THE PRODUCTION OF PHENOXY HERBICIDES

Phenoxy herbicides are of great significance in New Zealand because of their strength and selectivity. They include a group of herbicides consisting of a benzyl ether, of which the best known are 2,4,5-T and 2,4-D. This article focuses on 2,4-D and the herbicide formulations made from it.

2,4-D is manufactured from 2,4-dichlorophenol in a four step process:

Step 1 - Phenol neutralisation
The (acidic) phenol is neurtralised with caustic soda.

2,4-dicholorophenol + NaOH $\rightarrow$ sodium dichlorophenate (NaDCP) + H_2O + heat

Step 2 - NaMCA production
Sodium monochloroacetate is produced in another exothermic reaction.

monochloroacetic acid (MCAA) + NaOH $\rightarrow$ sodium monochloroacetate (NaMCA) + H_2O

Step 3 - Condensation
The NaDCP is condensed with NaMCA to produce Na 2,4-D - the sodium salt of 2,4-D.

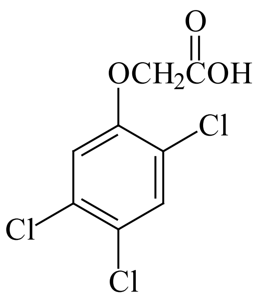
NaDCP + NaMCA $\rightarrow$ sodium 2,4-dichlorophenoxyacetate + NaCl

Step 4 - Final ageing
The Na 2,4-D is aged by the slow addition of NaOH to ensure that the phenol content is less than 0.5 w/w%.

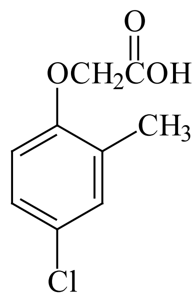
This Na 2,4-D is then converted to its ethyl hexyl ester, emulsified and sold as a herbicide.

INTRODUCTION

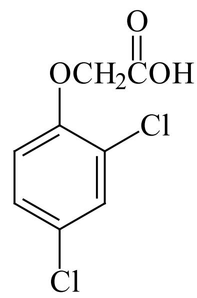
Phenoxy herbicides, such as those shown below, and have been in use since 1944. 2,4,5-T and 2,4-D were synthesised by Pokorny in 1942, and 2,4-D has been manufactured in New Zealand since 1962. It is currently the most significant phenoxy herbicide in New Zealand. 2,4,5-T was made by Dow AgroSciences in New Zealand until November 1987 and sold until December 1988, but it is no longer sold here due to its environmentally hazardous properties.



2,4,5-T



MCPA



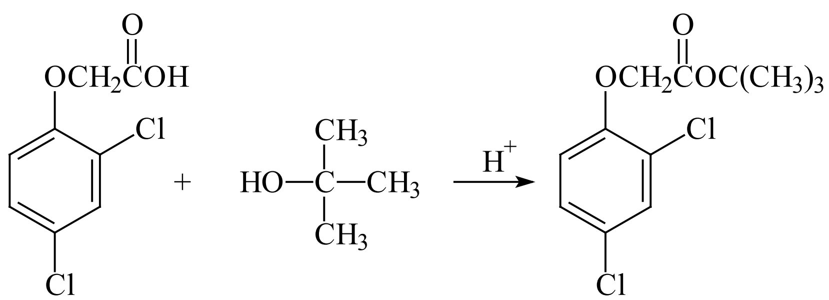
2,4-D

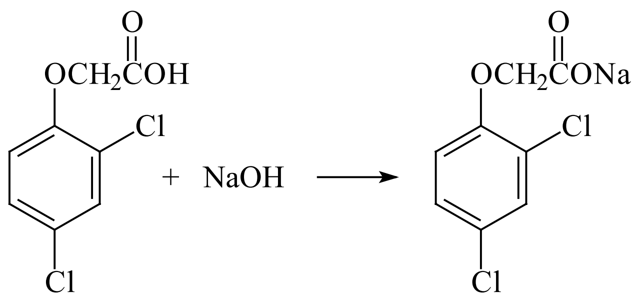
Uses of 2,4-D
2,4-D is a highly selective herbicide, affecting broad-leaved weeds (e.g. clover) and woody vegetation, while being harmless toward cereals. **Table 1** lists the herbicides made by Dow AgroSciences that contain 2,4-D and their uses.

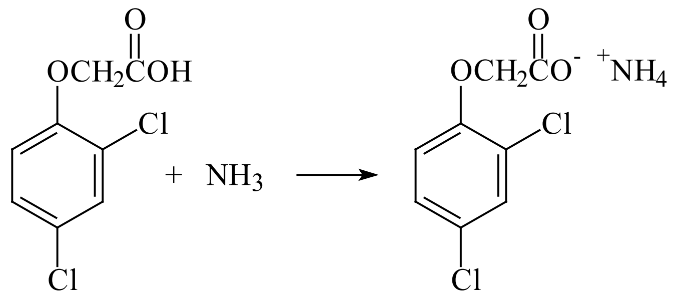
Table 1 - A selection of commercial herbicides containing phenoxy herbicides

Commercial name	**Phenoxy component**	**Other component(s)**	**Use**
2,4-D Amine	amine salt of 2,4-D	—	Broadleaf weeds in cereal areas
2,4-DB Herbicide	sodium salt of 2,4-DB	—	Broadleaf weeds in lucerne and new pasture
Banvine	amine salt of 2,4-D	amine salt of dicamba	Broadleaf weeds in turf and waste areas
2,4-D Ethyl hexyl ester	ethyle hexyl ester of 2,4-D	—	Broadleaf weeds in pasture
MCPA	potassium salt of MCPA	—	Broadleaf weeds in pastures and cereals
MCPB	sodium salt of MCPB	—	Broadleaf weeds in pastures and some crops
Tordon 50-D	amine salt of 2,4-D	amine salt of picloram	Perennial broadleaf weeds

Reactions
2,4-D can react in esterification, acid base and amine salt forming reactions as follows:







These reactions are used to synthesise herbicides with specific properties for commercial use.

THE MANUFACTURING PROCESS

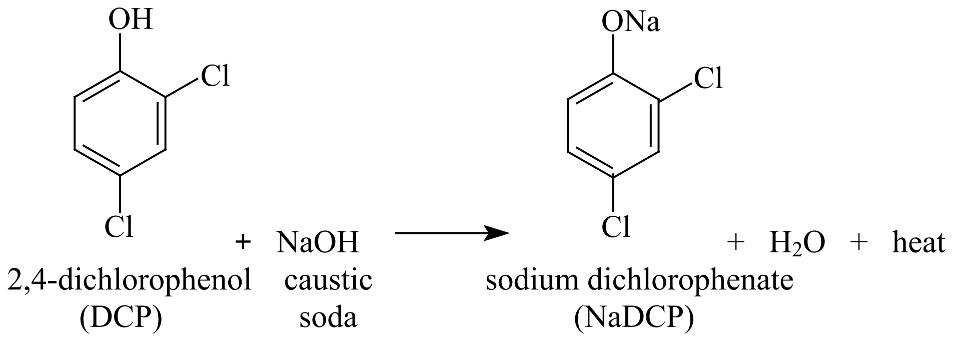
Phenoxy herbicides were made by Dow AgroSciences in New Zealand until December 1997. The process involved three stages. Firstly, 2,4-dichlorophenoxyacetate was produced. This was then converted into a variety of pure products, which in turn were formulated into commercial herbicides.

Production of 2,4-dichlorophenoxyacetate

2,4-dichlorophenoxyacetic acid (2,4-D) is produced from its sodium salt, which is in turn manufactured from 2,4-dichlorophenol in a four step process, and is converted into a variety of products. The conversion of 2,4-dichlorophenol (DCP) into sodium 2,4-dichlorophenoxy acetate[1] (Na 2,4-D) can be broken into four steps: neutralisation; NaMCA production; condensaton reaction; and ageing.

Step1 - Phenol neutralisation

The neutralisation step refers to the neutralisation of DCP with caustic soda. Sufficient caustic soda is added to create alkaline conditions although not all of the DCP is neutralised during this step. The neutralisation is exothermic with heat removed through a cooling jacket on the reactor. The product from this neutralisation is sodium dichlorophenol (NaDCP).



Step 2 - NaMCA production

NaMCA is produced by the neutralisation of monochloroacetic acid (MCAA) with caustic soda, which is an exothermic reaction. The heat of reaction is removed by reacting these two chemicals in a heat exchanger prior to adding the NaMCA to the reactor.

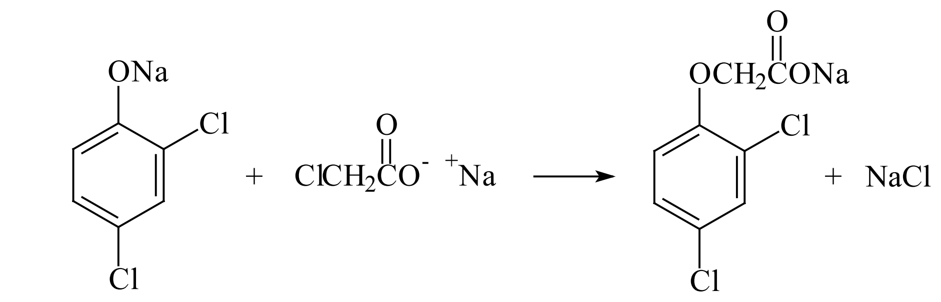
[1] *Note on nomenclature:* sodium phenolate and sodium phenate are the same species (a benzene ring with an ONa substituent) whereas phenoxide is the anion (a benzene ring with an O^- substituent).

$$\mathrm{ClCH_2C(=O)OH} + \mathrm{NaOH} \longrightarrow \mathrm{ClCH_2C(=O)O^-\ {}^+Na} + \mathrm{H_2O} + \text{heat}$$

monochloroacetic acid (MCAA) → sodium monochloro acetate (NaMCA)

Step 3 - Condensation

The NaMCA then condenses the NaDCP to produce Na 2,4-D. This reaction is highly exothermic with the heat of reaction removed through a cooling jacket on the reactor.



sodium dichlorophenate (NaDCP) + sodium monochloro acetate (NaMCA) → sodium 2,4-dichloro phenoxy acetate

Unwanted side reactions do occur but are kept to a minimum through the choice of optimum operating conditions. NaMCA and water undergo a reaction that produces sodium glycollate and hydrochloric acid.

$$\mathrm{ClCH_2C(=O)O^-\ {}^+Na} + \mathrm{H_2O} \longrightarrow \mathrm{HOCH_2C(=O)O^-\ {}^+Na} + \mathrm{HCl}$$

sodium monochloro acetate (NaMCA) → sodium glycollate

Due to the alkaline nature of the reaction mixture, any HCl formed is immediately neutralised with caustic soda to sodium chloride and water. NaMCA also reacts with caustic soda to produce sodium glycollate and water. For this reason the stoichiometric ratio of MCAA and caustic soda is strictly controlled to avoid build-up of excess caustic soda.

$$\mathrm{ClCH_2C(=O)O^-\ {}^+Na} + \mathrm{NaOH} \longrightarrow \mathrm{HOCH_2C(=O)O^-\ {}^+Na} + \mathrm{NaCl}$$

sodium monochloro acetate (NaMCA) → sodium glycollate

Step 4 - Final ageing

As the raw materials are used up, the speed of reaction slows because the unreacted material is at a low concentration in the reaction mass. An ageing period is required to ensure the phenol content of the Na 2,4-D is below 0.5 w/w %. During the ageing step, caustic soda is slowly added to the reaction mass to react with any remaining phenol. The addition rate is controlled so that alkaline conditions are maintained in the reactor.

Conversion to active species
The production of 2,4-D is the first step in the production of the following actives:

DMA 6 sequestered (i.e. it will not form complexes with hard water)
2,4-D amine technical
2,4-D ethyl hexyl ester
2,4-D concentrate
2,4-D wet acid

These actives are then used as the base for several herbicides that are formulated on site.

Different processes are used to convert 2,4-D into the various actives. The process of converting 2,4-D into 2,4-D ethyl hexyl ester is described below as an example. In producing all of the actives listed above, 2,4-D undergoes an acidification, and then either a neutralisation or an esterification depending on which active is desired.

Production of 2,4-dichlorophenoxy ethyl hexyl ester
The conversion of 2,4-D into 2,4-D ethyl hexyl ester involves two stages; an acidification stage, and an esterification stage.

Step1: acidification
The purpose of the acidification process in the production of 2,4-D ethyl hexyl ester is firstly to provide the means to separate the product of the reaction step from undesirable components, such as sodium glycollate and sodium chloride; and secondly to transform the reaction mass to the acidic state from which the esterification can take place.

The four steps in the acidification and their function are:

· Acidification / Separation - involves acidifying the reaction mass, and mixing, settling and separating the aqueous layers that form.

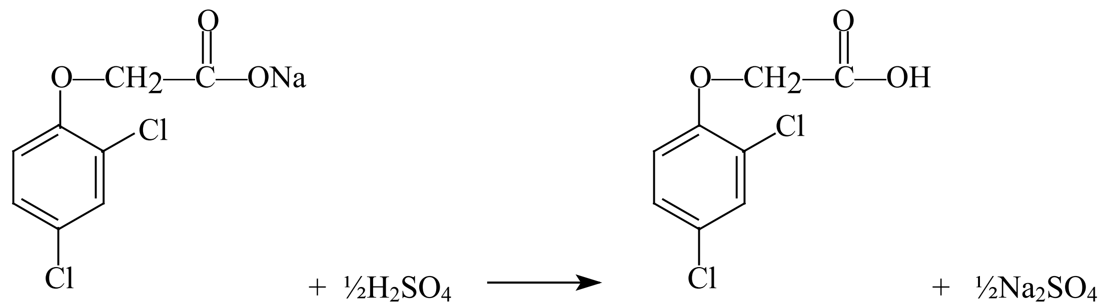
· First water wash - removing undesireable components from the product.

· Second water wash - removing further undesireable components from the product.

· Xylene wash - product which is miscible in the separation and wash waters is removed with xylene.

The acidification step involves adding water, sulphuric acid, 2-ethyl hexanol and xylene to the 2,4-D reaction mass. During the acidification step the 2,4-D is converted to 2,4-D acid.

Separation of the product from the undesirable side components is achieved by exploiting the differing solubility's of the components in water and xylene. The undesirable components are all very soluble in water, but insoluble in xylene; whilst the 2,4-D acid is soluble in xylene but only slightly soluble in water. The mixture is agitated for a period and when the agitator is stopped, two distinct layers form - a water layer, which contains most of the undesirable components, and a product layer that contains the 2,4-D acid and only a small amount of the undesirable components.



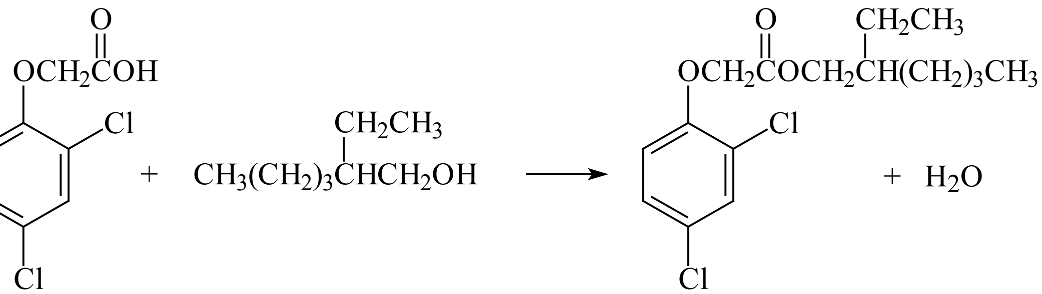
sodium 2,4-dichloro phenoxy acetate — sulphuric acid — 2,4-dichlorophenoxy acetic acid

The small amount of undesirable components that remain in the xylene layer after the acidification are removed with two water washes.

To ensure that all of the 2,4-D acid is collected, the water layers from the acidification and wash stages are treated with xylene to remove any 2,4-D acid that may have been soluble in the water.

Step2: esterification

The esterification of 2,4-D acid is the final step in the production of the herbicide active 2,4-D ethyl hexyl ester. During this stage 2-ethyl hexanol is added to the 2,4-D acid together with the xylene from the xylene wash. A catalyst is also added to aid the esterification. The esterification reaction is carried out at a high temperature, which is achieved by applying steam to the vessel jacket.



2,4-dichlorophenoxy acetic acid — 2-ethyl hexanol — 2,4-D ethyl hexyl ester

In common with esterification reactions generally, this reaction is reversible - that is water reacts with the ester to give acid plus alcohol - this reverse reaction is known as hydrolysis. It is important to remove the water that is formed to prevent the hydrolysis step from occurring. Water is removed with the aid of xylene. Water, xylene and 2-ethyl hexanol form an azeotrope which is continuously distilled off and then cooled in a condenser. When cooled, this mixture splits into two phases - a water phase that contains a small amount of 2-ethyl hexanol, and a xylene / alcohol layer. The water layer is run off into another vessel whilst the xylene / 2-ethyl hexanol layer is recycled to the reactor. This cycle continues until esterification is complete.

Once the esterification is complete, a vacuum is applied to the reactor. The reason for applying the vacuum is that the xylene and 2-ethyl hexanol boil at a much lower temperature when under a vacuum, requiring less energy to be applied to the reactor to boil off the components. The xylene and 2-ethyl hexanol that is distilled off is no longer recycled to the reactor but is drained into another vessel. The reactor remains under vacuum until almost all the xylene and 2-ethyl hexanol is driven off the reaction mixture.

Analyses of the product include estimates of:

Total ester concentration
Total free acid, which includes unreacted 2,4-D acid and phenol
Specific gravity

A gas/liquid chromatographic scan is run to check for impurities. The GLC indicates the ester concentration and the amount of xylene that is left in the ester at the end of the reaction.

Formulation - making a user product
2,4-D ethyl hexyl ester is largely water-insoluble, and so cannot be usefully mixed with water on its own. This product is marketed in an emulsifiable form - an "emulsifiable concentrate" or "EC".

Water is the obvious dilutant for spraying purposes, being the cheapest, most readily available and innocuous medium. It is therefore desirable to set up the product in a form which will emulsify readily in water.

Even if the product is an excellent quality ester, its biological efficiency, i.e. its useful efficiency, will be seriously restricted if it is not formulated so as to emulsify freely in water. 2,4-D ethyl hexyl ester formulations are composed of: a solvent, the ester and an emulsifier. The emulsifiers used are usually a blend of anionic and non-ionic agents, the mixture being chosen so as to achieve desirable emulsion properties in the presence of either hard or soft water - as would be commonly found on farms throughout the country.

The properties of a mixture which come under close scrutiny, especially when a new formulation is being established, include:

- Specific gravity
- Clarity
- Flash point (temperature at which vapour presence becomes high enough for an explosive mixture to be formed with air)
- Chemical stability of the EC and of the emulsion
- Physical stability of the emulsion
- Stability of the EC under normal conditions of storage with particular reference to precipitation's or solidification
- Spontaneity of emulsification of the EC.

Each batch of 2,4-D emulsifiable concentrate produced is tested in terms of properties such as these.

ENVIRONMENTAL IMPLICATIONS

The various products containing 2,4-D are used as herbicides. They have low acute toxicity to animals, but are toxic to fish. There should be no adverse environmental effect if used in accordance with label instructions. The problems associated with the related phenoxy herbicide 2,4,5-T relate to TCDD (2,3,7,8-tetrachlorodibenzo-D-dioxin) - an impurity that it commonly contains which is absent in 2,4-D.

The manufacture of these products has little effect on the environment. Waste air and aqueous streams are treated before discharge to the environment. Other wastes are incinerated in an approved high temperature incinerator.

All rain water that falls on site is retained in ponds on site until analysis confirms that it is safe to release it.

Original article compiled by Andrew Syme (Dow AgroSciences). Edited by Heather Wansbrough with reference to:

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