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EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

THE RADIOLYTIC AND PYROLYTIC DECOMPOSITION OF ORGANIC COOLANTS

V. THE THERMAL DECOMPOSITION OF o-, m- AND p-TERPHENYL IN THE PRESENCE OF ATTAPULGUS CLAY

by

G. JUPPE and H. RAU

1967

ORGEL Program
Joint Nuclear Research Center
Ispra Establishment - Italy
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E R R A T U M

The radiolytic and pyrolytic decomposition of organic coolants

V. The thermal decomposition of o-, m- and p-terphenyl in the presence of attapulgus clay.

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Please insert p. 7 , 2nd § after the following sequence :

"... and 61% p-terphenyl were finally formed."

" H. Nordmeyer [13] observed isomerisation and cracking when pyrolysing om-2 with attapulgus clay."

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Published in the same series :

THE RADIOLYTIC AND PYROLYTIC DECOMPOSITION OF ORGANIC COOLANTS

I. G. Juppe, M. Alvarenga and H. Hannaert ; The Pyrolytic Decomposition of Terphenyls ; EURATOM Report EUR 1647.e (1964).

II. G. Juppe, G. Wedekind, H. Rau and G. Schütz ; The Postpyrolysis of Preirradiated OM2 ; EURATOM Report EUR 3287.e (1967).

III. G. Juppe, H. Rau and F. Dorpema ; The Radiolysis and Pyrolysis of m-Terphenyl and m-Terphenyl-d_{14} ; EURATOM Report EUR 3172.e (1967).

VII. G. Juppe and H. Rau ; The Pyrolysis of High Boiling Residue ; EURATOM Report EUR 3158.e (1966).

SUMMARY

The kinetics of the pyrolysis of pure o-, m- and p-terphenyl and of material mixed with Attapulgus clay were studied. 10 to 12 times more o-, m- and p-terphenyl was decomposed in the clay catalyzed experiments and a strong isomerisation of o- into m- and p-, and m- into p-terphenyl appeared. Twice as much benzene and diphenyl was formed in the clay added runs. Similar differences were obtained for the quaterphenyl, triphenyl and triphenylbenzene formations. From the catalyzed experiments 50 times as much total gas was found consisting of 37 % hydrogen, 19 % methane, 7 % ethane, 2 % propane, 1.5 % n-pentane, 3.8 % isopentane, 2.5 % ethylene, 0.4 % acetylene, 0.9 % propene and 2 % butenes. The uncatalyzed runs yielded 82 % hydrogen, 4 % methane, 1 % ethane, 0.4 % propane, 0.2 % n-pentane, 0.3 % isopentane, 10 % ethylene, 2.8 % acetylene, 1.2 % propylene and 2 % butenes. It is suggested that the thermal decomposition of pure terphenyls follows a radical mechanism while the clay catalyzed pyrolysis follows a carbonium ion mechanism.

C O N T E N T S

K E Y T O T H E T A B L E S

K E Y T O T H E F I G U R E S

Previous tests performed by Atomics International[1] and by AECL[2] have shown that a fixed bed of Attapulgus Clay followed by a back up filter can effectively be used for the removal of organic and inorganic impurities from an ORGEL type coolant. The absorption of these impurities increases with increasing temperature. Only at temperatures above 400°C was a satisfactory purification of the radio-pyrolyzed coolant achieved.

At these high temperatures Attapulgus Clay could act as Lewis acid, especially when traces of water as promotor are present. This type of catalyst is known to initiate the decomposition of aromatic compounds like benzene, di- and terphenyls at temperatures well below those necessary for the pyrolytic decomposition. The di- and terphenyls intended to be recovered after radio-pyrolysis in an ORGEL reactor by the clay method would thus be decomposed by the purification process itself.

In the present investigation this question was studied by pyrolyzing o-, m- and p-terphenyl alone and in mixture with Attapulgus clay and comparing the kinetics of the thermal decompositions.

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1) G.O. Haroldsen and I.W. Florence, NAA Report SR-6905 (1962)

2) I.H. Duerksen and D.H. Charlesworth, AECL-Report 1683 (1963)

1 - INTRODUCTION (*)

The catalytic action of classical Lewis acids on the thermal decomposition of aromatic compounds is well established. More than sixty years ago V. Thomas[3] found that treatment of benzene with ferric chloride resulted in the formation of a black solid. Benzene is known to give resins and dark coloured solids on treatment with aluminium chloride or bromide under drastic thermal conditions[4]. P. Kovacic[5] recently investigated the oxidative polymerisation of benzene catalyzed by the Lewis acids aluminium-, molybdenum- and ferric chloride; polymerisation under remarkably mild conditions is only achieved when copper chloride as oxidant was added. R.D. Swisher[6] reported the isomerisation of the terphenyls using various amounts of aluminium chloride at temperatures ranging from 140°C to 220°C and observed the formation of 65 to 70% m-terphenyl regardless of whether o-, m- or p-terphenyl was used. The aluminium chloride catalyzed isomerisation of the three terphenyl isomers was again studied by G.A. Olah and M.W. Meyer[7]. At 220°C an equilibrium mixture was obtained which consisted of 63% m-, 37% p-terphenyl, and no o-isomer.

---

3) V. Thomas, Compte rend. 126, 1211 (1898)

4) C.H. Thomas, "Anhydrous Aluminium Chloride in Organic Chemistry", Reinhold Publ.Corp., New York, N.Y. 1941, p.716

5) P. Kovacic and A. Kyriakis, J.Americ.Chem.Soc. 85, 454 (1963)
P. Kovacic and R.M. Lange, J.Org.Chem. 28, 968 (1963)
P. Kovacic and F.W. Koch, J.Org.Chem. 28, 1864 (1963)

6) R.D. Swisher, U.S.Patent 2363, 209 (1944) (Monsanto Chemical Co.)

7) G.A. Olah and M.W. Meyer, J.Org.Chem. 27, 3682 (1962)

(*) Manuscript received on December 23, 1966.

Pure oxide catalysts have been investigated only to a minor extent. Manganeous and nickel oxide promote the thermal decomposition of benzene at elevated temperatures[8]. Oxides of barium, zinc, aluminium, lead and silicon were found to be effective only at temperatures above 6oo°C[9]. The effect of alumina-silica cracking catalyst and nickel-silica hydrogenation catalyst on the thermal decomposition of benzene was investigated by V.N. Ipatieff and G.S. Monroe[1o]. They found an increased rate for the destruction of the aromatic molecules. The formation of toluene from benzene was reported.

More recently in a French patent M. Jaymond and B. Germain[11] described the isomerisation of o-, m- and p-terphenyl in the presence of silica clays. Starting with o-terphenyl at 22o°C, 39% m- and 61% p-terphenyl were finally formed.

---

8) I. Ostronisslenski and I. Burshanadse, cit.Chem.Zentr. 81, I, 1711 (191o)

9) C. Smith and W. Lewcock, J.Chem.Soc. 1o1, 1453 (1912)
V. Ipatieff, J.Americ.Chem.Soc. 55, 3696 (1933)
Y. Kosaka, J.Fuel Soc. (Japan) 7, 892 (1928)

1o) V. Ipatieff and G.S. Monroe, J.Americ.Chem.Soc. 69, 71o (1947)

11) M. Jaymond and B. Germain, French patent Fr 1,345,o21 (C1C07c) (Progil S.A.)

2 - MATERIALS AND METHODS

2.1 - MATERIALS

All three terphenyls were samples commercially available[12]. m-Terphenyl was purified by distillation from traces of p-impurities. The o-terphenyl was recrystallized several times from methanol until gas chromatographic purity had been achieved.

The sample of Attapulgus clay had a composition listed in table 1. Further physical and chemical properties of the material have been described by H. Nordmeyer[13].

TABLE 1 - COMPOSITION OF ATTAPULGUS CLAY (wt.%)

SiO_2	66,0	K_2O	1,91	Ga	10^{-4}
TiO_2	0,53	CO_2	0,45	Sr	10^{-4}
Al_2O_3	13,46	SO_4	0,05	Mb	10^{-4}
Fe_2O_3	4,14	V	10^{-3}	Tl	10^{-4}
FeO	0,20	Y	$2\ 10^{-4}$	Be	$4\ 10^{-5}$
MnO	0,06	Zr	$2\ 10^{-4}$	B	$4\ 10^{-5}$
MgO	10,00	Ba	$2\ 10^{-4}$	Cu	$4\ 10^{-5}$
CaO	2,64	Cr	10^{-4}	Ag	$4\ 10^{-5}$
Na_2O	0,08	Zn	10^{-4}	Pb	$4\ 10^{-5}$

12) Merck, Darmstadt

13) H. Nordmeyer, The Retention of Organic and Inorganic Compounds on Clay Minerals, Part I, Basic Studies, EURATOM-Report 2646e (1966)

The material having a particle size between 24 and 48 mesh was dried at 120°C until a constant weight had been achieved. It was used immediately afterwards.

2.2 - PYROLYSIS

The preparation and the pyrolysis of the samples were carried out as previously described[14].

Oxygen enclosed in the inner layer of the sample tubes was carefully removed by heating them for 4 hours at 480°C ± 10°C and applying a vacuum of better than 10^{-4} mm. The samples were pyrolyzed simultaneously in pairs, one containing 2,0 g of pure terphenyl, the other 2,0 g terphenyl and 200 mg Attapulgus clay. The chosen temperature of 451°C was measured continuously by thermoresistance and did not fluctuate more than ± 1°C around the set point.

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14) G. Juppe, M. Alvarenga and H. Hannaert, EURATOM-Report 1647e (1964)

2.3 - ANALYSIS

2.3.1 - GASEOUS PRODUCTS

The determination of the total gas was performed in a conventional gas line as previously described[14]. Benzene and low boilers had been separated before by condensing them in a carbon dioxide/acetone mixture. The mass spectroscopic analyses of hydrogen, methane, ethane, ethylene, acetylene, propane, propene, n-butane, i-butane, 1-butene, 2-butene, n-pentane and i-pentane and the sum of the pentenes were performed on an Atlas Spectrometer, type CH-4[15].

2.3.2 - LIQUID PRODUCTS

The gas chromatographic analysis of benzene, diphenyl, the three terphenyl isomers, the quaterphenyl and triphenyl benzene isomers and the rest of the high boiling products were carried out by injecting trichlorobenzene solutions containing an inner standard. A 2,5 m CsCl-column was used. The raise in temperature over a 150°C range was maintained at 20°C per second[16].

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15) W. Beyrich, S. Facchetti and A. Marrel, EURATOM Internal Report (not available)

16) G. Barbero, F. Geiss and B. Versino, EURATOM Internal Report (1962) (not available)

3 - R E S U L T S

3.1 - FORMATION OF GASES

A comparison of the total gas formation during the pyrolysis of the pure terphenyls and the terphenyls + Attapulgus clay is given in fig. 1. The composition of the gas originating from the pyrolysis of o-terphenyl without additives and with added Attapulgus clay is listed in table 2.

TABLE 2 - COMPOSITION OF GAS (mole %)

	O-TERPHENYL	O-TERPHENYL + ATTAPULGUS CLAY
HYDROGEN	79-82	33-41
METHANE	3,1-3,7	14-19
ETHANE	0,9-1,0	5,2-7,2
ETHYLENE	6-10	2,0-2,5
ACETYLENE	1,6-2,8	0,2-0,4
PROPANE	0,3-0,4	1,0-2,1
PROPYLENE	0,8-1,2	0,5-0,9
n-BUTANE	1,0	0,1-0,3

	O-TERPHENYL	O-TERPHENYL + ATTAPULGUS CLAY
i-BUTANE	0,4-0,6	0,2-0,5
1-BUTENE	0,7-1,0	11-15
2-BUTENE	1,1	12-17
n-PENTANE	0,2	1,2-1,5
i-PENTANE	0,2-0,3	3,0-3,8
PENTENES	0,1-0,2	0,3-0,4

3.2 - FORMATION OF LIQUIDS

A comparison of the experimental data for the formation of benzene from the pyrolysis of pure o-terphenyl and from o-, m- and p-terphenyl + Attapulgus clay is illustrated in fig. 2. In fig. 3 the rates of diphenyl formation from the terphenyl isomers with and without Attapulgus clay are compared.

The rates of the observed decrease in o-, m- or p-terpheryl during their thermal decompositions with and without Attapulgus clay are listed in fig. 4-6. The kinetics of the formation of o- terphenyl from m- or p-terphenyl + Attapulgus clay is also described in fig. 4. Data about the formation of m- and p-terphenyl from o-, m- resp. p-terphenyl are listed in fig. 5 resp. 6.

The kinetics of the formation of o,o-[17], o,m-, o,p-[18], m,m-[19], m,p-quaterphenyls and the sum of all quaterphenyls, triphenylbenzenes and triphenylenes from the thermolysis of o-terphenyl with and without Attapulgus clay are described in fig. 7 to 12.

The experimental data about the formation of high boilers originating from the thermal decomposition of o-, m- or p-terphenyl with and without Attapulgus clay as additive are graphically illustrated in fig. 13.

On the basis of a first order reaction for the formation of benzene, diphenyl, m-terphenyl, p-terphenyl, o,o-quaterphenyl, o,m-quaterphenyl, o,p-quaterphenyl, m,m-quaterphenyl, m,p-quaterphenyl, as well as the sum of all quaterphenyls, triphenylbenzenes and triphenylene, the formation of high boilers and the decrease in o-, m- and p-terphenyls, the approximate initial rate constants have been determined and are listed in table 3:

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17) including triphenylene

18) including 1,2,4-triphenylbenzene

19) including 1,3,5-triphenylbenzene

TABLE 3 - RATE CONSTANTS [mg/g h]

	O-TERPHENYL		M-TERPHENYL		P-TERPHENYL	
	PURE	WITH AC[a]	PURE	WITH AC[a]	PURE	WITH AC[a]
Ø	-	2,1	-	1,75	-	1,5
$Ø_2$	-	5,2	-	2,1	-	1,5
o-$Ø_3$	16[b]	1040[b]	-	30[c]	-	20[c]
m-$Ø_3$	3[c]	640[c]	9[b]	520[b]	-	280[c]
p-$Ø_3$	1,5[c]	120[c]	-	30[c]	7[b]	360[b]
o,o-$Ø_4$[d]	4	14	-	6	-	-
o,m-$Ø_4$	0,5	1,2	-	-	-	-
o,p-$Ø_4$[e]	1,1	1,5	-	-	-	-
m,m-$Ø_4$[f]	0,2	1,6	-	-	-	-
m,p-$Ø_4$	0,1	0,9	-	-	-	-
sum $Ø_4$[g]	4	18	-	8	-	-
HB	14	79	10	27	20	31

a) Attapulgus clay
b) decrease
c) formation
d) including triphenylene
e) including 1,2,4-triphenylbenzene
f) including 1,3,5-triphenylbenzene
g) including triphenylene, 1,2,3- and 1,3,5-triphenylbenzene

Table 4 shows the composition of the liquid products after 5 hours' pyrolysis at 451°C of pure o-, m- and p-terphenyl and of o-, m- and p-terphenyl in mixture with Attapulgus clay.

TABLE 4 - COMPOSITION OF LIQUIDS (%)

	O-TERPH.	O-TERPH. + Ac[a]	M-TERPH.	M-TERPH. + Ac[a]	P-TERPH.	P-TERPH. + Ac[a]
BENZENE	0,31	0,59	-	0,55	-	0,55
DIPHENYL	1,15	1,70	0,4	0,8	0,3	0,6
o-TERPHENYL	92,8	23	-	6	-	4
m-TERPHENYL	1,5	43	-	54	-	36
p-TERPHENYL	0,30	17	-	32	-	48
o,o-QUATERPH.[b]	0,04	0,31	-	-	-	-
o,m-QUATERPH.	0,09	0,47	-	-	-	-
o,p-QUATERPH.[c]	0,25	0,64	-	-	-	-
m,m-QUATERPH.[d]	0,98	0,46	-	-	-	-
m,p-QUATERPH.	0,04	0,31	-	-	-	-
SUM QUATERPH.[e]	1,7	3,75	-	2,25	-	0,6
HIGH BOILERS	4,0	15,0	3,2	7,1	6,4	10,9

a) Attapulgus clay

b) including triphenylene

c) including 1,2,4-triphenylbenzene

d) including 1,3,5-triphenylbenzene

e) including triphenylene, 1,2,4- and 1,3,5-triphenylbenzene

4 - D I S C U S S I O N

4.1 - FORMATION OF GASES

4.1.1 - TOTAL GAS

A comparison of the formation of gases originating from the pyrolysis of the three pure terphenyl isomers and when mixed with Attapulgus clay shows the following:

There is appr. 1,5 times more gas obtained from m-terphenyl and 2 times more from o-terphenyl than from p-terphenyl in both the catalyzed and uncatalyzed experiments.

Comparing the total gas formation pure o-terphenyl exhibits a rate of total gas production appr. 5o times smaller than o-terphenyl in the presence of Attapulgus clay.

4.1.2 - GAS COMPOSITION

The gas compositions from the pyrolysis of terphenyl with or without clay catalyst show significant differences:

The hydrogen content for the pyrolysis of pure o-terphenyl is as high as 97-82% but drops in the presence of Attapulgus clay to less than half of this value. At low conversions, 33% of the total gas is analyzed to be hydrogen. This value increases to 41% hydrogen after the conversion of 79% of the initial o-terphenyl.

At the beginning of the Attapulgus catalyzed reaction, 19% of the total gas consists of methane, 7,2% of ethane, 2,1% of propane, 1,5% of n-pentane and 3,8% of isopentane. The corresponding percentages from the uncatalyzed runs are considerably lower: 3,7% methane, 1,o% ethane, o,4% propane, o,2% n-pentane, o,3% isopentane.

The formation of n-butane seems to be an exception: when pyrolyzing pure o-terphenyl 1,o% of the total gas is analyzed to be n-butane. When adding Attapulgus to the experiments only o,3% of the total reaction gas consists of n-butane.

The gas mixture of the Attapulgus experiments contains less unsaturated hydrocarbons than the reaction gas originating from the uncatalyzed runs: 2,5% (1o%) ethylene, o,4% (2,8%) acetylene, o,9% (1,2%) propylene are formed in the clay catalyzed (uncatalyzed) experiments. The formation of 1- and 2-butene is an exception. In the catalysed runs 1,0 % (1,1 %) of the total gas formed is analyzed to be 1-butene (2-butene). In the clay catalyzed experiments 15% (17%) of the total gas is found to be 1-butene (2-butene).

Although the hydrogen content in the reaction gas increases with progressing conversion, the content of saturated and unsaturated hydrocarbons decreases.

4.2 - FORMATION OF LIQUIDS

A comparison of the formation of liquid products originating from the pyrolysis of pure o-, m- and p-terphenyl and the corresponding material mixed with Attapulgus clay shows the following:

4.2.1 - FORMATION OF BENZENE AND DIPHENYL

The formation of benzene and biphenyl from o-, m- or p-terphenyl can only for the uncatalyzed experiments be described as resulting from zero order reactions. The formation of these compounds from the Attapulgus catalyzed runs follows a higher reaction order.

Compared with the pyrolysis of pure o-terphenyl an appr. two times increased rate of benzene formation is observed when pyrolyzing the terphenyl in the presence of Attapulgus clay.

A similar behavior is observed for the biphenyl formation from the pyrolysis of o-, m- and p-terphenyl. An appr. 60%, 300%, 150% increased rate of production of biphenyl results from the clay catalyzed o-, m- and p-terphenyl pyrolysis.

4.2.2 - TERPHENYL DECREASE

At the beginning of the reaction in both the uncatalyzed and clay catalyzed runs, the disappearance of terphenyls follows appr. a first order reaction. There appear, nevertheless, great quantitative differences which are due to catalysis:

Under the same thermal conditions 12, 1o and 12 times more o-terphenyl, m-terphenyl and p-terphenyl respectively are decomposed in the clay catalyzed processes.

4.2.3 - TERPHENYL ISOMERISATION

The partial isomerisation of o- into m- and p-terphenyl and m- into o- and p-terphenyl under thermolysis conditions was well established some time ago. The rates of the zero order reactions for the uncatalyzed processes are nevertheless very small: Starting from o-terphenyl and at 451°C only 1,5% m-terphenyl and o,3% p-terphenyl can be detected by vapor phase chromatography after 5 hours' pyrolysis time.

The isomerisation reaction becomes the main reaction when Attapulgus clay is present during the pyrolysis of o-, m- or p-terphenyl. After 5 hours and at 451°C, 43% and 17% of the o-terphenyl have been changed to the m-isomer and p-isomer. Similar results are obtained for the m-terphenyl isomerisation. Under the same thermal conditions, 32% of the initial m-terphenyl underwent isomerisation to p-terphenyl, but only 6% of o-terphenyl are formed. p-terphenyl under the same reaction conditions gives 4% o- and 48% m-terphenyl.

It is difficult to assign even a formal reaction order for the catalytic isomerisation of the individual terphenyls, at least at higher conversion rates. Finally an equilibrium between the three terphenyl isomers is approached being approximately the same regardless of whether o-, m- or p-terphenyl was used as starting terphenyl: the terphenyl composition of the final pyrolysis product at 451°C approaches finally a terphenyl content of appr. 16% o-terphenyl, 48% m-terphenyl and 37% p-terphenyl.

4.2.4 - QUATERPHENYL FORMATION

A major fraction of the products of the pyrolysis of o-, m- and p-terphenyl with and without clay additives consists of quaterphenyls, triphenylbenzenes and triphenylene.

The formation of the sum of these compounds follows in all cases approximately first order kinetics.

The rate of formation for these C_{18}-products is considerably higher of the clay catalyzed experiments than of the non-catalyzed runs:

o-terphenyl mixed with Attapulgus clay gives four times the formation of quaterphenyls, triphenylbenzenes and triphenylene as does the uncatalyzed process. The analyses for the individual C_{18}-compounds supply additional information:

During the pyrolysis of o-terphenyl the presence of Attapulgus clay causes an increase in the rate of production of the following compounds: o,o-quaterphenyl + triphenylene (8 times), o,m-quaterphenyl (5 times), o,p-quaterphenyl + 1,2,4-triphenylbenzene (5 times), m,m-quaterphenyl + 1,3,5-triphenylbenzene (4 times) and m,p-quaterphenyl (4 times). At 17% of the total, o,p-quaterphenyl + 1,2,4-triphenylbenzene are the main products formed, followed by m,m-quaterphenyl + 1,3,5-triphenylbenzene (12%), o,m-quaterphenyl (11%), o,o-quaterphenyl + triphenylene (8%) and m,p-quaterphenyl (8%). Also after the uncatalyzed o-terphenyl decomposition a similar composition of the quaterphenyl fraction is obtained: the main product is o,p-quaterphenyl + 1,2,4-triphenylbenzene (15% of the quaterphenyl fraction), followed by m,m-quaterphenyl + 1,3,5-quaterphenyl (7%), o,m-quaterphenyl (6%), o,o-quaterphenyl + triphenylene (3%), and m,p-quaterphenyl (3%).

4.2.5 - HIGH BOILER FORMATION

The formation of high boilers from the pyrolysis of o-, m- and p-terphenyl alone or in mixture with Attapulgus clay can be reasonably well described as resulting from a first order reaction. There appear, nevertheless, great quantitative differences between the catalyzed and the uncatalyzed processes:

The catalyzed pyrolysis of pure o,m- and p-terphenyl produced 5, 2,5 and 1,5 times respectively the amounts of high boilers formed during the uncatalyzed pyrolysis of the three terphenyl isomers.

Appr. 45% of the high boiler fraction from pure o-terphenyl consist of quaterphenyls. The high boiler fractions from the clay catalyzed experiments contain more compounds of higher molecular weight: Only 25%, 31%, and 6% of the high boilers formed during the thermal decomposition of o-terphenyl, m-terphenyl, and p-terphenyl respectively in the presence of Attapulgus clay can be analyzed to be quaterphenyls or other C_{18}-compounds.

4.3 - MECHANISM OF MINERAL CLAY CATALYSIS

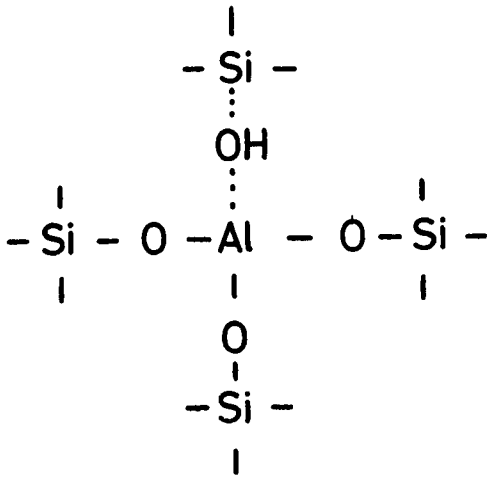
Sulphuric and phosphoric acids and Friedel Crafts catalysts (halides of boron and aluminium) catalyze the cracking and isomerisation of aliphatic hydrocarbons, alkylation reactions and the polymerization of olefins. It is well established, that all these reactions proceed by a carbonium ion mechanism. Friedel Crafts halides are designated Lewis acids, they react with water or other hydroxylic compounds with the liberation of protons:

$$AlCl_3 + H_2O \quad === \quad H_2O....AlCl_3 \quad === \quad H^+(AlCl_3OH)^-$$

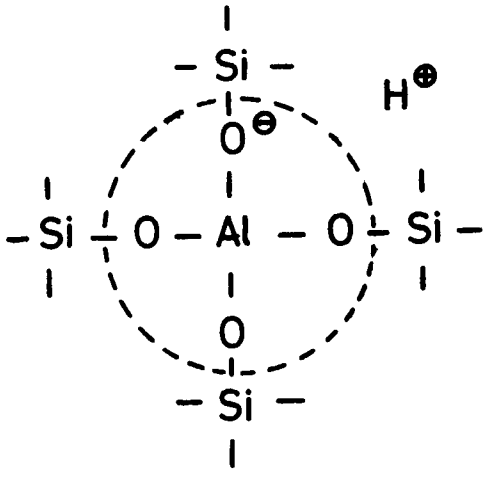
These protons or the protons from inorganic acids are then responsible for the formation of carbonium ion intermediates of organic compounds.

However, natural and synthetic clay also catalyze cracking and isomerisation reactions of aliphatic compounds, alkylation reactions and olefin polymerizations. The participation of carbonium ions as intermediates of this catalysis also, has only recently been proved [20].

In alumina silicates both Lewis acid sites (I) and Brönsted acid sites (II) can be formulated:



(I) Lewis acid site



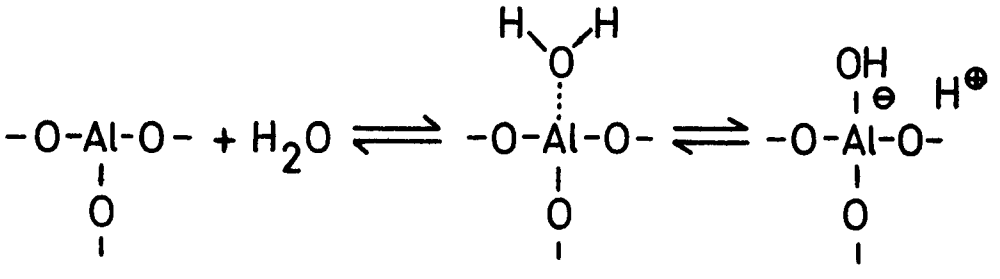
(II) Brönsted acid site[21]

---

20) H.F. Leftin and W.K. Hall, Proc. 2nd International Congress on Catalysis (Editions Technip, Paris 1961) 1, 1353
A.N. Webb, ibid, 1, 1289

21) The negative charge is probably delocalized within the dotted circle because of the high electronegativity of oxygen atoms

The Brönsted structure could be proven by T.J. Gray[22] on the basis of differential thermal analysis and X-ray spectroscopy. Brönsted acid sites can be formed directly (I) or by the hydration of alumino silicates by i.g. constituent water of the material:



The resulting protons initiate the formation of carbonium ions with aromatic compounds which are intermediates of the pyrolysis reaction and therefore undergo consecutive reactions. For the reaction of terphenyl with Lewis or Brönsted acids, the following reaction sequences are proposed:

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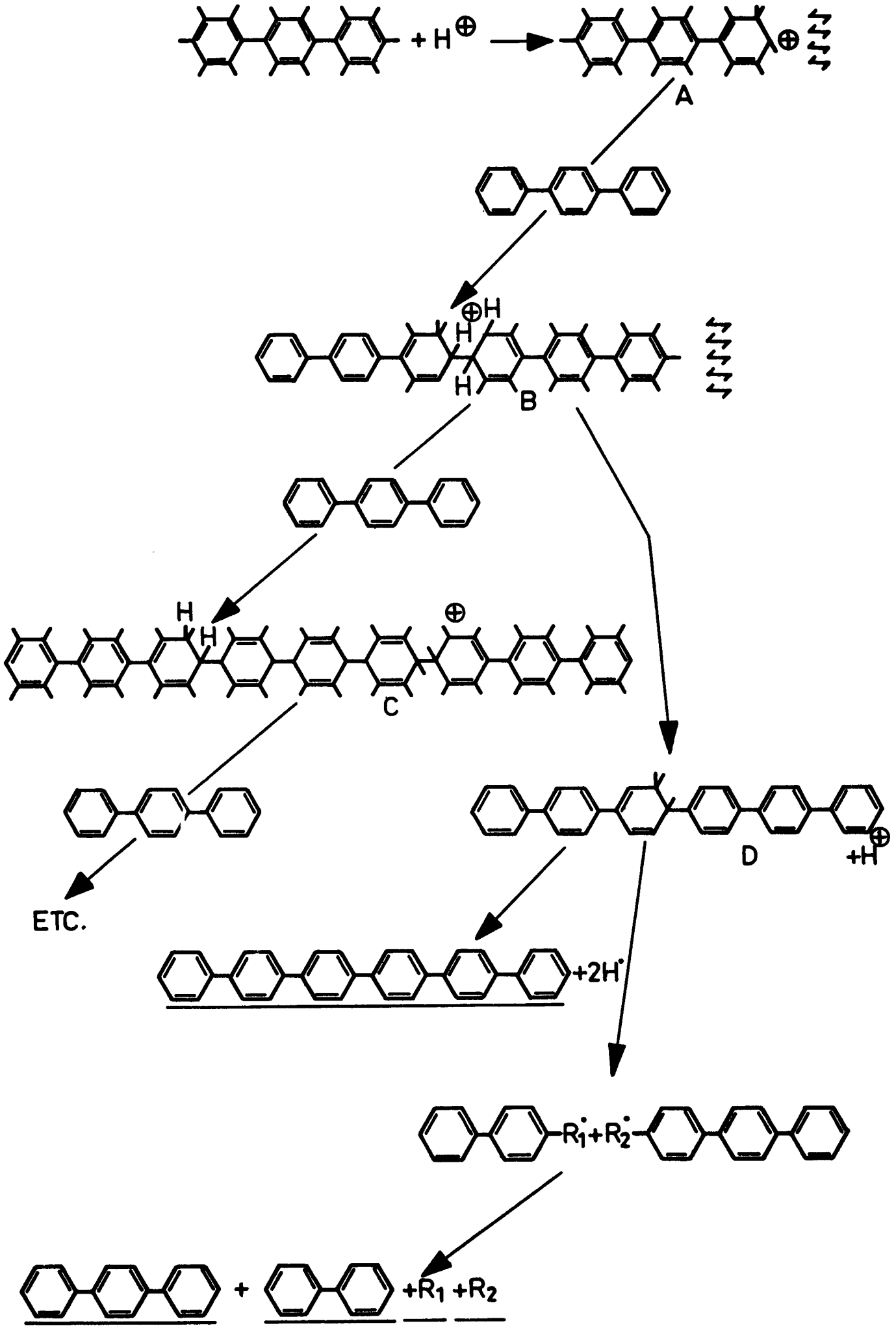
22) T.J. Gray, J.phys.Chem. 61, 1341 (1957)

CARBONIUM ION OPERATED REACTION MECHANISM



The Attapulgus clay catalyzed decomposition of terphenyls would thus lead to the formation of hydrogen atoms and aryl radicals just like the uncatalyzed thermal decomposition. In addition to this formation of alkyl radicals, leading to saturated and unsaturated hydrocarbons, and of dihydrogenated and fully aromatic hexaphenyls is to be expected.

4.4 - ATTAPULGUS CATALYSIS ON TERPHENYL PYROLYSIS

The kinetic results obtained in this investigation can consequently be explained on the following basis:

4.4.1 - TOTAL GAS FORMATION

A strong increase in the rate of hydrogen and saturated and unsaturated aliphatic hydrocarbon formation results when Attapulgus is present during the thermal decomposition of o-, m- and p-terphenyl. The above carbonium ion mechanism leads to the formation of hydrogenated aromatic cations (A,B,C) and hydrogenated hexaphenyls (D). The thermal decomposition of these entities into hydrogen radicals, aliphatic substituted phenyl and polyphenyl radicals and aliphatic radicals is expected to proceed more readily than the pyrolytic decomposition of fully aromatic systems, due to the lower bond strength involved. In conclusion to this a high formation of hydrogen and saturated and unsaturated alkanes as final reaction products is in agreement with our reaction mechanism.

4.4.2 - BENZENE, DIPHENYL AND QUATERPHENYL FORMATION

A two-fold increase in the rate of benzene, diphenyl and quaterphenyl formation is found when comparing the Attapulgus clay catalyzed pyrolysis of o-, m- or p-terphenyl with the uncatalyzed pyrolysis. The thermal destruction of hydrogenated intermediates (A,B,C,D) formed in the carbonium ion operated mechanism leads to the formation of phenyl and lower phenyl radicals in addition to the intermediate formation of aliphatic radicals. These aromatic radicals will form lower aromatic molecules, either by hydrogen abstraction from dihydroaromatics or, less likely, by chain and final dimerisation reactions as postulated for the uncatalyzed pyrolysis.

4.4.3 - HIGH BOILER FORMATION

The increase in the production of high boiling compounds during the pyrolysis of o-, m- and p-terphenyl in the presence of Attapulgus clay is even greater than that for the benzene, diphenyl and quaterphenyl formation. The high boiler fraction contains a large amount of compounds of higher molecular weight than quaterphenyls, i.e. mostly hexaphenyls.

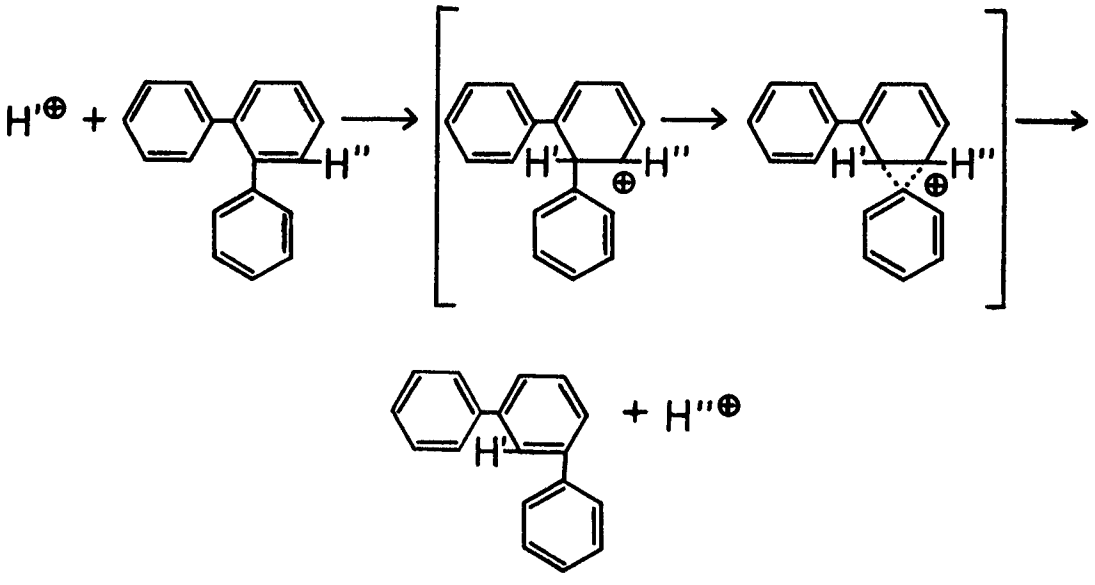
This is also in agreement with the carbonium ion operated mechanism discussed above: the main reaction products should be hexaphenyls and, to a lower extent, nonaphenyls.

4.4.4 - TERPHENYL ISOMERISATION

Friedel Crafts catalysts are known to promote the isomerisation of aliphatic hydrocarbons. When 2-methylnaphthalene is treated at elevated temperatures with aluminium chloride, the thermodynamically more stable 1-isomer is nearly exclusively formed.

It is therefore not surprising, that Attapulgus clay performs a similar action on polyphenyls; a considerable part of o-terphenyl is converted into the m- and p-isomers. A similar observation is made for the p- and m-terphenyl decomposition in the presence of Attapulgus clay.

As precursor of the reaction a carbonium ion of the type I is to be expected. This ion, without entering the further reaction steps of the discussed mechanism, looses a proton of the adjacent position under isomerisation by phenyl migration:



Experiments with ^{14}C-labelled o-terphenyl could verify whether this intramolecular reaction actually takes place and, if so, whether the adjacent carbon atom of the migrating ring (as formulated above) or the original atom is forming the new C-C-bond between the aromatic nuclei.

5 - C O N C L U S I O N S

The following conclusions can be drawn from our results:

1) A very pronounced effect of acid catalysis is observed when treating o-, m- or p-terphenyl at higher temperatures with Attapulgus clay. The proposed carbonium ion operated mechanism explains the following experimentally found results:

   a) A high evolution of gaseous compounds is observed when treating o-, m- or p-terphenyl at high temperatures (425°C) in the presence of Attapulgus clay. The gas mixture contains saturated and unsaturated hydrocarbons to a large extent.

   b) Each of the three terphenyl isomers is isomerised to the other two terphenyls. An equilibrium is finally reached with any of the three isomers as starting material in which the presence of p- and m-terphenyls predominates.

   c) A rate of high boiler formation is observed which is three times greater than under uncatalyzed conditions. The high boilers formed contain to a high percentage compounds of higher molecular weight than quaterphenyls, i.e. mostly hexaphenyls.

2) The use of Attapulgus clay for the removal of fouling and decomposition capacities from a used coolant is not to be recommended at higher temperatures. The di- and terphenyls of the radio-pyrolysis mixture, intended to be quantitatively recuperated, are to a large extent decomposed by the purification process itself and isomerized to p-terphenyl, which is highly undesirable in an organic coolant mixture.

A C K N O W L E D G E M E N T

The authors take pleasure in acknowledging the work of Dr. S. Facchetti, Dr. B. Versino, Mr. S. Marell and Mr. H. Vissers for determining the analytic results. We also thank Dr. H. Hannaert for valuable discussions.

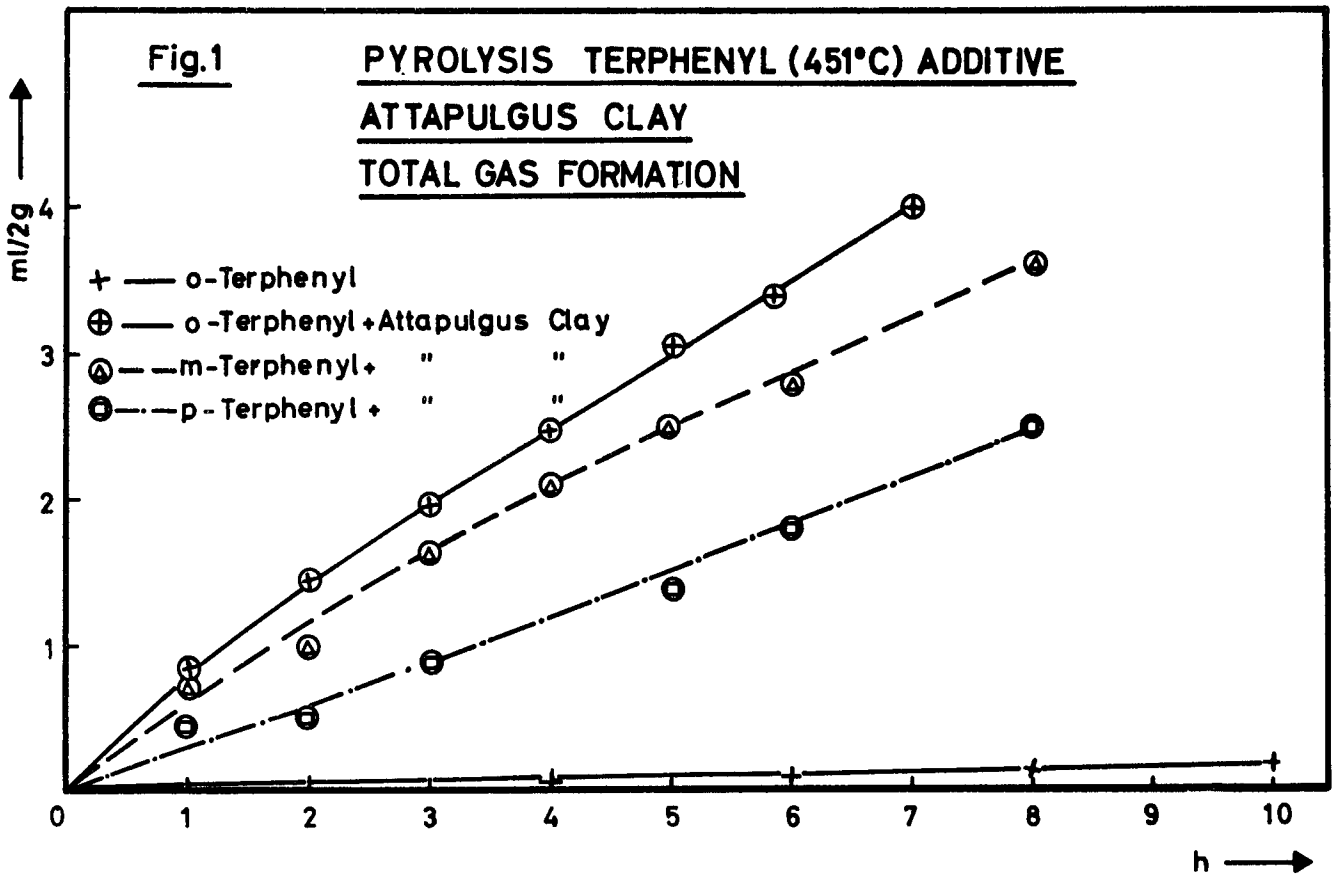


Fig.1
PYROLYSIS TERPHENYL (451°C) ADDITIVE
ATTAPULGUS CLAY
TOTAL GAS FORMATION
ml/2g
o-Terphenyl
o-Terphenyl + Attapulgus Clay
m-Terphenyl + " "
p-Terphenyl + " "
0
1
2
3
4
5
6
7
8
9
10
h

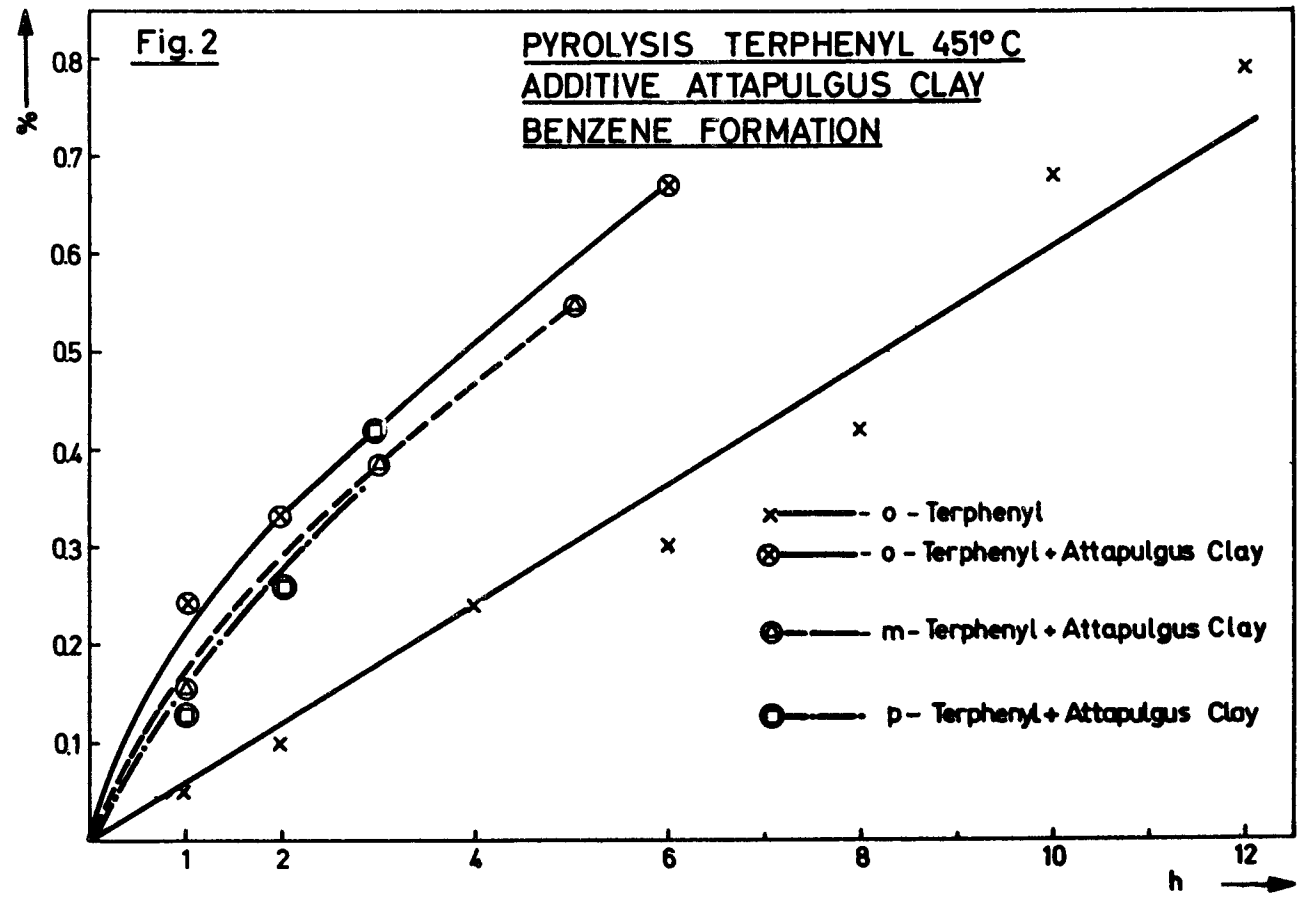


Fig.2
PYROLYSIS TERPHENYL 451° C
ADDITIVE ATTAPULGUS CLAY
BENZENE FORMATION
%
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1
2
4
6
8
10
12
h
o - Terphenyl
o - Terphenyl + Attapulgus Clay
m - Terphenyl + Attapulgus Clay
p - Terphenyl + Attapulgus Clay

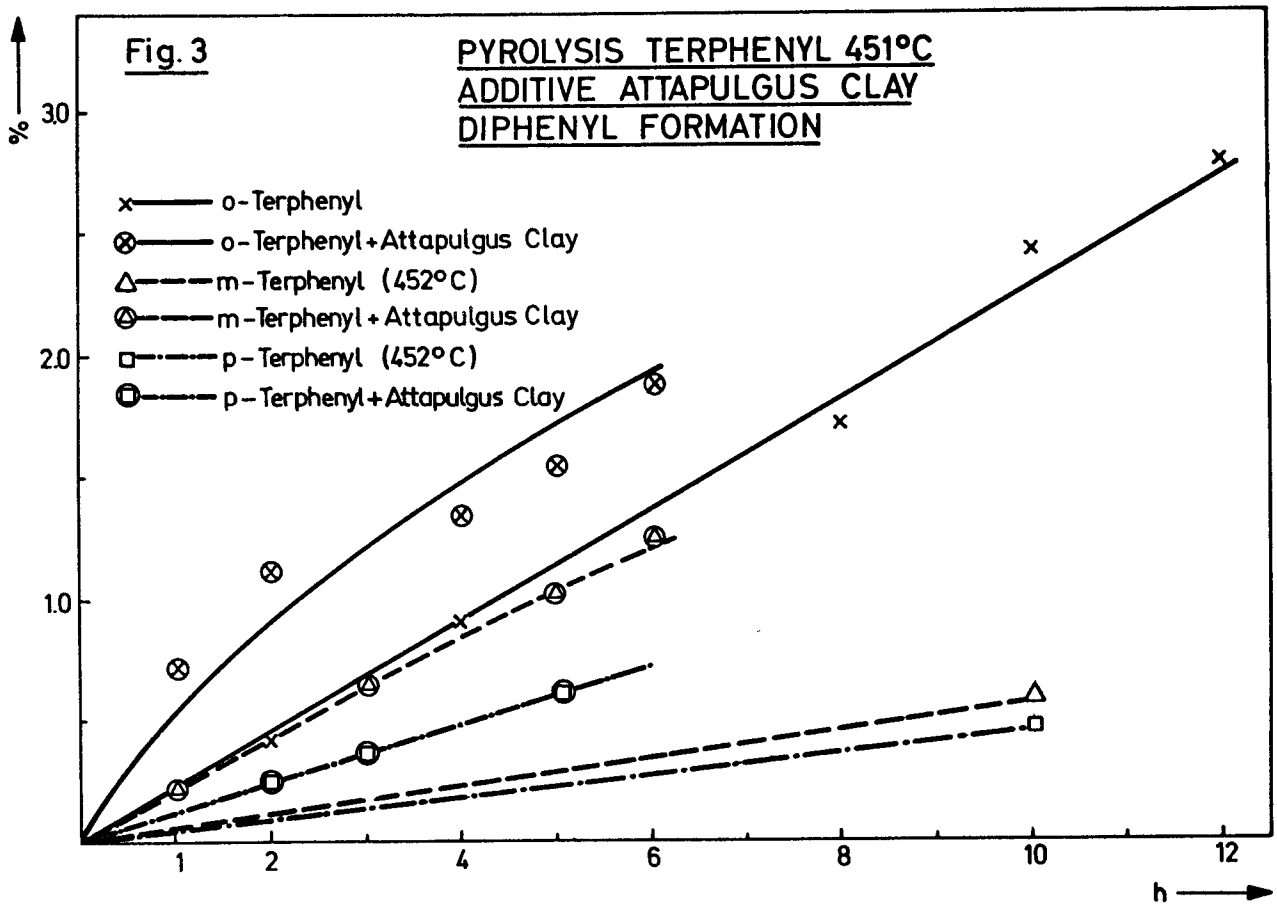


Fig. 3
PYROLYSIS TERPHENYL 451°C
ADDITIVE ATTAPULGUS CLAY
DIPHENYL FORMATION
%
3.0
2.0
1.0
o-Terphenyl
o-Terphenyl + Attapulgus Clay
m-Terphenyl (452°C)
m-Terphenyl + Attapulgus Clay
p-Terphenyl (452°C)
p-Terphenyl + Attapulgus Clay
1
2
4
6
8
10
12
h

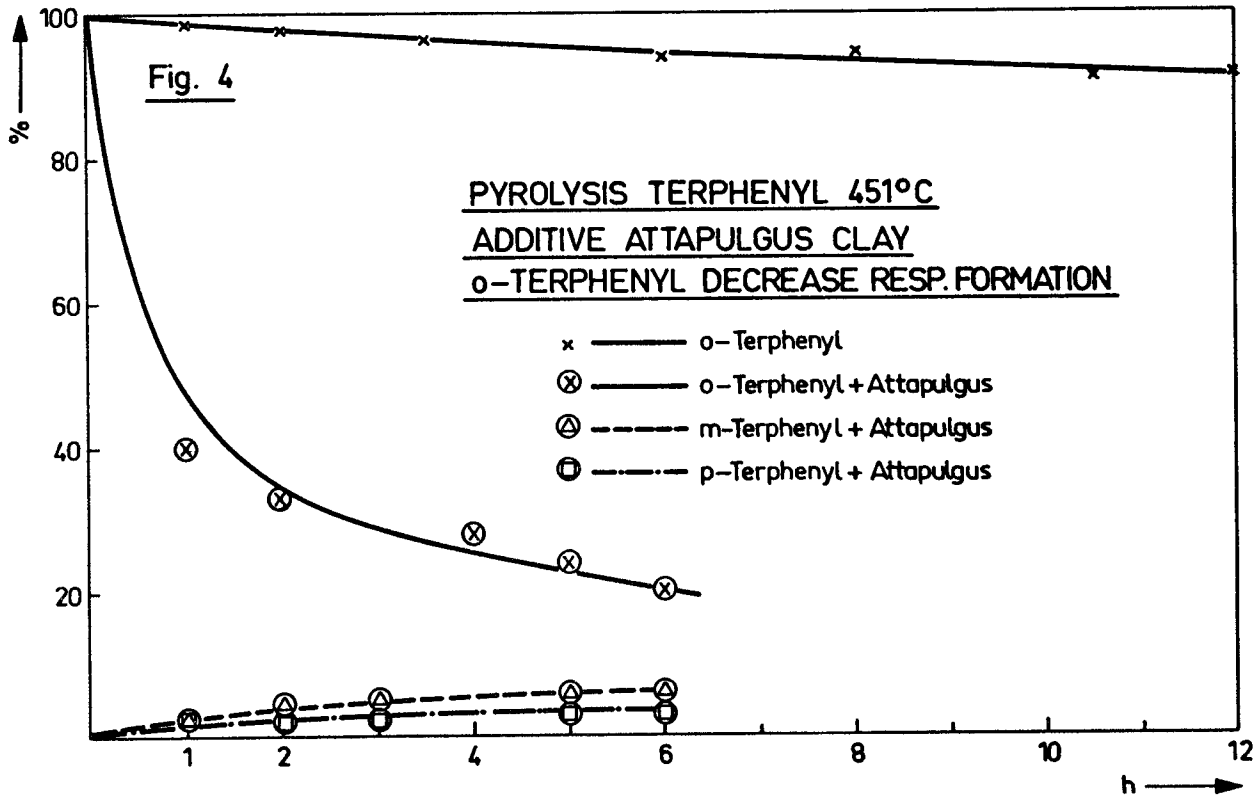


Fig. 4
%
100
80
60
40
20
PYROLYSIS TERPHENYL 451°C
ADDITIVE ATTAPULGUS CLAY
o-TERPHENYL DECREASE RESP. FORMATION
o-Terphenyl
o-Terphenyl + Attapulgus
m-Terphenyl + Attapulgus
p-Terphenyl + Attapulgus
1
2
4
6
8
10
12
h

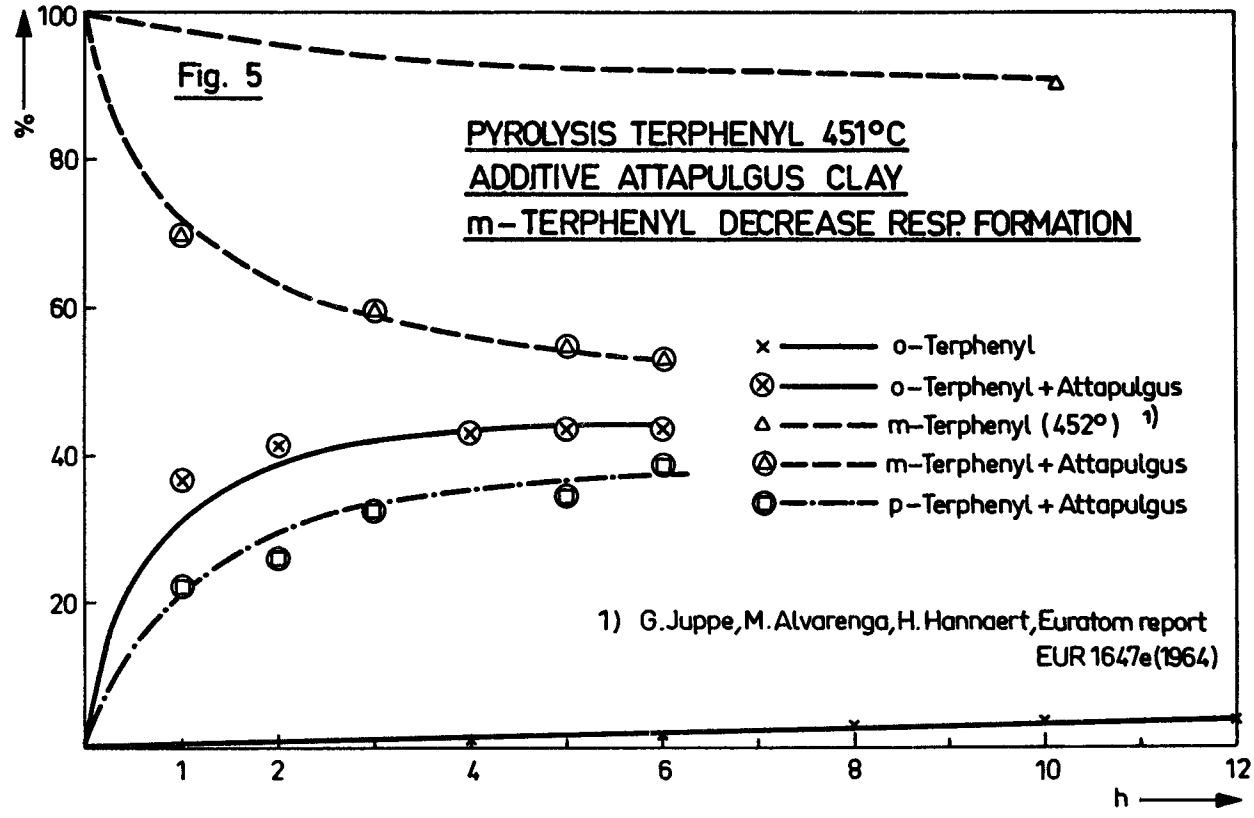


Fig. 5
PYROLYSIS TERPHENYL 451°C
ADDITIVE ATTAPULGUS CLAY
m-TERPHENYL DECREASE RESP. FORMATION
%
100
80
60
40
20
1
2
4
6
8
10
12
h
o-Terphenyl
o-Terphenyl + Attapulgus
m-Terphenyl (452°) 1)
m-Terphenyl + Attapulgus
p-Terphenyl + Attapulgus
1) G. Juppe, M. Alvarenga, H. Hannaert, Euratom report EUR 1647e (1964)

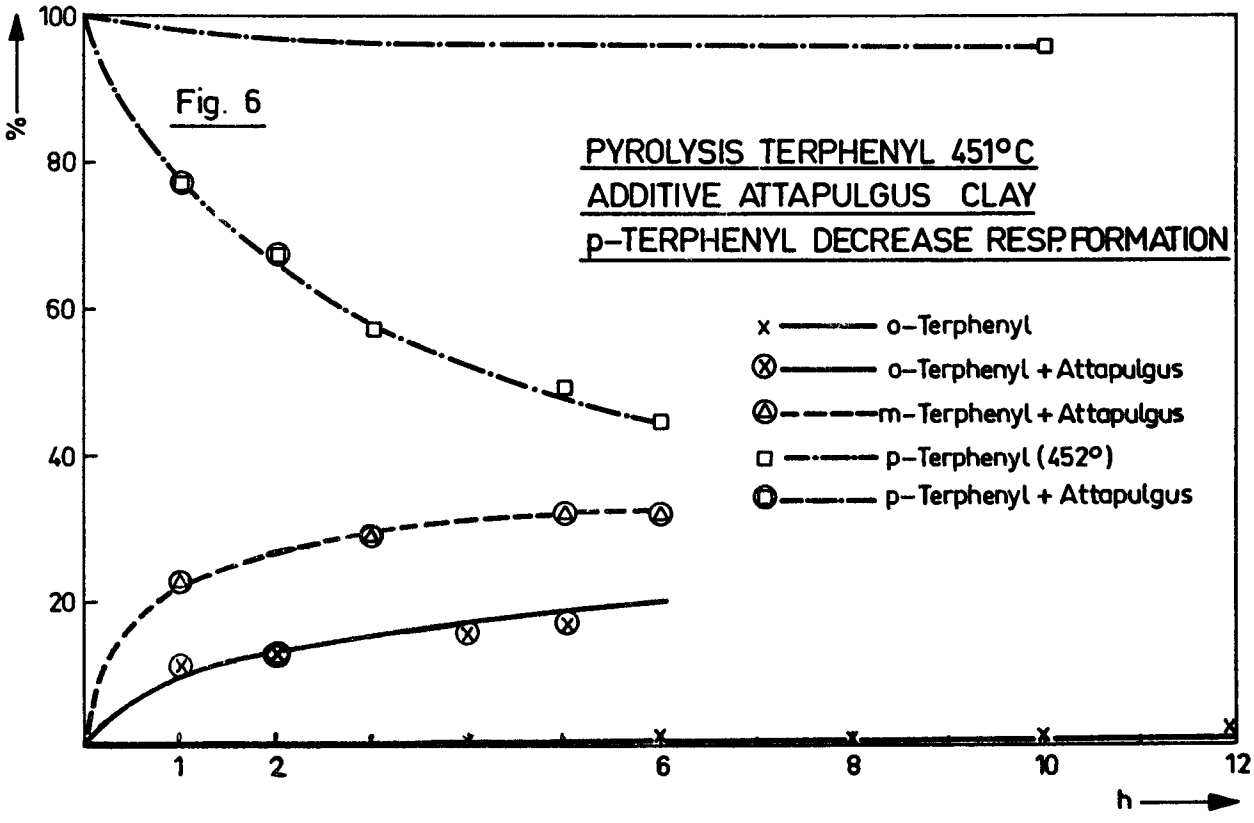


Fig. 6
PYROLYSIS TERPHENYL 451°C
ADDITIVE ATTAPULGUS CLAY
p-TERPHENYL DECREASE RESP. FORMATION
%
100
80
60
40
20
1
2
6
8
10
12
h
o-Terphenyl
o-Terphenyl + Attapulgus
m-Terphenyl + Attapulgus
p-Terphenyl (452°)
p-Terphenyl + Attapulgus

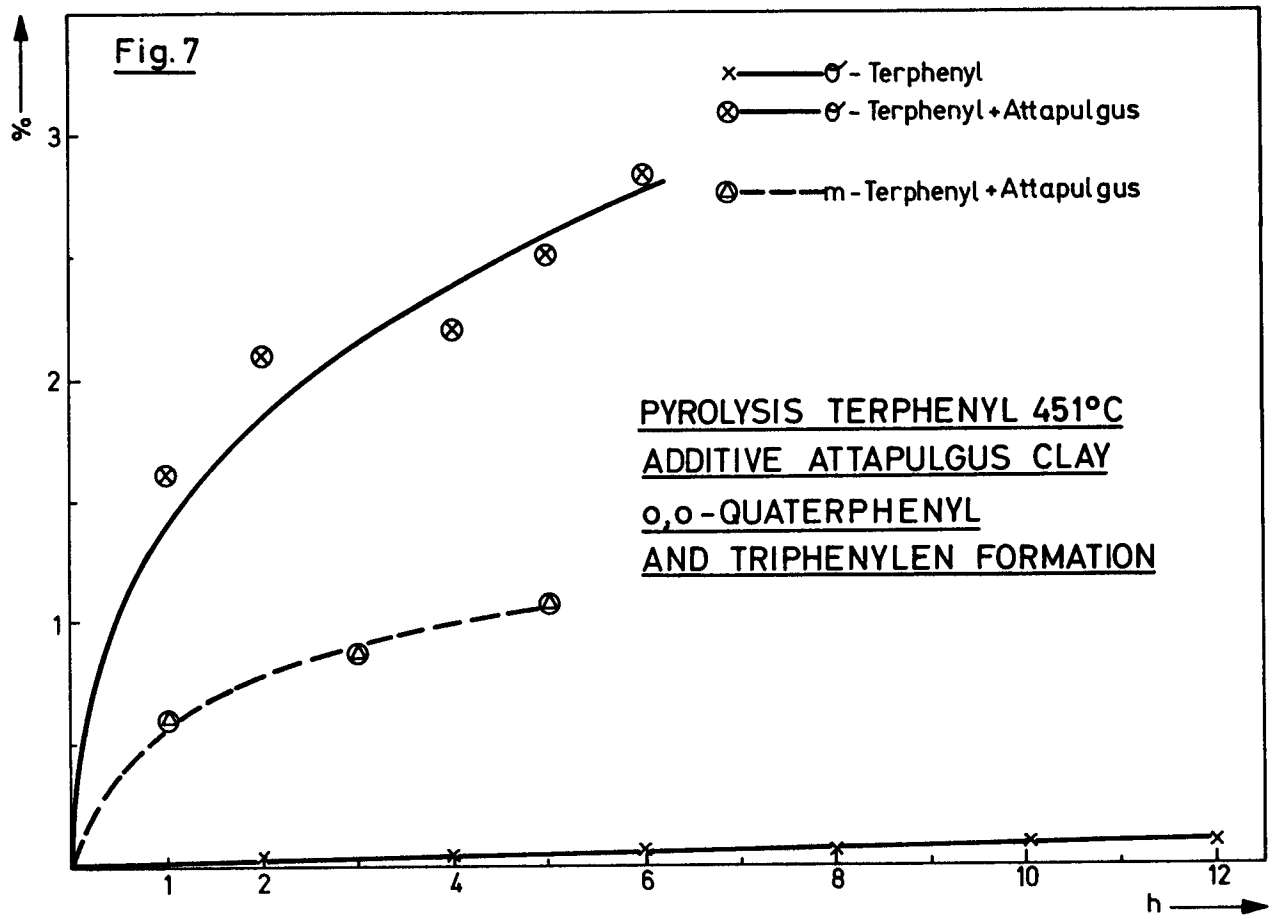


Fig. 7
%
3
2
1
× ——— o- Terphenyl
⊗ ——— o- Terphenyl + Attapulgus
△ - - - m - Terphenyl + Attapulgus
PYROLYSIS TERPHENYL 451°C
ADDITIVE ATTAPULGUS CLAY
o,o - QUATERPHENYL
AND TRIPHENYLEN FORMATION
1
2
4
6
8
10
12
h

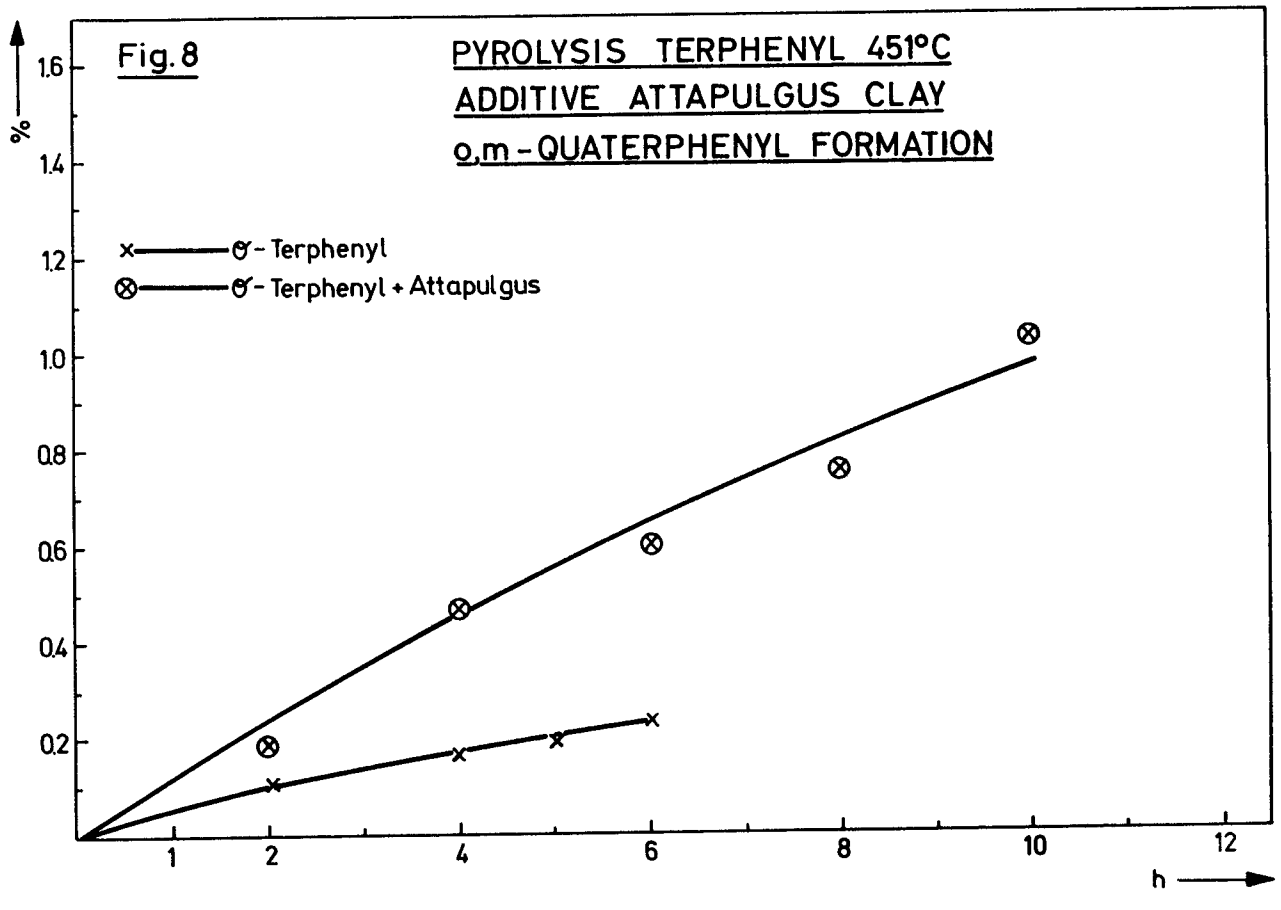


Fig. 8
PYROLYSIS TERPHENYL 451°C
ADDITIVE ATTAPULGUS CLAY
o,m - QUATERPHENYL FORMATION
%
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
× ——— o- Terphenyl
⊗ ——— o- Terphenyl + Attapulgus
1
2
4
6
8
10
12
h

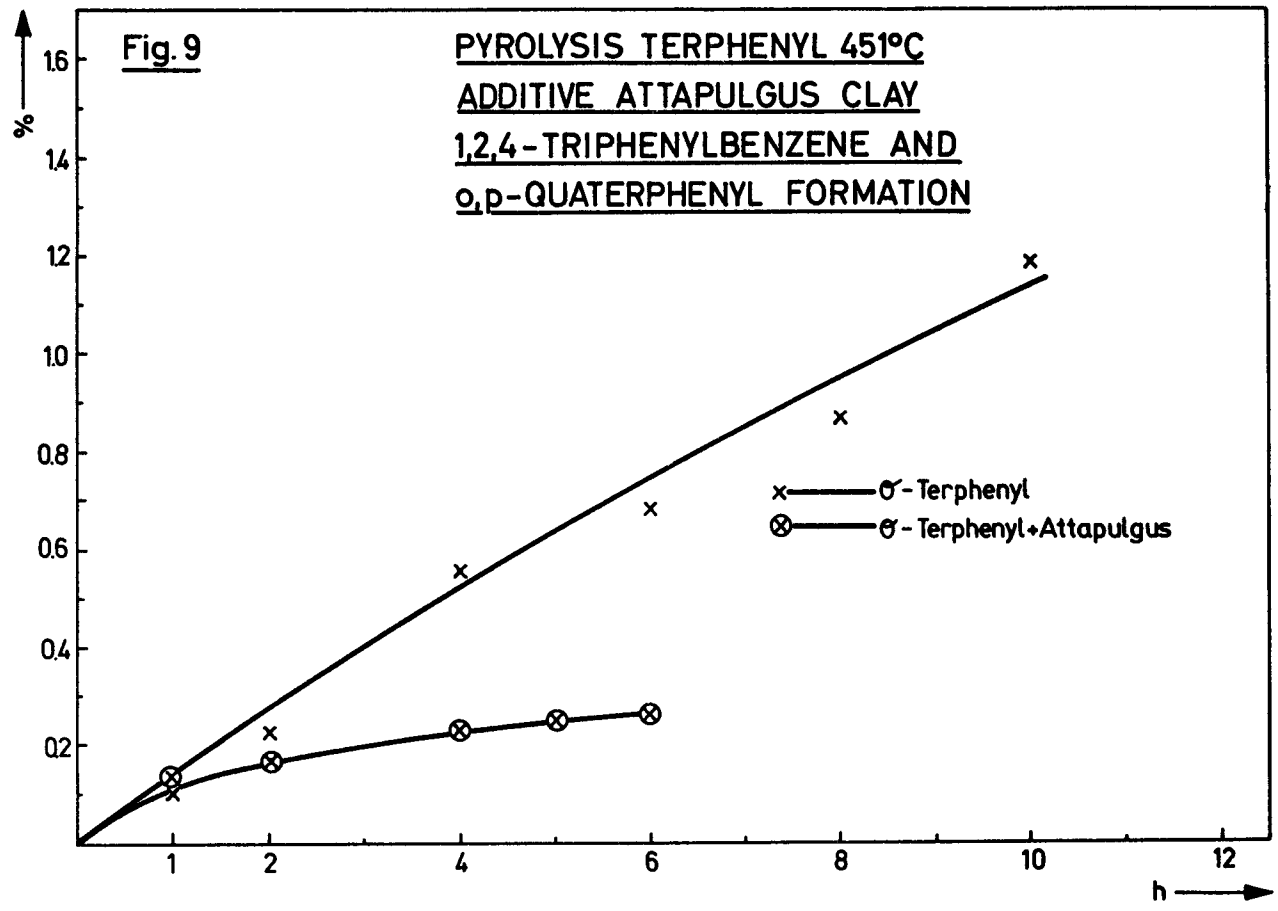


Fig. 9
PYROLYSIS TERPHENYL 451°C
ADDITIVE ATTAPULGUS CLAY
1,2,4-TRIPHENYLBENZENE AND
o,p-QUATERPHENYL FORMATION
%
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
1
2
4
6
8
10
12
h
o-Terphenyl
o-Terphenyl+Attapulgus

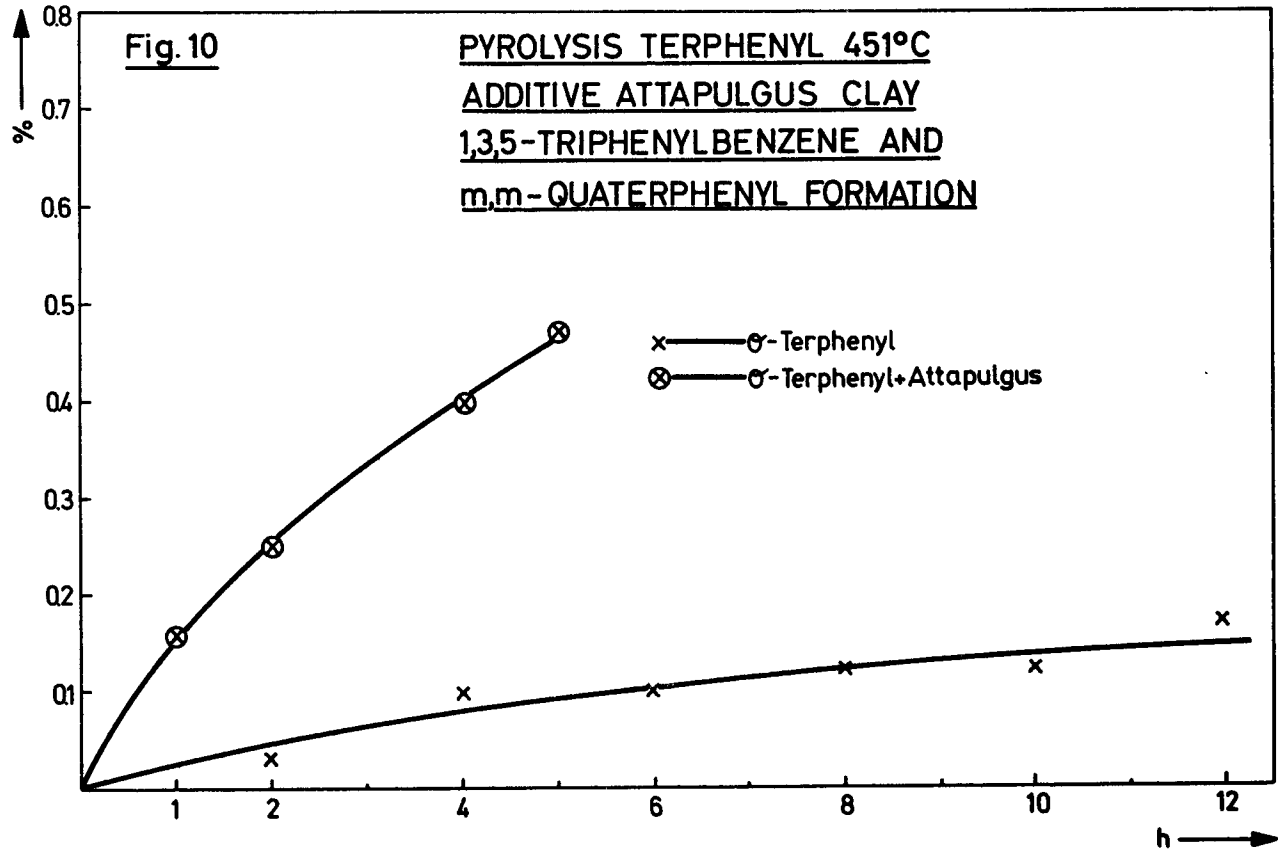


Fig. 10
PYROLYSIS TERPHENYL 451°C
ADDITIVE ATTAPULGUS CLAY
1,3,5-TRIPHENYLBENZENE AND
m,m-QUATERPHENYL FORMATION
%
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1
2
4
6
8
10
12
h
o-Terphenyl
o-Terphenyl+Attapulgus

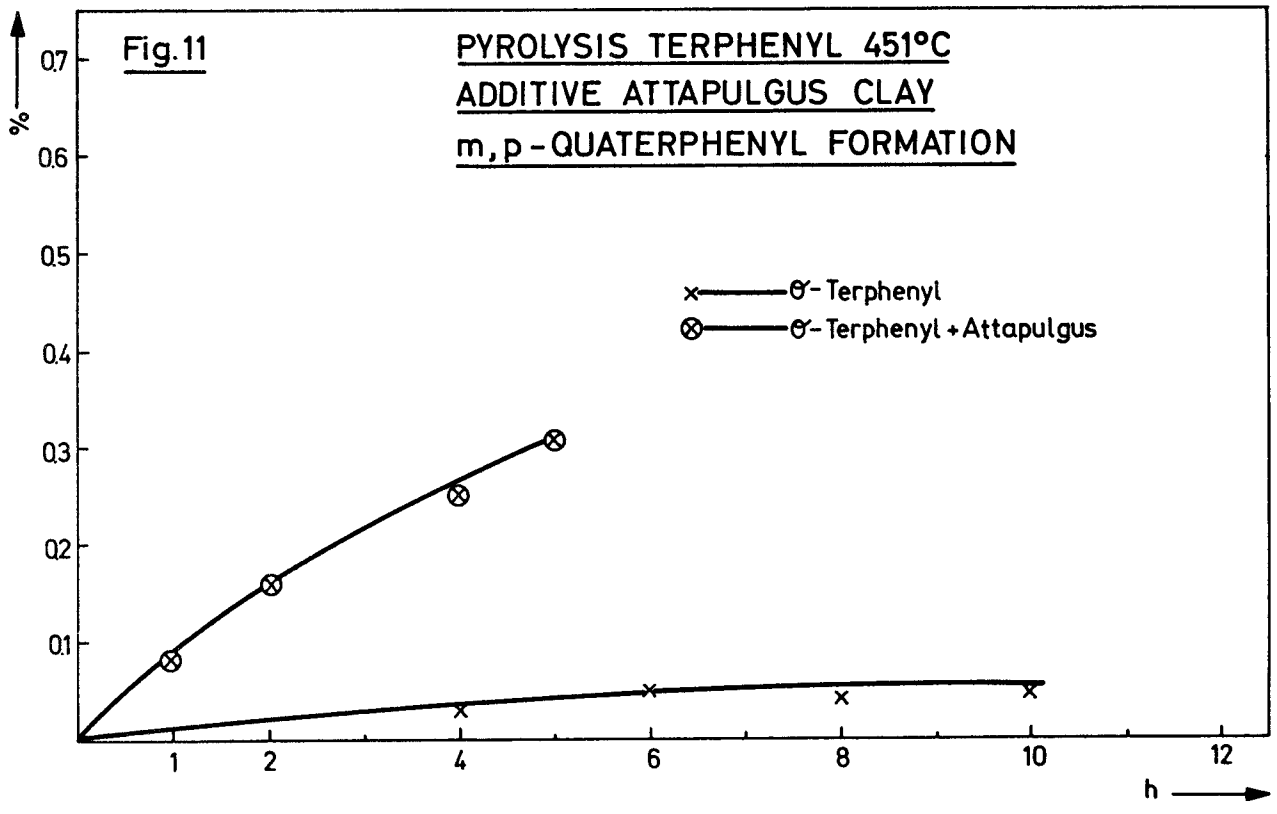


Fig.11
PYROLYSIS TERPHENYL 451°C
ADDITIVE ATTAPULGUS CLAY
m,p-QUATERPHENYL FORMATION
%
0.7
0.6
0.5
0.4
0.3
0.2
0.1
o-Terphenyl
o-Terphenyl + Attapulgus
1
2
4
6
8
10
12
h

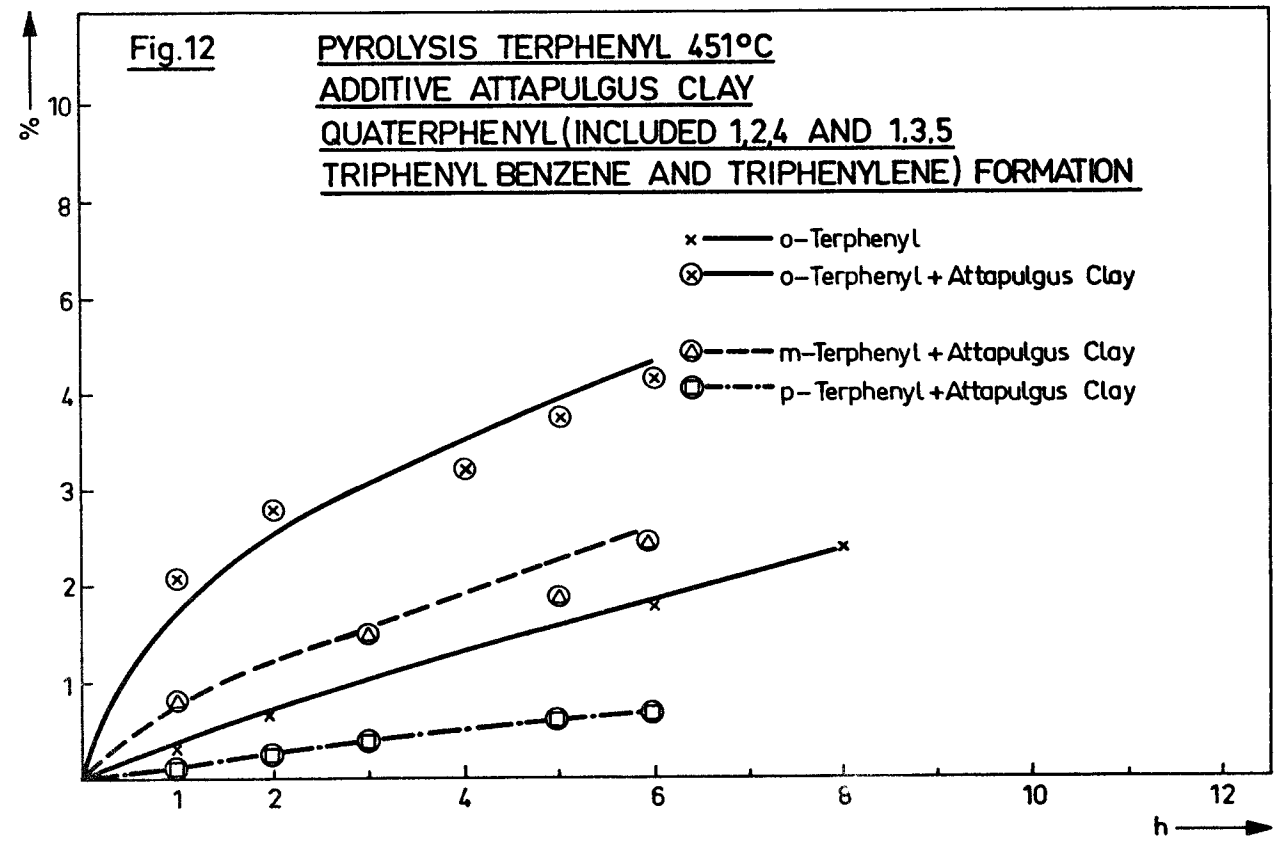


Fig.12
PYROLYSIS TERPHENYL 451°C
ADDITIVE ATTAPULGUS CLAY
QUATERPHENYL (INCLUDED 1,2,4 AND 1,3,5
TRIPHENYL BENZENE AND TRIPHENYLENE) FORMATION
%
10
8
6
4
3
2
1
o-Terphenyl
o-Terphenyl + Attapulgus Clay
m-Terphenyl + Attapulgus Clay
p-Terphenyl + Attapulgus Clay
1
2
4
6
8
10
12
h

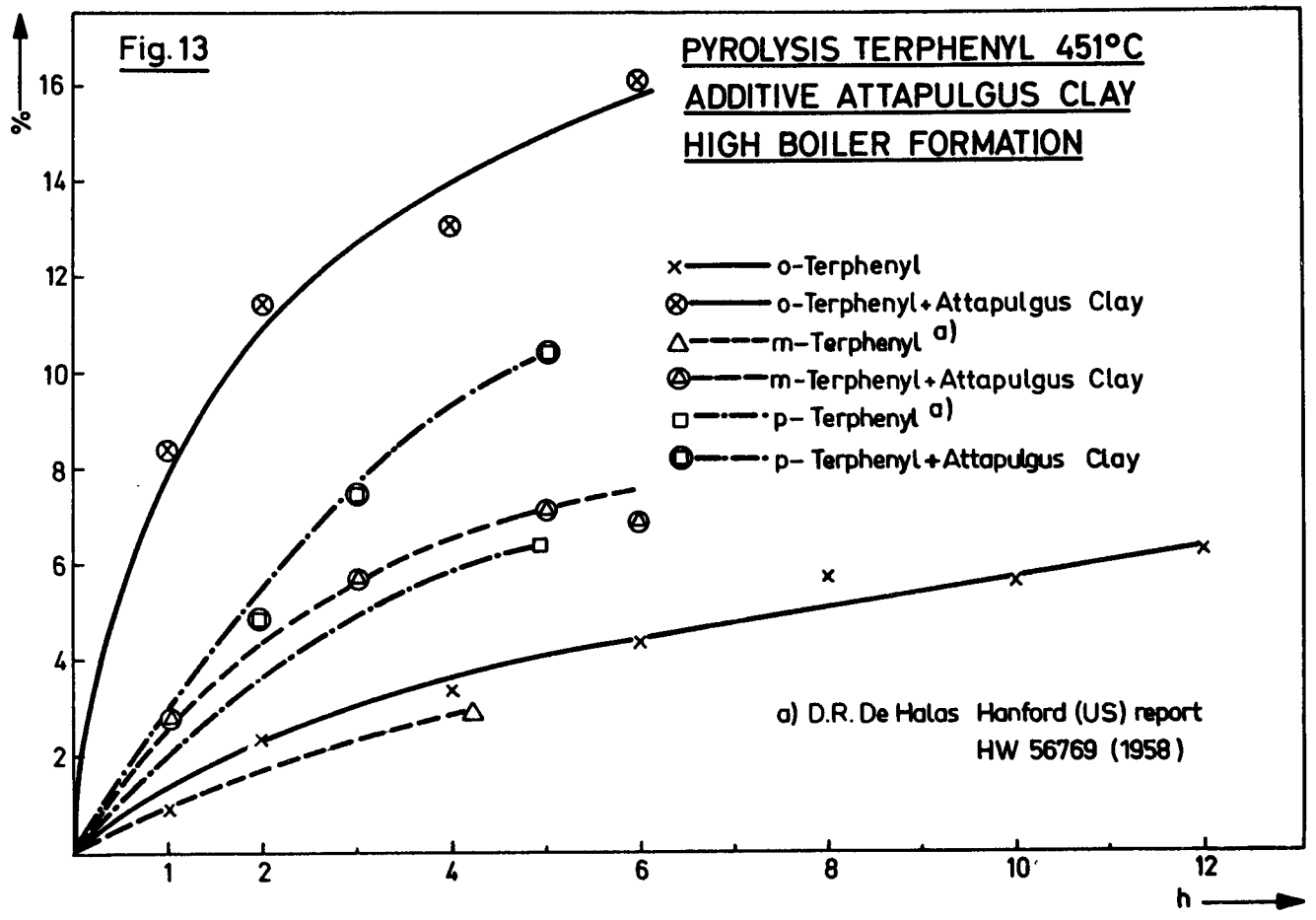


Fig. 13
PYROLYSIS TERPHENYL 451°C
ADDITIVE ATTAPULGUS CLAY
HIGH BOILER FORMATION
%
16
14
12
10
8
6
4
2
1
2
4
6
8
10
12
h
o-Terphenyl
o-Terphenyl + Attapulgus Clay
m-Terphenyl a)
m-Terphenyl + Attapulgus Clay
p- Terphenyl a)
p- Terphenyl + Attapulgus Clay
a) D.R. De Halas Hanford (US) report
HW 56769 (1958)

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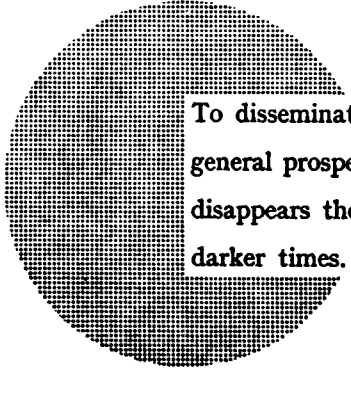

To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel