What's New In Agrochemical Formulation?

Reviewing Some Novel Technologies and Approaches

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INTERNATIONAL CROP-SCIENCE CONFERENCE & EXHIBITION

Organised By PMFAI PESTICIDES MANUFACTURERS & FORMULATORS ASSOCIATION OF INDIA

iFormulate

A Little About iFormulate

Founded in 2012 by two experienced industry professionals

Diverse experiences, knowledge and wide range of contacts

Polymers, materials science, chemistry, imaging, dyes, pigments, emulsion polymerisation, biocides, pharma, agrochem, FMCG, food, anti-counterfeiting, environmental, formulation etc…

Consultancy, innovation, marketing, business development, strategy, regulatory, training, events, R&D

Complementary Network of Associates

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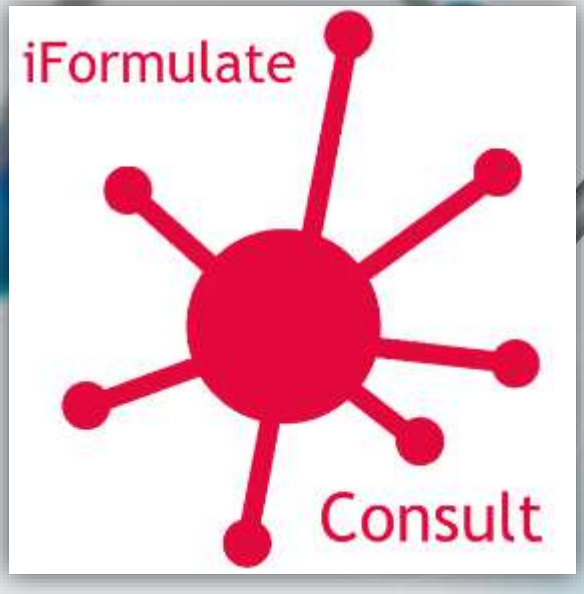
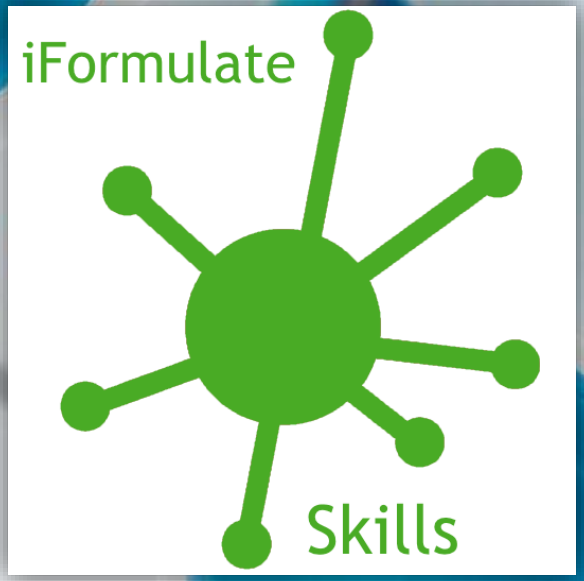
Our Services





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Some of our Agrochemical Activities

Individual client projects

- Supporting formulation development and trouble shooting
- Scouting for novel formulation technologies
- Positioning new technologies in the market

Training

- Introduction to Agrochemical Formulation Strategies – in-person and online training via ATI (Informa)

Reports

- Agrow Formulations Report 2017 (Informa Agrow) – including some material from today's presentation
- Further in planning

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Overview

- Formulation Trends: 2017 vs 2013
- Are Old Formulation Types Really Dying Out?
- Is Nanotechnology Really A Big Thing?
- Is Microencapsulation A Big Thing Then?
- Complex Mixture Formulations and Resistance
- Summary

FORMULATION TRENDS

Are The 2013 Formulation Trends Continuing?

- Growth in biopesticides use and the technological challenges of these products ✓
- More stringent regulatory requirements for formulation additives ✓
- Decline in the development of dust powders and solvent based formulations & growth in water based products, water dispersible granules, oil dispersions; ?
- Increased use surfactants/ adjuvants to enhance the biological activity/efficacy ✓
- Increase in significance of generic producers, especially China ✓
- More difficult and costly development and registration of new AI, especially in EU ✓
- Growth in outsourcing of formulation development work (speed/cost) ?
- More patent activity for new formulations, adjuvants and additives. ✓

Source: Agrow Formulations Report 2013, A.Knowles – summarised in Agrow Formulations Report 2016

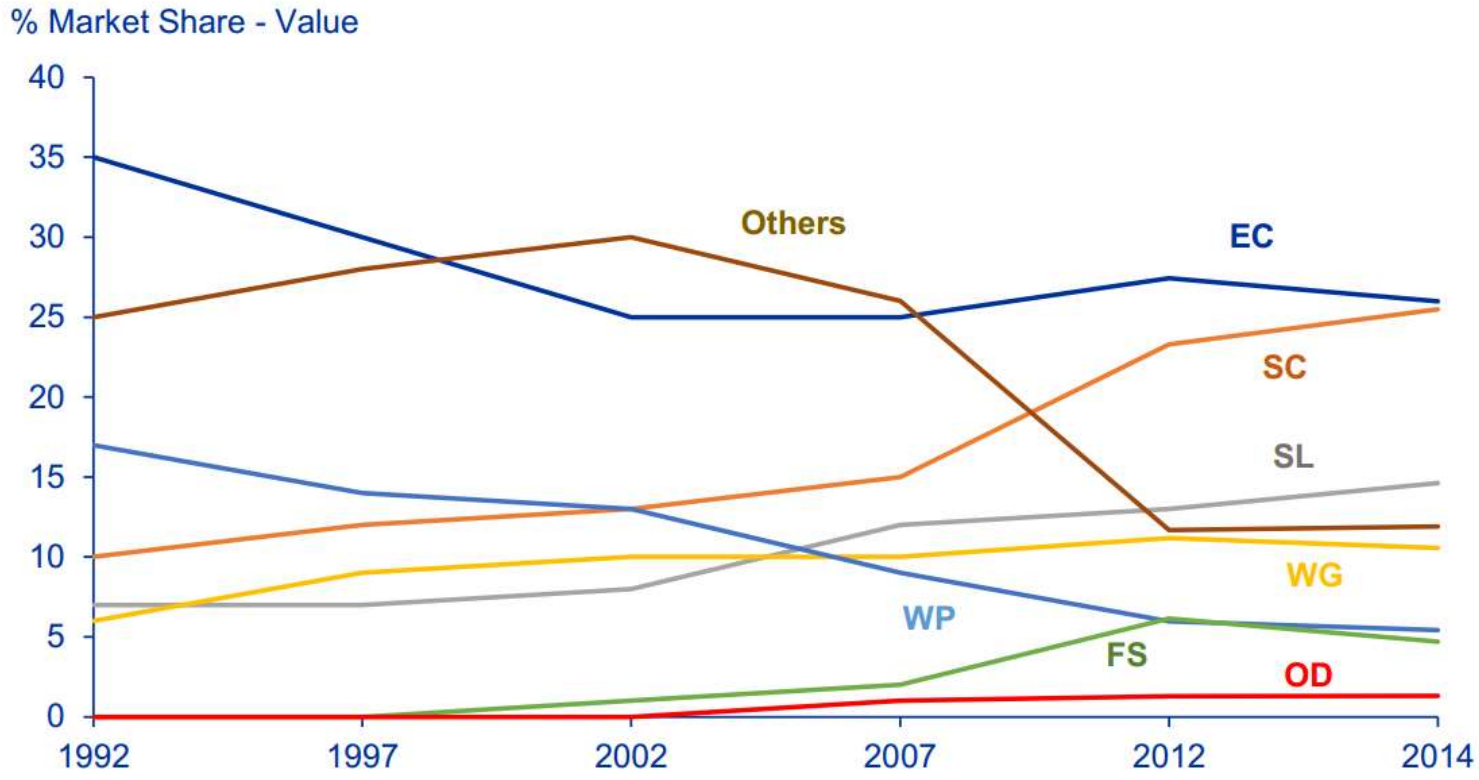
“New” Industry Trends Relevant to Formulation 2017

- Increase in pesticide resistant strains (weeds and pests) being reported
- Integration of herbicide treatments with planting of crop strains (GM or conventional) with deliberate herbicide resistance
- Integrated crop management (ICM) and integrated pest management (IPM) practices
- Restrictions and prohibitions for specific “big-name” pesticide active ingredients, e.g. EU restrictions on neonicotinoid insecticides and debates on the carcinogenic potential of glyphosate
- Increasing automation in the application of crop protection products.

Source: Agrow Formulations Report 2016

ARE OLD FORMULATION TYPES REALLY DYING OUT?

Formulation Types by Value: Old Data 2014



Key Drivers

SC – Soybean Fungicides and Insecticides/Rynaxypyr/Cereal fungicides
SL – Non-selective herbicides/herbicide tolerant crops
FS – Seed treatment / GM Crops
WP – China (older products), Japan (Jumbo and One-Shot formulations)
WG – Europe cereal herbicides and vines

Source: M.Phillips (Phillips McDougall) at Informa C&C Berlin 2017

Reports of the Death of EC Have Been Exaggerated

Number of AIs Listed for Main Formulation Types (BCPC Online Pesticide Manual)

Code	Description	No of AIs 2016	No of AIs 2013	Change 2013-2016
EC	Emulsifiable Concentrate	459	339	+35%
WP	Wettable Powder	401	297	+35%
SC	Suspension Concentrate	322	288	+12%
GR	Granule	258	197	+31%
WG	Wettable Granule	196	193	+1.5%
SL	Soluble Liquid	136	113	+20%
DP	Dustable Powder	134	100	+34%
UL	Ultra-low volume (ULV) Liquid	59		
FS	Flowable Concentrate for Seed Treatment	51		
EW	Oil in Water Emulsion	40	38	+5%

IS NANOTECHNOLOGY REALLY A BIG THING?

What Happened To Nanotechnology?

"Nanomaterials are chemical substances or materials that are manufactured and used on a very small scale. Their structures range from approximately 1 to 100 nm in at least one dimension" (ECHA)

Much attention and activity in many industries, including agrochemicals

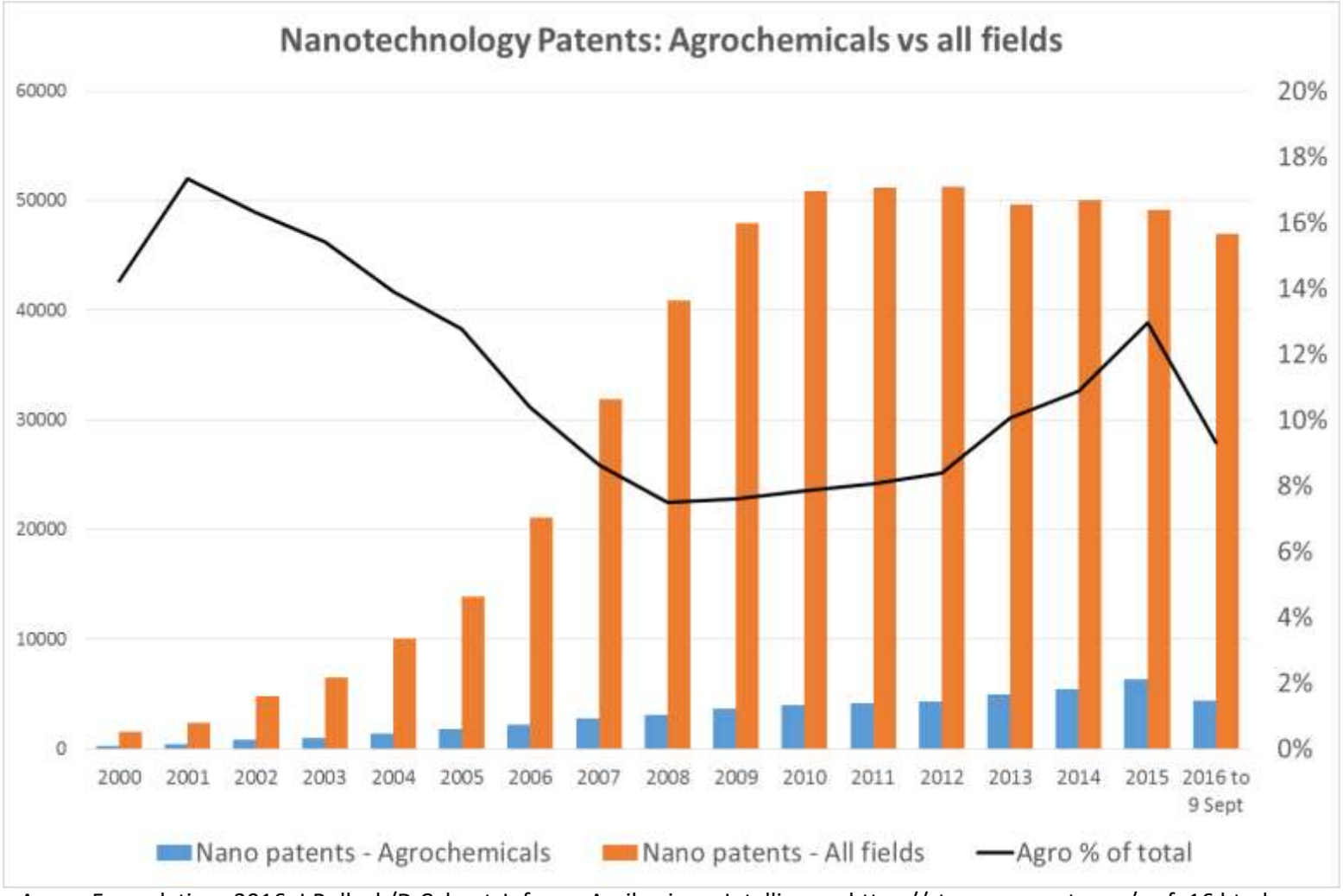
Often (but not always) refers to **particles** where properties change dramatically once they are nanosize

- Solubility and hence bioavailability (e.g. pharma – "difficult" low solubility actives)
- Encapsulation, transport and release (e.g. pharma drug delivery)
- Electronic properties (e.g. quantum dots for displays)
- Optical properties (e.g. sunscreens)
- Surface properties (e.g. nanostructures for coatings)

In parallel: Scrutiny of safety issues (e.g. food, cosmetics)

- Potentially more toxic than non-nano alternatives

Nanotechnology: The Plateau?



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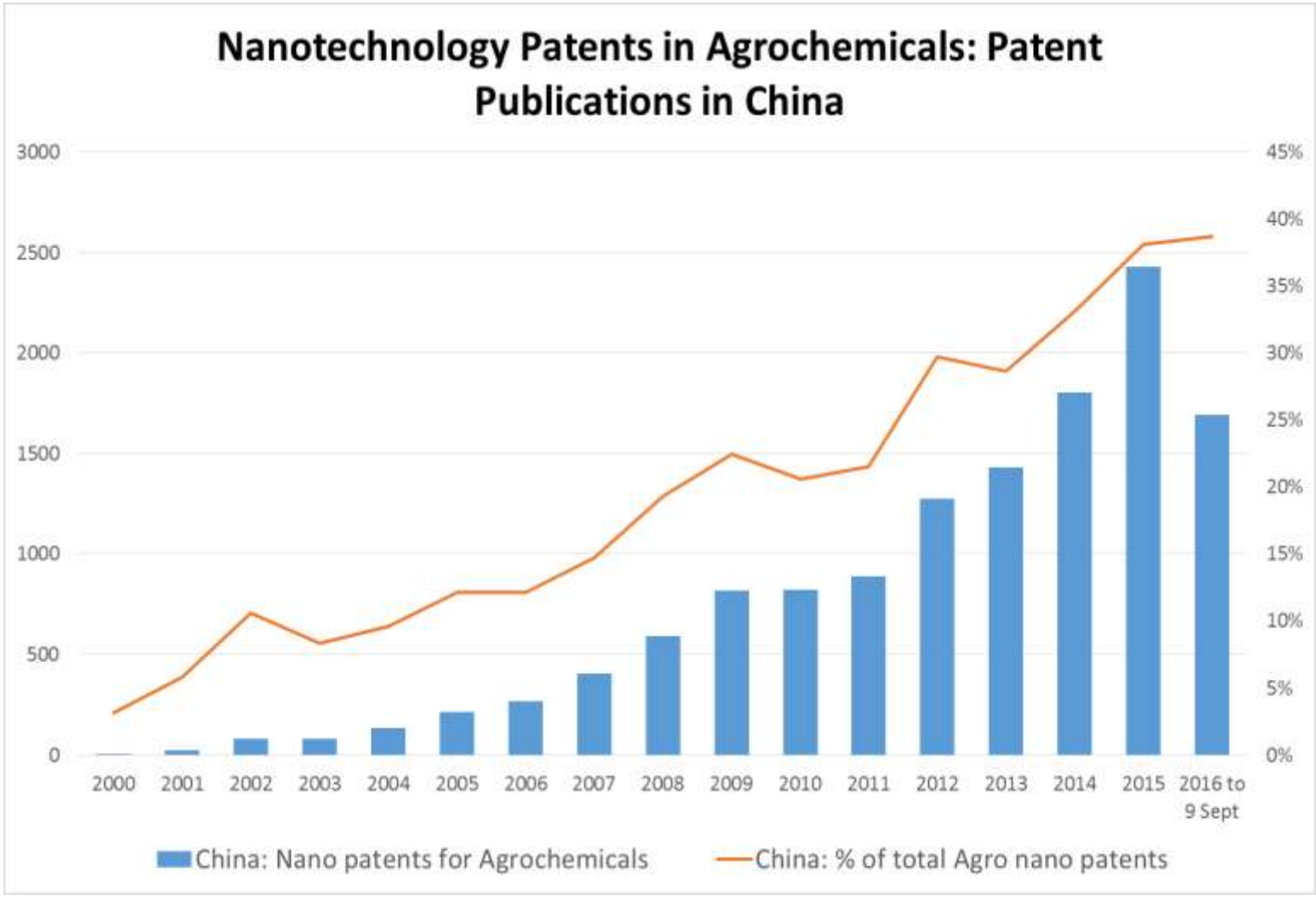
Who is Patenting Nano for Agrochemicals?



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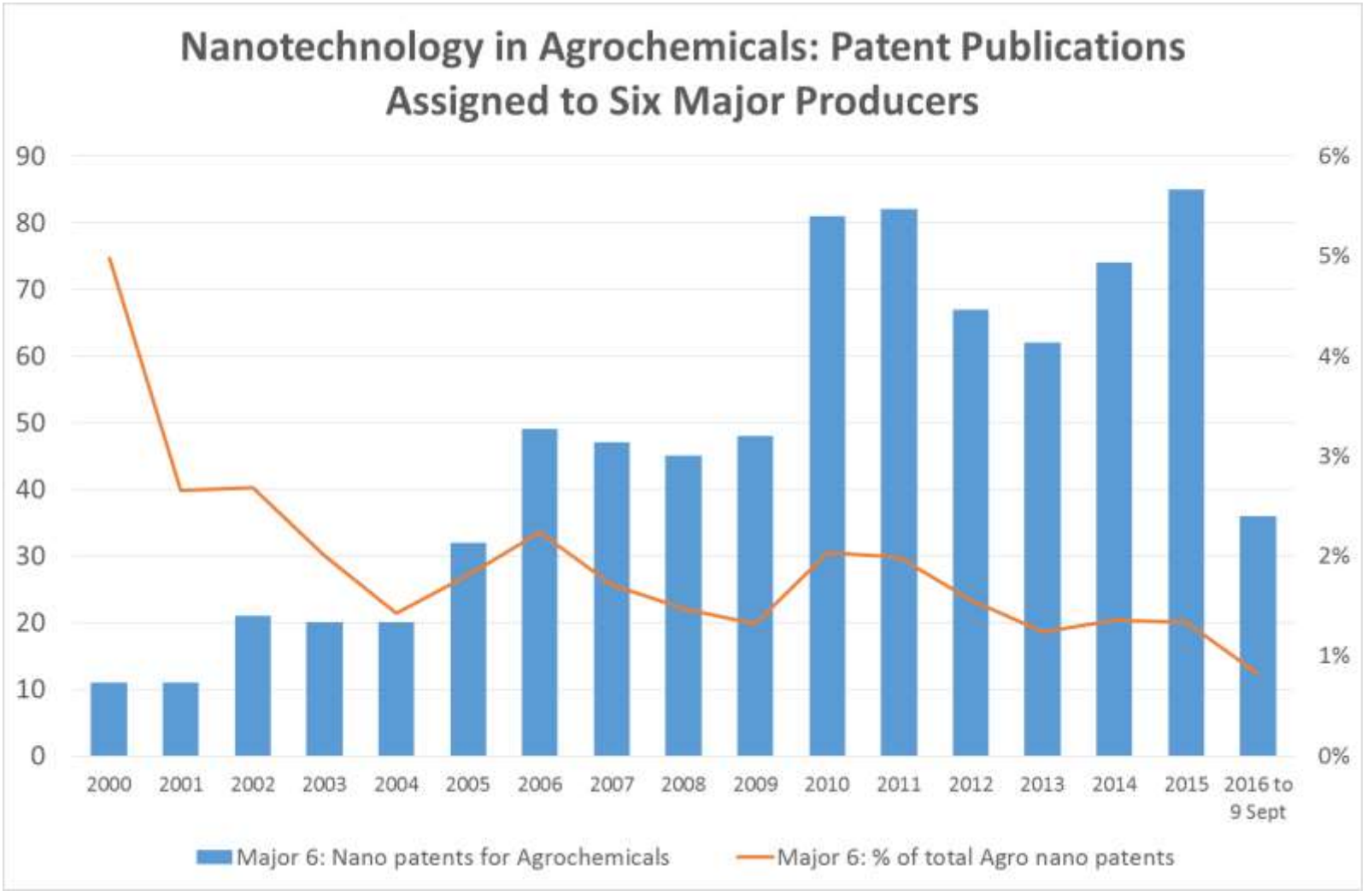

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Nanotechology: A Commercial Prospect – or not?

"There are over 3,000 patents worldwide for potential agrochemical usage of nanotechnology"

"However, "in reality, today very few, if any, intentionally manufactured nano-sized formulations exist on the market"

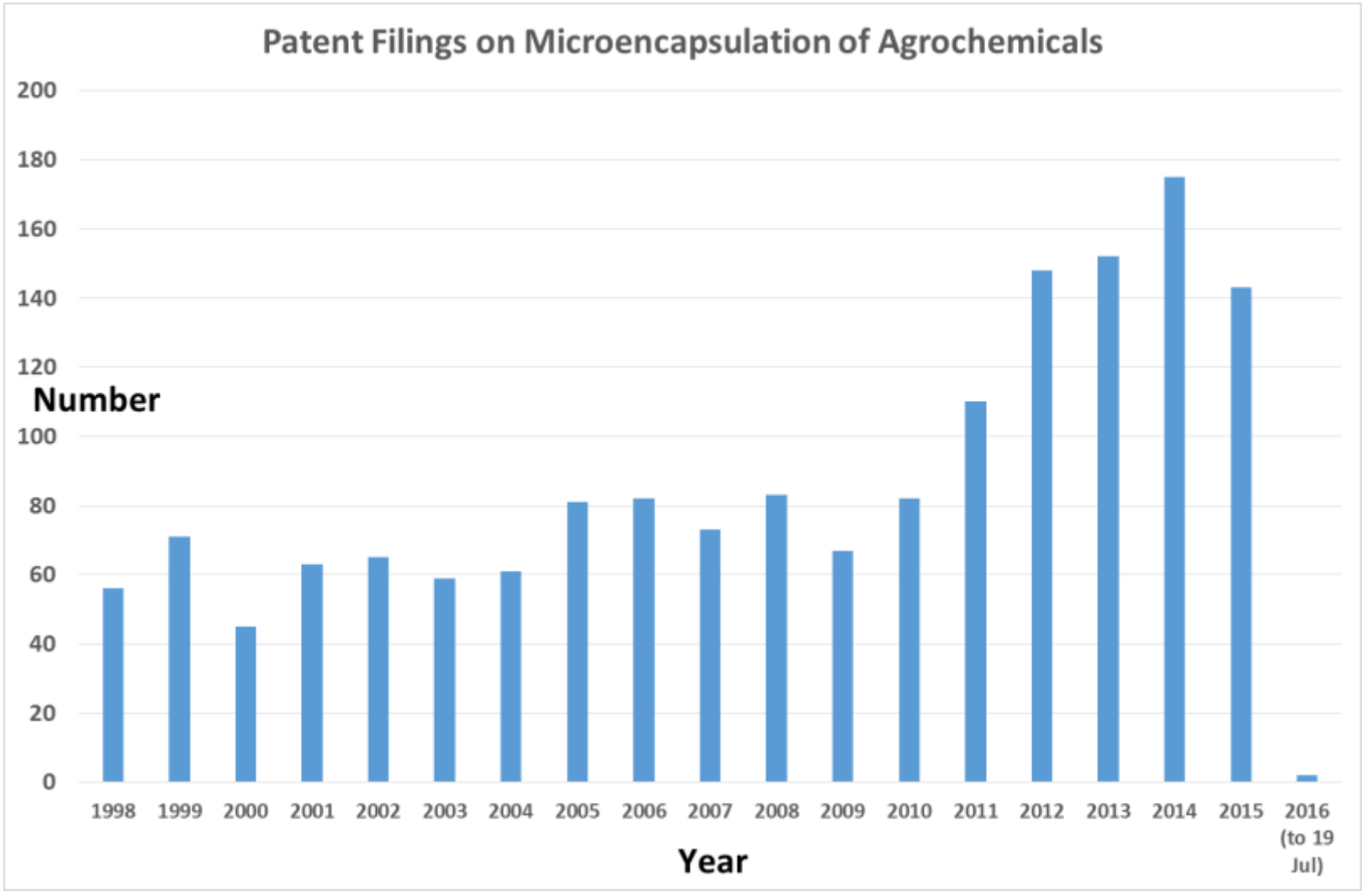
"Agrochemical large companies are constantly exploring the possibilities offered by nanotechnology, among other innovative technologies. However, at present, no significant data have been obtained in the development and impact of these products. **Nanotechnology is not seen by agrochemical industry as a technology that will have a major impact** on the crop protection industry in the foreseeable future and so far no agrochemical product is intentionally manufactured as a nanomaterial by these companies."

EU JRC Scientific and Policy Reports, Claudia Parisi, Mauro Vigani and Emilio Rodríguez-Cerezo, ISBN 978-92-79-37917-8 via https://ec.europa.eu/jrc/sites/default/files/ipts_jrc_89736_(online)__final.pdf

Despite numerous publications on potential safety issues and novel particles, our survey of launches and announcements confirms this position – for agrochemicals

IS MICROENCAPSULATION A BIG THING THEN?

Microencapsulation of Agrochemicals: Patents Only



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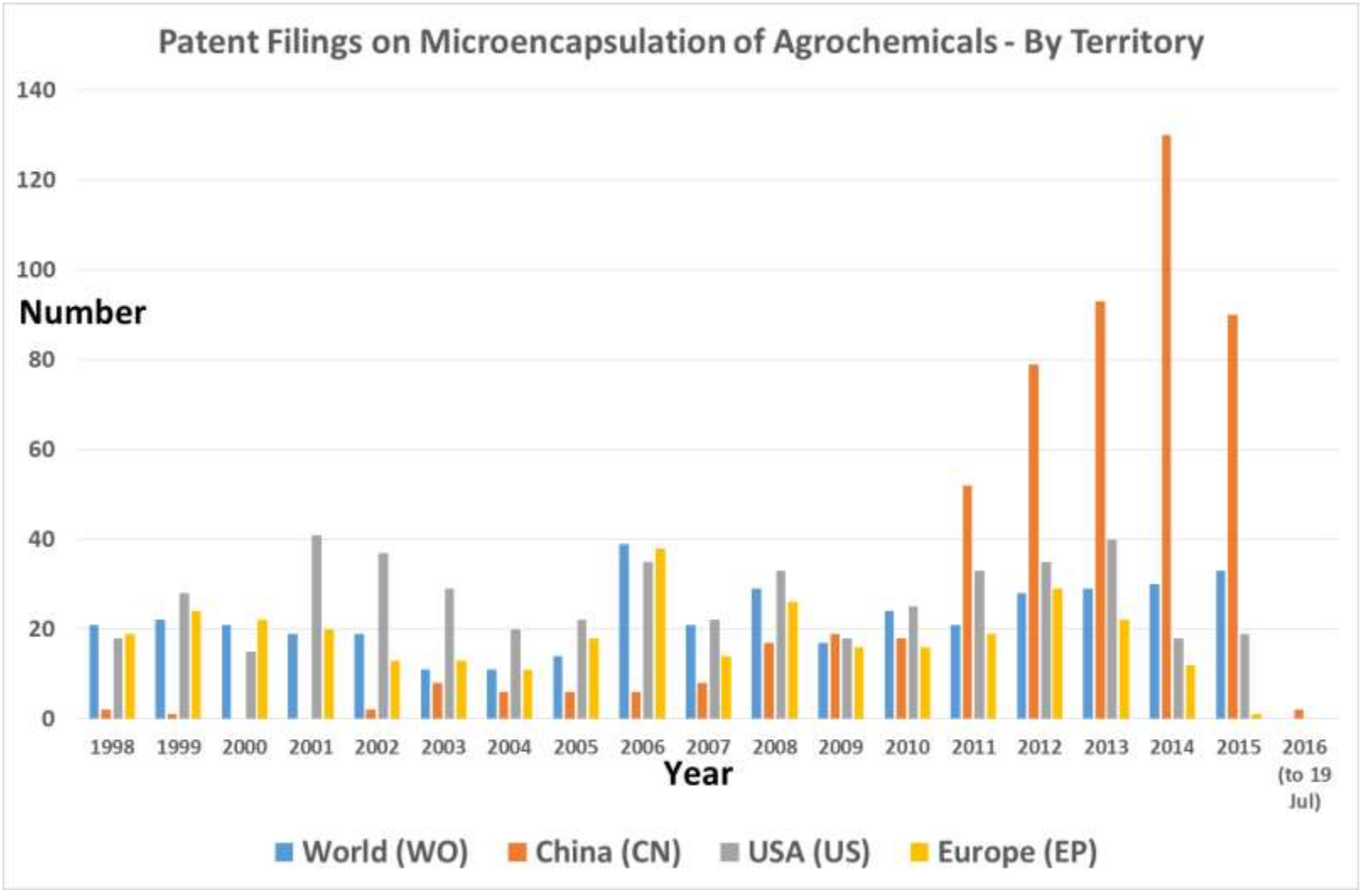
Data from Google Patents

Where is the Patent Spike Coming From?



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Patent Filings in Microencapsulation by the Agrochemical Majors

Year	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
Syngenta	1	3	4	6	5	2	1	4	7	2	2	2	3	4	10	2	0	4
Bayer	3	5	3	4	2	1	1	0	3	3	4	1	1	0	0	0	0	0
BASF	0	2	0	0	0	0	1	1	2	0	5	4	2	1	7	1	6	1
Dow	0	0	0	0	0	0	0	0	1	0	3	3	2	2	7	6	1	3
DuPont	0	2	0	2	0	1	0	1	5	1	3	1	0	2	0	2	0	0
Monsanto	0	0	0	1	1	1	0	3	0	0	2	0	0	1	0	1	1	4

Some Examples of Recent Activity in Microencapsulation and Controlled Release of Agrochemicals (1)

- Microencapsulation of the fungicide tebuconazole in seed coatings using solvent evaporation;
- Molecular encapsulation of the fungicide carbendazim using cyclodextrins.
- Microencapsulation to allow stable high concentration formulations of low-melting solid active ingredients (e.g. fluroxypyr-meptyl) EP2773193A1
- Incorporation of tebuconazole in porous hollow silica nanospheres, to provide controlled release properties. AI dissolved in solvent and combined with tetraethyl orthosilicate. Droplets volatilized to produce nanospheres incorporating AI
- Alginate/chitosan nanoparticles as carrier for paraquat. Calcium chloride was added to sodium alginate solution containing AI. Chitosan solution added to form the nanoparticles
- Polycaprolactone nanocapsules used to encapsulate the herbicides ametryn, atrazine and simazine

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COMPLEX MIXTURE FORMULATIONS AND RESISTANCE

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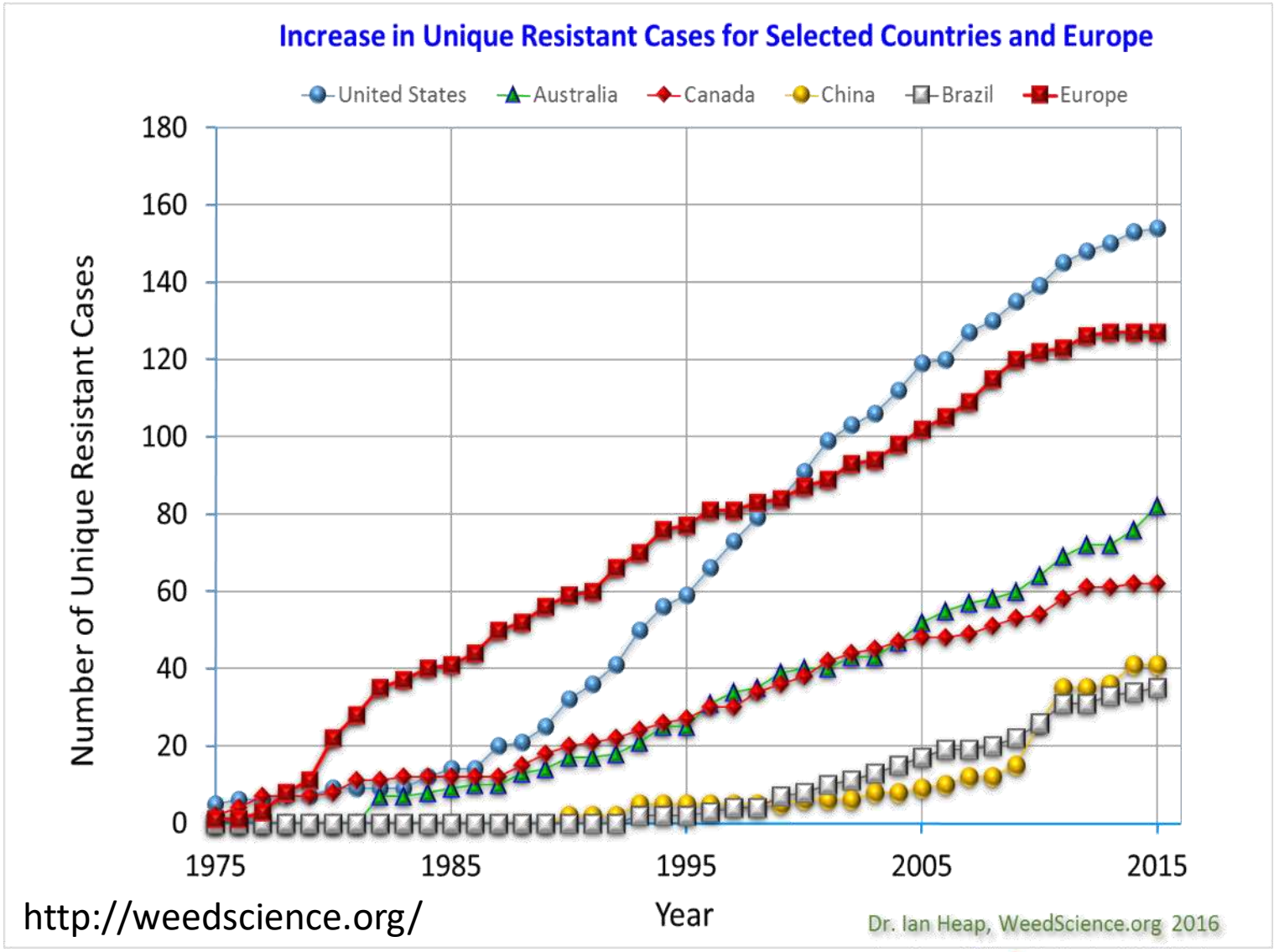
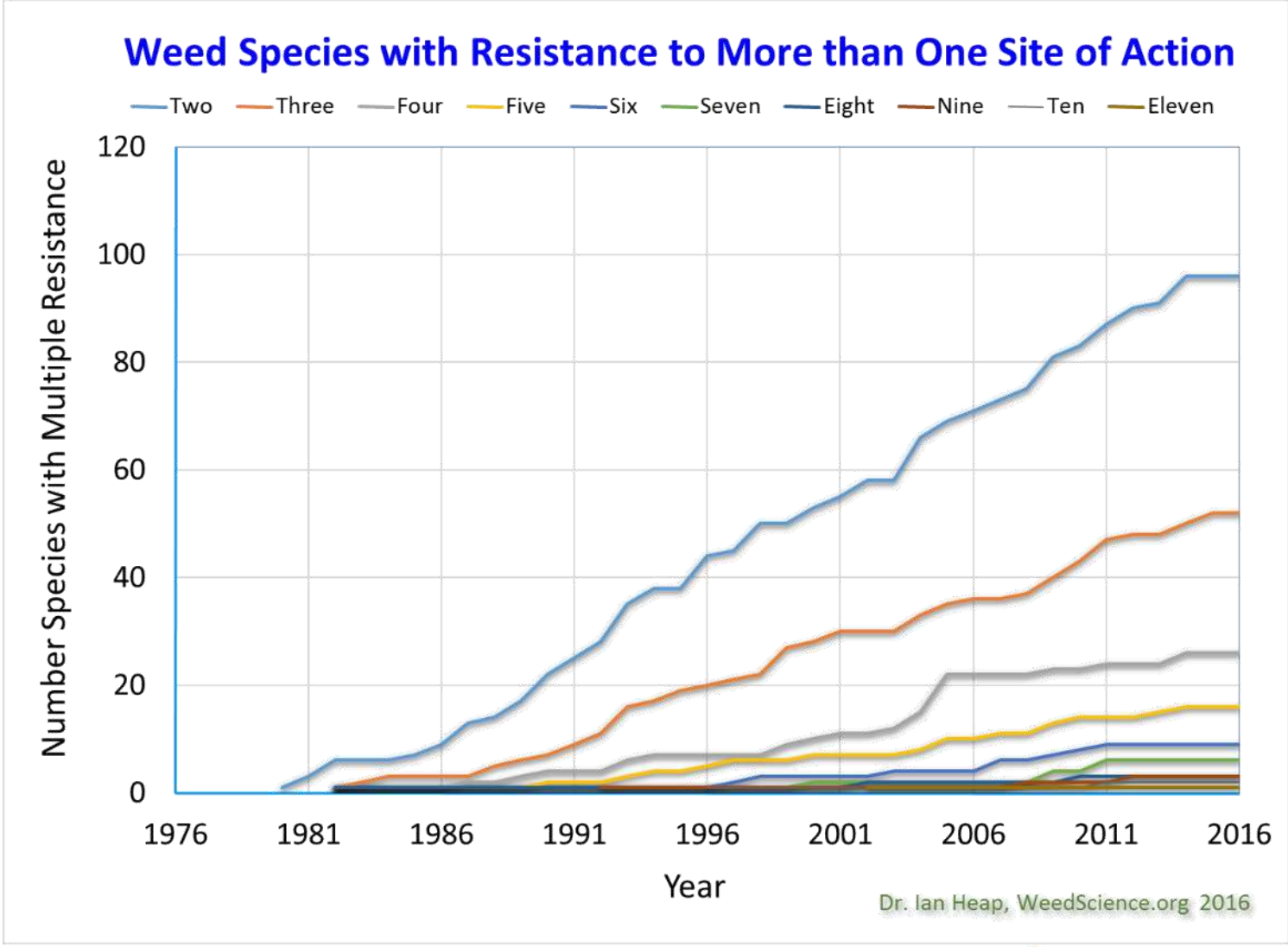
Herbicide Resistance: All Regions, but USA Dominates



Developing Multiple Resistance



Example of Herbicide Mixture Formulations: Acuron (Syngenta)

Active	Class	Group HRAC/WSSA	Proportion	Solubility mg/l	M.Pt °C	VP mPa	Log K_{ow}
Bicyclopyrone	triketone	F2/27	0.65%	1.19×10^5	65.3	<0.005	-1.2
Mesotrione	triketone	F2/27	2.6%	1.5×10^4	165	<0.00569	<-1.0
S-Metolachlor	chloroacetamide	K3/15	23.4%	480	-61.1	3.7	3.05
Atrazine	1,3,5-triazine	C1/5	10.93%	33	175.8	0.0385	2.5
Benoxacor	Herbicide safener for metolachlor	-	<5%	38	104.5	1.8	2.6
MSDS declares <10% propylene glycol and 47.45% “trade secret” Liquid product							

- Syngenta Acuron video http://youtu.be/ApeR5piwLLM via http://www.knowmoregrowmore.com/8636/understanding-the-acuron-corn-herbicide-formulation/
- Described as formulated with liquid capsule suspension technology: ZC (a mixture of Capsule Suspension (CS) and Suspension Concentrate (SC)

SUMMARY

Summary: Agrochemical Formulation 2017

The growth of “new” types (SC, WG etc) at the expense of EC, WP etc appears to have halted (by number at least)

- No good data on formulation types by market value
- Growth of “old” types may be related to increasing generic share
- Appearance of new solvents for EC may be a big factor?

Innovation in formulation appears to be very fragmented

- Publication rate in nanotechnology is not matched by visibility of commercial products
- Publication rate activity in microencapsulation is similarly high, but with relatively few products on the market
- Patent activity from China – how significant is this internationally

Thank You…and Questions

Workshop:
New Developments in Agrochemical Formulation
Friday 10th Nov!

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