From active substance to product – the formulation is the key

Crop protection isn't simply a question of using the right active substance: the success of a product also depends on delivering the active substance in the right formulation*.

The science of Formulation Technology involves incorporating the active substance into a final product that is the most practical for the user, and which guarantees that a small amount of active substance is distributed evenly over a large treated area. An important consideration is whether the crop protection agent will be applied by spraying, irrigation or broadcasting, or whether treatment should be in the form of a seed-coating. This article discusses the various factors that have to be taken into account when developing the right formulation for a particular active substance. It will also introduce the formulation types that have been developed for the most commonly used types of spray application.

High demands made of formulations

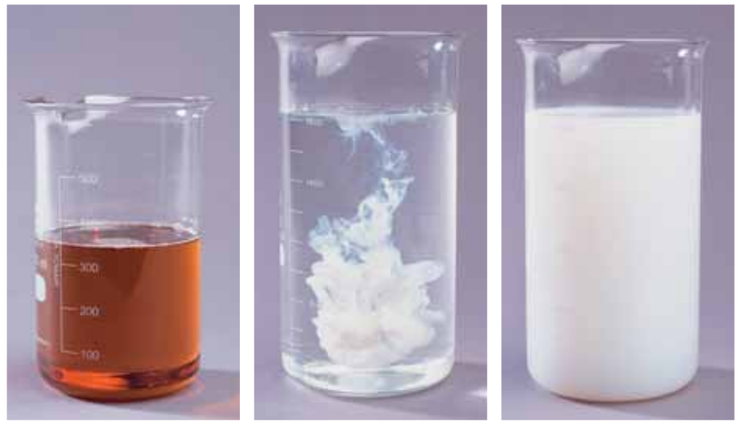
The choice of formulation is determined by the type of use, the crop to be treated, the cultural methods most commonly used in the region, and any specific requirements on the part of the user. But the wide range of formulation types that have been developed also follows from variation in the physico-chemical properties of the active substances themselves. Among these, melting point, solubility and chemical stability are important factors. Another determinant is whether the active substance shows systemic redistribution, or only contact activity. A particularly important aspect of the formulation is that it should aim to optimize factors such as retention, penetration, rain-fastness and spreadability, so that the active substance can express its full biological activity.

The development of a formulation also involves testing further important criteria such as crop compatibility, environmental behaviour, and toxicity. Moreover, it is important that the product, once sold, remains stable in storage under various conditions, retaining its activity for at least two years.

Being able to meet these challenges relies on the availability of a selection of different formulation types: EC, EW, SL, SC, WG, and more recently, CS, SE and OD. Special products, such as slug pellets and several other application types, are also available – for example for use in gardens.

Solution, Emulsion, Suspension or Granule

One of the most important considerations for the user in the field is that the crop protection product should remain in a stable mixture with water in the spray tank. This presents formulation technologists with a real challenge, because there are very few products that are fully soluble in water. For this reason, many formulations are prepared in the form of concentrated emulsions or suspensions in readiness for use. Other formulations are sold as organic solvents or granules that form an emulsion or suspension only after being diluted with water in the spray tank. Emulsions contain the active substance dissolved in finely-distributed oil droplets, whereas suspensions contain the active substance in the form of finely-distributed solid particles.



Diluting an emulsifiable concentrate (EC) in water produces an emulsion.

Emulsifiable concentrates (EC)

ECs have long been, and remain one of the most important formulation types for applying crop protection agents to cereals. The farmer buys a liquid product, in which the components of the formulation comprise a homogeneous solution. An emulsion is formed only after dilution with water. This might, for example, be a micro-emulsion with droplet sizes of between 0.01 and 0.1 µm. Apart from a slight bluish shimmer resulting from light dispersion (the so-called Tyndall-Effect), the micro-emulsion appears to the user as a clear solution, because the individual droplets cannot be seen with the naked eye. However, most EC-formulations comprise a macro-emulsion with a droplet size of between 0.1 and 10 µm when diluted with water. Because the larger droplets reflect light, macro-emulsions appear as typical milky-white spray mixtures.

The importance of the solvent

The development of an EC-formulation starts with the search for a suitable solvent or mixture of solvents that meets the following criteria: it must be toxicologically and ecotoxicologically safe, and should have low flammability. According to the demands the formulation and the active substance have to meet, further substances may be introduced, for example to optimize the spreadability of the spray mixture or to promote the penetration of the active substance into the plant. Finally, the appropriate emulsifier system must be selected, so that the emulsion remains sufficiently stable for spray application following dilution with water.

The challenge of stability

Once prepared by the user, an emulsion must remain stable for at least 24 hours without forming significant amounts of deposits in the form of oil, cream, or sediment. It is also vital to avoid crystallization of the active substance in the spray mixture, because this could lead to blockage of the spray nozzles or the pump filter during application.

What used to be considered an acceptable degree of crystallization is no longer thinkable for a modern EC-formulation. On the one hand, the demands made by the user have sharply increased; on the other

* The preparation called the „formulation" is identical to the product as sold.

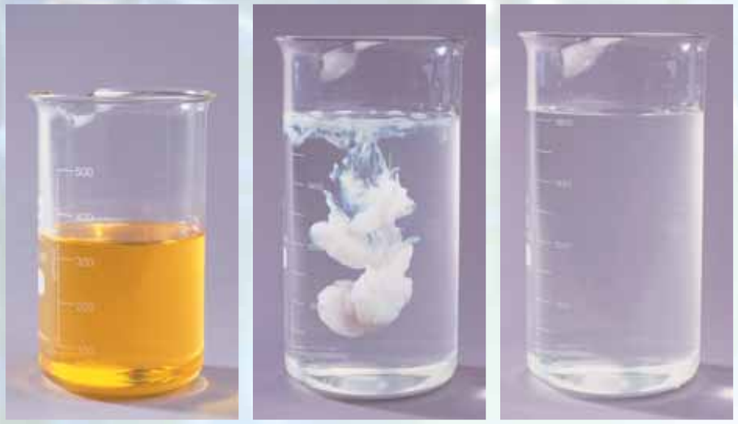
hand, modern application equipment and application methods require emulsions of the highest quality in order to allow the crop protection agent to be distributed evenly across the treated field. A further consideration is that the quality criteria for the registration of new products have become significantly more stringent.

Careful with mixtures!

All formulation types have to be tested for their miscibility with other crop protection products, fertilisers and additives, because they must retain their biological activity and crop compatibility in mixtures with these products. Each individual formulation is a finely-tuned „system“ in itself. Mixing formulations in the spray tank inevitably leads to various degrees of unfavourable interaction between the inert ingredients present in the different formulations. At worst, gel-formation, coagulation or sedimentation can make the spray mixture totally unusable. This places the onus on users to restrict themselves to mixtures that have been fully tested and validated.

Soluble liquids (SL)

The water-soluble, liquid concentrates (Soluble Liquids), like the EC and EW, contain the active substance in dissolved form. However, SLs differ from ECs and EWs in that every component of the formulation is dissolved in the water-based spray mixture – which is why the latter is always a clear solution. This means that SL-formulations can only be developed for active substances that are sufficiently water-soluble. A minimum spray mixture volume is usually recommended for SL-formulations. Nevertheless, localized concentration of the product can lead to some degree of crystallization if the spray mixture is not properly stirred.



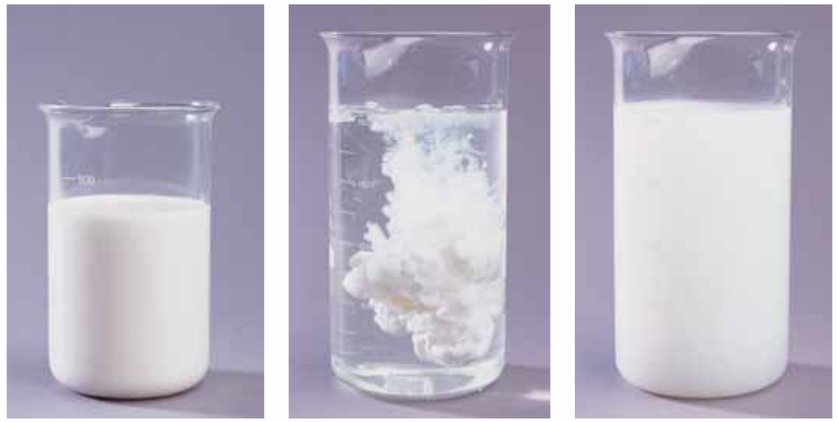
Dissolving a soluble concentrate (SL) in water results in a clear solution.

Emulsions in Water (EW)

EW-formulations are emulsions in water. The emulsion can comprise a liquid active substance, or otherwise one that has been dissolved in solvents. This means that considerably less solvent is applied to the crop compared with EC-formulations. With an EW, the emulsion has already been established in the sold product, and is only diluted in the spray mixture. EW-formulations have the advantage that they show little tendency to form crystals in the spray mixture. EWs can also be in the form of either micro- and macro-emulsions. However, EW-formulations are uncommon, because few active substances are liquids or possess the suitable solubility properties.

Suspension concentrates (SC)

In SC-formulations, the active substance is present as a solid that is finely-distributed in particles of between 1 and 4 µm in size. The particles are held in suspension in the water-based medium through the addition of so-called dispersing agents; this effect involves mutual repellency between the particles; and in combination with other substances that form net-like structures, the dispersing agents also prevent sediments from forming. One disadvantage though is that the product's high viscosity generally makes it more difficult to empty the packaging completely. The fact that the active substance is present in crystalline form also means that its biological availability is lower than with EC, EW and SL formulations. This is why SCs are most suitable when a high degree of contact exposure of the host organism is the main aim.



Mixing a suspension concentrate (SC) with water produces a suspension. The active substance is present as finely-distributed particles.

Water dispersible granules (WG)

For insoluble active substances, wettable powders (WP) used to be the preferred formulation type; however, these tend to form dust and are difficult to dose out. Nowadays, these problems are solved by choosing water dispersible granules. These are dust-free in practice, and allow the inclusion of large amounts of active substance in the product, so WGs are particularly useful for active substances that need to be applied at high rates. In this way, even if production costs are relatively high, the cost per hectare can usually be kept down. WGs generally show good crop compatibility, so they are often used for more sensitive crops, such as grapevine.

Capsule suspensions (CS)

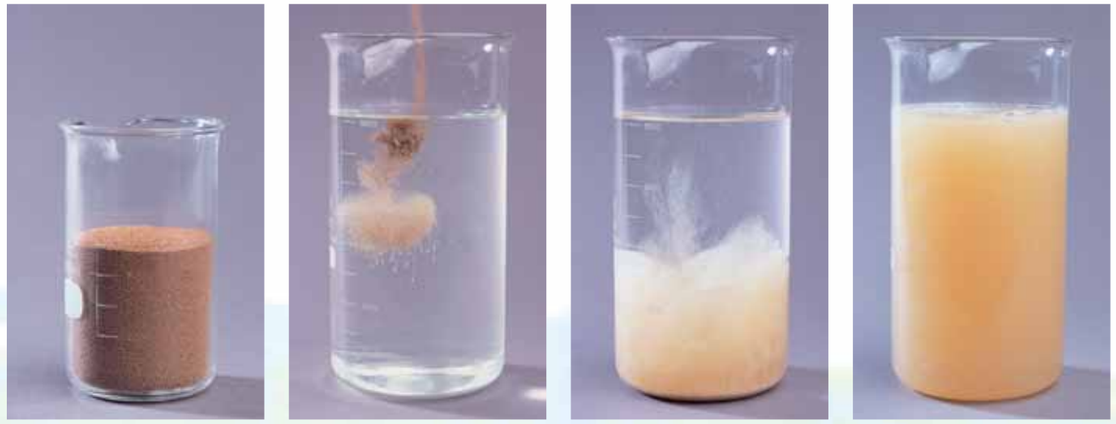
Capsule Suspensions are the best choice if an active substance shows problems with stability, or needs to be released in the environment in a controlled manner. The active substance can be present within the capsule either dissolved or dispersed in the liquid phase. The internal phase of the capsule is usually a solvent. The capsule is present in the product and later, in the spray mixture, in suspension. A CS is made from an emulsion that already contains the active substance; the other component is the capsule wall, the characteristics of which determine the release kinetics of the CS formulation.

Suspoemulsions (SE)

A suspoemulsion is a combination of the SC and EW formulation types. The continuous phase comprises water, in which both solid particles and emulsion droplets are finely distributed. This formulation type is especially suitable wherever two active substances with starkly contrasting solubility profiles or melting points need to be mixed. The emulsion phase can also contain additives that promote the systemic activity of the active substance.

Oil dispersions (OD)

Many (new) systemic active substances cannot be formulated as ECs because of their particular properties. Because the optimal activity of these active substances depends on their entering the plant, alternatives are needed in which the active substance is present in solid form. The Formulation Technology Unit at Bayer CropScience has developed various concepts involving oil dispersions (OD) in order to achieve the required levels of biological activity and crop compatibility. In an OD, a solid active substance is suspended in an oil. The oil also serves as a carrier for additives and/or a safener. Diluting the OD in water can produce various spray mixtures: if the active substance is itself water-soluble (as in many herbicides), then an emulsion results; if the active substance shows low water solubility (as in many insecticides), a suspoemulsion results.



Stirring water-dispersable granules (WG) into water makes them spread spontaneously.

Mixing an oil dispersion (OD) with water results in a suspoemulsion.

Outlook

In the context of the steadily increasing demands of modern crop protection, new, optimized variations on existing formulation types – and of course new concepts – will always be required. This is the task assumed by the Formulation Technology Unit at Bayer CropScience. Formulation technology is an interdisciplinary scientific undertaking, with special relationships to the disciplines of colloid chemistry and interfacial physics, in which technical chemistry plays an essential role.

In one of the next issues of Courier, you will be able to read about how efficient modern spray applications can be, and how formulation technology can improve the distribution of the active substances on, and within, the plant. ■