Fine hairs, wax crystals, water-repellent membranes etc. are all capable of inhibiting the transport of active substances into plants. Innovative approaches are needed to help the active substances overcome these hurdles at the plant surface. The figure shows the surface of a potato leaf at a very high magnification.

Innovative formulation technology

Effective **escorts** into the green tissues

Active substances may play the starring role in crop protection agents, but they have to be helped along by various additives if they are to express their full potential. Some additives, for example, remove barriers that would otherwise prevent the active substances from reaching their site of activity. Bayer CropScience's formulation technologists develop individual chemical escorts for the various molecules.

Maize, barley and wheat have many enemies: weeds compete with them for nutrients, fungi penetrate into their tissues, and insect pests attack their roots, leaves and fruits. If these enemies are to be controlled properly, crop protection agents must be designed in such a way that they can fulfil their intended uses. An effective active substance on its own is not enough: like the star of a football team, it needs the support of other team members if it is to succeed. "Without the right formulation, even the best of active substances is worth nothing", explains Dr. Hilmar Wolf, Group Leader, Fungicide Formulations at Bayer CropScience. And the active substances, which arrive at the plant enclosed in fine spray droplets, must first of all reach their actual site of action. Various barriers can get in the way. For example, many leaf surfaces are covered in fine hairs or tiny wax crystals, which cause most liquids to roll off.

In order to help the substances protect the various types of crop plant, the researchers must develop different strategies. An active substance applied to attack mites or germinating fungal spores through direct contact must be active at the leaf surface. Alternatively, if the intention is to control sucking insects – such as aphids – that bore into plant tissues, then the active substance needs to penetrate and to become as widely distributed in the plant sap as possible. This is why the chemical packaging around the molecule is so important. The researchers mix the active substance with various other molecules that cushion the impact of the spray droplet or reduce its surface tension on the plant. In this way, they ensure not only that the droplet stays on the leaf surface, but also that it spreads thinly over as large an area as possible, so that the active substance can quickly penetrate into the leaf.

Bayer CropScience's formulation specialists must keep abreast of trends in active substance chemistry and application technology. For example, active substance molecules are getting bigger and bigger these days: they are also usually less soluble – and thus more difficult to push into the plant. The trend in spray technology is towards larger droplets, because smaller droplets are more likely to be carried by wind, thus causing a loss of coverage. Applying fewer, larger droplets means that the active substance is much less evenly distributed over the plant surface than it would be by many, finer droplets. So Bayer CropScience's researchers must create a solution for each situation – in other words, a tailor-made formulation.

A good formulation of a crop protection agent comprises a mixture of various molecules besides the active substance. Dispersing agents, for example, ensure that finely-ground particles of active substance rapidly become evenly distributed within the spray tank during the process of dilution. If, however, the active substance is present in an organic solvent, then so-called emulsifiers are needed to bring about the formation of fine emulsion droplets in the water of the spraying solution. Other substances are used to extend the shelf-life of the mixture, by preventing it from forming lumps, and thus blocking the spray nozzles. Then come the so-called

adjuvants, which are there to help the active substance reach its target. Only when the perfect combination of various additives is achieved can the crop protection agent express the full potential of its activity. "The bioavailability of the active components, either on, or in the plant, is the major factor underlying their efficacy: it determines how quickly the active substance becomes available or reabsorbed", explains Dr. Rolf Pontzen, Laboratory Leader in the Formulation Department at Bayer CropScience.

Bioavailability is all

"Modern crop protection agents are usually based on highly-active molecules with complex structures, the synthesis of which is complicated, and for that reason, very expensive", continues Pontzen. "We must try to protect as many plants as we can using as little active substance as possible." Theoretically speaking, five to ten grammes of a substance would be sufficient to cover all of the leaves in a five hectare field with the thinnest film imaginable. And in some cases, the activity of modern compounds is so high that a film this thin could actually work.

As soon as the plant surface has been successfully coated with a film, the next hurdle arises. The outermost cell layer of the leaf – the epidermis – is protected by the cuticle, a wafer-thin, water-repellent membrane. The cuticle may be only about a micrometer thick, but it protects the plant very effectively against excessive loss of water via evapotranspiration from the leaves. In many plant species, this layer is also covered in tiny wax crystals – a severe impediment to the penetration of crop protection agents.

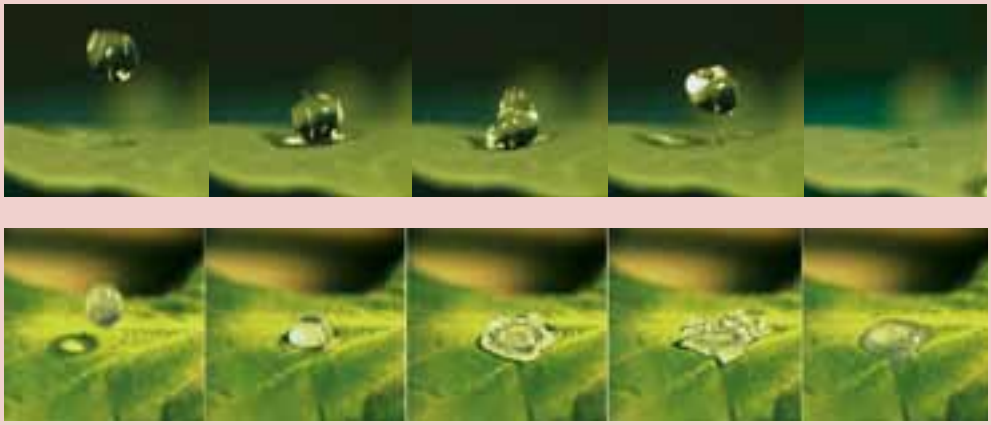
Overcoming this is a considerable challenge. Take, for example, the activity of the herbicide Laudis® OD (OD stands for "oil dispersion"), for which both optimal coverage of the plant surface and rapid penetration into its tissues are essential. Here, a sophisticated formulation ensures that the spray solution containing the Laudis active substance tembotrione becomes evenly distributed between the wax crystals, thus ensuring optimal contact with the leaf surface. Other components of the formulation then greatly facilitate penetration into the leaf. More than 90 percent of the active substance succeeds in entering the plant over the course of a single day. In order to control a weed plant, tembotrione must become distributed throughout its tissues by spreading as effectively as possible via the vascular system. The herbicide inhibits specific vital enzymes in the leaves of plants that protect them against the effects of UV-light: this causes photosynthesis to come to a standstill, and ultimately brings about the death of the weed. "Herbicides can only really express their full potential if they are transported in both elements of the plant's vascular system – the xylem and the phloem", explains Pontzen. "In fact, this would also apply to the crop plants themselves if we didn't protect them by adding substances called safeners to the crop protection agent," continues the formulation specialist. Safeners ensure that the treated crop plants – but not the target weeds – are able to metabolise the active substance quickly, so that only the latter are killed off.

Finding ways through the green barrier

The researchers have a useful instrument that allows them to investigate treated leaves – the scanning electron microscpe. "This allows us to take a look at what the additives in the spray deposit are doing on the leaf surface", says Pontzen. For example: what the film coating on the leaves looks like, or how the particles of active substance and additives are arranged in relation

Keeping droplets in the picture

Crop protection agents are most commonly applied to the field in the form of aqueous solutions. When the tiny droplets impact onto the water-repellent leaf surface of an oilseed rape plant, they simply run off (upper pictures), and thus fail to reach their intended target, the site of action in the plant. To make sure that the spray droplet does indeed stay on the plant surface, Bayer researchers equip the product with special substances that cushion the impact or reduce the droplet's surface tension. In this way, they ensure that the spray droplet adheres firmly to the leaf (lower pictures) and moreover, that it spreads itself over a large area, so that the active substance can penetrate rapidly, and subsequently spread to all parts of the plant. The more efficient these processes, the less product the farmer needs to apply to the crop.



Source:
Bayer research, 20, 2008

The formulation specialists Dr. Rolf Pontzen (left) and Dr. Hilmar Wolf are trying to identify additives capable of keeping the complex crop protection agents on target – in other words, helping them to reach their active sites.

to each other. In some cases, the special additives facilitate the penetration of the active substance by softening up the cuticle. In other cases, they actually inhibit penetration by causing the active substance to crystallize out of solution. Either of these effects can be vital, depending on the circumstances. If a crop protection agent is intended to prevent germinating spores from penetrating, then it must be capable of prolonged action at the plant surface. For this reason, some fungicide mixtures contain two active substances. "For these fungicides, it is particularly important that the conditions are balanced to favour both active substances: the one that needs to penetrate into the plant, and the other that remains in the spray deposit on the leaf," says the crop protection specialist. This means that the fungal pathogens within the leaf are controlled, but also that the entire plant is provided with a film to protect it against new infections. Adjuvants are used to ensure that the active substances become, as it were, lodged onto the leaf – only gradually entering the plant in regular doses over a period of several days. These examples show that Bayer CropScience's formulation scientists have found various ways of overcoming the green barrier. ◀

Wafer-thin protection

Some crop protection agents need a special formulation to help them to penetrate into the leaf – because the epidermis, the outermost layer of cells, is covered by the cuticle, a wafer-thin, water-repellent membrane. The latter is usually no more than a micrometer thick, and it prevents the plant from losing too much water via evaporation from the leaves. The cuticle thus presents crop protection agents with a barrier that is extremely difficult to overcome. Bayer CropScience's researchers create special formulations that help the active substance to penetrate into the leaf quickly and effectively. Or they encapsulate the active substances so cleverly that these are able to remain on the cuticle for longer, and can thus be gradually released at the leaf surface. This scanning electron microscope picture shows a spray deposit containing the active substance thiacloprid on a barley leaf.