7^{th} INTERNATIONAL CONFERENCE ON ADJUVANTS FOR AGROCHEMICALS

Cape Town, 8-12 November 2004

PREFACE

Cape Town was the venue for the seventh in the series of International Symposia on Adjuvants for Agrochemicals. The programme provided a forum for 165 delegates from the agrochemical and speciality chemical industries, and researchers to discuss new chemistry and advances in adjuvant application and science since the last conference in Amsterdam in 2001. As the series of symposia has progressed, the focus has broadened considerably to encompass a wide variety of adjuvant functions, useful not only for herbicides, but also insecticides, fungicides, PGRs and foliar fertilizers, and to address a wider range of practical issues.

The symposium succeeded in covering a wide range of topics and emphasised the multi-disciplinary nature of adjuvant R&D. Having a broad understanding of the individual sciences involved is vital to both devising appropriate evaluations, and the correct interpretation of results. The leading organisation represented at the conference in having this breadth of approach was clearly the Forest Research Institute, New Zealand (www.forestresearch.co.nz).

Papers on new formulations or adjuvants were sometimes lacking in robust biological data where the results of field trials were presented. These were often insufficiently replicated, with treatment lists lacking the minimum range of comparisons from which to draw firm conclusions. Similarly, papers focusing on explaining biological performance sometimes missed the important practical considerations of the influence of spray application conditions *eg* ultimately affecting droplet size, or shear effects.

Topics rather under-represented were issues of commercial and practical importance to built-in adjuvant systems. In these, cost-effective, safe and environmentally sound performance is acutely important, alongside the drive for high concentration products and robustness throughout the supply chain to target crops and pests.

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SUMMARY

Markets

Speakers reviewed the global adjuvant market (>$1 billion, growing at 3% *pa*), local markets and their regulatory requirements, issues and drivers for change. The USA dominates with 35% world market share. Markets for surfactants, oils, buffers, anti-foams, stickers, fertilizer blends, compatibility aids, drift control agents, *etc* were discussed. GM crops and more generic herbicides are presenting good opportunities for adjuvant manufacturers.

Regulatory Affairs

Regulatory requirements and timelines differ greatly between countries. From the USA there was optimism that the 2004 Pesticide Registration Improvement Act will stimulate the approval process for new 'inerts'. In Europe, data package needs vary considerably between countries. Approval times vary from 4 – 30 months.

New Adjuvants & Formulants

Several new surfactants with good safety and environmental profiles were presented as possible replacements for alkylphenol ethoxylates (APE). These included Cesalpinia Chemicals' new class of anionic alkylpolyglucoside esters and ethoxylated cardanol (Unitop Chemicals). Degussa Goldschmidt presented results on organosilicones for use as emulsifiers in EC's and a polyether replacement for APE dispersants in SC's. Non-aqueous formulations have been researched by several companies. Huntsman has been studying oil dispersions as liquid alternatives to WG's for hydrolytically unstable actives such as sulfonylureas. Helena has been using surfactants to solubilise free acid forms of phenoxy and benzoic acid herbicides. Lipophilic glyphosate salts were prepared and formulated in oil for application through CDA units by the Victorian Chemical Company. BayerCropScience has been developing improved formulations of phenmedipham based herbicides. When mixed with cold, hard water EC's were liable to crystallisation problems, blocking filters and nozzles. New improved technology has been developed, based on phosphoric-acid-ester solvents, castor-oil emulsifiers and alkyl-arylpolyglycolether–phosphate up-take enhancers. Akzo Nobel introduced ethyl hydroxyethyl cellulose polymers which have similar visco-elastic properties to polyacrylamides.

Biological Performance

Amongst herbicides, glyphosate and sulfonylureas featured strongly. Glyphosate topics included the control of spray drift and the development of 'hybrid' adjuvants suitable for enhancing the activity of both glyphosate and lipophilic mixture partners. Problems of mineral ions in water to glyphosate and iodosulfuron were discussed and solutions evaluated. Not all ions are antagonistic, as magnesium can enhance the activity of foramsulfuron in the presence of appropriate HLB surfactants. Rainfastness of iodosulfuron and mesosulfuron mixtures was investigated and effective adjuvants described.

The organosilicone surfactant Zipper was reported to increase the efficacy of abamectin and cyromazine on populations of *Liriomyza trifolii* showing reduced sensitivity, and significantly extend pymetrozine residual control of *Aphis frangulae* on potatoes. When the combination was applied in higher spray volumes, spray liquid flowed down petioles and stems to the soil increasing the potential for root uptake, which is particularly effective. Spinosad efficacy on *Thrips palmi* could be increased by the addition of Dyne-Amic.

A styrene-acrylate based sticker maintained levels of disease control on potatoes by mancozeb following rain, in Dutch trials. Results from the Czech Republic suggested that Silwet L-77 can improve control of Fusarium head rot in malting barley and reduce mycotoxins. Super-spreading organosilicone surfactants can be used to reduce spray volumes in New Zealand vines from 1500 L/ha to less than 200 L/ha, while substantially increasing work rates and decreasing application costs. Ghent University reported that surfactants can have a direct lethal effect on zoospores of *Phytophthora* and *Pythium* spp.

Non-pest control applications for adjuvants included reducing spray volumes and improving penetration into bunches of an emulsion used to dry sultana grapes; enhancing PGR effects on breaking apple tree dormancy; adding adjuvants to foliar nutrient sprays to improve deposition and uptake; and improving lodging control of winter wheat by CCC and prohexadione-calcium.

Spray Drift Control

A session was devoted to drift and included practical and more theoretical papers. An example from one experiment was the reduction in the volume of driftable glyphosate spray droplets from 58% to 17% by the most effective adjuvant. The overall conclusion was that the whole context in which drift control agents are used is critical: atmospheric conditions, spray equipment operation, nozzles, and target surface characteristics will all affect whether adjuvants, seemingly promising in the lab, are effective in the field.

Mode of Action & Methodologies

The Forest Research Institute in New Zealand contributed a number of papers on the effects of adjuvants on uptake and translocation, seeking to model and predict effects. Radio-label studies with active ingredients and surfactants representing a range of physico-chemical properties were combined with scanning electron microscope observations on spray deposits. Other papers reported on the movement of surfactants themselves into leaves. Two powerful visualisation techniques were presented. Confocal laser scanning microscopy is a non-destructive technique that uses a laser beam to optically section samples and visualise penetration and transport of fluorescent chemicals in living plants. Studies with various surfactants with contrasting HLBs were illustrated. Chlorophyll fluorescence during photosynthesis can be used to screen sprayed plants for effective adjuvants in an automated system with a robot-arm and laser-camera. Finally, a design for a novel single droplet applicator for use in studies on deposition and movement into targets was described.

7th INTERNATIONAL SYMPOSIUM ON ADJUVANTS FOR AGROCHEMICALS

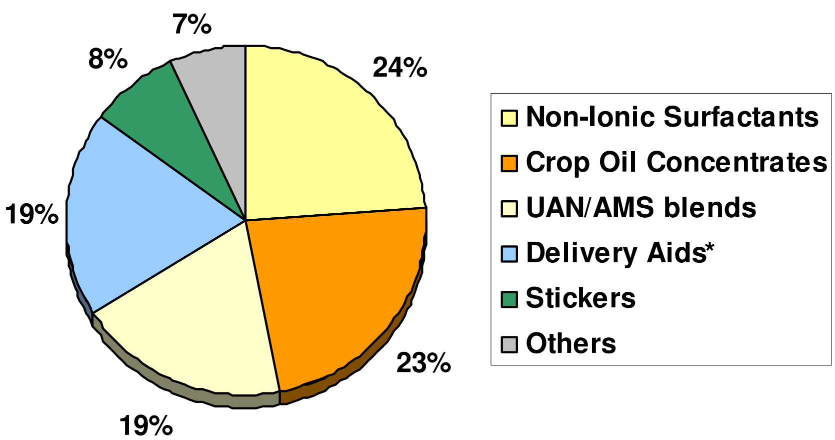
1. MARKETS

1.1 Global Market

Allen Underwood (Helena Chemical Company, USA) reviewed the global adjuvant market and drivers for change[1]. Total adjuvant market value is difficult to estimate, but is believed to be over $1 billion (end-user level), growing at 3% *pa.*, and is clearly strongly related to the overall market for agrochemicals.

Adjuvant markets in particular countries have two main determinants. Firstly, their regulatory requirements, and the duration and cost of meeting these; and secondly, the labels on prospective partner agrochemicals and where liability lies for lack of efficacy or crop injury from off-label use. Given the relative ease of introducing new adjuvants in the US Mid-West and the predominance of post-emergence herbicide use on maize and soya, the US share of the adjuvant market is disproportionately high at about 35%. Here, non-ionic surfactants and various types of crop oil concentrates (mineral or vegetable oils or esterified derivatives) each have about 25% market share, with a move to the former. Adjuvants based on UAN or ammonium sulphate, and delivery aids (including buffers, anti-foams, compatibility and drift control agents) take around 20% each. Anti-drift adjuvants have become very popular recently. Spreader-stickers have just under 10% share.

Figure 1. Estimated US market shares of adjuvant categories



* Compatability aids, buffers/acidifiers, anti-foams, drift control agents

The impact of the move to herbicide tolerant GM crops has been reduced because of the increase in glyphosate use and its response to adjuvants. Also, the rising use of generic herbicides has presented a good opportunity for adjuvant manufacturers.

1.2 South Africa

The South African agrochemical market is worth $250 million (distributor level) according to **Andre Schreuder, Villa Crop Protection (South Africa)**[2]. This comprises 39% herbicides, 34% insecticides, 24% fungicides and 6% PGRs. Major crops are maize (3 million ha), cereals (0.8 million ha), sugarcane (0.2 million ha), vines (0.12 million ha) and fruit (0.1 million ha).

Opportunities for adjuvants are believed to be under-exploited as current sales are only 2.5% of all agrochemicals compared to the global mean of 5%. A particular opportunity now exists to complement the use of glyphosate on GM corn. Recent stimulation to the market has been the increase in use of a number of sulfonylurea herbicides as post-patent expiry prices have dropped. Prospective adjuvant suppliers need to work closely with agrochemical manufacturers to secure label recommendations, and with distributors to offer technical support, ideally to exclusive rights. Market research has shown that these are especially valued, in addition to clear demonstrations of efficacy and focused market positioning. Farmers are more cost-conscious, but will trust recommendations if supported by other influencers, such as researchers and food processors.

112 adjuvant products were registered on 1 September 2004, noted **Ian Brink (Spectrum Research Services, South Africa)**[3] **and Arthur Keegan, (Volcano Agroscience (Pty) Ltd, South Africa)**[4]. In contrast to the market share profile of adjuvant types in the USA, these are dominated by acidifiers and buffers (31%). Surfactants take only 19%, as do oils. Water quality is a particularly recognised issue in South Africa. The dominant position of acidifers/buffers was greatly helped by the mid 1980's innovation of adding a pH sensitive dye to products. Besides the use of such adjuvants to optimise spray water pH for organophosphate, carbamate and pyrethroid insecticides, fertiliser blends are used to reduce the antagonism of dissolved salts to glyphosate, tralkoxydim, iodosulfuron and tribenuron, in particular.

2 REGULATORY AFFAIRS

2.1 USA

The US Pesticide Registration Improvement Act (PRIA) became law in 2004. This will provide greater resources, including a dedicated inerts department at the EPA. **Warren Stickle (Chemical Producers and Distribution Association, USA)** was optimistic that this should provide considerable impetus to the approval of new 'inerts'[5]. A tiered review process for has been introduced for inerts in which, for example, existing data or FDA approval for food uses will be considered first before asking for more hazard data; and the magnitude of the incremental exposure involved in pesticide use could be regarded as a non-significant extra risk alongside current exposure in approved uses in other industries. Current issues include pressure to disclosure of all inert ingredients by weight on pesticide labels, and assembling a list of inerts to be included in the planned endocrine disruptor screening programme.

2.2 Europe & ROW

The European regulatory arena was reviewed by **Hans de Ruiter, (SurfaPlus Netherlands)**[6]. Pending harmonisation, data requirements and timelines differ greatly between countries. Factors such as whether the adjuvant is built-in to the formulation or a tank-mix and whether the latter are included as label recommendations can be important. In some countries, *eg* France, comprehensive field testing is required, but in others, *eg* Germany, proof of biological efficacy is not needed. In some countries, *eg* Belgium, adjuvants are regarded as pesticides and appropriate data are therefore mandatory. The time taken to get a new adjuvant approved varies from 4 months in Germany, 12 months in the UK, 18 months in France, to 30 months in Spain.

A paper by **Beata Bialek (Volcano Agroscience (Pty) Ltd, South Africa)** overed similar ground and specifically outlined the registration procedure for adjuvants in South Africa[7]. Efficacy data are required and applications are generally processed within 6 months.

3. NEW ADJUVANTS & FORMULANTS

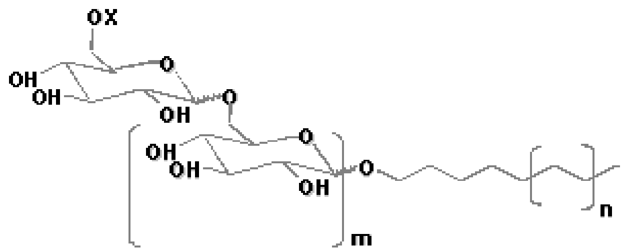
3.1 APE Alternatives

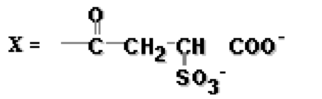
A number of new adjuvants or formulants with good safety and environmental profiles were presented as possible replacements for alkylphenol ethoxylates or tallow amine ethoxylates. These included several of natural origins and readily biodegradable.

A laurylpolyglucoside citrate sodium salt is the lead in a new class of anionic alkylpolyglucoside esters from **Cesalpinia Chemicals (Italy)** under the Eucarol AGE® brand name[8]. An aqueous solution with a 30% active content has a pH of 5.5 (2% in water at 20°C), a CMC of 0.008% with surface tension of 26.6 mN/m. It has inherent biodegradability of >90% and ready biodegradabily of 68%. It is not irritating to eyes or skin and has acute oral toxicity > 5000 mg/kg.

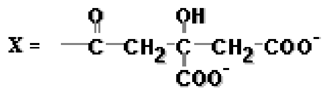
Spray solutions with added Eucarol AGE® had good physical stability when added to EC or SC formulations. Full compatibility between different active ingredients was claimed. Data from field trials were presented. Eucarol AGE® was tank-mixed with phenmedipham mixtures in sugar beet and mesotrione + atrazine in maize at reduced rates of herbicides. Comparisons were made with the same herbicide treatments using a tallow amine ethoxylate surfactant, and herbicides applied alone at full rates. Good weed control with no crop phytotoxicity was reported. However, these trials were not robust tests. Only one trial of each type, each with only two replicates, was reported. Trial design should have included at least an equivalent lower herbicide rate treatment with no added adjuvants, and three replicates. No statistical analysis was attempted.

Eucarol AGE® product range (m: glucosidation degree; n: -CH2- units in hydrophobic alkyl chain).

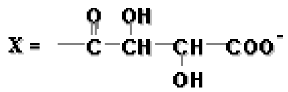




Alkylpolyglucoside Sulfosuccinate



Alkylpolyglucoside Citrate



Alkylpolyglucoside Tartrate

Wetcit® is a blend of orange oil, borax and several surfactants developed by **Oro Agri (South Africa),** originally developed under the name of Dustcon® as an environmentally friendly product for dust control in mines and on roads[9]. Preliminary studies have shown 0.05% to 0.1% addition to spray solutions to have good adjuvant effects, while at higher concentrations it exhibits miticidal, insecticidal and fungicidal properties. Toxicological, eco-tox and biodegradation data were presented with illustrations of wetting effects, but no biological data were reported.

Cardanol is an alkylphenol (3-pentadecadienyl phenol) derived from cashew nuts. Amongst various surfactants prepared by **Unitop Chemicals (India)**[10]. Cardanol ethoxylate with 13.4 mole EO had the greatest ability to reduce surface tension, but this was said to be inferior to nonylphenol ethoxylates. When cardanol ethoxylates were used in combination with calcium linear alkyl benzene sulphonate as an emulsification system for EC formulations, they compared favourably to nonylphenol ethoxylates. Biodegradation studies showed 20% cardanol 13 EO remaining after 28 days incubation compared to 77% of nonylphenol 8 EO.

Ingo Fleute-Schlachter (Degussa Goldschmidt, Germany) presented results on two lipophilic silicon-based surfactants for use as emulsifiers in EC formulations, Break-Thru S 240 and Break-Thru OE 441[11]; and a replacement for APE dispersants in SC formulations, Break-Thru DA 646[12].

Break-Thru S 240 (trisiloxane)
$(CH_3)_3SiO-[(CH_3)RSi]_x-OSi(CH_3)_3$
x = 1
R = $-C_3H_6O-EO_n-PO_m-H$
Break-Thru OE 441 (siloxane)
$(CH_3)_3SiO-[(CH_3)RSi]_x- [(CH_3)_2Si]_y-OSi(CH_3)_3$
x > 5
R = $-C_3H_6O-EO_n-PO_m-H$
y > 10

Although acceptable formulation properties were inferred no data were presented. Biological data were limited to one field trial with the herbicide + safener combination clodinafop-propargyl and cloquintocet-mexyl (Topik), in which levels of control of blackgrass (*Alopecurus myosuroides*) were too low to provide reliable data.

Break-Thru DA 646
$R-(C_2H_3R'O)_n-H_n > 5$
R = alkyl
R' = H or phenyl

Physico-chemical properties of Break-Thru DA 646 and performance with a sulphur SC fungicide showed superior effects to an alternative anionic tristyrylphenol based dispersing agent.

Performance as a dispersant was optimized by using styrene oxide in the polyether and varying the number of aromatic groups. The ratio of ethylene oxide to the hydrophobic moiety introduced by the starting alcohol and the styrene oxides gives an HLB of 11. DA 646 is not irritating to skin and eyes and shows benign aquatic toxicity i.e. LC_{50} was determined to be 15 mg/l on *Brachydanio rerio,* and EC_{50} on *Daphnia* is 73 mg/l.

Break Thru DA 646 surface tension of aqueous solutions compared to tristyrylpenol dispersant (w/w concentration, mN/m).

	0.1%		0.25%		1.0%	
	DA 646	TSP	DA 646	TSP	DA 646	TSP
Static ST	43.1	45.0	37.2	44.4	34.9	41.3
Dynamic ST	62.1	70.6	51.9	66.2	43.6	57.9

3.2 Non-Aqueous Formulations

Non-aqueous formulations (oil dispersions) ave been the subject of research by several companies for various reasons. **Huntsman (Belgium)** have been studying oil dispersions as liquid alternatives to wettable granules for hydrolytically unstable actives such as sulfonylureas, and discussed the properties necessary for effective disperants to give stable formulations[13]. The development of non-aqueous dispersants has its origins in the printing and paints industries. Products developed for these uses are mainly polymeric in nature and a theoretical basis for selection is the configuration of the stabilizing chain in the solvent medium. Some typical non-aqueous adjuvant media were characterised according to their Hildebrand solvent parameter. The Hildebrand parameter is the square root of the cohesive energy density. Put simply, this is the energy needed to remove a molecule from its nearest neighbours, divided by the total volume of the moved molecule. A set of dispersants was selected to make formulations of the fungicides copper hydroxide, mancozeb and carbendazim. These were chosen because they represent different types of disperse phase, namely inorganic metal hydroxides, metal salts and organic compounds. Dispersancy was investigated using simple rheological measurements. It was found that the suggested dispersants were not always effective in making stable non-aqueous formulations. The main stabilization mechanisms were discussed and the results explained in terms of the standard colloidal model. Simple rheological measurements proved rapid means of giving useful preliminary information. The overall conclusion was that the best strategy for oil dispersion formulation development is very similar to aqueous-based dispersion:

- First, make colloidal stable dispersion;
- Then adjust viscosity with a thickening agent to prevent sedimentation.

Helena (USA) has been using surfactants to solubilise free acid forms of phenoxy and benzoic acid herbicides[14]. These can have advantages of rainfastness, low volatility, spray mix compatibility (*eg* fertilizers) and efficacy. Activity of 2,4-D acid on *Conyza canadensis* was noted as being particularly useful with the recent advent of glyphosate resistant populations of this species in the USA. In addition, these can also give the usual surfactant benefits of improved target coverage. Examples of such surfactants include ethoxylated or propoxylated adducts of aliphatic and aromatic alcohols, acids, and esters.

Lipophilic salts of glyphosate were prepared and formulated in oil for application through CDA units by the **Victorian Chemical Company (Australia)**[15]. The preferred amines for forming lipophilic glyphosate salts were found to be tertiary dimethylamines of the structure $(CH_3)_2N\text{-}R$. Dimethyl cocoamine was a typical example. Tertiary amines which are sterically hindered such as tributylamine or didecylmethylamine could not be induced to form suitably stable complexes.

It was found that primary or secondary lipophilic amines generally resulted in glyphosate salts which were prone to crystallise out of lipophilic mixtures more easily than the corresponding salts of tertiary amines. Lab studies showed good rainfastness, but no useful field data were presented.

3.3 Polymers

James Hazen (Akzo Nobel Surface Chemistry, USA) introduced ethyl hydroxyethyl cellulose (EHEC) which has similar visco-elastic properties to polyacrylamide polymers currently used for controlling drift[16]. EHEC is produced with a wide range of characteristics modified by molecular weight and degree of substitution by ethyl and/or ethylene oxide units per anhydroglucose unit. These have been branded as the Adsee® product range. Evaluation of candidates was reported using studies on viscosity, droplet size and drift, taking into account practical factors such as shear in recirculating sprayers.

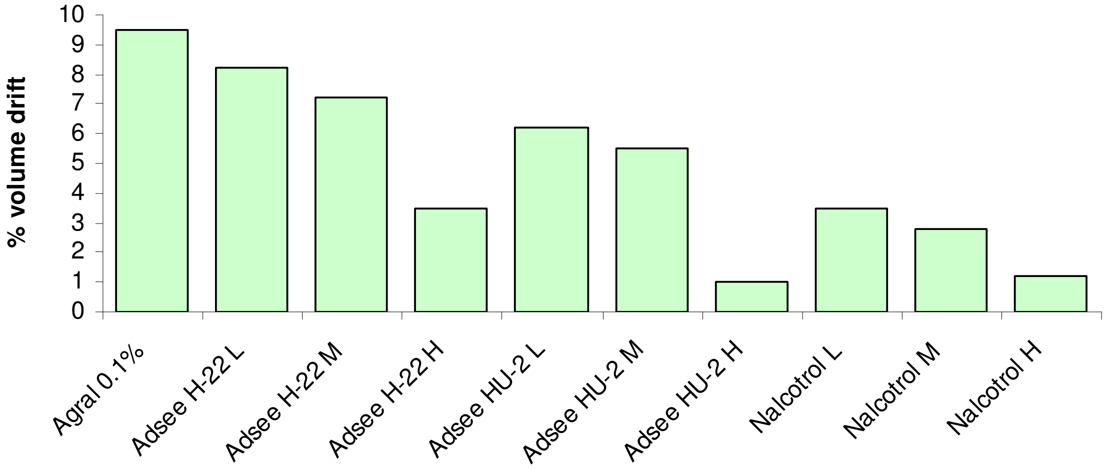
Viscosity measurements were made with various concentration solutions of Adsee® products over several shear rates and compared with Helena's anti-drift agent Nalcotrol II (polyvinyl polymer). Results indicated that some members of the range could match the performance of Nalcotrol II at half to quarter rates.

Effect of Adsee® polymers and other adjuvants on spray droplet sizes and distribution.

	Concentration (%)	VMD (µm)	% Volume < 100 µm
Agral	0.1	242	8
Adsee H-22 (low MW)	0.0625	314	6
	0.125	329	4
	0.25	357	2
Adsee HU-2 (high MW)	0.0625	348	4
	0.125	375	2
	0.25	458	1
Nalcotrol II	0.0625	363	4
	0.125	394	3
	0.25	419	2

Spray drift measurements showed that Nalcotrol II was unexpectedly more effective than suggested by droplet size and distribution data.

Effect of Adsee polymers and other adjuvants at different concentrations on spray drift (L = 0.0125%. M = 0.125%, H = 0.25%)



Finally, because it was suggested that apparently pump shear stable products can be less effective in the presence of glyphosate, studies were conducted adding adjuvants to Roundup Original and spraying through a re-cirulating sprayer. Adsee® polymers were centrifugal pump shear stable and on a par with Strike-Zone® in controlling droplet size. STA-PUT Plus®, however, was not effective in this system.

Ewald Sieverding, (Degussa Goldschmidt, Germany) presented a new tank mix adjuvant based on emulsion polymer technology[17]. A colloidal suspension of a cross-linked polymer based on partially neutralized acrylic acid and acrylamide is dispersed in oil (as described in PCT patent application WO 03/015512). Pamacea® is a water-in-oil emulsion polymer adjuvant which does not spread, but improves retention through increased viscosity of the spray solution. Static surface tension of a 0.1% w/v solution was 65.5 mN/m. The product contains about 28% co-polymers, 24% oil and 38% water. The remainder comprises emulsifiers to stabilise the product, and to invert the product to an oil-in-water preparation when added to the tank.

Water quality is a possible issue as extremes of water hardness can lead to insufficient (hard water) or excessive (soft water) swelling of polymers and resultant adverse effects on viscosity. Performance in recirculating farm sprayers was reported to be good with respect to any adverse effects of shear or line clogging. Droplet diameter was increased by upto 40-50% depending on nozzle type.

Field trials results showed promising effects on the efficacy of cereal fungicides and PGRs. Nineteen trials were conducted over three seasons. Results from only two of the 11 fungicide trials were illustrated. In these (see table below) there were significant benefits in persistence of effect, and a slow-release effect was hypothesised.

Enhancement of residual activity of Opus Top (epiconazole + fenpropimorph) on control of *Septoria tritici* in winter wheat.

	Mean infected area of leaf 2			
	22 DAT		35 DAT	
Untreated	12.1	b	65.8	a
Opus Top 0.7 L/ha	0.9	c	17.2	b
Opus Top 0.7 L/ha + Pamacea 1 L/ha	0.2	c	3.7	c

Values in columns followed by a common letter are not significantly different at p = 0.05.

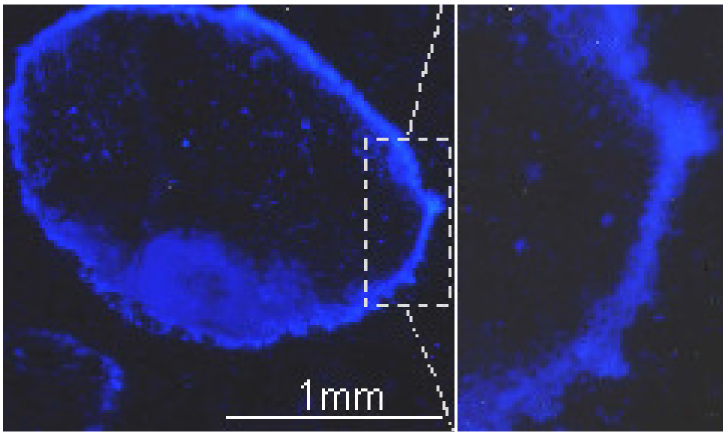
3.4 New Bayer Formulations

Two papers on new formulation technologies were presented by **BayerCropScience (Germany)**[18, 19]

Firstly, improved formulations of phenmedipham based herbicides for weed control in sugar beet have been developed. Formerly, when the EC formulations in the Betanol® product range were mixed with cold, hard water crystallised active ingredients could block filters and nozzles. To overcome these problems, a new technology was developed, based on phosphoric-acid-ester solvents, castor-oil based emulsifiers and alkyl-arylpolyglycolether–phosphates as up-take enhancers. Associated with less crystallisation from the new formulation was markedly faster absorption of active ingredients. Uptake into *Chenopodium album* one hour after treatment was less than 30% for both phenmedipham and desmedipham applied in standard formulations. When applied in the new formulation, uptakes of 50-60% where achieved by one hour.

Secondly, the effect of formulation components on the stability and foliar delivery behaviour of fungicide suspo-emulsions (SE) containing emulsified oil adjuvants was studied. Crystal growth, spray application and uptake behaviour of a series of SE formulations containing a crystalline ai or fluorescent pigment and an emulsified oil adjuvant were investigated. Surfactants, oils and other adjuvant types were varied and applied in different water volumes. Surfactants enhanced crystal growth while polymers such as polyvinyl alcohol reduced this substantially. On grapevine leaves, surfactants with low surface tensions gave high wetting SE's that exhibited run-off at high spray volumes. This gave ai and adjuvant-induced phytotoxicity through localised overdosing. Surfactants with high surface tensions gave less run-off and smaller deposit sizes on leaf surfaces. Smaller deposit sizes were found to give greater uptake through greater association between ai crystals and the oil adjuvant. Deposit size depended both on the surface tension of the spray solution and the spray volume.

Deposit of suspo-emulsion illustrating annulus formation.



Microscopic observations showed crystals and oil to be associated in a ring at the periphery of the dried spray droplets. The mechanism responsible for this appeared to be pinning of the edge of the drying drop by the ai crystals and subsequent transport of ai and emulsion droplets to the periphery by capillary action. This annulus formation was considered to be a possible mechanism by which ai and adjuvant associate on the leaf surface, resulting in enhanced uptake.

3.5 Others

Peter Jones (Victorian Chemical Company, Australia), described the development of what was termed a 'hybrid' adjuvant for glyphosate[20]. There was little formulation detail and only illustrative biological data. Hot-Up is a blend of oil, surfactant and ammonium source for use with glyphosate in warm climates and hard water. A stable formulation was apparently achieved. Blends of cationic or anionic surfactants plus non-ionic surfactant were used to achieve stable, homogeneous formulations. Those including cationic surfactants were better at enhancing activity.

Dave Humble (Degussa Goldschmidt Chemical, Germany) discussed new organosilicone surfactants (of unspecified structure) with DST values similarly low to conventional organosilicones, but which spread very much less[21]. These were found to perform well in field trials with several herbicides, although data were only illustrative. Improving rainfastness of halosulfuron was particularly noted.

4. BIOLOGICAL PERFORMANCE

4.1 Weed Control

In sessions devoted to weed control, herbicides featuring most often were glyphosate and various sulfonylureas.

Improving the efficacy *per se* of glyphosate seems to have declined in interest with low costs and the widespread use of ammonium sulphate. However, **John Nalewaja's (North Dakota State University, USA)** contribution relating to the latter still indicated some lack of understanding as to its mode of action with respect to magnesium and bicarbonate antagonism, in contrast to the better understood preferential precipitation of calcium[22]. Calcium sulphate is precipitated so preventing the formation of the glassy calcium salt of glyphosate, but although magnesium sulphate is highly soluble, this does not seem to have registered. The mechanism of bicarbonate antagonism does not seem to have attracted any investigation either.

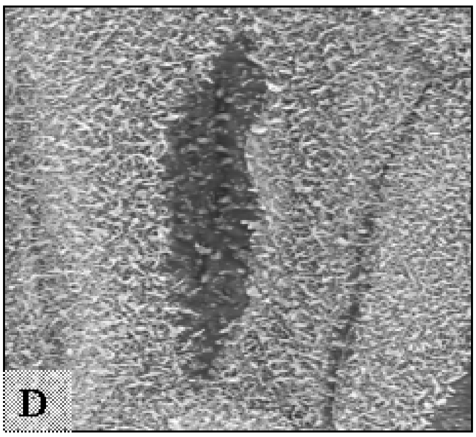
Glyphosate papers generally addressed practical application issues such as controlling spray drift (see Section 5) and the use of mixture partners in glyphosate tolerant crops. Often, these partners are more lipophilic compounds with consequently contrasting requirements for adjuvant physical properties. **Greg Lindner (Uniqema, USA)** presented data from a joint project with Agriliance Crop Protection Products (USA) to find a 'hybrid' adjuvant suitable for mixtures of glyphosate and herbicides such as clethodim (Select)[23]. A typical useful situation would be for the control of volunteer glyphosate tolerant corn in soya. High fructose corn syrup (HFCS) is the key component of Superb HC, now sold by Agrilance in the USA. Adjuvant blends of HFCS (25% w/v), NIS (alkylpolysaccharides, phosphate esters, sorbitan esters, mono- and diglycerides, polysorbates, and ethoxylated alkylamines were found to be most suitable at 25% w/v) and mineral oil (50% w/v). When applied with herbicides individually, these blends were at least as good as tallow amine ethoxylate conventionally used with glyphosate and crop oil concentrates used with lipophilic herbicides, and maintained good activity when applied with mixtures. However, although these data were interesting, much more comprehensive results from trials with mixtures would be needed to form a critical view on their potential. For instance, weed species should be carefully selected and treatment lists designed to indicate levels of control from glyphosate and partners alone and in mixture, particularly with regard to any antagonism that might be expected. The paper also contains a background review of the evolution of 'crop oil concentrates' from '83:17' mineral oils, through seed (vegetable) oils and esterified seed oils, to 'high surfactant oils'.

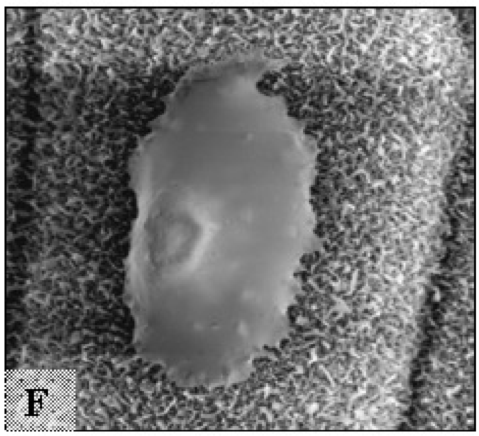
Brian de Villiers (Agricultural Research Council, South Africa) described how iodosulfuron (Hussar) is antagonised by bicarbonate ions in spray water[24]. A proprietary adjuvant blend of non-ionic surfactant and UAN was able to overcome this antagonism. Ammonium nitrate was found to be the most effective component, but urea was also effective at higher rates. The latter was possibly an effect of higher pH increasing the absorption of iodosulfuron. The herbicide was also antagonised when co-applied with foliar nutrient products. This was overcome by the addition of ammonium nitrate, mono- or diammonium phosphate, but not by urea.

Per Kudsk (Danish Institute of Agricultural Sciences) reported that the rainfastness of Atlantis WG and Cossack WG (different ratios of iodosulfuron-methyl and mesosulfuron) could be improved by methylated vegetable oil adjuvants[25]. Three adjuvants, an anionic surfactant, Genapol LRO and methylated vegetable oils, Actirob B and Renol were tested. Outdoor grown *L. perenne* and *A. myosuroides* (4-leaf stage) and *B.napus* (2-leaf stage) were sprayed and a rain simulator used to apply 5 mm rain 1, 3 or 6 hours after treatment at 20 mm/h. All adjuvants improved herbicidal activity similarly, but differed in their effects on rainfastness. All significantly improved rainfastness of both herbicides, but Renol performed significantly better than the other adjuvants on Atlantis WG and Genapol LRO was the least effective. Generally Cossack WG was less adversely affected by rain than Atlantis WG. Both herbicides with all three adjuvants were more rainfast on *B. napus* compared to the two grasses. This is possibly because this species is extremely difficult to wet and rain droplets readily coalesce and bounce-off. This paper was an excellent example of the ideal way to design experiments to determine the biological effects of adjuvants on herbiicide activity by generating and comparing dose responses, and the logic for this was explained.

Studies on the effects of water quality on the efficacy of foramsulfuron by **Zenon Woznica, Agricultural University of Poznan (Poland)** revealed the surprising finding that magnesium chloride enhanced weed control[26]. Enhancement was greatest in the presence of low to medium HLB secondary alcohol ethoxylate surfactants, but magnesium chloride was strongly antagonistic in the presence of high HLB surfactants from this series. Magnesium chloride is highly hygroscopic and benefits may be related to deposit and/or cuticle hydration. Magnesium chloride increased water retention regardless of surfactant HLB. SEM studies, however showed that spray deposits with high HLB surfactants seemed to haye poor contact with leaf surfaces, probably restricting foramsulfuron absorption. These experiments were conducted in the greenhouse and would need to be confirmed in field trials. The benefits of humectants are usually less clear under field conditions.

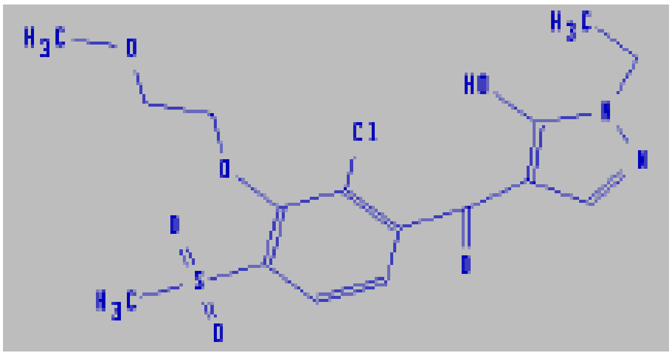
Scanning electron micrograph of spray deposits of formasulfuron (16 g/ha) on yellow foxtail leaves. D with Tergitol 15-S-7 (low HLB). F with Tergitol 15-S-40 (high HLB).





Nelson Keeney, DowAgroSciences described investigations into optimising the herbicidal efficacy of a benzoyl pyrazole[27]. XDE-350 is a discontinued broad spectrum HPPD inhibitor herbicide with pre- and post-emergence activity, controlling many grasses and broadleaf weeds common in corn and cereals.

4-[2-Chloro-3-(2-methoxyethoxy)-4-methylsulfonylbenzoyl]-1-ethyl-5-hydroxy-pyrazole (XDE 350)



A partially systematic evaluation of the effects of varying surfactant hydrophobe and the degree of ethoxylation was made in order to optimize the herbicidal activity of XDE-350.

Ethoxylated phosphate esters were very effective adjuvants and the following prior art in the patent literature was noted:

- Use of acidic phosphate ester surfactants in conjunction with a basic co-surfactant to stabilize a microemulsion of glyphosate and oxyfluorfen (US 6,667,276; Maier and Wuertz).
- Use of ethoxylated alkyl phosphate to improve the efficacy of several herbicides by modulation of the hard water antagonism. (WO2001026463; Nufarm)
- Use of a multi-component adjuvant matrix comprising a fatty acid ester, a phosphate of a fatty acid alcohol ethoxylate/propoxylate and free oleic acid to improve the efficacy of a series benzoyl pyrazoles, similar chemistry to XDE-350 (US 6,514,910; BASF).
- Use of ethoxylated C4-C12 alcohol phosphate esters with 2-10 polyethoxylate chains for enhancing the phytotoxicity of glyphosate (US 5,180,414; Aventis, formerly R-P)

Ethoxylated alkyl phosphate esters were significantly more effective than either ethoxylated aryl or alkylaryl phosphate esters. Linear alcohol phosphate esters performed better than branched alcohol phosphate esters. The number of moles of ethoxylation of the linear alcohol also influenced the phytotoxicity of XDE-350. With a C12-C14 linear alcohol ethoxylate phosphate ester, here was a trend for greater efficacy was associated with a lower degree of ethoxylation over the range tested (3 – 8 moles of ethylene oxide)

In other experiments, when UAN was added to XDE-350 applied with Spraymate X-77 non-ionic surfactant to *Abutilon theophrasti*, uptake increased three-fold and translocation to the roots was four times greater.

Two other papers were presented which contained little data or insufficient information to be of interest. **Prakash Jadhav, United Phosphorus Limited (India)** described a field trial in India which showed that adding increasing amounts of ethoxylated sorbitan ester to tallow amine ethoxylate increased the efficacy of an undisclosed sulfonylurea mixture[28]. **Rajender Balyan, CCS Haryana Agricultural University (India)** reported results from a field trial in India testing the response of fenoxaprop to surfactant[29].

4.2 Insect Control

Insect control trials in the Netherlands with the organosilicone surfactant Zipper® were reported by **Frank Dirkse (Modify B.V.)**.

Zipper®

1,1,1,3,5,5,5-heptamethyltrisiloxanyl propyl-hydroxyl [ethylene/propylene oxide]

In greenhouse ornamentals, Zipper® enhanced the efficacy of abamectin and cyromazine on populations of serpentine leafminer (*Liriomyza trifolii)* showing reduced sensitivity[30]. Since larvae of *L. trifolii* feed on the mesophyll, improved control can only be explained through increased foliar uptake of abamectin and cyromazine. However, at an organosilicone rate of 200 ml/ha in 1000 litres of spray stomatal infiltration is not possible, so the increased penetration must have taken place through enhanced cuticular penetration.

In field trials on potatoes, addition of Zipper® to pymetrozine (Plenum®) significantly extended residual control of melon aphid (*Aphis frangulae*)[31]. Previous studies have reported improvements in the efficacy of pymetrozine control of the closely related cotton aphid (*Aphis gossypii*) by the addition of organosilicone surfactant. When the combination was applied in higher spray volumes, spray liquid flowed down petioles and stems to the soil increasing the potential for root uptake which is particularly effective. This resulted in an improvement of the persistence of efficacy from 14 to 28 days.

Effects of Zipper® (400 ml/ha) on the control of melon aphid by pymetrozine (150 gai/ha) at two spray volumes.

	Mean live aphids/leaf			
	7 DAT		16 DAT	
Untreated	669	a	1149	a
Pymetrozine 250 L/ha	18	b	170	b
Pymetrozine 250 L/ha + Zipper	3	cd	26	c
Pymetrozine 500 L/ha	7	bc	18	c
Pymetrozine 500 L/ha + Zipper	6	cd	6	d

Values in columns followed by a common letter are not significantly different after transformation.

Melon thrips, *Thrips palmi* are a serious pest of vegetable crops in South Florida[32]. Field trials conducted by **Helena** on phaseolus beans showed that the effects of SpinTor 2SC (Spinosad) could be increased by the addition of Dyne-Amic®, claimed Helena. This was indicated by reductions in larvae and adults, and increased marketable yields.

Dyne-Amic®
Polyalkyleneoxide modified polydimethylsiloxane, polyoxypropylene-polyoxyethylene block copolymer plus methylated vegetable oils

4.3 Disease Control

Growing grapes for wine in New Zealand can involve 10-14 spray rounds per season, applying 15-20 different products and total rates of 70-80 kg/ha. High water volumes (1000-1500 L/ha) are used because spray retention and penetration into the canopy and fruit bunches is important but difficult. An extensive research programme was conducted by the **Forest Research Institute** to evaluate the super-spreader Du-Wett® and spreader-sticker Bond Xtra® in conjunction with low spray volumes using hydraulic and air-assisted sprayers[33]. Both adjuvants enabled similar or better fungicide performance from spray volumes down to less than 200 L/ha, while providing better coverage and improved spray deposition on bunches. In addition to improving disease control, work rates increased by up to 22% and application costs per hectare were up to 26% less in programmes including the adjuvants.

Ghent University (Belgium) found that surfactants can inhibit sporangia formation and have a direct lethal effect on the zoospores of *Phytophthora* and *Pythium* spp[34]. The mode of action largely relies on inhibition of motility rapidly followed by lysis. Atplus MBA1301, a monobranched C13 alcohol alkoxylate, and PRO1, a formulation of 25% rhamnolipids of *Pseudomonas aeruginosa* in oil, were found to give excellent disease control of chicory in a commercial situation.

FullStop®, a styrene-acrylate based sticker maintained the level of disease control on potatoes by mancozeb following rain, applied alone or in mixture with Zipper ®organosilicone surfactant in trials conducted by **Modify**[35]. Performance was superior to Bond® or Nufilm 17®, particularly in the absence of rain

FullStop®
Styrene-acrylate based sticker
Zipper®
1,1,1,3,5,5,5-heptamethyltrisiloxanyl propyl-hydroxyl [ethylene/propylene oxide]
Bond®
Styrene-butadiene based sticker
Nufilm 17®
Di-l-p-menthene based sticker

Results from the **Czech Republic Agricultural Research Institute** suggested that Silwet L-77 could give promising improvements in control of Fusarium head rot in malting barley and reductions in mycotoxins[36]. However, the effects of adding Silwet L-77 were not compared within the same season.

4.4 Crop Manipulation and Improvement

Sultana grapes are drying before harvest with a vegetable oil and potash emulsion to speed dehydration and produce high quality, pale golden fruit. Although extremely high volumes are applied, waxy berries and tight bunches limit penetration of the oil emulsion. This causes slow and uneven dehydration necessitating additional drying costs for growers and reducing dried fruit quality. **Robyn Gaskin (Forest Research, New Zealand)** reported that a laboratory study identified an alkylsilicone surfactant, Break Thru OE444, that substantially reduced surface tension of the drying oil and increased spreading of on grapes four-fold[37]. The adjuvant was stable in the high pH environment of the drying emulsion. No phytotoxicity was associated with addition of the adjuvant to the drying oil. A field trial on commercial vines, using an oil soluble UV fluorescent dye, determined that adding Break Thru OE444 and halving the spray volume increased coverage of bunches and improved penetration into bunch centres. The moisture content of fruit at harvest was significantly less than in the standard full volume treatment, eliminating the need for and cost of dehydration. Fruit quality was significantly improved. The net profit to growers would be increased markedly relative to conventional practice.

Most apple trees grown in the Western Cape, South Africa receive applications of a chemical rest-breaking agent at the end of winter to reduce the incidence of growth abnormalities associated with insufficient winter chilling. A new product with a formulation based on a mixture of inorganic and organic nitrogen sources was evaluated by **IAAS (Netherlands)**[38]. Applications were made to mature ‘Golden Delicious’ apple trees at two sites over three seasons. The product was applied with a penetrant, Acer®, with Acer® plus a humectant, with Acer® plus oil, or with Acer® plus a humectant plus either a mineral or a vegetable oil. Acer® plus the humectant tended to have positive effects on bud break, fruit set and fruit size. The penetrant may increase speed of uptake whilst the humectant may prolong the time available for uptake.

Acer® : Alkoxylated fatty amine

Work on **apples in South Africa and citrus in Israel** showed the potential for adjuvants to be added to foliar nutrient sprays to improve deposition and uptake [39, 40].

Break-Thru S-240 and Adpros 85 SL enhanced reduction in height and improved the control of lodging of winter wheat by CCC and prohexadione-calcium in field trials in **Poland** [41].

Break-Thru S-240
α-1,1,1,3,5,5,5-heptamethyltrisiloxanyl propyl –Ω-hydroxypoly [ethylene/propylene oxide]
Adpros 85 SL
Methylated rape seed oil

5. SPRAY DRIFT CONTROL

Several speakers addressed the use of drift control agents. The overall conclusion was that the whole context in which they are used is critical. **Ali Musa Bozdogan (University of Cukurova, Turkey)** reviewed the known effects of adjuvants on spray drift[42]. Wind velocity is obviously important, and temperature and relative humidity affect evaporation and, therefore, droplet size in flight. Characteristics of the target surface affect droplet bounce and retention. Spray droplet formation and deposition can be influenced by the physical properties of the spray solution, and adjuvants such as those based on polyacrylamides may influence droplet size and retention on targets.

Interest in spray drift retardants is driven by economics of on-target application, fear of penalties for non-target injury and concern for movement of spray into safety buffer zones. The US Spray Drift Task Force, a consortium of 38 agricultural companies, showed that spray drift increases as droplet size decreases. During a 3-m fall in a 5-km/hr cross wind, a 100-micron-diameter droplet of water will move 15 m off target compared to 5 m for a 200-micron-diameter droplet. Commonly used drift control agents in North America include non-ionic polyacrylamide and an anionic copolymer of polyacrylamide. Additionally, there has been some use of a modified guar derivative.

5.1 Polymers

Polyacrylamides have been used to affect spray droplet size and bounce with resulting improvements in deposition. Experiments to determine the effects of such a polymer on droplet bounce from pea leaves was reported by **Simon Rose, (Ciba Specialty Chemicals, UK)**[43]. Droplets of a glyphosate solution bounced over 11cm, but the addition of 100 ppm of an anionic polyacrylamide polymer reduced this to less than 1.5 cm. More effective was 2000 ppm tallow amine 20 EO surfactant (<5mm) or a combination of the two (2mm). AMS is often used to increase the solubility of such polymers, and was shown to have a small reduction in the control of bounce by both polymer and TAE.

Glyphosate efficacy enhancement by polyacrylamides alone and mixed with tallow amine ethoxylate (TAE) surfactant in tank-mix and built-in formulations was studied **(Mickey Brigance, Adjuvants Unlimited Inc., USA)**[44]. Good effects were found regardless of TAE content. There was a tendency for greater enhancement of glyphosate efficacy by lower anionic charge density of the polyacrylamide, but molecular weight (MW) had no effect. As greater deposition is clearly related to higher MW it was suggested that there may be an alternative mode of action regarding improved efficacy.

In a study reported by **Gene Wills, (Mississippi Agricultural and Forestry Experiment Station, USA).** four drift control agents based on polymers and ammonium salts were evaluated in conjunction with glyphosate formulated with (Roundup UltraMax) or without surfactant (Rodeo)[45]. The volume of driftable spray droplets (<144 microns diameter) of glyphosate was 58 and 56% for glyphosate with no drift control adjuvant both with and without surfactant, respectively, and was variously reduced from 5 to 41 percentage points by the addition of four drift control adjuvants. Two weeks after treatment, control of four weeds was assessed and showed small differences between treatments. Not surprisingly, the most marked were the beneficial effects of all adjuvants on Rodeo. Spray patterns were essentially unchanged by the addition of drift control agents.

5.2 Influence of Spray Equipment etc.

Harry Combellack (Spray Smart Enterprises, Australia) presented results of experiments with SST 0107/03, a new biodegradable wetter comprising a mixture of polyoxyalkylene alcohols[46]. It is more effective at spreading on waxy surfaces than the commonly used alkoxylated alcohol, BS 1000, and was surprisingly shown to reduce droplet drift. In preliminary studies with 13 different nozzles, an overall drift reduction of around 60% was achieved when compared to a reference 03XR nozzle spraying BS 1000. Unexpectedly, the reduction in drift was more like that for an organosilicone and almost equal to that for an emulsifiable mineral oil. Droplet spectra data show that SST 0107/03 generates significantly less volume of driftable droplets (<100 µm) than BS 1000 or water. Dynamic surface tension is similar to BS 1000 at 30 Hz as tested, but less drift could be partly due to the lower equilibrium surface tension as well an increase in polarity. It also shows that effectiveness of SST 0107/03 in lowering drift is greater when sprayed through high shear nozzles such as the XR range. This may occur because of its different micelle structure. The level of drift reduction achieved implies that it should enable a 10003 XR to be given a two star LERAP-Low Drift rating if used with this wetter.

Oleg Nicetic (University of Western Sydney, Australia) noted that the effects of an oil adjuvant on spray droplet size and drift were dependent on nozzles[47]. Wind tunnel and droplet sizing experiments with Malvern 200 laser diffraction analyser clearly demonstrated that the impact of oil on droplet spectra and spray drift is highly dependent on the nozzle type, orifice size and pressure at which the liquid is applied. Increasing oil concentration in sprays can, in some instances, increase the impact of the oil on droplet spectra but emulsifier concentration in the oil had no impact. For flat fan and hollow cone nozzles, oil tended to increase droplet size and reduce the percentage of drift-prone droplets. However, for injet nozzles, reduced droplet size and increased proportions of drift-prone droplets were recorded. Drift reduction was more pronounced for hollow cone nozzles than for flat fan nozzles and the impact of oil on drift from injet nozzles is unlikely to have practical implications. Recommendations should be specific for nozzle type, orifice size and operating pressure.

Two papers were presented by **Pieter Spanoghe (Ghent University (Belgium)** on work designed to provide data to validate FYDRIMO ("FYsisch DRIft MOdel" or Physical Drift Model) recently developed by Ghent University[48,49]. Products formulated as SC, EC, WP, WG formulations were evaluated. A literature review on the effects of various types of adjuvants was supplemented by experiments to classify the effects of different adjuvants on spray droplet volume median diameter when sprayed through various types of nozzles. Droplet size distribution was measured by using laser diffraction. An anti-drift polymer was included with some treatments. The validation of the model with wind tunnel measurements showed good results

6. MODES OF ACTION & METHODOLOGIES

6.1 Biokinetic Studies at FRI, New Zealand

Alison Forster, Jerzy Zabkiewicz and Robyn Gaskin have been continuing to study the modes of action of adjuvants with respect to enhancing uptake of active ingredients at the Forest Research Institute in New Zealand.

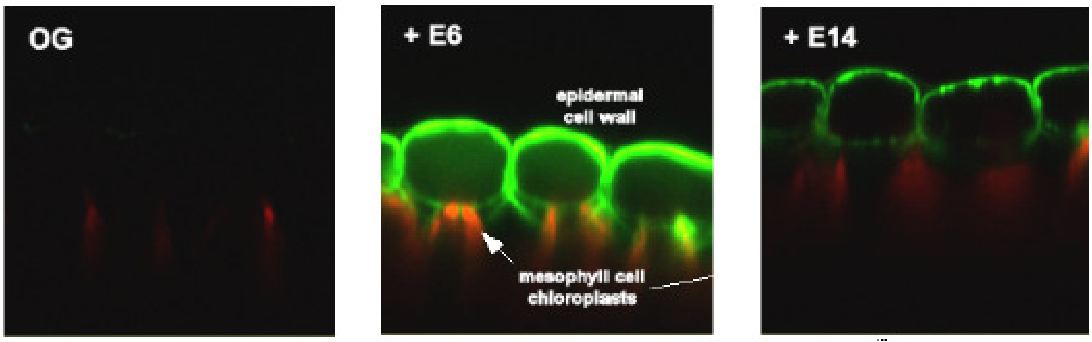
2-deoxy-D-glucose, 2,4-dichlorophenoxy-acetic acid and epoxiconazole have lipophilic characteristics from very low to very high and have been used model active ingredients. These were applied at a range of concentrations, in the presence and absence of four surfactants, to the leaves of three species (*Chenopodium album*, *Hedera helix* and *Stephanotis floribunda*) to evaluate the relationship of initial dose applied to uptake per unit area[50]. Silwet L-77 trisiloxane ethoxylate, mean EO of 7.5), triethylene glycol monododecyl ether (C12EO3), hexaethylene glycol monododecyl ether (C12EO6) and decaethylene glycol monododecyl ether (C12EO10) induce varying degrees of deposit spreading. Uptake of ai was shown to be strongly related to the effective initial dose per unit area after spreading. However, there were also significant differences related to other effects of specific surfactants on uptake.

In other experiments, scanning electron microscope observations were made on spray deposits on leaves of *Chenopodium album*[51]. A range of C12 alcohol ethoxylate surfactants with 3, 6, or 10 EO units and Silwet L-77 were studied with the same three model active ingredients as in the study reported above. The appearance of precipitates from the droplet solution with various adjuvants during drying was related to the pattern of uptake of epoxiconazole and 2,4-dichlorophenoxy-acetic acid. However, in the case of deoxyglucose, a much more polar compound, the precipitates observed on eaf surfaces did not adequately explain uptake trends.

The efficacy of systemic agrochemicals depends on a combination of deposition, retention, uptake, and translocation. Hydrophilic molecules are readily transported in either the phloem or the xylem, though their initial movements through the cuticle, epidermal cells and into the mesophyll are not understood well. Adjuvants can assist foliar uptake, and, in theory, if adjuvants could reach the cell membranes promote translocation. Localised contact phytotoxicity due to formulation or concentration of specific ai's can reduce translocation. A non-herbicidal model compound, 2-deoxyglucose (DOG) and several surfactants, known not to cause contact phytotoxicity on *Chenopodium album*, were used to evaluate the relationship of mass uptake by this polar molecule to its subsequent short term (24h) translocation out of the treated leaf [52]. Surfactants studied were Silwet L-77, triethylene glycol monododecyl ether, hexaethylene glycol monododecyl ether and decaethylene glycol monododecyl ether, all believed to be non-phytotoxic. Translocation over this period was directly proportional to uptake and the surfactants tested did not directly affect subsequent short term translocation out of the treated leaf. Either they do not penetrate far into the leaf tissues, or they do not have any effect on cell permeability, at these concentrations.

Confocal Laser Scanning Microscopy (CLSM) is a non-destructive technique that uses a laser beam to optically section samples. It has been used to visualise the penetration and transport of fluorescent chemicals in living plants[53]. While most pesticides do not fluoresce and thus, cannot be visualised by CLSM, fluorescent dyes with similar physicochemical properties to pesticides can be used to simulate their uptake and translocation in intact plants. CLSM was used to investigate the effects of two aliphatic alcohol surfactants with different mean molar ethylene oxide contents (E6 and E14), on the uptake of Oregon Green dye (log Ko/w –2.4), into broad bean leaves.

CLSM visualization of Oregon Green (OG) applied alone or with more lipophilic (+E6) or less lipophilic surfactant (+E14), 24 hours after treatment.



The qualitative results obtained were compared with the measured uptake of the dye. Whilst the addition of E6 increased uptake of Oregon Green into bean leaves, E14 had no effect. However, both surfactants modified the distribution of the dye within the epidermal and mesophyll cell layers. CLSM showed that Oregon Green alone diffused slowly through the cuticle and was transferred to mesophyll cells via epidermal cell walls. E6 increased sequestration of the hydrophilic dye within epidermal cells and slowed its vertical diffusion. E14 did not cause the dye to partition into epidermal cells and thus enhanced diffusion relative to E6, but slowed the vertical movement of dye *per se*. CLSM has enabled us to visualise, *in vivo*, how surfactants can affect the movement of a compound within an intact leaf. It has provided evidence that certain surfactants may alter diffusion pathways and the speed of transfer of compounds from the cuticle to mesophyll cells, information which traditional gross uptake measurements are unable to provide.

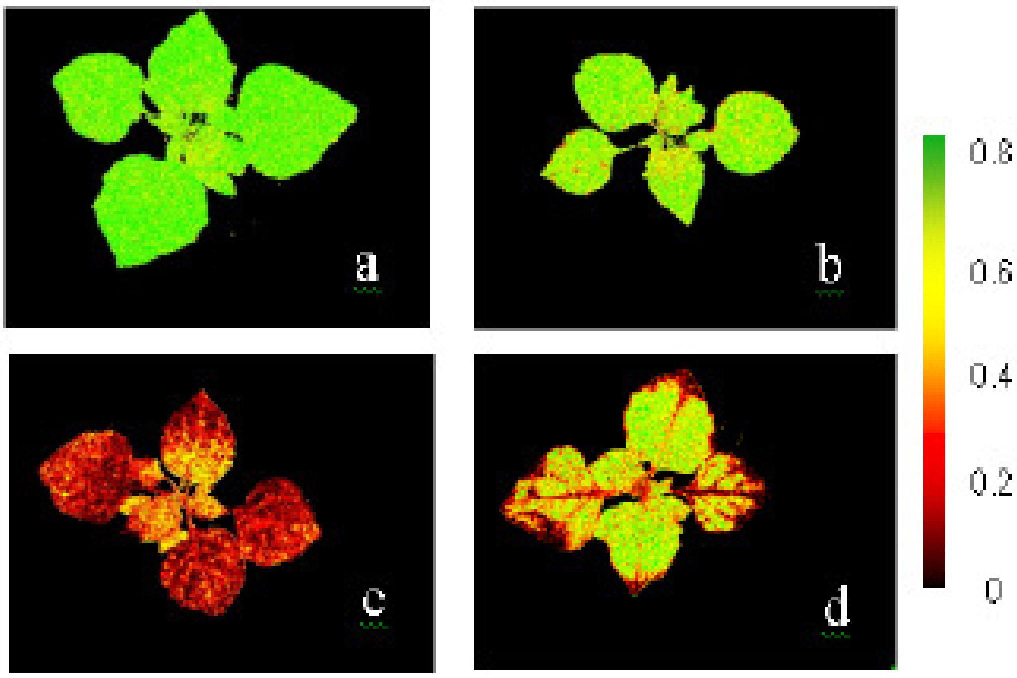
6.2 Surfactant Uptake

Although spray droplets dry down in minutes, uptake can continue for days. Penetration of isolated tomato (*Lycopersicon esculentum*) fruit cuticular membrane (CM) by a homologous series of octylphenoxy polyethoxylated surfactants with mean EO units per molecule of 3, 9.5, 12.5, 16, and 40 was examined using infinite and finite dose diffusion systems. Results were reported by **Peter Petracek (Valent BioSciences Corporation, USA)**[54]. The time course for infinite dose diffusion from donor solution through an interfacing CM to a receiver solution was characterized by lag and linear phases. As polarity increased with EO content, lag phase increased and flux decreased. The time course for finite dose diffusion was described by lag, linear, and plateau phases. Lag phase was not a function of EO content and extended well beyond apparent donor droplet drying. Linear phase penetration rate was linearly related to log EO. Penetration approached a plateau 648 h after droplet application and ranged from a total of 17% for the most polar to 85 % for the most lipophilic of the amount applied. It was pointed out that as these surfactants were mixtures with a wide range of degrees of ethoxylation, with the high HLB surfactant it could be the more lipophilic shorter chain molecules penetrating.

6.3 Rapid Screening Technique

Hans de Ruiter (SurfaPlus R&D, Netherlands) demonstrated how the relative increase of chlorophyll fluorescence during photosynthesis can be used to compare the influence of adjuvants on the activity of herbicides[55]. This allows the accurate and non-destructive screening of sprayed plants in the first minutes and hours after application. Automated imaging and quantification of the relative increase of fluorescence at the whole plant level is now possible. A robot-arm enables a laser-camera to visualise chlorophyll fluorescence, moving rapidly between plants, making large-scale screening possible. The use of this technology for monitoring bentazon, glufosinate and glyphosate action was demonstrated.

Effect of adjuvants on bentazon activity (2 HAT) as measured by efficiency of photosynthesis (green = high; red = low) via chlorophyll fluorescence. a) untreated; b) bentazon alone; c) bentazon + polyglycerol derivative; d) bentazon + organosilicone surfactant Break Thru S 240. (NB. A video clip can be downloaded from www.surfaplus.com)



6.4 New Micro-Droplet Generator

Studying spray droplet behaviour with plant foliage is facilitated if individual droplets can be generated and their subsequent behaviour on impact observed or measured. Devices of several designs for producing single droplets have been developed. The common failing of these designs is that they all depend on droplet fall distance to provide droplet velocity differences. In general there is little or no control apart from capturing droplets of different sizes at their terminal velocity, which means using the device at different heights from the target surface. **Jerzy Zabkiewicz (Forest Research, New Zealand**) described a novel, simple single droplet generator that uses gas pressure pulses to generate the droplets[56]. This works by applying pulses of pressurised gas to a liquid contained in a chamber, forcing out droplets through a nozzle in the bottom plate of the generator. A solenoid valve is rapidly opened and closed to create pressure pulses. There are no moving parts in contact with the liquid, making the generator simple to build, robust, and also easy to clean. It is robust and easy to use with the potential to be used with a wider range of spray formulations and operating conditions than previously possible.

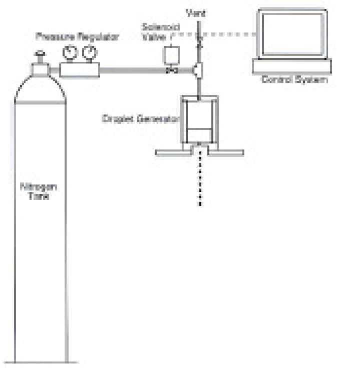


Figure 1. Pneumatic droplet generator system (4).

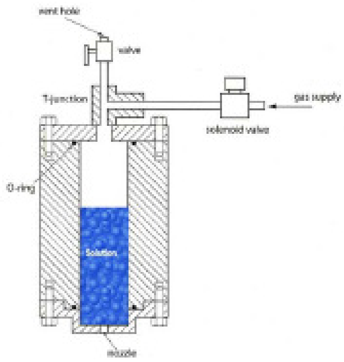


Figure 2. Original droplet generator body (4).

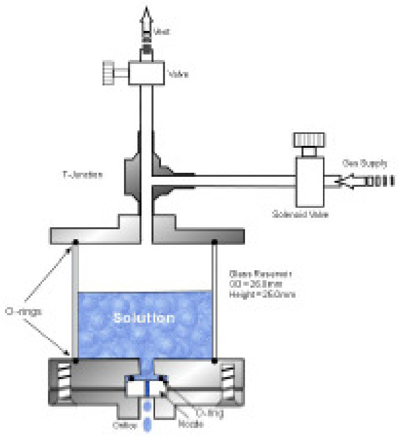


Figure 3. Droplet generator design for use with agrichemical solutions.

Figure 4. Photograph of agrichemical droplet generator body.

In South Africa, *Botrytis cinerea*, (Botrytis bunch rot) is best controlled by optimising the coverage of fungicides on pedicels, rachises, laterals and berry bases rather than berry skins. **Jan-Cor Brink, University of Stellenbosch (South Africa)** desribed a protocol developed to visualise and quantify spray deposits within grape bunches[57]. Bunches were sprayed with different volumes of a mixture of fenhexamid and a yellow fluorescent pigment, illuminated, visualized under a stereo microscope, and inner bunch parts were digitally photographed at 20x magnification. Several image contrasting and filtering processes were performed and area of deposited pigment in selected areas was quantified. It was commented on in discussion of the paper that the dye should have been checked for surfactant properties.

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7. **Registration procedure for adjuvants with special reference to South Africa.**
   Beata Bialek, Volcano Agroscience (Pty) Ltd

NEW ADJUVANTS AND FORMULANTS

8. **Development of alkylpolyglucoside esters for tank-mix adjuvants application (mesotrione).**
   Alberto Colombo, Cesalpinia Chemicals.

9. **Evaluating a new bio-rational orange oil-based multipurpose adjuvant.**
   Erroll Pullen & Dirk Uys, ORO Agri (South Africa).

10. **Card phenol ethoxylates: economical natural origin, non-petro origin - biodegradable surfactants against alkyl phenol ethoxylates.**
    Dharmaraya Shetty, Unitop Chemicals (India).

11. **New dispersion additive for suspension concentrate formulations.**
    Ingo Fleute-Schlachter, Degussa Goldschmidt.

12. **Improvement of emulsifiable concentrates through siloxane surfactants.**
Ingo Fleute-Schlachter, Degussa Goldschmidt.

13. **Developments in non-aqueous dispersants for built-in adjuvant based flowable formulations.**
Emmanuel Paris, Huntsman.

14. **The utilization of surfactants in the solubilization of phenoxy and benzoic acid herbicides.**
Johnnie Roberts, Helena Chemical Company.

15. **Glyphosate in oil.**
Robert Killick, Victorian Chemical Company.

16. **Spray Drift Experiments with Adsee® Ethyl Hydroxyethyl Cellulose as a Tank Mix Adjuvant.**
James Hazen, Akzo Nobel Surface Chemistry.

17. **New technology tank mix adjuvants based on emulsion polymers.**
Ewald Sieverding, Degussa Goldschmidt AG.

18. **Biological optimisation of sugar beet herbicides.**
Rainer Suessmann, BayerCropScience (Germany).

19. **Effect of formulation components on the bulk stability and foliar delivery behaviour of suspo-emulsion formulations containing built-in adjuvants.**
Malcolm Faers, Bayer CropScience.

20. **Development of a hybrid adjuvant for glyphosate.**
Peter Jones, Victorian Chemical Company.

21. **Super-spreading not required for efficacy of organo-siloxanes as adjuvants for herbicides.**
Dave Humble, Degussa Goldschmidt Chemical.

WEED CONTROL

22. **Optimizing glyphosate efficacy via application technology.**
John Nalewaja, North Dakota State University.

23. **Oil and saccharide adjuvant for herbicides (glyphosate & mixture partners).**
Greg Lindner, Uniqema.

24. **Influence of carrier water, foliar feeds and adjuvants on iodosulfuron activity.**
Brian de Villiers, Agricultural Research Council of South Africa.

25. **Adjuvant effects on the rainfastness of iodosulfuron-methyl + mesosulfuron formulations.**
Per Kudsk, Danish Institute of Agricultural Sciences

26. **Enhancement of foramsulfuron efficacy with magnesium chloride.**
Zenon Woznica, Agricultural University of Poznan.

27. **Influence of spray tank adjuvants on the foliar activity of a benzoyl pyrazole on a series of grasses and broadleaf weeds.**
Nelson Keeney, DowAgroSciences

28. **The influence of ethoxylated sorbitan ester co-surfactants in enhancement of adjuvancy effects of tallow amine ethoxylates on herbicide activity of sulfonylureas in wheat.**
Prakash Jadhav, United Phosphorus Limited.

29. **Wild oat (*Avena Ludoviciana*) and wild canary grass (*Phalaris Minor*) control in wheat by fenoxaprop applied with and without surfactant.**
Rajender Balyan, CCS Haryana Agricultural University (India).

INSECT CONTROL

30. **Improved control of populations of Serpentine Leafminer *Liriomyza trifolii* with reduced sensitivity to abamectin and cyromazine by addition of the organosilicone Zipper.**
Frank Dirkse, Modify B.V.

31. **Improved control of organophosphate and pyrethroid resistant populations of *Aphis frangulae* in potatoes with pymetrozine by addition of the organosilicone Zipper.**
Frank Dirkse, Modify B.V..

32. **Management of Melon Thrips, *Thrips palmi* Karny (Thysanoptera: Thripidae): Use of an agricultural spray adjuvant to increase efficacy of SpinTor.**
Robert E. Mack, Helena Chemical Company.

DISEASE CONTROL

33. **Adjuvant prescriptions to lower water volumes and improve disease control in vineyards.**
Robyn Gaskin, Plant Protection Chemistry, Forest Research.

34. **Control of *Phytophthora cryptogea* in the hydroponic forcing of witloof chicory with a non-ionic synthetic surfactant and a rhamnolipid-based biosurfactant formulation.**
Kris de Jonghe, Ghent University.

35. **Fullstop: A new sticker for the application of protectant fungicides.**
Ian Brink, Spectrum Research Services and Frank Dirkse, Modify B.V.

36. **Protection of malting spring barley against *fusarium* spp using fungicides and Silwet L-77 adjuvant.**
Marie Vanova, Agriculture Research Institute .

CROP MANIPULATION & IMPROVEMENT

37. **Adjuvants improve the evenness and efficiency of drying sultana grapes.**
Robyn Gaskin, Plant Protection Chemistry, Forest Research.

38. **Effect of penetrant and humectant adjuvants on the Efficacy of a rest breaking agent on Golden Delicious apple.**
Robert Butselaar, IAAS.

39. **Adjuvants affect apple leaf and fruit calcium and nitrogen concentrations following calcium nitrate sprays.**
Michael North & John Wooldridge, Agricultural Research Council of South Africa.

40. **"Bonus-NPK" - A unique formulation for foliar nutrition: an optimal yield and quality booster for citrus**
Oded Achilea, Haifa Chemicals Ltd.

41. **Adjuvant effects on plant growth regulators in winter wheat.**
Stanislaw Stachecki, Institute of Plant Protection, Poznan.

SPRAY DRIFT CONTROL

42. **A review of the effects of adjuvants on spray drift in pesticide applications.**
Ali Musa Bozdogan, University of Cukurova.

43. **Effect of polyacrylamide formulations on bioefficacy of glyphosate.**
Mickey Brigance, Adjuvants Unlimited Inc.

44. **The effect of high molecular weight anionic polyacrylamide polymers on the droplet bounce of glyphosate solutions.**
Simon Rose, Ciba Specialty Chemicals.

45. **Influence of drift control adjuvants on applications of glyphosate.**
Gene Wills, Mississippi Agricultural and Forestry Experiment Station.

46. **A wetting agent that unexpectedly reduces drift.**
Harry Combellack, Spray Smart Enterprises.

47. **Influence of agricultural mineral oil on droplet spectra and spray drift.**
Oleg Nicetic, University of Western Sydney.

48. **The influence of different formulations on spray performance and drift potential.**
Pieter Spanoghe, Ghent University.

49. **The influence of adjuvants on spray performance.**
Pieter Spanoghe, Ghent University.

MODES OF ACTION & METHODOLOGIES

50. **Mechanisms of cuticular uptake into living plants: influence of xenobiotic dose and surfactant on uptake.**
Alison Forster, Plant Protection Chemistry, Forest Research.

51. **Spray formulation deposits on leaf surfaces and xenobiotic mass uptake.**
Alison Forster, Plant Protection Chemistry, Forest Research.

52. **Foliar uptake and translocation relationships for polar xenobiotics.**
Jerzy Zabkiewicz, Plant Protection Chemistry, Forest Research.

53. **Visualising surfactant effects on foliar uptake using confocal laser scanning microscopy.**
Robyn Gaskin, Plant Protection Chemistry, Forest Research.

54. **Infinite and finite dose diffusion of octylphenoxypolyethoxylated surfactants through isolated cuticles.**
Peter Petracek, Valent BioSciences Corporation.

55. **Fluorescence imaging for investigating the efficiency of formulations and adjuvants.**
Hans de Ruiter, SurfaPlus.

56. **A new single droplet generator for high speed impact and adhesion studies of agrichemical spray formulations.**
Jerzy Zabkiewicz, Plant Protection Chemistry, Forest Research.

57. **Development of a protocol to quantify spray deposits on grape bunches.**
Jan-Cor Brink, University of Stellenbosch.

EXHIBITORS

Speciality Chemical Suppliers

Akzo Nobel	www.surface.akzonobel.com
Clariant	www.pa.clariant.com
Degussa	www.break-thru.com
GE Advanced Materials	www.gesilicones.com
Huntsman	www.huntsman.com
Marubeni	www.chemdot.com

Adjuvant Manufacturers/Distributors

Helena Chemical Company	www.helenachemical.com
IAAS	www.iaas.nl
OroAgri	www.oroagri.com
Plaaskem	www.plaaskem.co.za
Villa Crop Protection	www.villacrop.co.za

Contract Research Organisations

agroTechnology Research, Inc	www.agrotechnologyresearch.com