Journal of Crop and Weed, 14(2): 130-136 (2018)

Conventional and futuristic smart herbicide formulations for environment friendly weed management : A review

D. K. HAZRA

ICAR-AINP on Pesticide Residues, Directorate of Research
Bidhan Chandra Krishi Viswadyalaya, Kalyani-741235, Nadia, West Bengal

Received: 05-01-2017; Revised: 18-04-2018; Accepted: 07-05-2018

ABSTRACT

Annual worldwide crop losses due to weeds are estimated to comprise approximately 10-15per cent of attainable production among principal food sources. Worldwide consumption of herbicides represents 47.5per cent of the 2 million tons of pesticide consumed each year. Heavy use of herbicides has given rise to serious environmental and public health problems. It is therefore imperative to develop new herbicide formulations that are highly effective, safe to the users and non targets and economic. In this sense, smart herbicide formulations have become necessary in recent years, since they often increase herbicide efficacy at reduced doses. The review article will encompass the detail components of various types of herbicide formulations with an emphasis on possible new innovations in formulation technologies.

***Keywords*:** Adjuvant, contamination, delivery system, formulations, herbicide, micro-encapsulation, weed control

Weeds reduce the yield and quality of valuable commercial crops, ornamentals and forestry (Bahadur *et al*., 2015). Weeds also damage crops and other landscapes in a secondary way, serving as hosts for a variety of insects, mites, nematodes and disease causing agents. In industrial settings, weeds interfere with the safety and management of utilities, highways, railways, runways and waterways. Typically, pure herbicide molecules are of limited value to the end user (Anon., 2010). To control weeds effectively, select control methods carefully and use them properly. Chemicals, tillage, crop competition, cropping rotation, mowing and fire are alternative weed control methods that may be used alone or in combination with two or more tactics. Available time, labour, equipment and other costs as well as types of weeds and areas infested need to be considered while planning a weed control program. The use of herbicides as pre- and post-emergence treatment can control weeds, before and after their emergence from the soil so that crop can germinate and grow in a weed free environment or with minimum competition during their tender and seedling stage (Parker, 2005; Roy *et al*., 2015). Choice of an herbicide depends on the crop being grown, expected weed infestation, soil type, desired duration of control, crop use, crop sequence and cost.

To give them practical value and usable, most herbicides are combined with appropriate solvents or surfactants to form a product called a *formulation*. Herbicides are available as formulations and rarely as the pure chemical. In addition, a given chemical may be formulated in a variety of differing formulations and sold under different trade names (Mathur, 1999). The primary reason for formulating herbicide is to allow the user to dispense it in a convenient carrier, such as water. The primary purpose of the carrier is to enable the uniform distribution of a relatively small amount of herbicide over a comparatively large area. In addition to providing the consumer with a form of herbicide that is easy to handle, formulating an herbicide can enhance the efficacy of the herbicide, improve the shelf-life of the herbicide and protect it from adverse environmental conditions in storage or transit (Dobrat *et al*., 1995).

Herbicide formulations must have the following desirable features (Mulqueen, 2003; Geisler *et al*., 2004): (i) to obtain a high biological effectiveness throughout the time required to control harmful weeds; (ii) to enable the management and application of herbicides; (iii) to reduce the use of solvents and or select solvents that are dangerous or toxic; (iv) to minimize or avoid the adverse environmental effects on organisms that are not the cause for herbicide application (fish, crops, *etc*.) (v) to ensure safer use of herbicides by workers and users; (vi) to extend the range of herbicide application, and (vii) to be physically and chemically stable through time and at the same time compatible with other formulations that could be present in mixing systems of the application equipment.

A single herbicide is often sold in several types of formulations. Abbreviations are frequently used to describe the formulation. Common abbreviations and their interpretations are listed in the table1. The amount of weedicide and the kind of formulation are listed on the product label. For example, an 80 per cent SP contains 80 per cent by weight of herbicide and is a 'soluble powder'. If it is in a 10kg bag, it contains 8 kg of *a.i.* and 2 kg of inert ingredient. Liquid formulations indicate the amount of *a.i.* in ml per litre. For example, 40% EC means 400 ml of the *a.i.* per litre in an emulsifiable concentrate formulation.

Email: dipakipft@gmail.com

Table 1: Abbreviations and interpretation of different formulations

Abbreviation	Interpretation	Abbreviation	Interpretation
CS	Capsule suspension	SC	Suspension concentrate
EC	Emulsifiable concentrate	WG	Water dispersible granule
EW	Emulsion in water	SP	Soluble powder
SE	Suspo-emulsion	TB	Tablet
SG	Water soluble granule	GR	Granule
SL	Soluble liquid	ZC	A mixed formulation of CS & SC
WP	Wettable powder	ZW	A mixed formulation of CS & EW

Types of herbicides formulations

Herbicides in developing countries of Asia and Pacific region are mainly available as dust, wettable powder, emulsifiable concentrate, solution *etc*. (Seaman, 1990). These types of formulations are now known as 'conventional' or 'old technology' or 'classical' or 'traditional' because of their increased dose or repeated applications to get desired bio-efficacy (Rüegg *et al*., 2007). More than 70 per cent herbicides flow into the environment and residue in plant products in process of application through old formulations. Inefficient use of herbicides causes a series of food safety and environmental problems (Gupta, 2004). With the increasing awareness of toxic effects of conventional formulations, there is a significant trend towards switching over from such old herbicide formulations using petroleum and organic solvent based constituents to user and environment friendly smart and innovative herbicide formulations (Green *et al*., 2007).

Drawbacks of conventional herbicide formulations

Wettable Powders (WP) **[Example: Atrazine 50% WP]**

Wettable Powder formulations are applied as suspensions after dispersion in water. They consist of one or more herbicides which are blended and mixed with inert diluents and surfactants (Tadros, 1995). The herbicide can be either a liquid or solid. Wetting agents are used to facilitate the wetting of the particles in water. A dispersing agent is added to prevent any flocculation of the suspension before it is applied. Some disadvantages are that they require constant and thorough agitation in the spray tank, are abrasive to pumps and nozzles, may produce visible residues on plant and soil surfaces and can create an inhalation hazard to the applicator while handling (pouring and mixing) the powder (Das *et al*., 2014).

Emulsifiable Concentrates (EC) **[Example: Alachlor 50% EC]**

Emulsifiable concentrate formulations are a blend of herbicide, organic solvent and surfactants. When the solution is diluted into water, a spontaneous milky emulsion forms with dispersed phase droplets in the size range of 1 to 10 ìm (Fig. 1). When sprayed, this dilute emulsion gives a uniform and accurate application of herbicide on the crop, which is essential for effective weed control (Macbean, 2012). However, they may have potentially greater phytotoxicity than any other formulations; are more easily absorbed through skin of humans or animals; and contain solvents that may cause deterioration of rubber or plastic hoses and parts of pump.

Soluble Liquids (SL) **[Example: Glyphosate 41% SL]**

A soluble concentrate is a clear solution to be applied as a solution after dilution in water. Soluble concentrates are based on either water or a solvent which is completely miscible in water (Fig. 2). Solution concentrates are the simplest among the formulation types and merely require agitation into water in the spray tank. However, the number of pesticides which can be formulated in this way is limited by two factors, the solubility and hydrolytic stability of the herbicide in water (Mollet *et al*., 2001). This can sometimes lead to flocculation of other tank-mix partners such as SCs or ECs. Because SLs can contain the salt form of an herbicide, the overall salt concentration in the spray tank can be higher than for other formulations.

Trends towards smart and safer herbicide formulation technologies

However, there has been a dramatic shift from WP formulations to WG (water dispersible granule), from EC to EW (Emulsion in water). SCs have also increased in popularity due to their environmental advantages, being water based and their ease of application due to spontaneous dispersion in water during dilution (Malqueen, 2003). The new formulations (Table 2) in recent years has gained considerable attention to achieve a number of objectives namely broader formulation inerts, solvent reduction, safer solvent selection, safer surfactant components with low toxicity, low skin irritation, enhanced biodegradability, long term physical and chemical stability, enhancement of bio-efficacy by

Fig. 1: Mixing of emulsifiable concentrate in water produces milky emulsion blooms

Fig. 2: Mixing of soluble liquid in water results a clear solution (Photo Courtesy: Bayer Crop Science)

Fig. 3: Mixing of suspension concentrate in water results a stable suspension (Photo Courtesy: Bayer Crop Science)

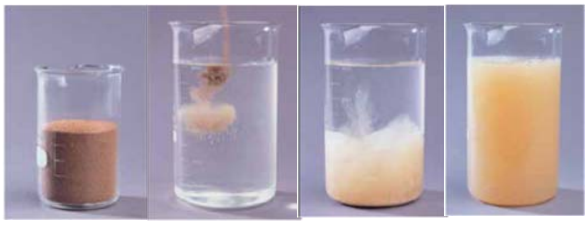

Fig. 4: Mixing of water dispersible granules in water makes spontaneous dispersion (Photo Courtesy: Bayer Crop Science)

incorporation of adjuvants, controlled and sustained release and compatibility of various formulations in tank mixes (Hewin International, 2000). These challenges require good knowledge of colloid and surface science as well as the key factors involved in formulating complex systems (Knowles, 2005).

***Suspensions Concentrates (SC)* [Example: Penoxulam 21.7 %SC]**

A liquid flowable or suspension concentrate formulation contains tiny particles of herbicide suspended in a liquid (usually water) and milled to reduce the average particle size (Fig. 3). Herbicides that are more dense than water require suspension agents to be added to prevent the solids from settling in the packaged product (Gasic *et al*., 2012). Among other inert components, wetting agents are usually needed to keep the solid surfaces wetted in water because most herbicides tend to be hydrophobic. Flowables typically have a higher viscosity than water alone, because of the presence of thickeners or suspension aids. Developing a flowable is a balancing act between the need to keep the viscosity high enough that particles do not sink rapidly, but low enough that the material pours out or pumps easily. Water-based suspension concentrate formulations offer many advantages such as: high concentration of insoluble herbicides, ease of handling and application, safety to the operator and environment, relatively low cost and enable water soluble adjuvants to be built-in for enhanced biological activity (Tadros, 2005).

***Water Dispersible Granules (WDG/WG)* [Example: Sulphosulfuron 75% WG]**

Water dispersible granules, also known as dry flowables, are like wettable powders instead of being dust like; they are formulated as small, easily measured granules (Knowles, 2008). Water-dispersible granules must be mixed with water to be applied. Once in water, the granules break apart into fine particles similar to wettable powders (Fig. 4). The formulation requires constant agitation to keep them suspended in water. The percentage of herbicide can be high, sometimes as much as 90 per cent by weight. They are becoming more popular because of their convenience in packaging and use, being non-dusty, free flowing granules which should disperse quickly when added to water in the spray tank.

***Emulsions in Water (EW)* [Example: Butachlor 50%EW]**

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,

Table 2: A comparison of handling, application and performance characteristics of different herbicide formulations

Formulations	Mixing or loading hazards	Phytotoxicity	Effect on application equipment	Agitation required	Method of application	Compatible with other formulations
Granules (GR)	Safe	Safe	-	No	Soil	-
Wetteble powders	Dustinhalation	Safe	Abrasive	Yes	Foliarand soil	Highly
Dry flowables / water dispersible powders (WDG / WDP)	Safe	Safe	Abrasive	Yes	Foliar and soil	Good
Soluble powders (SP)	Dust inhalation	Usually safe	Non-abrasive	No	Foliar and soil	Fair
Emulsifiable concentrates (EC)	Spills and plashes	Possible	May affectson rubber parts	Yes	Foliar and soil	Fair
Suspension concentrates (SC)	Spills and plashes	Possible	May affectson rubber parts	Yes	Foliar and soil	Fair
Solutions (SL)	Spills and plashes	Safe	May affects on rubber parts	Yes	Foliar and soil	Fair

the emulsion has already been established in the sold product, and is only diluted in the spray mixture (Gasic *et al*., 2006). Because they are water based, oil-in-water emulsions can have significant advantages over emulsifiable concentrates in terms of cost and safety in manufacture, transportation and use (Zhang , 2004). EWs can also be in the form of either micro or macro-emulsions. However, EW-formulations are uncommon, because few active substances are liquids or possess the suitable solubility properties.

***Microencapsulations (CS)* [Example: Pendimethalin 38.7%CS]**

Microencapsulated herbicides are mixed with water and sprayed in the same manner as other sprayable formulations. After spraying, the capsule wall breaks down and slowly releases the herbicide (Beestman, 2003). Microencapsulated materials have several advantages like highly toxic materials are safer for applicators to mix and apply, delayed or slow release of the herbicide prolongs its effectiveness, allowing for fewer and less precisely timed applications and herbicide volatilizes more slowly; less is lost from the application site (Fernandez, 2007).

Ways of making microcapsules

- physical methods
- phase separation
- interfacial polymerization
- entrapment

Herbicide release mechanisms

- Enzymatic digestion
- Diffusion
- Membrane dissolution
- Mechanical fracturing
- Temperature change

Parameters affecting rate of release

- Polymer type
- Degree of cross-linking
- Capsule wall thickness
- Capsule size (surface area to volume ratio)
- Physical state of the *a.i.*

Possible new innovations in herbicide formulation technology

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) herbicides cannot be formulated as ECs because of their particular properties. Because the optimal activity of these herbicides depends on their entering the weed, alternatives are needed in which the active substance is present in solid form. In an OD, a solid active substance is suspended in 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, then an emulsion results; if the active substance shows low water solubility, a suspoemulsion results.

Spreading Oil (SO)

The surface spreading formulations are oil based formulations which can be applied by dropping on water surface and after application the formulation spreads to the whole water surface within a few seconds. Basically these formulations are stable dispersion of water insoluble liquid or solid in oil. When these formulations are applied on the water surface the herbicide maintains a smooth networking film on the water surface.

Microemulsions (ME)

Microemulsions are thermodynamically stable water-based systems containing water-insoluble herbicides. In addition, microemulsions are composed of extremely tiny particles (similar to micelles) that can be as small as 0.01 micron (Hiromoto, 2007). This makes the diluted product transparent because light scattering is reduced. It is commonly believed that microemulsions can provide superior efficacy relative to macroemulsion formulas having the same level of activities. It is believed that the small size of the emulsion droplets may allow for better transport of the herbicide through cell membranes thereby resulting in enhanced efficacy (Zabkiewicz, 2001). Microemulsions are considered to be infinitely stable, thereby providing improved stability over traditional macroemulsion systems.

Nanoemulsions

Nanoemulsions have a particle size of less than 200 nm, which makes the systems inherently transparent/ translucent and kinetically stable (Nair *et al*., 2010). Herbicides formulated with nanoemulsions having a lower surfactant concentration than microemulsions and surfactants are considerably more environmentally friendly and are cost effective and economical (Izquierdo *et al*., 2005). Low-energy emulsification methods are applied to produce nanoemulsions (Sadurni *et al*., 2005). The energy stored could promote smaller-sized nanoparticles of longer life.

Tablets (TB)

Tablet formulations are similar to water-dispersible granules. They are small, easily handled, easily measured dosage form that must be mixed with water to be applied. Once in water, the tablets break apart into fine particles similar to wettable powders. The percentage of herbicide in the product can be high, sometimes as much as 95 percent by weight. The formulations are produced by compaction in a tablet press machine. Tablets share many of the same advantages of water-dispersible granules. Effervescent Tablets (WT) invention relates to an effervescent tablet utilizing the acid-alkali neutralizing reaction to produce self-dispersion of herbicides. The effervescent tablet has high stability, convenient operation, high dissolution speed and safe and non-dusty. Floating Tablets (FT) are slow release tablets which after application in water bodies floats on the surface of water due to low specific gravity and specific inert ingredients. The floating tablets offer a simple and practical approach to achieve increased surface residence time for the dosage form and sustained herbicide's release. Preparing the herbicides in a floating dosage form can control the extent of bioavailability for such poorly water-soluble herbicides. These types of formulations act target specific with lower doses of the herbicide compared to general formulations which mix throughout the whole water body and require high doses. This particular technology can be utilized for the development of controlled release product as a safe alternative to conventional product for the control of aquatic weed like water hyacinth, algae etc in wet land like transplanted rice field.

Quality Control

Herbicides are by their very nature toxic substances; hence, a great deal of concern has centered on safety (Sopeña *et al*., 2008a). The laws dealing with herbicide safety are very strict and will become even stricter in the future. Besides legal restrictions, herbicides are also subject to stringent quality control standards like any other manufactured product. Most large herbicide manufacturers have highly developed quality control laboratories that test each herbicide for potency, emulsification, density, color, pH, particle size and suspension. If the company makes more than one herbicide, the product's identity must also be verified. An herbicide must be stable, easy to apply, and easy to store. Shelf-life must extend past two years. In accelerated tests, the herbicide is subjected to high temperatures for a short period, and then checked for effectiveness. Labels must be easy to read and meet all regulations. The manufacturer keeps files for each raw material, herbicide, formulation, and packaged item, and samples are stored for three years.

Formulations and mixing

Two or more herbicides are often *mixed* together for a single application. Only those materials that are compatible should be mixed together. Incompatibilities are often indicated on the product label. Proper mixing begins with filling the spray tank with at least half the water you intend to use. The materials are then added in the following order:

1. Adjuvants for antifoaming, buffers, compatibility
2. Wettable powders, water dispersible granules, or dry flowables (WP, WDG, DF)
3. Water soluble (S, SP)
4. Liquid flowables (SC)
5. Emulsifiable concentrates (EC)
6. Other adjuvants
7. Drift control agents

The remaining water is added to the spray tank once materials are added.

Spray Adjuvants

Adjuvants are non-herbicide materials added to spray mixes to improve the performance of the herbicide application. These additives are commonly categorized as *utility* or *activator* adjuvants (Azbkiewicz, 2000). Activators can be thought of as products that improve herbicide performance after the spray has contacted the leaf surface. Utility adjuvants improve your ability to get the herbicide to the leaf surface. Activator adjuvant products perform several functions - they serve as wetting agents (or spreaders), stickers, humectants and penetrants. A wetting agent reduces the surface tension of water, so that a droplet beads less, lays flatter on the leaf surface, and covers more leaf surface area. A sticking agent helps the herbicide ingredients, particularly dry ingredients that were suspended in water, stay on the leaf surface after the water has evaporated. The sticking agent remains as a thin film holding the herbicide in place so that it can be absorbed, and prevent wash-off. A humectant retains moisture, or absorbs water vapor from the air to prevent reduce net evaporation. Keeping the deposited herbicide surrounded by moisture as long as possible prevents the herbicide from crystallizing on the leaf surface and increases absorption of the herbicide into the leaf. An oil-soluble penetrating agent increases the movement of the herbicide into and eventually through the cuticle so that the herbicide can absorbed into the outer layer of cells. Drift inhibitors or thickeners are used to control drift. These may be powders, granules, or liquids that cause the spray solution to be more cohesive; less subject to wind shear as it leaves the nozzles so as to reduce the amount of very small spray droplets.

Antifoaming agents

Air gap filling or mechanical agitation in partially full tanks can cause excessive foaming. Antifoaming agents cut down on frothing so that the tank can be filled more easily. These are usually silicone containing products that are used in relatively small amounts to breakdown the foam.

Calculations in herbicide application

Uniform application of herbicides at proper rates is essential for effective weed control. A slight variation in the rate of application with some herbicides may result in poor control of the weeds or injury to the crops or the environment, causing a loss of time, effort, and money. So, correct calculation of herbicide doses is very important prior application.

$$\text{Quantity of commercial produce required (kg ha}^{-1}\text{)} = \frac{\text{Rate of herbicide application (}a.i.\text{ kg ha}^{-1}\text{)} \times 100}{\%\text{ herbicide } a.i.}$$

Example

Rate of atrazine (herbicide) application ha^{-1} = 1.25 kg

Herbicide in commercial product = 50% WP

Quantity of commercial product of atrazine to be required ha^{-1}

$$= \frac{1.25 \times 100}{50} \text{ kg}$$

$$= 2.50 \text{ kg}$$

Conclusion

The development of new herbicide formulations and new fields of application for the herbicides already in existence may be comparable to the development of new herbicides. The cost and time required for the development of new formulations may be even less than that required for the development of new herbicides. Current resources are directed toward the development of safer herbicides, for the worker and for the environment, as well as toward more efficient application and formulation technologies. In the context of the steadily increasing demands of modern weed management, new, optimized variations on existing formulation types – and of course new concepts–will always be required. 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.

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