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Ecological Production Technology of Phenoxyacetic Herbicides MCPA and 2,4-D in the Highest World Standard

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*„Selectivity is a major goal in modern synthetic chemistry”
Bartman W., Trost B. M.*

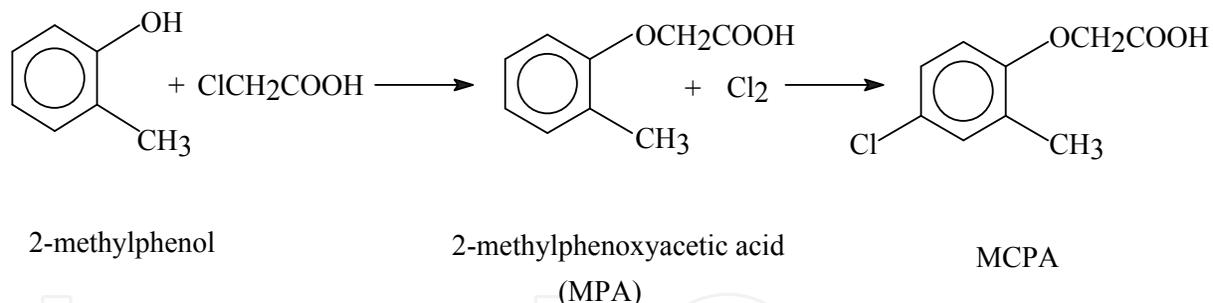
1. Introduction

Herbicides MCPA (4-chloro-2-methylphenoxyacetic acid) and 2,4-D (2,4-dichlorophenoxyacetic acid), which belong to the group of chlorophenoxyacetic acids, have been produced in Poland since the break of the sixties in the scale of many thousands of tons per year, which constitutes 5-7% of the world's production. Acids and their salts are exported to all continents. An advantage of herbicides within this group is their harmlessness for man and environment in doses used in agriculture. The condition is the high content and purity of the active substance in utility preparations. Unfortunately, classic technologies based on the reaction of phenols chlorination or their derivatives used until today all over the world do not ensure high purity, and significant quantities of highly toxic chloroorganic waste compounds originate in the production process. The main cause lies in the low selectivity of the reaction of chlorination of phenols' aromatic ring. Numerous producers enrich the purity of chlorophenols with the method of rectification. As our research has shown, in the process of rectification and while burning post-rectification wastes, dioxines and dibenzofurans can originate.

Below we present research conducted in the Institute of Industrial Organic Chemistry (IPO) in Warsaw with strict cooperation with production plants „Rokita Agro” in Brzeg Dolny and „Organika Sarzyna” in Nowa Sarzyna over the development of technologies of chlorophenoxyacetic herbicides. Commonly used „classical” technologies of production of MCPA and 2,4-D are based on two subsequent reactions – chlorination of phenol or 2-methylphenol and the reaction of the obtained chlorophenol with chloroacetic acid (MCAA), commonly called condensation. The first stage – chlorination reaction – is critical for the nature of the entire reaction, i.e. the number of operations, selection of equipment, purification methods, wastes. Electrophilic reaction of chlorination of aromatic phenol ring is non-selective. Isomers and polychlorinated compounds are always originated. In order to increase the selectivity of reaction and the purity of the the final product, various technologies of chlorination and purification of chlorophenols are used all over the world,

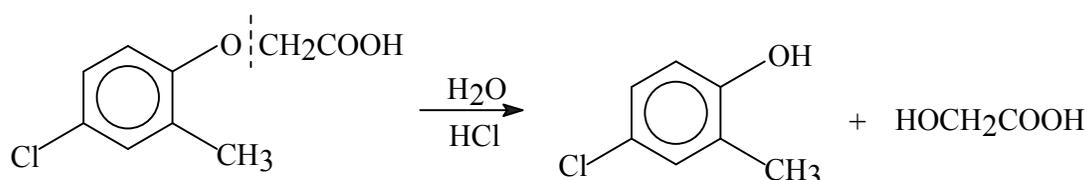
with that 40% of waste chloromethylphenols was originated. The preparation Chwastoks R-30 had a good opinion among its users. It did not freeze in winter in unheated warehouses, it perfectly dissolved in water. It was cheap. In IPO a comparative research of the activity of MCPA-70 with pure MCPA was conducted, and the activity of each chloromethylphenoxyacetic acids separately, and also their mixtures. It appeared that isomeric 6-chloro-2-methylphenoxyacetic acid had a high biological activity, and in the mixtures the synergism of activity was observed. After 10 years of MCPA-70 production in a small installation in 1972 a new production facility of 4500 tons per year capacity was started without substantial changes in technology. In the discussed decade in the European market there appeared MCPA preparations of high purity, without free chloromethylphenols containing 80-90% of the pure active component. In the technologies sulfuryl chloride was used as a more selective chlorinating agent, and sometimes additionally vacuum rectification of technical 4-chloro-2-methylphenol. Chemische Werke Schwarzweide in GDR started the production of MCPA basing on sulfuryl chloride on the license purchased in Great Britain. The technology based on sulfuryl chloride is currently commonly used by chemical companies all over the world.

Skeeters was the first to describe in 1956 the MCPA synthesis through chlorination of 2-methylphenoxyacetic acid (MPA) in 1,2-dichloroethane (Skeeters et al., 1956). In the seventies such a method was used in industry. It was a new generation technology, below referred to as the reverse method, and the obtained product - „MCPA 90“. The diagram of the reaction is presented below.

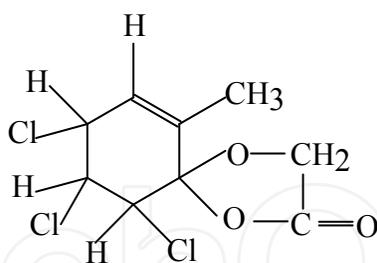


The aromatic ring of MPA acid is less prone to electrophilic substitution, and the side chain is a steric hindrance for creating the isomer 6-chloro-. In the reaction of MPA, chlorination selectivity of 80-90% is achieved, i.e. higher than in the classical method, where sulfuryl chloride without purification of the product by rectification is used. In the reverse technology a barrier which is difficult to lift is the high melting temperature of MPA (157°C) and the low solubility (7%) in organic solvents. Chlorination of MPA acid without solvents in hot water cannot be performed to the end and there remains 20% of non-chlorinated MPA. In Bratysława, the chlorination of 20-30% of water solution of MPA sodium salt MPA in the temperature of 90-100 °C was used on the industrial scale. The final product, containing 90% of the active substance, contained 5% of isomer 6-chloro- and 3-6% of free MPA (Rapoš et al, 1960). Chimzawod in Ufa, USSR, launched a multi-ton installation of MPA acid chlorination in 7% solution in solvent. The license with the full equipment was purchased from the Fisons company (Great Britain). The MCPA purity was 85-90%, the product contained 1-3% of free MPA, efficiency about 92% (Moszczyński, 1971).

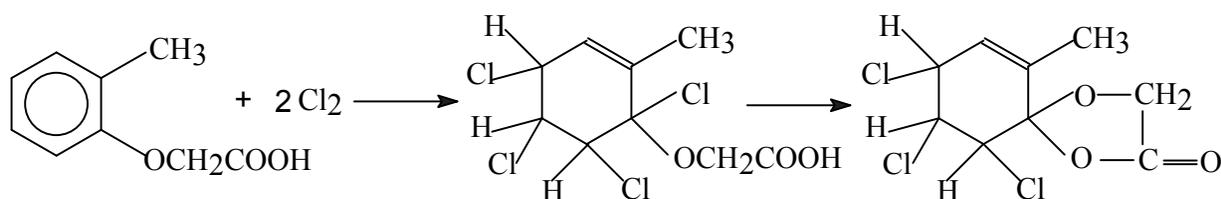
In Poland, in 1976, after the complete redevelopment of MCPA-70 system (Moszczyński et al., 1975), a new generation reverse technology was developed and used in industry. MPA acid heated with tetrachloroethylene (TCE) in post-condensation mass (brine) forms an eutectic of melting temperature of 100°C. It enables the separation of the liquid organic phase MPA/TCE from brine effluent from the post-condensation mass. The organic phase of MPA/TCE without drying was chlorinated in the temperature of 90-100°C. TCE was removed from the post-chlorination mass with the use of distillation with water vapour. The obtained product was of 90% purity, with a mix of 7-9% of isomer 6-chloro-, and up to 3% of free chloromethylphenols. With the evaluation of efficiency in precise balance tests, 3 to 5% of the product was missing, and the quantity of free chloromethylphenols was higher than the quantity derived from MPA. In the technology used in Ufa, MPA before chlorination was effectively dephenoled by the extracting method, and in spite of that, in the final product chloromethylphenols were present. In patent literature the low efficiency of MPA chlorination attracts attention, as well as the lack of material balance of reaction. We have recognized that as a normal known phenomenon of breaking MPA and MCPA ether bonding in the presence of hydrogen chloride according to the following diagram:



The hydrolysis research which we performed did not confirm the presence of such a reaction in the conditions of MCPA synthesis, in the MPA post-chlorination mass there was found and separated several per cent and a compound with spirolactone structure was identified. An identical compound was depicted earlier by H. Lund (Lund, 1958).



H. Lund suggests the mechanism of spirolactone origination, a derivative of MPA, based on joining 2 molecules of Cl_2 to the aromatic ring before the formation of cyclic ketal (spirolactone) according to the diagram:



He refers to known phenols reactions, which in the process of long-lasting chlorination, after saturation of all the places with chlorine, form cyclohexanones. It is difficult to agree with

$$V = k[\text{ArO}^-] [\text{ClCH}_2\text{COO}^-]$$

In the temperature $<90^\circ\text{C}$, in the water alkaline environment its speed is low, while in the temperature of $90\text{-}110^\circ\text{C}$ full substrate reaction occurs after 1 hour (Moszczyński, 1994). pH has very clear influence on this speed, and the concentration of ions of phenoxy ArO^- and hydroxyl OH^- depends on pH. Both mentioned nucleophilic agents compete with each other in the reaction with substrate – apart from the main reaction there occurs hydrolysis of chloroacetic acid into glycolic acid. Hydrolysis of substrate makes the reaction's kinetics more complicated, and the formula of speed of reaction of synthesis of MPA needs to be corrected.

Hydrolysis of chloroacetic acid has a course which is clearly distinct from the main reaction. According to Berhenke and Britton, it occurs both in acidic environment and in alkaline environment and in the range of pH 3 – 10 it has similar speed. (Berhenke, Britton, 1946). Occurrence of hydrolysis both in the acidic and lightly alkaline environment as well as acceleration of speed of hydrolysis in the final stage of MPA synthesis along with sodium chloride accumulation proved by this research confirm that the reaction proceeds according to the mechanism $\text{S}_{\text{N}}1$. With pH = 11 – 11,5 MCAA hydrolysis is 5,5%, and with pH = 12 – 12,5 it increases to 42%, which suggests that with a greater concentration of OH^- the reaction proceeds according to the bimolecular mechanism type $\text{S}_{\text{N}}2$ with the participation of OH^- ions. This research confirms the findings of Dawson and Pycock (Dawson, Pycock, 1936) that the reaction of MCAA hydrolysis is a combination of mechanisms $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$.

For research on the optimalization of parameters of MPA synthesis with the use of mathematical model the following parameters were accepted as critical: reagent molar ratio (X_1), reagent molar ratio (X_2), pH (X_3). Optimum values of variables X_1 and X_2 marked by experiment and calculated for the synthesis of MPA are respectively 0,8-1, and 3,3-3,7 mol/dm³.

pH of reaction environment has a critical influence on the efficiency of MPA synthesis. With pH $<9,5$ MPA synthesis does not occur, while with pH >11 , ion ArO^- loses in the competition with ion OH^- . The optimum value of pH indicated on the mathematical model is 10-10,7.

In the period of MCPA production with the reverse method in „Organika Sarzyna” in the seventies, countries classical technologies of chlorination of 2-methylphenol with sulfuryl chloride used in different were modernized. New regioselective catalysts combined with vacuum rectification of technical 4-chloro-2-methylphenol were commonly used. It meant an improvement of the purity of preparations with over 90 to 96% of active substance.

IPO for the third time has joined the competition in the market, overtaking, in terms of modernity, all technologies based on sulfuryl chloride. MCPA of 98% purity was offered directly from the synthesis, without purification and wastes, with an outstanding simplification of technology.

After several years of research on regioselective catalysts of chlorination of MPA with chlorine, sodium hypochlorite and *t*-butyl, a laboratory synthesis „MCPA 98” of 98% of purity of active substance was developed. In May 1992 a combined research-implementation team, composed of 25 specialists from IPO was assigned, W. Moszczyński, I. Górska et al., and 19 from „Organika Sarzyna”, including T. Jakubas, J. Peć to conduct technical tests,

supervising redevelopment of construction and to conduct the launch of production. Synthesis of MCPA 98 consisted in one-stage condensation of MCAA with *o*-cresol to MPA and chlorination of MPA in water in room temperature with the use of sodium hypochlorite against amine catalyst (Moszczyński et al., 1992). A simple laboratory technology appeared to be unrepeatable in industrial conditions. For two years of 1/2-technical and technical tests not a single manufactured unit of product of >94% purity was obtained.

In the laboratory in glass all syntheses without exception had selectivity and efficiency of 98-99%. Meanwhile, with any multiplication of scale in glass and apparatuses from 50 l to 2,5 m³ after exceeding the stage of about 2/3 pure chlorination *para*- suddenly broke down and a product of 90-94% purity of isomer *para*- was originated. Only the research of W. Moszczyński on the mechanism of reaction showed that we deal with a new, unknown in this group of compounds, aromatic free radicals reaction of 99% selectivity (Moszczyński, 1998). Free radicals reactions, as opposed to ion reactions, are highly selective, but sensitive to the conditions of reactions and dozens of external agents, and anytime there may occur a break of chain generation of radicals and return to the ion mechanism of a lower selectivity. Phenol reactions occupy a special place in this group. They are subject to reactions with such free radicals, which in other cases are inactive. There are proofs that with the presence of unpaired electrons delocalized into the aromatic ring, the replacement only occurs into the location *orto*- or *para*- (Dermer & Edmison 1957). The presence of free radicals was proved by EPR method at the University of Wrocław (Jeziński et al., 1999). It allowed to discover and eliminate radicals inhibitors and easily repeat the synthesis on an industrial scale. The installation launch took place in 1995. For the third time a new MCPA production installation was assembled with the full automatic control of the technological process and continuous chlorination and educing of MCPA acid. In the table below a standard of active substance of domestic MCPA was shown, according to the technology from 1976 and the last from 1996 with the purity declared in that time by leading western producers (Moszczyński et al. 2010). MCPA 98 from „Organika Sarzyna” is the best in all parametres.

No.	Parametres	MCPA 90 „Organik a Sarzyna” 1976	MCPA AK 20 The Netherlands prospectus 1992	MCPA BASF Germany prospectus 1992	MCPA 98 „Organika Sarzyna” 1995
		[%]			
1	MCPA	85-90	96.0	94.0	97-98
2	6-chloro-2- methylphenoxyacetic acid	8-14	1.0	1.5	0.7
3	2-methylphenoxyacetic acid (MPA)	2	1.0	1.5	0.2
4	4,6-dichloro-2- methylphenoxyacetic acid	2	1.5	2.5	0.2
5	chlorocresols	1-3	0.5	0.5	traces

Table 1. Comparison of MCPA quality standards.

are liquid preparations soluble in water, easy to use and prepare working liquids. Previously used sodium salt 2,4-D, so called Pielik, in the form of powder was poorly soluble in water, and in hard water residues of magnesium, calcium and iron salt were precipitated. In 1968 a brand new production installation 3000 tons per year was launched. As was shown in the diagram above, the synthesis of 2,4-D is based on two subsequent reactions of chlorination and condensation. This method is used by producers of 2,4-D in all countries, invariably since the first synthesis published in 1941 by J. Pokorny (Pokorny, 1941). Below, this technology is referred to as „classical”. This method is based on easily available resources and the standard production equipment, which makes it generally accessible. A disadvantage to this method is the low quality of the product, burdened with 10-12% of undesired chlorophenoxyacetic acids, as well as free chlorophenols.

In the process of production as a result of standard purification of the product with the method of crystallization and washing there are originated 15 tons of wastes per 1 ton of 2,4-D, burdened with chloroorganics, chlorophenoxyacetic acids, chlorophenols, glycolic acid and sodium chloride. With multi-thousand scale of production, it means a serious environmental problem. For several thousand tons of annual production for many years there were created many thousand tons of wastes in the solid form and in liquid wastes. In some manufactured units there was confirmed the presence of nanogram quantities of highly toxic dioxines. Technology 2,4-D required research and solutions eliminating dioxines. Thermal processing, including burning of chloroorganic compounds, particularly chlorophenols, conduces originating dioxines. For some period waste chlorophenols were separated from the liquid wastes and chlorinated up to pentachlorophenol PCF, a known fungicide used mainly for the preservation of railway sleepers. In the first period in the installation 500 tons of 2,4-D per year, chlorophenol wastes were oxygenated with sodium hypochlorite on separated uncovered ground fields, a technology of Ostrowska J. IPO. The breakthrough occurred only after condensation was mastered at the beginning of the nineties, thanks to using several metre long reactors with stirrers for the reaction of disintegration of chlorophenols with sodium hypochlorite and additional cleaning of liquid wastes on biological treatment plant.

The border of purity of 2,4-D in the classical technology is determined by 90% of isomer 2,4-DF in the process of phenol chlorination and 96% of the active substance in acid and preparations 2,4-D after crystallization and washing.

Composition of 2,4-D obtained in the classical technology [% GC]	
chlorophenols	0.3
<i>o</i> -chlorophenoxyacetic acid	2.0
<i>p</i> - chlorophenoxyacetic acid	0.4
2,6-di chlorophenoxyacetic acid	0.9
2,4- di chlorophenoxyacetic acid	95.6
2,4,6-tri chlorophenoxyacetic acid	0.3

Table 2. 2,4-D obtained in the classical technology. (Białek, Moszczyński, 2009).

For many years of production of 2,4-D on bigger and bigger installations, apart from the cumulation of wastes, a weak link was the poor efficiency of condensation reaction, maximum 90% of calculated on 2,4-dichlorophenol. In particular manufactured units, it

varied up to several per cent. The reacting mass, initially thin, sometimes as a result of a violent reaction and salting out the product, was getting thick so quickly that it could not be stirred and it was thrown out of the hatchway from the reactor. Never ending experiments with a change of concentration and order of introducing products, molar ratio, temperature and height of pH gave no results. During the synthesis, in the course of reacting of chloroacetic acid pH was changing, which required adding sodium lye. The measurement and adjustment of pH was done by hand and as a rule – delayed in relation to the speed of reaction. As it was mentioned above, in „Organika Sarzyna” was produced since 1962 on IPO technology 4-chloro-2-methylphenoxyacetic acid (MCPA, Chwastoks). In the reaction of condensation of 4-chloro-2-methylphenol with chloroacetic acid there occurred similar difficulties. They were mastered only after partial continuity of the process and using automatic adjustment of pH with the help of pH-metre controlling the dispensing of MCAA and sodium lye.

The causes of difficulties occurring at MCAA and phenols condensation were only explained by the research of Moszczyński over the mechanism of the main reaction and the competitive MCAA hydrolysis reaction depicted before (Moszczyński, 1999). The research concerned the reaction of *o*-krezol with chloroacetic acid, but they are of a general nature and they can be related to 2,4-dichlorophenol (2,4-D) and other alkilo- and chlorophenols. Particular phenols depending on the substituents and solubility of the final chlorophenoxyacetic acid react in a slightly different way. The maximum industrial capacity of condensation in MPA synthesis is 92%, while in 2,4-D synthesis 97% is achieved.

The composition of mass after condensation of raw 2,4-dichlorophenol with MCAA acid was shown below in table 3.

Composition of post-condensation mass	[%GC]
<i>o</i> -chlorophenoxyacetic acid	2.5
<i>p</i> - chlorophenoxyacetic acid	0.5
2,6-dichlorophenoxyacetic acid	7.4
2,4- dichlorophenoxyacetic acid	84.6
2,4,6-trichlorophenoxyacetic acid	1.2
<hr/>	
<i>o</i> -chlorophenol	0.0
2,4-dichlorophenol	2.2
<i>p</i> -chlorophenol	0.0
2,6-dichlorophenol	1.1
2,4,6-trichlorophenol	0.4
NaCl	
glycolic acid	
water	

Table 3. Composition of reaction mass after condensation of raw 89% 2,4-DCP with MCAA.

Purification of acid with crystallization method has a limited efficiency. Isomer 2,6 is easily eliminated, while 2-chlorophenoxyacetic acid is hard to dissolve and remains in 2,4-D. 2,4-D of 96% purity of active substance is obtained. Rectification of about 89% raw 2,4-dichlorophenol is non-economical and threatened with originating dioxines in cube residue. The difficulty in mastering the technology of selective chlorination, purifying raw 89% 2,4-

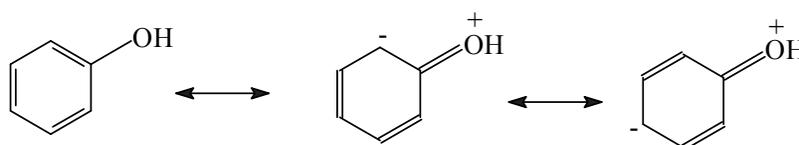
dichlorophenol or technical 2,4-D acid is soundly confirmed by the EU position regarding purity of commercial 2,4-D and its derivatives.

In the countries of the European Union, after the process of verification and re-registration according to the directive 91/414/EWG, only preparations of the highest quality were allowed into the market, broadly tested, man friendly and natural environment friendly. In the nineties, over one half of active substances used in preparations of plant protection was recalled from sales. With allowing a plant protection agent into the market full chemical specification and toxicity tests of all pollutions of the active substance which were found in the quantity of over 0,1% were required.

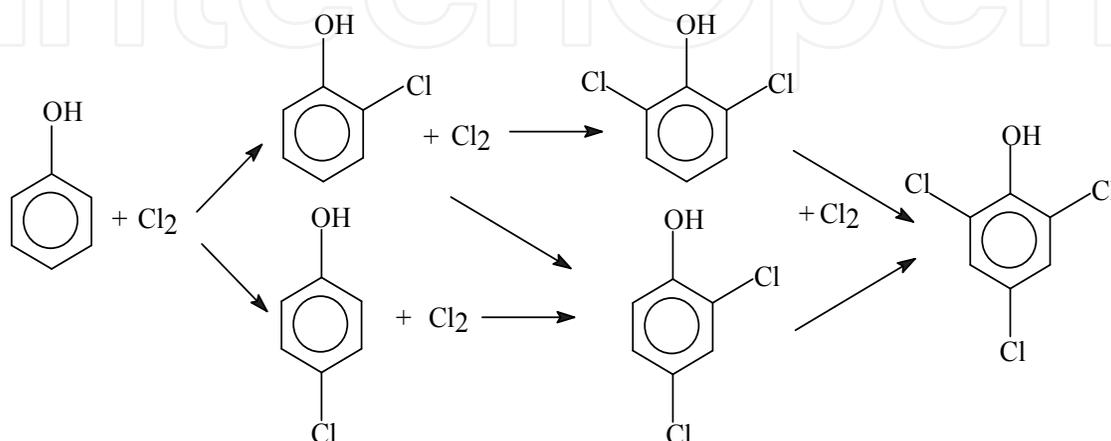
In the meantime, the working team for toxicological and ecotoxicological evaluation appointed under directive 91/414 EEC (over 200 of open and closed sorts of research) 2,4-D, consisting of 12 producers and suppliers of preparation 2,4-D in the European Union, including DowElanco Europe UK, Nufarm-Agrolinz Austria, Rhone-Poulenc France and AH Marks Co Ltd. UK submitted to the European Committee for registration 2,4-D of the quality of 96% of active substance. This standard was approved for UE producers by the directive 2001/103/EC of 28.11.2001. Maintaining the traditional standard 96% of active substance 2,4-D, in spite of a great pressure of environmentalists, shows difficulties in obtaining product of a higher purity.

Moszczyński and Białek have conducted a vast research on selectivity of reaction of phenol chlorination to 2,4-dichlorophenol (Białek, Moszczyński, 2009).

Phenol is a substrate which easily undergoes electrophilic substitution in aromatic ring. Additional pair of electrons from hydroxyl group after delocalization and because of mesomerism shifts to moves in aromatic ring which results in higher density of electrons in *ortho*- and *para*- positions.



Substitution in the ring with an electrophilic agent is fast but not regio- and chemoselective. Just after using 1 M of chlorine for 1 M of phenol a mixture of six products is formed (Watson, 1985).



The following conclusion can be drawn from the scheme above: obtaining *p*-chlorophenol as an intermediate product in synthesis of 2,4-dichlorophenol is much more advantageous than obtaining *o*-chlorophenol which is followed by forming 2,4-dichlorophenol and 2,4,6-trichlorophenol or even 2,6-dichlorophenol.

It is commonly known that many factors are included in the selectivity of reaction. Electron density in the substrate molecule – active phenol centres are located in the position *ortho*-, *para*- with preference for *para*-. The dissociation of hydroxyl group in phenol in different conditions of pH influences the orientation of electrophilic substitution. The activity of electrophilic agent is of crucial significance. Chlorine molecules are a strong electrophilic agent reacting violently with active aromatic substrates. The decisive significance should be ascribed to steric effect and catalysts. Intermolecular hydrogen bondings through hydroxyl group are formed in melted phenol. The association of molecules makes it more difficult to replace in the position *ortho*-. A similar effect is achieved at phenol chlorination in strong acids and polar proton dissolvents. The presence of hydrogen bondings in phenols was confirmed by IR methods and proton NMR method.

Our research mostly concerned catalysts and chlorinating agents, including high-molecular ones.

It is not necessary to use catalyst during the synthesis of 2,4-dichlorophenol from melted phenol and gaseous chlorine. The process of chlorination stops at 2,4,6-trichlorophenol. Substitution of next chlorine atoms is only possible when Friedel-Crafts catalysts are used. It was stated that Lewis acids used at chlorination of less active substrates do not influence the selectivity of substitution of highly reactive phenols. Catalysts from amines group direct substituents into *ortho*- position. Catalysts used by Moszczyński in MPA production appeared to be totally inactive. Sulphur catalysts have a limited directing effect. The combination of Lewis catalysts with sulphur compounds resulted with a high regioselectivity into *para*- position. Probably in the reaction a high-molecular complex is originated, where the catalytic effect interferes with the steric effect.

There were also performed tests of chlorination with the reverse method, i.e. phenoxyacetic acid (PA). Przondo, in cooperation with fellow workers in the installation 1/2-technical in Chemical Plants „Rokita”, did research on chlorination of PA acid with chlorine in alkaline water solution. Satisfactory results were not achieved. The process required significant dilutions of the reaction mass. The technology appeared to be highly waste-generating and the selectivity of chlorination not much better than at phenol chlorination (Dudycz et al. 1985).

Our team IPO and Rokita continued research on the reversed process. Using *tert*-butyl hypochlorite in the place of chlorine (t-BuOCl) of spatially developed molecule. A high selectivity of chlorination was achieved (98%) and purity of 2,4-D up to 99% of active substance. A very high selectivity of chlorination reaction is the result of the interference of two steric effects – side chain and volumetric molecule t-BuOCl (Moszczyński et al. 2008). A negative side to the technology is the necessity of operating flammable t-BuOCl and t-BuOH.

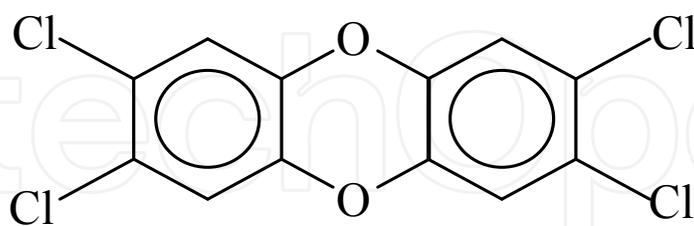
A technology based on sulfuryl chloride was developed and confirmed in the 1/2 technical scale results presented by Watson (Watson, 1974). The process is easy to implement and control. A negative side is the necessity of SO₂ recycling.

Three new methods of 2,4-D synthesis were developed, each of them of > 95% selectivity. The barrier of 90% selectivity of isomer 2,4-D in phenol chlorination was lifted. Results were shown below in table 4.

Chlorinating agent, catalyst,	Cl ₂	Cl ₂ catalytic complex, Lewis acids, sulphur compounds	SO ₂ Cl ₂ catalytic complex	<i>tert</i> -BuOCl phenoxyacetic acid, reverse method
Selectivity of chlorination [%]	90	96	98	98
Production scale	industrial	industrial (Moszczyński et al., 2002)	experimental (Moszczyński et al., 2009)	laboratory

Table 4. Progress in selectivity of the process of chlorination in technology 2,4-D.

While discussing the technology of production of 2,4-dichlorophenol, the problem of trace pollutions must be mentioned, which includes remains of catalyst, present always in industrial water iron, polychlorinated compounds, cyclohexenones derivatives. There may also appear polychlorodibenzodioxines and polychlorodibenzofurans. Trace pollutions in 2,4-DCP are undesired, because they influence the quality and stability of 2,4-D. Iron compounds may worsen the hue, remains of sulphur catalysts - odour, form during storing liquid forms slimy residues and also, as an effect, decrease the durability of 2,4-D preparations. Used by some 2,4-D producers, the vacuum rectification of technical 2,4-DCP is efficient, but it threatens with dioxines forming. In the tests of vacuum rectification of technical 2,4-dichlorophenol there was formed about 15% of post-distillation tars, containing significant quantities of dioxines, including the most toxic 2,3,7,8-TeCDD and TeCDF, which was shown below in table 5.



2,3,7,8-TCDD

Authors have developed the technology of removing catalysts and trace pollutions (Moszczyński et al. 2005).

2,4-dichlorophenol obtained with the method of phenol chlorination in the presence of catalysts is washed off with mineral acid, it is neutralized to pH >10,5 and dilutes with water to 50%. A suspension of mineral sorbents is introduced to chlorophenolate obtained in this way. Chlorophenolate with sorbents is stirred for 30 minutes and the introduced sorbents are filtered, which are then destroyed thermally.

Congener PCDD / PCDF	Toxicity equivalency factor (TEF)	Congener content in an specimen, m_i [ng/g]	Toxicity TEQ $m_i \times \text{TEF}$ [ng-TEQ/g]
2,3,7,8-TeCDD	1	2.32	2.3200
1,2,3,7,8-PeCDD	1	51.71	51.7100
1,2,3,4,7,8-HxCDD	0.1	0.28	0.0280
1,2,3,6,7,8-HxCDD	0.1	16.22	1.6220
1,2,3,7,8,9-HxCDD	0.1	6.63	0.6630
1,2,3,4,6,7,8-HpCDD	0.01	0.76	0.0076
OCDD	0.0001	3.11	0.0003
2,3,7,8-TeCDF	0.1	10.69	1.0690
1,2,3,7,8-PeCDF	0.05	1.45	0.0725
2,3,4,7,8-PeCDF	0.5	1.50	0.7500
1,2,3,4,7,8-HxCDF	0.1	0.55	0.0550
1,2,3,6,7,8-HxCDF	0.1	4.58	0.4580
1,2,3,7,8,9-HxCDF	0.1	3.16	0.3160
2,3,4,6,7,8-HxCDF	0.1	0.17	0.0170
1,2,3,4,6,7,8-HpCDF	0.01	5.90	0.0590
1,2,3,4,7,8,9-HpCDF	0.01	0.00	0.0000
OCDF	0.0001	67.75	0.0068
Result in ng TEQ/g			59.15 ± 0,05

Table 5. Contents of PCDD/F in the cube residue from the distillation of 2,4-DCP (Białek, 2009).

Authors have developed the technology of removing catalysts and trace pollutions (Moszczyński et al. 2005).

2,4-dichlorophenol obtained with the method of phenol chlorination in the presence of catalysts is washed off with mineral acid, it is neutralized to pH >10,5 and dilutes with water to 50%. A suspension of mineral sorbents is introduced to chlorophenolate obtained in this way. Chlorophenolate with sorbents is stirred for 30 minutes and the introduced sorbents are filtered, which are then destroyed thermally.

Trace pollutions in purified 2,4-dichlorophenol are given below in table 6.

Iron contents [ppm]	Derivatives DPS [%]	PCDD/F [TEQ ng/g]
<5	<0.001	0.027

Table 6. Trace pollutions in purified 2,4-dichlorophenol.

The product contains trace pollutions PCDD/F in the amount allowed by technical producers norms.

The world production of 2,4-dichlorophenol without Russia, China and India is estimated for 44 000 tons per year. The current production of 2,4-DCP in Poland is 6 to 8 000 tons per year. It places our country in the strict world lead. After using in 2004 a new technology of selective chlorination of phenol, two barriers were lifted: chlorination selectivity increased from 89 to 96% and the purity of commercial acid 2,4-D from 96 to 98%. Waste chloroorganic compounds were decreased by one half in the production process, also organic pollutions introduced to the soil during agricultural operations were decreased by one half. Recommendations of directive 91/414 EEC on the improvement of ecological conditions in the production and usage of plant protection agents were implemented.

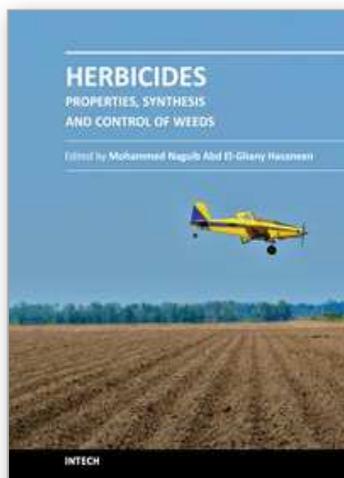
The author team W. Moszczyński, A. Białek, E. Makiela, B. Rippel, Listopadzki E., Okulewicz, Z. Dancewicz G. for the technology and product won prizes in national and world competitions, including:

- Złoty Orbital (Gold Orbital) of the monthly Rynek Chemiczny (Chemical Year), year 2004
- The main prize in the competition „Polish Product of the Future” („Polski Produkt Przyszłości”) in category „Technology of the Future” („Technologia Przyszłości”) organized by the Polish Agency for Enterprise Development, year 2004
- The Gold Medal with Mentions in the World Inventions, Research and Innovations Exhibition „Brussels Eureka”, year 2005.

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Herbicides - Properties, Synthesis and Control of Weeds

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This book is divided into two sections namely: synthesis and properties of herbicides and herbicidal control of weeds. Chapters 1 to 11 deal with the study of different synthetic pathways of certain herbicides and the physical and chemical properties of other synthesized herbicides. The other 14 chapters (12-25) discussed the different methods by which each herbicide controls specific weed population. The overall purpose of the book, is to show properties and characterization of herbicides, the physical and chemical properties of selected types of herbicides, and the influence of certain herbicides on soil physical and chemical properties on microflora. In addition, an evaluation of the degree of contamination of either soils and/or crops by herbicides is discussed alongside an investigation into the performance and photochemistry of herbicides and the fate of excess herbicides in soils and field crops.

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