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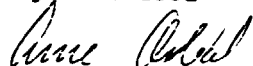
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Final report on initial phase of cooperation between KVK Agro, Chemical Works Organika-Sarzyna and Institute of Industrial Organic Chemistry.

Production of the herbicide MCPA (2-methyl-4-chloro-phenoxy acetic acid).

Project no. SI/POL/90/802

May 7th. 1992


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Abstract.

In cooperation between Chemical Works Organika-Sarzyna, Poland, and KVK Agro, Køge, Denmark, the latter has investigated the possibilities of implementing a new process for producing MCPA in the plant in Sarzyna.

KVK Agro has developed a new method for said production, which is simpler and in our opinion better than hitherto known methods. The method will significantly improve the quality of Organikas MCPA.

The plant in Sarzyna is suitable for the process and only minor changes is necessary before the process can be started. Part of the process already employed at Organika can be used as it is, followed by the inventive step of KVK Agro's process giving a great deal of the improvements (a better quality of the product). According to Organika the necessary chemicals are available in the neighbourhood of the factory.

The process has been demonstrated to people from Organika and their consultants from the Institute of Industrial Organic Chemistry in laboratory scale and in big scale.

A project is going on at KVK Agro with the aim of recirculation of the wastewater and conversion of sodium chloride in the water to a useful raw material.

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1. Introduction.

In April 1987 Chemical Works "Organika" in Sarzyna, Poland, initiated a project on expansion and modernization of their MCPA-plant. The project was expected to be supported by United Nations Industrial Development Organization (UNIDO). The project is described in a paper from The Slover Group, Texas. A member of this group contacted Sven Månsson at KVK Agro and asked for cooperation and technical assistance.

Chemical Works "Organika" wants to have a new process for production of MCPA with the purpose of improving the quality of the product in order to be able to sell to export markets. In cooperation with Institute of Industrial Organic Chemistry, who developed the process employed now, they look for companies with technology for MCPA-production and possibility to help with this technology.

Organika's initial intention was to be able to work with a well-known technique, used by many companies including Kemisk Værk Køge, the company from which KVK Agro is derived. Recently, however, KVK Agro has developed a new process, for which a patent is applied. This process will significantly improve the quality of the product and possibly benefit the environment.

KVK Agro proposed to bring this method into the discussion, because it is a much simpler method. We proposed a visit to the factory in order to find out, whether some of the equipment was suitable for the new method, to learn about Organika's method and to introduce our ideas.

2. Contact between the parties in the cooperation.

In the following text the companies/institutions are mentioned as

- 1) Organika = Chemical Works Organika-Sarzyna.
- 2) KVK Agro.
- 3) IPO = Institute of Industrial Organic Chemistry.

2.1. People involved in the cooperation.

The following people has been in contact with each other and participated in meetings, laboratory work and/or visits at the factories

- Mr. Wladyslaw Pilat, Organika.
Diplom chemical engineer, General director.
- Mr. Tadeusz Jakubas, Organika.
Diplom chemical engineer, Production director.
- Mr. Kazimierz Ratajczak, Organika.
Diplom chemical engineer, Research and technology manager.
- Ms. Stanislaw Murzyn, Organika.
Chemical engineer, Production chemist.
- Mr. Wieslaw Moszczynski, IPO.
Professor, D. Sc., Director.
- Ms. Iwona Gorska, IPO.
M. Sc. chemistry, Research chemist.
- Mr. Janusz Ostrowski, IPO.
D. Sc. agriculture, Professor of plant protection.
- Mr. Kurt Jensen, KVK Agro.
Director.
- Mr. Sven Månsson, KVK Agro.
Export Manager.
- Mr. Bjarne Holm-Jensen, KVK Agro.
Chemical engineer, Production manager.
- Mr. Arne Oxbøl, KVK Agro.
Chemical engineer, Agrochemical research.

2.2. Visits at Organika.

In november 1987 mr. Holm-Jensen and mr. Oxbøl visited Organika and met mr. Pilat, mr. Jakubas and mr. Ratajczak.

During the meeting, we were introduced to Organika and the presently employed method for production of MCPA. We inspected the factory to have a short introduction to the plant.

There was a mutual interest in continuing cooperation.

In april 1991 mr. Jensen, mr. Månsson, mr. Holm-Jensen and mr. Oxbøl visited Organika together with mr. Moszczynski, mr. Ostrowski and ms. Gorska.

Mr. Holm-Jensen and mr. Oxbøl demonstrated the process to ms. Gorska and ms. Murzyn through laboratory experiments and we went through the factory again to get a more precise description.

Mr. Jensen and mr. Månsson discussed the cooperation with mr. Pilat and mr. Moszczynski.

2.3 Visit at KVK Agro.

In July 1990 mr. Pilat, mr. Moszczynski and mr. Ostrowski visited KVK Agro and met mr. Jensen, mr. Månsson, mr. Holm-Jensen and mr. Oxbøl. The Polish side received a description of KVK Agro's method and the project including descriptive examples of the method.

After the first days meeting, the Polish side discussed internally and showed on the second day a very positive attitude to the project. They put many questions, which were answered. The main problem seemed to be content of sodium chloride in the wastewater. KVK Agro told about an idea to lower this content and promised to send further informations with mass-balance for water and sodium chloride.

Mr. Pilat and mr. Moszczynski received a copy of our method for analysis of MCPA, and mr. Oxbøl received a sample of MCPA-formulation from Organika.

2.4 Visit at Esbjerg Kemi.

In January 1992 ms. Gorska and ms. Murzyn visited Esbjerg Kemi together with mr. Holm-Jensen and mr. Oxbøl. The process was demonstrated in big scale, and ms. Gorska and ms. Murzyn was satisfied with what they saw. On the other hand they put many questions about equipment in general and methods, which was answered by letters after the visit.

3. Description of plants and chemistry.

3.1. Organika.

3.1.1. Introduction.

The factory is build in 1939 but due to the war the beginning of production was postponed to 1950. Since 1960 the factory produced agrochemicals, 50% of the factories total production. Among other productions are epoxy resins, silicone products and polyesters.

In the agrochemical division is also formulated imported, active ingredients. There is a mill installation present in the factory.

The productions are based on own technology, own chemical equipment made in own silicon cast iron foundry.

The MCPA plant is constructed in 1969/70 to produce 500 tons/year. It is however now producing 2000 tons/year. According to mr. Pilat, the plant is not good enough anymore, and the buildings are not constructed big and safe enough to build bigger and heavier equipment into it.

Organika has had a contact to Czechoslovakia and bought MCPA there, but this contact does not exist anymore.

The domestic market is 3000 tons/year and the export market 1000 tons/year.

3.1.2. The MCPA-plant.

The plant is situated on four floors in one building, partly outdoor. Equipment is listed below in short form. A more detailed description is in appendix 1.

3 reaction tanks with stirrer 3 m³ each made of steel for neutralisation of monochloroacetic acid.

4 reaction tanks with stirrer 3 m³ each made of glasslined steel for condensation of o-cresole with monochloroacetic acid.

2 reaction tanks with stirrer 2 m³ each for prechlorination.

4 tanks 3.5 m³ each for dissolving in tetrachloroethane.

3 reaction tanks with stirrer (3.5 m³, 4.5 m³ and 6 m³) for chlorination.

5 distillation columns for stripping the tetrachloroethane.

Storage tanks for formulations.

The plant capacity is 2000 tons/year (47 weeks in 3 shifts all week), which means the capacity is 253 kg/h).

In our opinion the plant is in relatively good condition and better, than we had expected. We believe, that our process can be performed in the existing plant with good results. Minor investments are necessary.

3.1.3. Organika's production method for MCPA.

The method employed by Organika is as follows in short form:

Initially a solution of 70% w/w monochloroacetic acid is neutralised with 30% w/w NaOH solution to pH = 6 at -30°C, yielding a solution of monochloroacetic acid sodium salt (app. 40% w/w of the monochloroacetic acid salt).

556 kg o-cresole (5.14 kmoles) is condensed with 1300 liters (1670 kg) of the abovementioned 40% w/w solution of monochloroacetic acid sodium salt (668 kg = 5.74 kmoles acid salt). 480 liters (638 kg) 30% w/w NaOH solution is added together with the other raw materials within 1 hour. The mixture is stirred for 2 hours more at 95-98°C.

After the reaction the mixture contains 3-4% w/w unreacted o-cresole, which is stripped in a column by steam and recirculated, leaving <0.5% w/w o-cresole in the mixture. The product is 2-methylphenoxyacetic acid.

App. 1 kmole chlorine is led into the mixture to chlorinate the phenoxy acid partly. Afterwards tetrachloroethane is added, the mixture is acidified and heated to 90°C in order to dissolve all the phenoxy acids in the tetrachloroethane. The water is removed, cooled and filtrated giving some phenoxy acid, which is recirculated. Chlorine is led into the tetrachloroethane solution to chlorinate the rest of the phenoxy acid. The temperature is 90-100°C. The product so obtained consists of 87% MCPA, 2% unchlorinated, 1% dichlorinated and 10% 6-chlorinated phenoxy acid based on total phenoxy acid.

The tetrachloroethane is removed by stripping in vacuum, and the product is dissolved in for example potassium hydroxide at alkaline pH.

Wastewater is treated together with other wastewaters on the factory, much of the treated water being recirculated.

For further details please see appendix 1.

3.1.4. The production method initially desired by Organika.

The method, Organika initially intended to learn, when the project started, is practically the same, as Kemisk Værk Koge has used for many years:

Chlorination of o-cresole with sulfurylchloride. The sulfur dioxide coming from the chlorination is to be recirculated as sulfurylchloride formed in a regeneration plant.

Distillation of raw chlorocresole to obtain a good quality of 4-chloro-o-cresole.

Condensation of 4-chloro-o-cresole with monochloroacetic acid.

Extraction of excess 4-chloro-o-cresole, which is to be recirculated.

The expectations is a product of 95% purity.

We were told, that a description of this project is made by a "projectbureau" before end of January 1990. Estimated pricelevel is 8-10 mill. US dollars for a completely new factory. We have not seen this project.

3.2. KVK Agro and Esbjerg Kemi.

KVK Agro is an independent, danish company, which produce, formulate and sell pesticides.

Esbjerg Kemi is also a producer and formulator of pesticides and cooperates with KVK Agro on phenoxy acids. Pilot plant and production plant for phenoxy acids is situated at Esbjerg Kemi.

3.2.1. KVK Agro's production method for MCPA.

KVK Agro's method is as follows in short form:

o-cresole is condensed with monochloroacetic acid in a manner different from, what Organika does today thereby increasing yield and decreasing sideproducts.

The reaction mixture is extracted with xylene, thereby decreasing the content of unreacted o-cresole in the mixture significantly.

The mixture of 2-methoxyphenoxyacetic acid is chlorinated with sodium hypochlorite at temperatures lower than 40°C and at neutral pH. A catalyst is necessary to obtain the better quality.

The mixture is acidified at app. 90°C, the product separated as a heavy oil, washed with a minor amount of water and dissolved in for example potassium hydroxide. The product so obtained has a purity of 98% based on total phenoxy acid in solution. The yield is 95% based on unchlorinated phenoxy acid.

Mecoprop (CMPP) can be made by this method as well as MCPA.

It is also possible to obtain technical acid by mean of well-known methods as for example flaking of the oily acid. This is outside KVK Agro's invention.

For a more detailed description please see appendix 2, which is part of the material, mr. Pilat and mr. Moszczyński received in july 1990, or eventually our patent description as mentioned below.

KVK Agro has applied for a patent in EP (PCT/DK 91/00208), US, Australia and Poland. The first written opinion from the European Patent Office is very positive saying that the process is novel and inventive.

3.2.2. Necessary equipment.

3.2.2.1. Condensation between o-cresole and monochloroacetic acid.

KVK Agro use a slightly different condensation technique though the chemistry is principally identical to the method employed by Organika. Ms. Gorska has explained, that IPO already has improved the method but not yet implemented it into the factory. According to discussions with ms. Gorska our method seems to be identical to the method developed by IPO.

The improved method can be performed in the same reaction vessels at Organika as the present method. Only slight changes are necessary, the difference between the methods being simultaneous addition of two raw materials instead of one.

In our opinion the reaction vessels for condensation are really good, so the condensation can continue in the system.

3.2.2.2. Removal of o-cresole.

Today Organika removes unreacted o-cresole by water-steam distillation from the condensation product. It is possible to do it perfectly well and we think this method can be continued. The consumption of sodium hypochlorite in the following chlorination reaction depends on how good this distillation is done, since sodium hypochlorite reacts with and destroys o-cresole.

We have seen very good samples and too bad samples of condensation product from Organika. They all give the same good end-product and in both cases waste-water contains no cresoles, but loss of o-cresole and sodium hypochlorite increases with decreasing effectivity of distillation.

Removal of o-cresole by steam distillation costs much energy, which is an argument for changing this step.

At KVK Agro the o-cresole is removed by extraction with xylene. It can be done in various systems either batchwise or continuously. Our experience is with continuous extraction while we have seen it done batchwise at Esbjerg Kemi. Organika has tanks enough for a batchwise extraction while a continuous extraction needs investment in new equipment.

According to ms. Gorska IPO has worked with this extraction but not yet implemented in the factory.

In both cases - water-steam distillation and extraction - removed o-cresole is recirculated, the yield based on o-cresole approaching 100%. In our opinion extraction is to prefer due to less energy consumption and generally better condensation products. On the other hand distillation has the advantage of using no organic solvents, and the equipment necessary is already present.

We have chosen not to propose a definite solution to this question since both principles are useful and maintaining the present system makes it easier to start the project and obtain the most desired advantage - a better quality. Furthermore we find it useful to discuss in details with the people of Organika and IPO.

3.2.2.3. Chlorination.

The inventive step of KVK Agro's process is the chlorination. In this step the selectivity of the chlorination is improved considerably compared to Organika's method and other known methods in producing phenoxy acids. Furthermore it is a simple process operating at neutral pH and ambient temperature.

The process is to be performed in a ventilated tank with stirrer and equipment for measuring pH, redox-potential and temperature. There is no particular demands on the tank material, since the sodium hypochlorite is consumed in the process momentary and pH is neutral. The temperature can be controlled by direct addition of ice, which give the most effective cooling and at the same time serves as a necessary diluent.

In the process is produced app. 100 kg MCPA per 1000 liters of waste-water. This is the disadvantage of the process giving more waste-water than most other processes.

Beside the reaction vessel a storage tank for sodium hypochlorite is necessary, the material of which must be resistant to the hypochlorite (rubber or some polymer material). Such a tank is available at Organika.

Other necessary storage tanks (for sodium hydroxide and hydrochloric acid) are present.

3.2.2.4. Isolation and formulation of the product.

When the chlorination is finished, we propose to set the MCPA free by addition of hydrochloric acid thereby precipitating the phenoxy acid as a heavy oil. The oil can easily be transferred to another tank in which it is washed free of sodium chloride with minor amounts of water. The washed, heavy oil can then be transferred into a suitable base f.ex. potassium hydroxide or dimethylamine. This procedure is very close to what Organika does now, since they obtain the product as an oil after having distilled the organic solvent from the chlorination step.

Acid-proof tanks for such a process is present (steel lined with carbon tiles).

3.2.2.5. Proposal of how to use Organikas plant.

At the meeting in Køge, july 1990, we presented a scheme of the process starting with o-cresole and ending with MCPA. We proposed to do a minimum of changes in order to be able to start the improvement very soon, which means that removal of o-cresole has to be done by steam distillation. Please find the scheme in appendix 3.

We calculated the capacity of the plant to be 5400 tons MCPA per year.

The main thing is, that we in principal are able to start "tomorrow" with the existing plant.

4. Calculation of cost prices.

Based on informations from mr. Ratajczak (copy of telex in appendix 4) we are able to compare the consumption of raw materials in the two processes. In the table below consumption of raw materials are listed for the two methods together with savings of each material by changing to KVK Agro's method. Savings with a negative sign indicate, that KVK Agro's method uses more of the raw material than Organikas method.

Table 1. Raw material consumption producing 1000 kg MCPA.

Raw material	Organika- method (tons)	KVK Agro- method (tons)	Savings (tons)
o-cresole	718	570	148
Chloroacetic acid (80% w/w)	881	700	181
Chlorine	577	410	167
NaOH (28% w/w)	3461	1750	1711
HCl (30% w/w)	957	1400	- 443
H ₂ SO ₄ (96% w/w)	-	72	- 72
NaOH (50% w/w)	-	950	- 950
Na ₂ CO ₃	108	2	106
Tetrachloroethane	144	-	144
Catalyst	-	10	- 10

In KVK Agro's method less o-cresole, chlorine and monochloroacetic acid are used. On the other hand more sodium hydroxide and hydrochloric acid are used. Most o-cresole and monochloroacetic are to be imported, while sodium hydroxide and hydrochloric acid are locally present.

5. Advantages of KVK Agro's process.

Our process has in our opinion the following advantages:

- 1) The chlorinated product has a very favourable distribution between the different, chlorinated species - >97% being the desired 4-chlorinated product.
- 2) There is no handling of chlorinated cresoles and therefore no smelling of them and no problems with discharging wasteproducts (6- and dichlorinated products).
- 3) The wastewater contains no cresoles at all, since they are destroyed in the chlorination process prior to the chlorination of the phenoxy acid.
- 4) No handling of chlorinated, organic solvent and therefore no emission to the environment.
- 5) Improved economy due to reduced raw materials consumption.
- 6) Reduced consumption of imported raw materials.

To illustrate the effect of changing to KVK Agro's method is below analysis of an Organika-product (Chwastox) and a KVK Agro product produced in pilot plant (50 liters).

Table 2. Analysis of MCPA-products.

Distribution of total phenoxy acids and chlorocresoles (% w/w).

	MPA	2C6MPA	MCPA	2,4DC6MPA	Chloro- cresoles	MCPA/ 2C6MPA
Chwastox	1.64	9.32	80.32	1.10	7.62	8.6
KVK Agro	0.14	0.35	98.76	0.74	-	280

The improved selectivity benefits the purpose of making products of export quality.

Avoiding handling of tetrachloroethane seems to be a big advantage, since tetrachloroethane is regarded as a very unpleasant chemical (Hommel: Handbuch der gefährlichen Güter, 2nd. edition, 1988, Merkblatt 646)

6. Waste water.

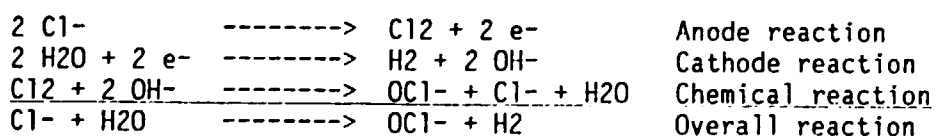
As mentioned previously the amount of waste water is a disadvantage of KVK Agro's process. It is necessary to remove phenoxy acids and most of the sodium chloride from it before discharging to the freshwater River San.

Removing phenoxy acids has to be done by extraction with xylene according to our experience. This leaves a waste water basically free of phenoxy acids.

Secondly sodium chloride has to be removed according to mr. Pilat and mr. Moszczynski. We have calculated the content of sodium chloride in the waste water in KVK Agro's and Organikas process and presented the results to mr. Pilat and mr. Moszczynski (appendix 5). Changing from Organikas method to KVK Agro's method raises the amount of sodium chloride in waste water from 1417 kg per ton MCPA to 1495 kg per ton MCPA which is 5.5% increase.

We do not consider this increase as a big disadvantage but we agree, that the amount is too big. Our proposal to mr. Pilat and mr. Moszczynski is to investigate the possibility of regenerating sodium hypochlorite from the sodium chloride by electrolysis. If possible, it will serve two purposes: Removing sodium chloride from the waste water and lower the costs of sodium hypochlorite.

Electrolysis of an aqueous solution of sodium chloride to chlorine, sodium hydroxide and hydrogen is well-known. The chlorine and the sodium hydroxide can afterwards be combined to sodium hypochlorite.



Our idea is, that the sodium chloride in the waste water is to be converted to sodium hypochlorite by this process without preceding purification of the waste water.

We have proposed use of a membrane cell, which represents the purest technology in chlorine production. The main question in treating a waste water with inorganic and organic impurities is lifetimes of electrodes and membrane. Another important question is current efficiency.

In order to answer this questions KVK Agro has initiated a cooperation with an expert in the field (Dr. Hans Holmberg, Synthelec, Lun' Sweden). He presented a report showing that the process is possible but not answering the above questions.

No optimization will be done before a principal decision about the whole project is taken. Please see section 7.

7. KVK Agro's proposal for further action.

7.1. Production using KVK Agro's process.

As the new process in all aspects, except for waste water seems to be better than the old one, we propose to begin a pilot production of MCPA in almost full scale in parallel to the normal production. In our opinion it is possible to find equipment in the factory in which it can be done. We know, that IPO has a pilot plant in Sarzyna for such purposes. Such a production will show to the people in Sarzyna the benefits of the new process, and selling the improved product might give improvements in the economical situation.

The waste water from the new process is neither better nor worse than the waste water from the old process and should cause no problems for pilot productions.

We propose to do the chlorination process only and to use the MPA produced now, since the major advantages is in the chlorination step. On the other hand we are willing to work with the condensation process, too, if we can avoid a conflict with IPO. They have told us, that they have started an optimization work, the results of which not yet are fully satisfying. We do not know why, but have been told about problems with pH-measurement.

Provided that we can find a suitable tank, the only things required by us are redox potential measurement (one electrode and a mV-meter), pH-measurement (one electrode and a pH-meter) and temperature control (preferably by addition of ice in the reaction mixture). The cost for electrodes and meters is about 1500 US dollars. We propose, that we buy the necessary equipment at a danish company, with which we have good experience.

We have been told, that ice and sodium hypochlorite is available in the factorys neighbourhood. The necessary catalyst has to be supplied from Denmark for the pilot production.

Since the season is over now, we propose to work quickly in order to use spare time at the factory before the start of next season. Before we start, negotiation between the parties should take place in order to settle the financial problems and Organikas eventual export of MCPA.

7.2. Conversion of waste chloride to hypochlorite.

When the chlorination process works, treatment of waste water becomes the most important part of the project. We propose, that we continue the cooperation with mr. Holmberg at Syntheled in order to get the full information about the possibility of the electrolysis. This shall include calculations of economical feasibility.

We know, that mr. Holmberg is willing to do the work. The price level for necessary experiments is 15.000 US dollars. This work has to be started as soon as mr. Holmberg has the time for it. If the process is possible, we propose a contact to a swedish supplier of membrane cells, ElectroCell Systems AB, Tæby, Sweden. KVK has been in contact with them before and discussed chlorine plants.

8. Conclusion.

A new process for producing MCPA has been demonstrated to Organika and IPO, and its advantages has been approved.

The MCPA-plant at Organika has been inspected and is considered suitable for the new process with minor changes. It is possible to start the new process very soon and obtain the major advantage - a better product.

The major advantages are a better product of export quality and elimination of a chlorinated, organic solvent.

The new process has a disadvantage in waste water. The amount of waste water means, that the same amount of sodium chloride is led to the recipient - the fresh water River San - as by the process employed now.

A process for purifying the waste water and at the same time regenerate a useful raw material is proposed and preliminary investigated. Further investigation awaits a decision of the continuation of the project.

Appendix 1.

Description of plant and process at Organika.

In the bottom floor are 3 reactors for neutralisation of monochloroacetic acid. Each is 2 m³, made of stainless steel and equipped with stirrer and coil and mantle for cooling water. The size of the coil was not stated. There are 9 holes in the top each app. 10 cm in diameter.

In the reactors are 70-80% MCA neutralised with 30% NaOH yielding a 40% solution of MCA Na-salt. The neutralisation takes place at 30°C.

On the 3rd. (upper) floor are 4 measuring tanks:

2 for MCA-solution which were rubberlined. Size not stated.

1 for o-cresol made of steel. Size not stated.

1 for 30% NaOH made of steel. Size not stated.

Additionally there are 4 condensation tanks, each 3.6 m³ glass lined. The reactors are all equipped with demister, stirrer and jacket for steam and cooling water.

550 l o-cresole with density = 1.01 kg/l at 50°C (app. 5.14 kmoles) are taken up in a condensation tank. Within 1 hour 1300 l MCA-solution with density = 1.28-1.29 kg/l at 20°C (app. 7.74 kmoles) are added together with 480 l 30% NaOH with density = 1.31 kg/l at 40°C (app. 4.62 kmoles). The temperature is 85-90°C. Stirring is continued for 2 hours at up to 98°C.

The gas ventilated from the reactors is passed through a demister to a carbon cooler, where the vapour condenses. The condensate (o-cresole and water) is led to a separation tank. After separation, the water is used for dilution of NaOH. The o-cresole is recirculated.

A storage tank is situated outside the building for MPA-condensation mixture (carbon steel).

Also storage tank(s) for stripped MPA-solution are situated there.

On the upper floor is a dosage tank (1200 l of carbon steel) for MPA-condensation mixture before the stripping columns. There is another, smaller dosage tank, which sometimes is used before the 3rd. column (reserve).

There are 3 stripping columns each app. 4.5 m high and 0.8 m in diameter. The top of the columns are on the upper floor.

On the upper floor are two tanks for distillate each 2 - 2.5 m³ made of steel.

After some reaction, the condensation mixture is pumped to a storage tank, from which it is pumped to the dosage tank for stripping. From the dosage tank it is run through 2 of the columns (500 l/h in each). The distillate is led through a carbon cooler to a separation tank, from which the o-cresole is recirculated. The stripping is done with steam (0.1-0.15 MPa). The amount was not stated, and there was no measurement of the temperature in the column.

The mixture contains about 25-26% MPA and 2-3% o-cresole before stripping and 20-23% MPA and up to 0.5% o-cresole after stripping.

If a better quality of MPA is desired, the first raffinate is pumped to the smaller dosage tank, from which it is run through the 3rd. column.

From the bottom of the columns the product is run to the storage tanks for MPA-solution.

On the upper floor are 2 tanks for prechlorination, each 2.5 m³ and rubberlined.

For prechlorination 1980 l MPA-solution (20%) with density app. 1.15 kg/l (2.74 kmoles) and 390 l tetrachloroethane is pumped to a prechlorination tank. 30 kg Cl₂ (0.42 kmoles) is added within 0.5 hour at 90-100°C.

On the 2nd. floor are 4 tanks for acidification, each 3.6 m³ and glass-lined with stirrer and jacket for steam.

On the 2nd. floor are 2 intermediate tanks (3.6 m³ - glass lined) with stirrer for organic phase after prechlorination and acidification.

The prechlorination mixture is run into the acidification tank and acidified with 20% HCl-solution at 90°C in order to dissolve all MPA and MCPA. 3 prechlorinations are mixed before acidification (2 from one and 1 from the other prechlorination-tank). The water-phase is removed, cooled and filtrated. The filtercake is recirculated. We did not see the the equipment for cooling and filtration.

The organic phase is run to the intermediate tanks.

On the 1rst. floor are 4 chlorination tanks (3.5, 4.5, 6.0 and app. 5.0 m³) each glass lined and without stirring.

There is also a cooler for tetrachloroethane and an absorber for HCl formed in the chlorination.

To the chlorination tanks Cl₂ is added with 60 kg/h at 90-100°C. HCl formed in the reaction is absorbed in the HCl-absorption tower.

On the ground floor is 5 destillators 5 m³ each (steel lined with carbon tiles) for destillation of tetrachloroethane. There are tanks for separation of destillate and finally storage tank for tetrachloroethane.

There are also storage tanks for MCPA-formulations.

After the chlorination, tetrachloroethane is watersteam destilled. The destillate is collected in a tank, where aqueous and organic phase are separated. The organic phase is pumped to storage tank, and the aqueous phase to waste (the aqueous phase is acidic).

The appropriate base (KOH, NaOH or dimethylamine) is pumped to the remainens in the destillator for dissolving the MCPA in the formulation at pH = 10-11 (8-9 for dimethylamine formulations).

Outside the building, in which the plant is situated, is a tank with 4 chambers for further purification/sedimentation of process water.

All process water from the process goes into this tank, from chamber 1 to chamber 2 and so on leaving the tank from chamber 4. Within a year the tank is filled with precipitate. Finally the waste water is treated chemically before discharging. This treatment is an oxidation with NaOCl taking place in a stirred tank.

Appendix 2.

Description of KVK Agro's invention.

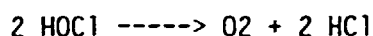
Detailed description of the invention.

There are three important aspects in the invention, all of them being responsible for a good result: The pH at which the chlorination takes place, the temperature and the catalyst.

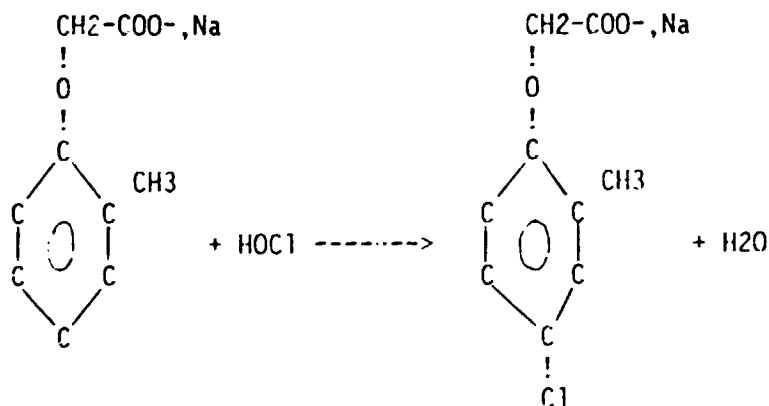
The pH differs considerably from the pH reported in most other papers on afterchlorination of phenoxy acids. We have worked with neutral or weakly alkaline conditions because the chlorinating agent giving only monochlorination is hypochlorous acid, HOCl. When chlorine, Cl₂, is dissolved in water, it enters in an equilibrium with HOCl. The equilibrium pH is 4.3. When pH is raised, the salt of HOCl, having an acid dissociation constant of 7.4, is formed.

It is therefore very important to have a pH higher than 6.3, at which pH practically no Cl₂ is present. On the other hand it is necessary, that the HOCl is not entirely converted to its salt. So, pH must be kept below 9.4, at which pH practically no HOCl is present. In practice we have found that pH between 7 and 9 is suitable.

The HOCl undergoes disproportionation into oxygen and hydrochloric acid on prolonged standing and under influence of light and heat:



We have found, that this reaction is of practically no importance at the lower pH-values in the interval compared with the chlorination reaction:



At the higher pH-values in the interval, the disproportionation reaction becomes more important compared to the chlorination reaction, resulting in a lower yield of chlorinated phenoxyacid based on NaOCl and a requirement of an excess of NaOCl. A pH of 8.5 or lower is found suitable to ensure a satisfactory yield on NaOCl.

The temperature is very important to the ratio between 4- and 6-chlorinated products. So the ratio drops from approximately 180 to 100 in chlorination of methylphenoxypropionic acid to produce MCP, when going from 10°C to 30°C.

The catalyst is very important to the ratio between 4- and 6-chlorinated product. The ratio raises from 8.0 in a chlorination without catalyst to 178 in a chlorination with catalyst.

The process is as follows:

o-cresol is condensed in the same way as 4-chloro-o-cresol with either a chloro-alkanoic acid or a lactone. The reaction mixture is water-steam distilled or extracted to remove excess o-cresol. The resulting mixture is cooled to the chlorination temperature, diluted with water to approximately 12-14% w/w 2-methylphenoxy-alkanoic acid.

After the chlorination, the mixture contains approximately 8-10% w/w 4-chloro-2-methylphenoxy-alkanoic acid. It can be isolated in many ways, depending on the end use. One method is to pump the mixture to equimolar amounts of mineral acid at ambient temperature. The acid crystallises as a fine powder, which can be filtrated and washed to remove inorganic salts. The wet powders can be formulated directly as aqueous solutions of salts or dried to yield a technical acid of high purity.

Another method is to heat the reaction mixture to 90°C and add the mineral acid to the mixture. Thereby the phenoxyalkanoic acid is set free as an oil. On cooling the acid crystallises as granules, which is easily filtrated and washed. Alternatively the oil can be washed and formulated without crystallization.

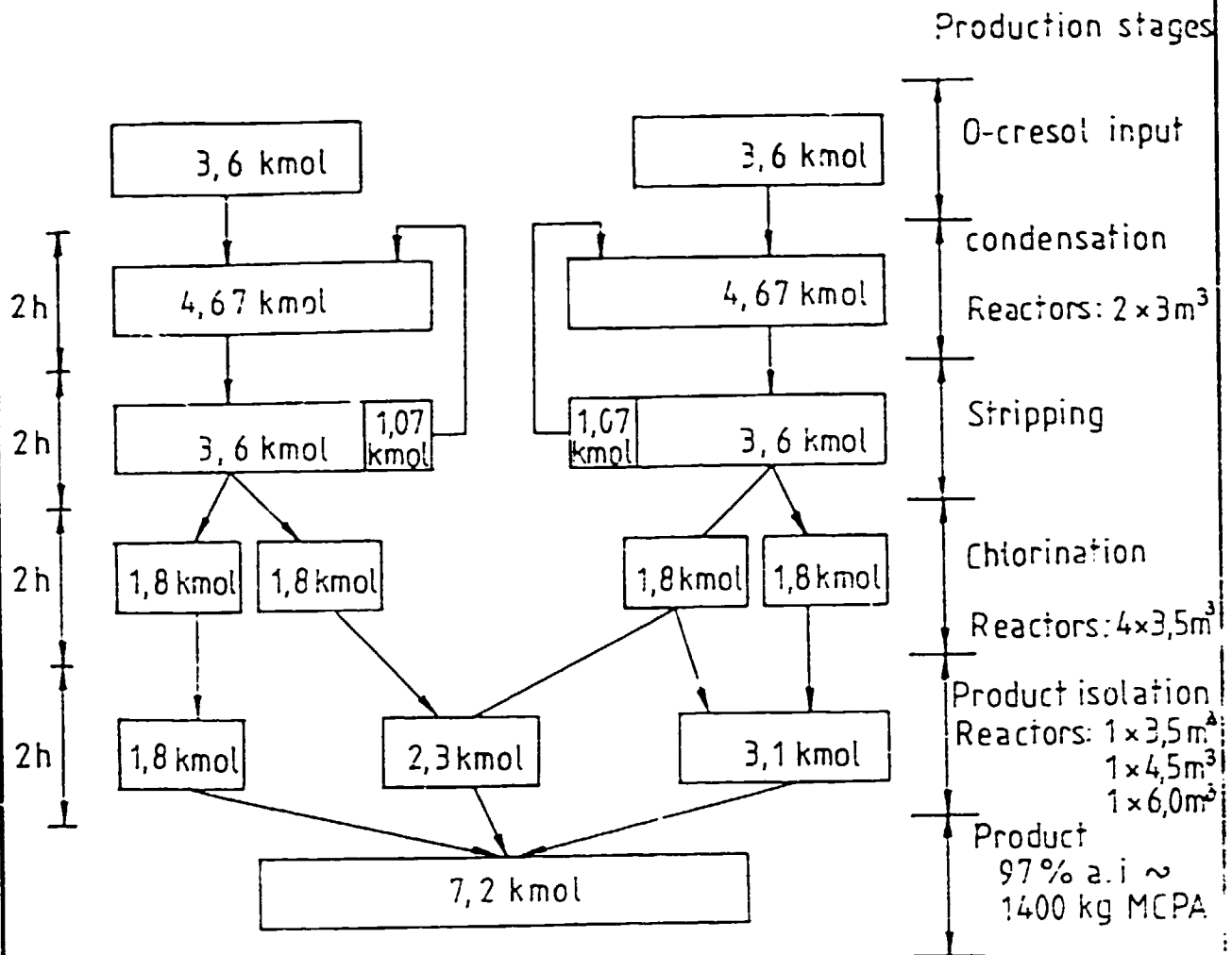
A third method is to extract the phenoxyalkanoic acid at 80°C into xylene and extract the phenoxyalkanoic acid out of the xylene into aqueous solutions of potassium hydroxide, dimethylamine or other bases, thereby forming a commercial solution of salt of phenoxyalkanoic acid.

During the chlorination stage o-cresol remaining after water steam distillation/extraction is oxidized by the NaOCl-mixture to watersoluble aliphatic acids. This oxidation is known in wastewater treatment, and it is a further benefit to the method, that no o-cresol is present in the waste water. Depending on the content of o-cresol an excess of NaOCl is necessary.

Appendix 3.

Scheme on proposed use of Organikas plant with KVK Agro's process.

O-cresol balance



Production capacity at the Organika Plant:

$$\frac{356 \text{ days} \times 24 \text{ h} \times 1400 \text{ kg MCPA} \times 0,9}{2 \text{ h}} \sim 5400 \text{ t MCPA/year}$$

Remarks: The stripping time is a guess.

0,9 is a efficiency level.

Matr:	TEKNISK SKOLE	Målestok	Tegn	
			Konf	

Appendix 4.

Cost price informations from Organika (copy of telex).

re: informations for kvk

' ' in answer to kvk letter of 13.4. -we are giving below informations re raw materials consumption for 1000 tons pure mol, figures are calculated on base of planned for 1990 standards of consumption of raw materials for production of chwastox extra (26 g/o mk 817 viscosity in 20 deg c = 1,179 g/cm³)

- 1) 0- creosol 98 o/o - 716 tons
- 2) monchlorine acid (?) - 881 tons
- 3) sodium hydroxide (in calc. for 100o/o - 969 t
- 4) hcl -in calc for 100 o/o - 287 t
- 5) 4-chloroethan 144t
- 6) liquit chlorine 577 tons
- 7) soda (waterless?) 108 t
- 8) potassium hydroxide (in calcul. for 100 o/o - 63 tons

in nearst time we will send to you sample of chwastox extra 10m³ with atest which is solivent of sodium - potassium salt of ucoa (66.7 sodium salth and 33/3 o/o potassium saltz

regards

ing.k.ratajczak.,

Appendix 1.

Mass-balance for sodium chloride in 3 processes for MCPA-production.

Køge, den 10. September 1990

CHEMICAL WORKS "ORGANICA-SARZYNA"
37-310 Nowa Sarzyna
POLEN

Zu Hd. von Herrn Direktor, Diplomingenieur Wladyslaw Pilat

Sehr geehrter Herr Pilat,

Wie Ihnen während unserer Sitzung in Køge am 19.-20. Juli 1990 versprochen, haben wir eine Übersicht über die Bildung von NaCl in den besprochenen Herstellungsverfahren für MCPA: dem SO₂Cl₂-Verfahren, dem NaOCl-Verfahren der KVK Agro A/S und dem jetzigen Organica-Verfahren ausgearbeitet. Wegen unseres Sommerurlaubs hat sich der Versand dieses Briefes und des Berichtes etwas verspätet, was wir bedauern.

Bemerkungen zum Bericht

Entscheidet man sich bei der Neutralisation für die Verwendung von lediglich HCl, bilden sich beim SO₂Cl₂-Verfahren 796 kg NaCl/Tonne MCPA gegenüber 1460 kg NaCl/Tonne MCPA beim NaOCl-Verfahren. Der Unterschied ist deutlich, aber allein die 796 kg müssen vor der Einleitung in Süßwasserflüsse zu Erwägungen Anlaß geben. Die für das NaOCl-Verfahren erforderliche Klärung sollte auch beim SO₂Cl₂-Verfahren stattfinden.

Entscheidet man sich, wo nur möglich in den beiden Prozessen, für die Verwendung von H₂SO₄, bilden sich beim SO₂Cl₂-Verfahren 293 kg Salze gegenüber 1630 kg Salze beim NaOCl-Verfahren. Wiederum ist der Unterschied deutlich, der aber eigentlich ohne Bedeutung ist, da die Ausleitung von Na₂SO₄ nicht viel besser sein kann.

Für die Verwendung von Schwefelsäure spricht, daß sie billiger ist.

Für die durchgehende Verwendung von HCl spricht, daß das gebildete NaCl eventuell Teil einer Elektrolyse mit Bildung von Cl₂/NaOCl würde und so wiederverwendet werden könnte. Das würde eine teilweise Ausscheidung von NaCl in den Abwässern bedeuten und eine mögliche wirtschaftliche Verbesserung des Prozesses. Als Alternativ könnte man das Wasser eindampfen und das gefällte Salz einem Chlorproduzenten als Teilzahlung für das NaOCl zugehen lassen. Wir, die KVK AGRO A/S, arbeiten zur Zeit an dieser Möglichkeit zusammen mit Experten auf dem Gebiet. In diesem Zusammenhang wurde am 28. August Herrn Mike Kosinski ein Telex geschickt mit einigen Fragen an Organika, Sarzyna.

Falls unsere angestellten Berechnungen über die NaCl-Bildung in Ihren jetzigen Prozess korrekt sind, bilden sich jetzt 1250-1420 kg NaCl. Das ist somit eine beträchtliche Menge, und ein Verfahren zur Entsorgung scheint, nach dem, was Sie uns während der Sitzung hier in Køge erzählten, auch erforderlich. Wenn Sie bereits jetzt Umstände sind, sich einer Menge von 1250-1420 kg zu entledigen, muß es möglich sein, auf gleiche Weise die kleine Extramenge loszuwerden.

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BANKFØR
A. S. ØYKKE BANK, DRIFBØR
GWIFT: ØYBA DK KK

Wir möchten jedoch betonen, daß ein Klärprozess, bei dem die Abwässer so sauber wie möglich werden, bei uns einen hohen Stellenwert hat. Wir bemühen uns deshalb sehr was diesen Elektrolysenprozess betrifft.

Wir sehen Ihren Äußerungen zu diesem Brief und zum Bericht entgegen und hoffen, in naher Zukunft die Diskussionen fortsetzen zu können.

Freundliche Grüße



Bjarne Holm-Jensen und Arne Oxbøl

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BERICHT

Das Salzgleichgewicht bei drei Verfahren zur Herstellung von MCPA

In dem folgenden wird die Herstellung von MCPA nach dem SO₂Cl₂-Verfahren, dem NaOCl-Verfahren bzw. dem Organika-Verfahren mit der Angabe, wo sich bei den drei Prozessen Salz bildet, kurz beschrieben.

I. Das SO₂Cl₂-Verfahren

Chlorierung:

o-Cresol + SO₂Cl₂ ----> 4-Chlor-o-cresol + andere Chlor-o-cresole + SO₂ + HCl

(ca. 92%)

Das Schwefeldioxid wird bei einer Reaktion mit Cl₂ zu SO₂Cl₂ regenerieren und die Salzsäure zur Fällung der Phenoxysäure oder an anderen Stellen in der Produktion verwenden.

Die Chlor-o-cresolmischung auf eine Reinheit von ca. 97-98% destillieren. Die Remanenz verbrennen.

Kondensation und Nachbehandlung:

50 kmol 4-Chlor-o-cresol mit 42 kmol Chloressigsäure umsetzen. Hierdurch bilden sich 36 kmol MCPA (7,2 Tonnen) und 6 kmol Glykolsäure. In der Mischung befinden sich 14 kmol nicht umgesetztes 4-Chlor-o-cresol.

Die Mischung mit ca. 14 kmol HCl oder 7 kmol H₂SO₄ neutralisieren und extrahieren.

Nach Extraktion mit Xylol, die Säure mit ca. 42 kmol HCl oder 21 kmol H₂SO₄ unter Erhitzung mit direkter Dampfzuleitung fällen.

Das Endvolumen beträgt ca. 30 m³, davon sind 7 m³ MCPA und 23 m³ Wasser.

Anschließend die Säure mit ca. 2 m³ Wasser waschen (10 m³ werden 5 mal verwendet).

Unterwegs bildet sich Natriumchlorid oder Na2SO4 wie folgt:

	<u>NaCl</u> (kmol)	<u>Na2SO4</u> (kmol)
Chlorierung	keines	keines
Kondensation	42	keines
Neutralisation	14 oder	7
Ansäuerung	42 oder	21
	i.g.	98
	oder	42 und 28

Entscheidet man sich für die Verwendung von nur HCl, enthalten die Abwässer:

$$\frac{98 \text{ kmol NaCl} \times 58,5 \text{ kg/kmol}}{25 \text{ m}^3} = 229 \text{ kg NaCl/m}^3.$$

Dieses entspricht:

$$\frac{98 \text{ kmol NaCl} \times 58,5 \text{ kg/kmol}}{7,2 \text{ Tonnen MCPA}} = 796 \text{ kg NaCl/Tonne MCPA.}$$

Falls man, wo nur möglich, H2SO4 anstatt verwendet, enthalten die Abwässer:

$$\frac{42 \text{ kmol NaCl} \times 58,5 \text{ kg/kmol} + 28 \text{ kmol Na2SO4} \times 142 \text{ kg/kmol}}{25 \text{ m}^3} =$$

$$98 \text{ kg NaCl} + 159 \text{ kg Na2SO4 pro m}^3.$$

Dieses entspricht:

$$\frac{42 \text{ kmol NaCl} \times 58,5 \text{ kg/kmol} + 28 \text{ kmol Na2SO4} \times 142 \text{ kg/kmol}}{7,2 \text{ Tonnen MCPA}} =$$

$$341 \text{ kg NaCl} + 552 \text{ kg Na2SO4 pro Tonne MCPA.}$$

II. Das NaOCl-Verfahren

Kondensation und Extraktion

50 kmol o-Cresol mit 42 kmol Chloressigsäure umsetzen. Hierdurch bilden sich 38 kmol MPA und 4 kmol Glykolsäure. In der Mischung befinden sich 12 kmol nicht umgesetztes o-Cresol.

Die Mischung mit ca. 12 kmol HCl oder 6 kmol H₂SO₄ neutralisieren und extrahieren.

Chlorierung und Nachbehandlung

Nach der Extraktion aufgelöstes Xylol abkochen, und die 38 kmol MPA mit ca. 42 kmol Cl₂ in der Form von NaOCl als eine 12% W/W Lösung chlorieren, die auch 42 kmol NaCl und 4 kmol NaOH enthält, die mit 4 kmol HCl oder 2 kmol H₂SO₄ neutralisiert werden. Bei der Reaktion bilden sich 42 kmol NaOH, die mit 42 kmol HCl oder 21 kmol H₂SO₄ neutralisiert werden.

Nach der Chlorierung die Säure mit ca. 42 kmol HCl oder 21 kmol H₂SO₄ unter Erhitzung mit direkter Dampfzuleitung fällen.

Es werden min. 100 kg MCPA/m³ produziert mit einem Ertrag bei der Chlorierung von ca. 95%. Aus 38 kmol MPA ist der Ertrag deshalb 36 kmol MCPA (7200 kg) in 72 m³ Lösung, wovon 65 m³ Wasser sind.

Anschließend die Säure mit 2 x 7 m³ Wasser waschen, die dann für die folgende Charge als ein Bestandteil der 65 m³ Verwendung finden.

Unterwegs bildet sich wie folgt:

	NaCl (kmol)		Na ₂ SO ₄ (kmol)
Kondensation	42		keines
Neutralisation	12	oder	6
Chlorierung			
mit Hypochlorit	42		keines
Neutralisation	46	oder	23
Fällung	42	oder	21
	1.g.		
	184		
	oder	und	50
	84		

Entscheidet man sich für die Verwendung von nur HCl, enthalten die Abwasser:

$$\frac{12 \text{ kmol NaCl} \times 58,5 \text{ g/kmol}}{65 \text{ m}^3} = 106 \text{ kg NaCl/m}^3$$

Dieses entspricht:

$$\frac{106 \text{ kg NaCl} \times 58,5 \text{ g/kmol}}{7,2 \text{ Tonnen MCPA}} = 1475 \text{ kg NaCl/Tonne MCPA}$$

Falls man, wo nur möglich, H_2SO_4 anstatt verwendet, enthalten die Abwässer:

$$\frac{84 \text{ kmol NaCl} \times 58,5 \text{ kg/kmol} + 50 \text{ kmol Na}_2\text{SO}_4 \times 142 \text{ kg/kmol}}{65 \text{ m}^3} =$$

76 kg NaCl + 109 kg Na_2SO_4 pro m^3 .

Dieses entspricht:

$$\frac{84 \text{ kmol NaCl} \times 58,5 \text{ kg/kmol} + 50 \text{ kmol Na}_2\text{SO}_4 \times 142 \text{ kg/kmol}}{7,2 \text{ Tonnen MCPA}} =$$

683 kg NaCl + 986 kg Na_2SO_4 pro Tonne MCPA.

III. Das Organika-Verfahren

Basiert auf Auskünfte, die wir während eines Besuches bei und aus einem Telex, das wir von Organika erhalten haben, konnten wir die folgende Aufstellung über das NaCl-Gleichgewicht im jetzigen Prozess ausarbeiten:

Kondensation und Extraktion:

5,19 kmol *o*-Cresol mit 5,36 kmol Chloroessigsäure umsetzen. Hierdurch bilden sich 3,66 kmol MPA und 1,70 kmol Glykolsäure. In der Mischung befinden sich 1,53 kmol nicht umgesetztes *o*-Cresol.

Die Mischung mit ca. 1,53 kmol HCl neutralisieren und sie wasserdampfdestillieren.

Kondensation und Nachbehandlung:

Nach der Wasserdampfdestillation 1 kmol Chlor in die Mischung leiten, wonach die Mischung durch Beigabe von ca. 4,36 kmol HCl völlig angesäuert wird. Anschließend die MPA-Mischung fertigchlorieren.

Nach der Chlorierung die Säure zur Salzformulierung extrahieren.

Zur Herstellung von 1000 Tonnen MCPA werden 881 Tonnen Chloroessigsäure 100% verwendet, entsprechend 0,535 kmol MCPA/kmol Chloroessigsäure. Aus 5,36 kmol Chloroessigsäure werden somit 2,87 kmol = 575 kg.

Unterwegs bildet sich NaCl wie folgt:

	NaCl (kmol)
Kondensation	5,36
Neutralisation	1,53
Chlorierung	1,00
Ansäuerung	4,36
insg.	12,25

Die Wassermengen sind uns nicht bekannt. Wir können aber die NaCl-Bildung pro Tonne MCPA errechnen:

$$\frac{12,25 \text{ kmol NaCl} \times 58,5 \text{ kg/kmol}}{0,575 \text{ Tonnen MCPA}} = 1246 \text{ kg NaCl/Tonne MCPA.}$$

Aus dem Telex von Herrn Ratajczak am 15. Mai 1990 geht hervor, daß 969 kg NaOH (100%) verwendet werden. Ich erlaube mir die Annahme, daß alles als 100% reines Material vorliegt, bestehend die Menge auf eine andere Weise zu rechnen ist:

$$\frac{969,000 \text{ kg NaOH} \times 58,5 \text{ kg/kmol NaCl}}{40 \text{ kg/kmol NaOH}} = 1417 \text{ kg NaCl/1000 kg MCPA.}$$

31. August 1990

Björna Holm-Lundgren und Anne Öxsti