2,1 kg. In tali condizioni, l'intervallo di valori, corrispondente a prodotti di buona lavorabilità, è compreso fra 0,1 e 4 dg/min.

Effettuando sugli stessi prodotti la determinazione nelle condizioni standard per il polietilene, il grado oscillerebbe fra valori tanto piccoli, da essere indeterminabili, e 0,3 dg/min.

b. Rigidità a trazione

Viene richiesto che la rigidità misurata su provini ottenuti per stampaggio e valutata come 100 volte il valore della sollecitazione richiesta per ottenere una deformazione dell'1% sulla lunghezza iniziale, con una velocità di trazione del 10% al minuto, sia compresa fra 80.000 e 100.000 p.s.i. per un tipo, e raggiunga il valore minimo di 180.000 p.s.i. per il secondo tipo di polipropilene.

L'apparecchiatura Amsler per le prove di trazione, di cui è dotato il nostro Laboratorio, non è munita di un sistema di ingrandimento dei grafici. Risulta quindi assai difficile apprezzare con la necessaria esattezza la deformazione dell'1% e il corrispondente valore del carico.

Le nostre determinazioni sul valore della rigidità vengono eseguite a flessione (Stiffness test D 747-48 T). I valori ottenuti sui materiali finora esaminati sono compresi fra 57.000 e 143.000 p.s.i. In base a dati in nostro possesso e riferentesi a materiali analoghi al polipropilene cristallino (Marlex 50) si può fissare il rapporto fra rigidità a flessione e rigidità a trazione in 1 : 1,4 circa. Perciò i valori da noi trovati corrisponderebbero, in una prova a trazione, a 79.800 e 200.200.

Siamo d'avviso che gli errori compiuti con questa arbitraria trasformazione risultano inferiori a quelli che si sarebbero compiuti tentando di apprezzare i valori della rigidità a trazione sui grafici ottenibili con la nostra apparecchiatura.

Per ottenere una conferma ai valori da noi calcolati e al rapporto 1 : 1,4 da noi assunto occorrerebbe eseguire prove sull'apparecchiatura Instron di cui è dotato il Laboratorio dell'Istituto di Ricerche Polymer a Terni.

Rileviamo ancora che la rigidità del polipropilene varia, più che con il grado del prodotto, con la percentuale di cristallino misurata in base all'estratto eptanico o alla densità. Aumentando la percentuale di prodotto cristallino e la densità aumenta, secondo una funzione lineare, anche la rigidità.

Pure avanzando qualche riserva in conseguenza delle valutazioni indirette da noi effettuate riteniamo possibile soddisfare le richieste avanzate nella lettera in esame in merito alla rigidità del polipropilene.

c. Deformazioni per sollecitazioni prolungate (creep).

Viene richiesto che i due tipi considerati di polipropilene, sollecitati rispettivamente con 1000 e 2000 p.s.i, alla temperatura di 60°C e per la durata di 1000 ore, non diano luogo ad una deformazione complessiva superiore al 10%.
Le prove debbono essere eseguite su provini di 0,02x0,125x inches, ottenuti per stampaggio.

Da parte nostra sono state effettuate finora solo prove orientative che hanno raggiunto la durata di 300 ore, con una sollecitazione di 1070 p.s.i. Il polipropilene sperimentato ha una viscosità intrinseca 3,27 e un re-

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siduo all'estrazione eptanica dell'85%, ed è uno fra i migliori fra quelli da noi esaminati.

A 60°C, con la sollecitazione di cui sopra, si ha una deformazione iniziale del 5%, raggiunta in 20 ore circa, e successivamente una deformazione approssimativamente costante (misurata nel tratto fra 100 e 200 ore) di 0,012%/h, corrispondente a 12% in 1000 ore. La deformazione complessiva in 1000 ore sarebbe quindi del 17%. Con sollecitazioni maggiori le deformazioni risultano logicamente più grandi. Ad es. con un carico di 1500 p.s.i., alla temperatura di 60°C si ha una deformazione iniziale dell'11% circa, oltre ad un incremento del 3,6% in 100 ore, corrispondente a 36% in 1000 ore. Le deformazioni permanenti corrispondenti a carichi più alti sono state da noi misurate solamente alla temperatura di 20°C.

Più precisamente con un carico di 2450 p.s.i., a 20°C, si ha una deformazioneiniziale del 12% circa e un incremento del 13% in 100 ore, corrispondente ad un valore di 130% in 1000 ore.

Se si assume, per il rapporto fra la deformazione a 20°C e quella a 60°C il valore di 1 : 3 ÷ 1 : 4, in conformità a quanto da noi rilevato per sollecitazioni più basse, la deformazione totale per una sollecitazione di 2000 p.s.i. a 60°C per 1000 ore può essere valutata in 300÷400%.

Sia pure facendo le debite riserve sui valori da noi valutati per interpolazione, riteniamo di poter affermare che sarà assai difficile soddisfare le richieste formulate in merito al creep del polipropilene. Potrà essere avvicinato il valore richiesto per il carico di 1000 p.s.i. ma è da escludere, sulla base delle nostre conoscenze, che si possa ottenere un materiale il quale, sottoposto ad un carico di 2000 p.s.i. a 60°C per 1000 ore si deformi in misura inferiore al 10%. Ciò anche se si potessero raggiungere valori assai elevati nella cristallinità e i pesi molecolari più elevati fra quelli ammessi in rispondenza dei valori del grado e della conseguente lavorabilità citati al punto 1 a.

Punto 2

Esula della nostra competenza.

Punto 3 - Stabilizzazione del polipropilene

1. Percentuale di stabilizzante

Riteniamo sia possibile rientrare nel limite massimo dell'1% previsto. I migliori risultati in fatto di stabilizzazione contro la degradazione termica sono stati da noi ottenuti con Santowhite Crystals e 2246.

2. Atossicità e permanenza dello stabilizzante

Si può rispondere affermativamente per quanto concerne la non volatilità dello stabilizzante se intesa come termine generico. Se invece fosse riferita a prove specifiche occorrerebbe conoscere le condizioni richieste da tali prove.
Circa l'atossicità dello stabilizzante i prodotti da noi consigliati sono di produzione U.S.A. (Il Santowhite è della Monsanto e il 2246 della American Cyanamid). Sarà perciò possibile controllare se essi siano considerati atossici dalla Food and Drug Administration. Un esame sulla tossicità di eventuali altri stabilizzanti dovrebbe essere eseguito secondo le norme di detto Ente, norme che non sono in nostro possesso.

3a. Variazioni del carico di rottura per ossidazione termica

Dopo condizionamento per 500 ore in aria circolante alla temperatura di 100°C e in assenza di luce si dovrà registrare una riduzione del carico di rottura non superiore al 50% del valore iniziale.
Non abbiamo finora eseguite prove di questo tipo. In base alle nostre conoscenze riteniamo che il polipropilene possa superare in modo soddisfacente questa prova.

3b. Variazione del carico di rottura per esposizione alla luce.

Dopo condizionamento per 500 ore in Fadeometro Atlas non si dovrà registrare una riduzione del carico di

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rottura superiore al 50% del valore iniziale.
Non abbiamo finora eseguito determinazioni di trazione sui provini esposti.
In base alle osservazioni effettuate sui provini finora esaminati rileviamo che con gli antiossidanti finora noti sia difficile ottenere la protezione richiesta contro l'azione della luce. I provini diventano fragili in periodi di esposizione che variano fra le 20 e le 150 ore. Solo con Santowhite sono stati registrati risultati migliori.
Il risultato richiesto si può invece ottenere includendo nel polipropilene 1-2% di carbon black. Una relativa protezione viene anche assicurata con uguali percentuali di ossido di titanio rutilo RA 50.
Occorre rilevare che i materiali finora posti a nostra disposizione erano ricchi in impurezze di cui ignoriamo l'influenza nei confronti della prova di stabilità alla luce. Un giudizio più obiettivo potrà essere emesso solo dopo aver esaminato campioni di polipropilene ad elevato grado di purezza.
Facciamo inoltre rilevare che la valutazione basata sulle variazioni del carico di rottura a trazione non è molto appropriata. Più significativa sarebbe una valutazione basata sulle variazioni del modulo elastico.

3c. Stabilità del colore

Dopo estrusione o stampaggio nelle normali condizioni operative il prodotto dovrà registrare variazioni di colore uniformi con una percentuale di bianco di almeno 65 e di giallo non superiore a 25.
Non disponiamo dell'apparecchiatura necessaria a misurare i valori citati. Inoltre, anche in questo caso, occorrerebbe partire da polipropilene molto puro mentre i campioni finora posti a nostra disposizione erano già colorati in partenza e dimostravano una forte tendenza ad imbrunire per effetto dei trattamenti termici subiti nel corso delle diverse lavorazioni.

Punto 4 - Corrosione degli stampi

Nel corso di 24 ore di stampaggio con stampi in acciaio a basso tenore di C non si devono notare corrosioni negli

stampi e non si devono notare odori percettibili.
Con i prodotti molto impuri sui quali abbiamo finora lavorato abbiamo notato fenomeni di corrosione a volte assai vistosi. Abbiamo anche notato, in correlazione con ciò, lo sviluppo di odore penetrante e sgradevole.

Abbiamo tentato di ovviare a questi inconvenienti con l'impiego di stabilizzanti, in particolare di tipo epossidico. Non abbiamo avuto modo di effettuare determinazioni quantitative dei miglioramenti ottenuti, che sono comunque assai sensibili nei confronti dei fenomeni di corrosione, del colore e, in misura minore, anche dell'odore.

Occorrerebbe disporre di prodotto puro per stabilire se detta stabilizzazione sia necessaria e se sia possibile soddisfare la richiesta sopra citata.

Punto 5

Non è di nostra competenza.

[illegible]/rsm.