Phytotoxicity of different classes of adjuvants

A study for Henkel KgaA, Düsseldorf, Germany

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1. Introduction

Foliar application of pesticides results in coverage of the leaf surface with surfactants that are included in the commercial formulation or included in the spray solution as tank-mix adjuvants. The subsequent foliar absorption of the surfactants can result in severe damage to the leaf tissue. This leaf damage may have (depending on the active ingredient) deleterious effects on the translocation of pesticides in the tissue beneath the drop deposit (Sherrick *et al.*, 1986). A reduced pesticide efficacy can be the result. Whether some degree of surfactant phytotoxicity is just beneficial for the efficacy of an active ingredient is not well-known at this stage. From the cosmetic point of view the surfactant-induced leaf damage is a drawback because growers do not want to sell products with necrotic spots on the surface (fruits, pot plants, flowers, vegetables etc.).

The phytotoxicity of surfactants is determined by the amount of surfactant deposited per unit of leaf area, penetration of the surfactant into the leaf and their cellular toxicity. On plants that are difficult to wet, the surfactant concentration in the spray solution determines the retention of spray solution and thus the amount of surfactant deposited on the foliage (De Ruiter *et al.*, 1990). Further, the physical-chemical properties of the surfactants play a dominant role. The phytotoxicity of surfactants depends on the EO (ethylene oxide)content and the physical size, the degree of branching, and the chemical nature of the hydrophobic region. Generally, surfactants with a low EO-content are more phytotoxic than surfactants with a high EO-content (Lownds & Bukovac, 1988; Matsui *et al.*, 1992; Gaskin, 1995). Measurement of the leakage of potassium ions from bean leaves (Silcox & Holloway, 1986b) demonstrated that surfactants with a low EO content of (4 EO) caused a lower leakage. The authors suggested that the poor water solubility of these surfactants caused this result. With regard to the influence of the structure of the hydrophobic region on the phytotoxicity, the relationships are less clear which is partly due to less systematic efforts on this subject. A linear chain of the hydrophobe may be more toxic than branched chains (Siegel & Halpern, 1964) or sorbitol- (Matsui *et al.*, 1992) or hexitan-based hydrophobes (De Ruiter & Meinen 1996). The length of the C-chains of ethoxylated alkylphenols is relevant to their uptake into different species; an optimum around C12/C13 was suggested (Silcox & Holloway, 1989). A reduction of phytotoxicity when increasing the size of the alkyl chain has been observed (Furmidge 1959). Ethoxylated alkylamine surfactants are relatively toxic to plant cells (Silcox & Holloway, 1986b; De Ruiter & Meinen, 1996). The degree of surfactant phytotoxicity depends on the type of surfactant and its structure as summarized above. Besides, the plant species is also relevant. Gaskin (1995) suggested an optimum for both EO-content and the hydrophobic size according to plant species.

In this study we applied the adjuvants on tomato (*Solanum lycopersicum* L.) and on wheat (*Triticum aestivum* L.) by using 1-µl drops and a spray. Individual application of 1-µl drops enables us to circumvent the influence of spray retention and the phytotoxicity is determined by surfactant penetration alone. Besides, the use of relatively large 1-µl drops results in more surfactant deposited per unit of leaf surface which enhances the sensitivity of the measurements.

The general scope of the project is developing substitutes for the persistent and phytotoxic ethoxylated nonylphenols. The objective of this study was to range the phytotoxicity of different adjuvant types. Biodegradability was one of the criteria used for the selection of the adjuvants.

2. Materials and methods

2.1. Plant material

Tomato ('Meran') and winter wheat ('Vivant') were grown in 11-cm diam. pots filled with a mixture of sand and humic potting soil (1:2, v/v). Tomato was thinned to one plant per pot and wheat was thinned to two plants per pot. The plants were grown in a greenhouse under the following conditions: additional light (high-pressure mercury lamps, 12 h), 18/12°C (light on/light off) temperature and 60/80 % relative humidity. The pots were placed on subirrigation matting which was wetted regularly with water and twice a week with nutrient solution. After treatment, the foliage was not wetted to prevent run off of the adjuvants. Tomato (7 cm tall) had 4 unfolded leaves at the time of treatment and wheat was treated at the 3-leaf stage (20 cm tall).

2.2. Adjuvants

Twenty-three adjuvants were tested and compared with a polyoxyethylene (10) nonylphenol. This adjuvant has a persistent character and was included as a reference compound. The other adjuvants belonged to the following classes; alkyl polyglycosides, polyalkoxy fatty alcohols, methylated polyalkoxy fatty acids, esterified polyalkoxy glycerol. The adjuvants are listed according to these groups in Table 1.

2.3. Application of adjuvant solutions and phytotoxicity

The adjuvants were applied in demineralized water at concentrations of 0.005, 0.05, and 0.5 % (w/v) by spraying the plants and using 1-µl drops. When spraying the plants, the solutions were applied with an air-pressured laboratory track sprayer delivering 400 L/ha at 303 kPa. A micro-applicator was used for applying separate 1-µl drops to a discrete and marked area of the adaxial leaf surface. Five discrete drops were applied in a 1.8-cm long row on the central region of the third leaf of tomato (avoiding the veins) and on the second leaf of wheat. The drops were applied to one of the two wheat plants per pot. Leaves were inspected visually at one, two, three and six days after treatment and a phytotoxicity rating (1 to 5) was recorded as described in Table 2. When there was a visual effect of the treatment on the size of the plants, fresh weight of the aerial parts was determined 1 week after treatment.

Table 1. List of products tested on phytotoxicity.

Class	Abbreviation of class	Carbon content alkyl chain[a]	PO/EO content[a,b]	Product name[f]®	Code
Polyalkoxy fatty alcohol	FAL-EO(PO)[e]	10-14	1.2 PO + 6.4 EO	Dehydol 980	A67
		12-14	5 EO	Dehydol LS 5	A68
		12-14	9.5 EO	Dehydol LS 9.5	A69
		12-18	2 EO	Dehydol LT 2	A70
		12-18	5 EO	Dehydol LT 5	A71
		10-18	5 EO	Mergital BL 589	A72
		16-18[c]	5 EO	Eumulgin ET 5L	A73
		16-18[c]	2 EO	Eumulgin VP 3370	A74
Alkyl polyglycoside	APG	8-10	-	Agrimul PG 220	A64
		12-14	-	Agrimul PG 600	A65
		8	-	Agrimul PG 3399	A66
Methylated polyalkoxy fatty acid	FAC-EO-ME	6-10	3 EO	Eumulgin ME 3516	A75
		6-10	6 EO	Eumulgin ME 3517	A76
		8-18	3 EO	Eumulgin ME 3401	A77
		8-18	6 EO	Eumulgin ME 3402	A78
Esterified polyalkoxy glycerol	G-EO(PO)[e]-E	12-14	7 EO	Cetiol HE	A79
		16-18[c,d]	40 EO	Eumulgin RT 40	A80
		16-18[c]	5 EO	Eumulgin CO 3371	A81
		16-18[c]	3 PO + 3 EO	Eumulgin CO 3522	A82
		16-18[c]	3 PO + 9 EO	Eumulgin CO 3523	A83
		16-18[c]	3 PO + 15 EO	Eumulgin CO 3524	A84
		16-18[c]	3 PO + 30 EO	Eumulgin CO 3525	A85
		16-18[c]	20 EO	Eumulgin CO 3393	A86
Polyglycerin polyhydroxystearat				KE 3190	A87
Polyoxyethylene alkyl phenol	AP-EO	9	10 EO	Dehydrophen 100	A88

[a] Products are polydisperse preparations.
[b] EO=ethylene-oxide, PO=propylene oxide.
[c] The alkyl chain is partly unsaturated.
[d] The alkyl chain is partly hydroxylated.
[e] Some compounds contain propylene oxide.
[f] ® Registered brand names of Henkel Company.

Table 2. Phytotoxicity rating.

Score	Description
1	no discoloration or necrosis
2	slight damage, no necrosis, curling leaf margins
3	necrotic spots
4	complete necrosis without loss of leaf turgor
5	complete necrosis of the droplet areas plus loss of leaf turgor

2.4. Experimental design and data analysis

The two species and the two methods of application were, for practical reasons, not compared in one experiment. Each of the four combinations, species with method of application, was conducted twice as a separate experiment. The experiments are listed in Table 3. The experiments were conducted as a randomized complete block with four replicates. Each block contained two untreated controls. The data from each experiment were subjected to analysis of variance using the Genstat 5 statistical package (Rothamsted Experimental Station, Harpenden, England). The means of treatment and groups of treatments were compared according to Fisher's LSD (0.05) test. The data were also analysed according the Monte Carlo method using 1000 randomizations, to check the validity of the F-test.

Table 3. Experiments in chronological order.

Experiment	Species	Application method	Date of treatment
1	Wheat	Spray	08-07-97
2	Wheat	Drops	15-07-97
3	Tomato	Spray	09-09-97
4	Tomato	Drops	30-09-97
5	Wheat	Spray	21-10-97
6	Wheat	Drops	04-11-97
7	Tomato	Spray	18-11-97
8	Tomato	Drops	09-12-97

3. Results and discussion

The residual variances of the separate experiments in time, investigating a certain combination of species with method of application was such that the data obtained from the two experiments could be pooled (Figure 1, 2 and Tables 4-9). The F-test was validated according to the Monte Carlo method, using 1000 randomizations. This analysis resulted in P-values comparable to the P-values in the F-table. Thus analysis of variance could be used to compare the different treatments.

Careful examination of the data revealed that, in general, necrosis was quite visible three days after treatment (Photos 1 and 2). The concentration dependence of the phytotoxic adjuvants was such that application at 0.005, 0.05, and 0.5 % resulted in no, a little, and severe necrosis, respectively. The data of the 0.5 %-application, recorded three days after treatment discriminated the best between the different adjuvants.

An example of a phytotoxic adjuvant, a polyoxyethylene fatty alcohol (Dehydol LS 9.5) is given (Figure 1). The polyoxyethylene (10) nonylphenol (Dehydrophen 100) included as a reference compound in this study was as phytotoxic as Dehydol LS 9.5 on tomato but less phytotoxic than this compound when applied on wheat (Tables 4-9, Figures 3-6). A methylated polyalkoxy fatty acid (Eumulgin ME 3402) is an example of an adjuvant that is phytotoxic on tomato and not phytotoxic on wheat (Figure 2)

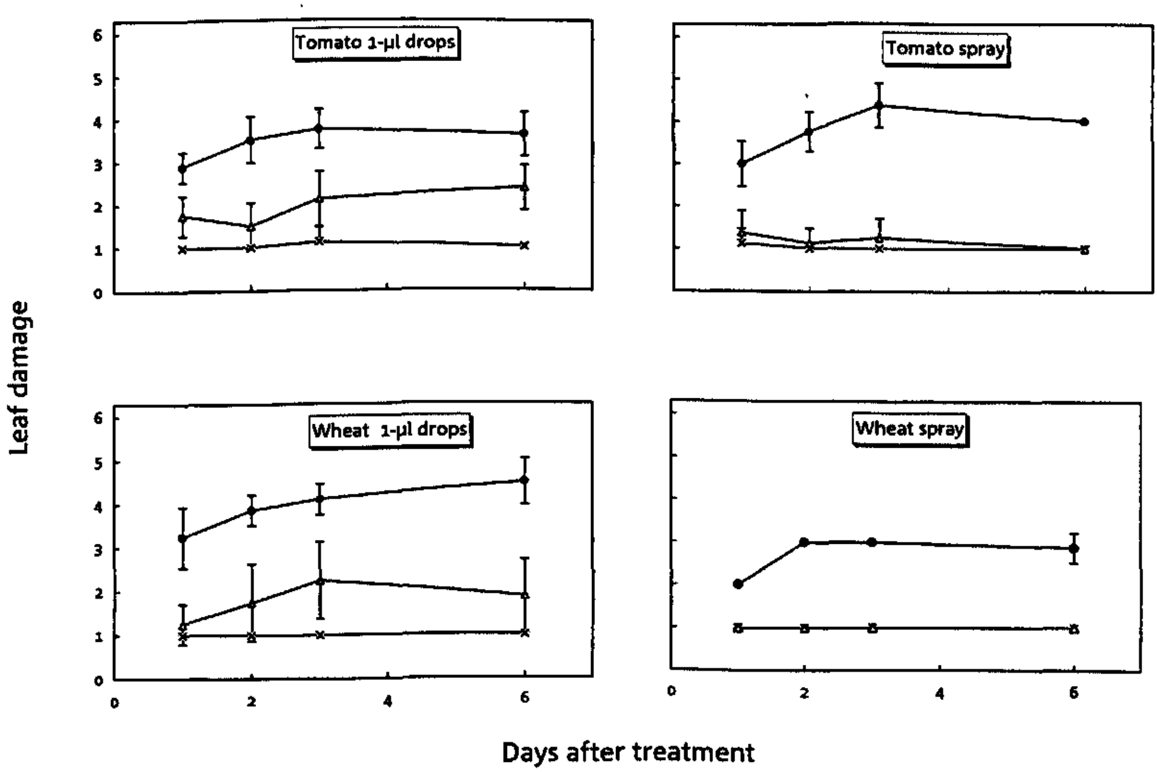

Figure 1. Influence of time and adjuvant concentration [0.005 % (x); 0.05 % (Δ); 0.5 % (•)] on the appearance of necrosis. The adjuvant tested was an ethoxylated fatty alcohol (Dehydol LS 9.5). Data are means (bar = SD) of two experiments with each four replications.

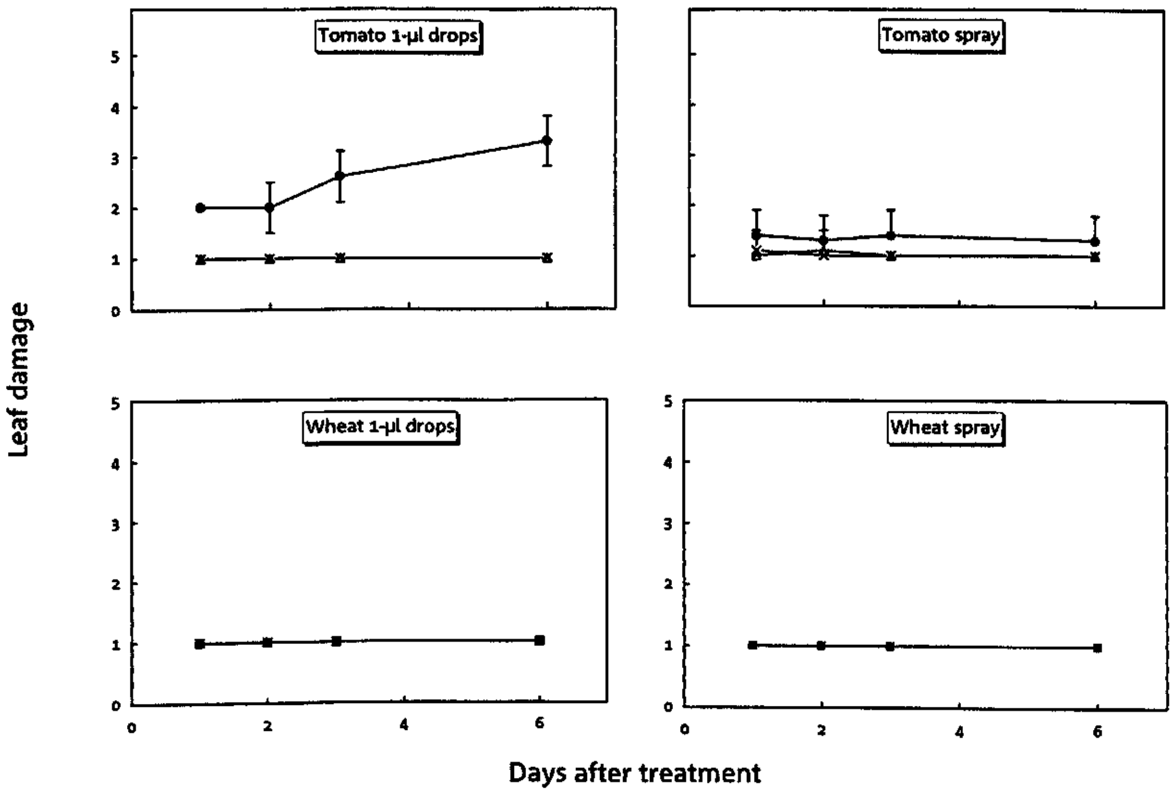

Figure 2. Influence of time and adjuvant concentration [0.005 % (x); 0.05 % (Δ); 0.5 % (•)] on the appearance of necrosis. The adjuvant tested was a methylated polyalkoxy fatty acid (Eumulgin ME 3402) Data are means (bar = SD) of two experiments with each four replications.

The data (Tables 4-9, Figures 3-6) indicate that tomato responded more strongly than wheat and that, generally, 1-µl drops resulted in more necrosis than a spray application. As was stated in the introduction the use of relatively large 1-µl drops resulted in more surfactant deposited per unit leaf surface in comparison with the spray application. We calculated that application of 1-µl drops will result in a ten times higher deposition of surfactant per unit of leaf surface than the application of the spray drops with a volume around 0.004 µl. We therefore expected the more severe necrosis observed when 1-µl drops were applied. The necrosis results from two steps: movement of the surfactants across the leaf cuticle and the subsequent interaction with the cell membrane. Our data presented in this study do not indicate the cause for the differences between adjuvant types. Cell membranes are relatively uniform with regard to the phospholipid bilayer as an essential structure in the membrane. At this stage we only suggest that it is more likely that the permeability of the cuticle and/or the apoplastic route from the leaf cuticle to the cell membrane via the primary cell wall may cause the differences between adjuvant types.
The cuticular surface of wheat is covered with epicuticular crystalline waxes and tomato has a smooth cuticular leaf surface (De Ruiter *et al.*, 1990). This difference in physical configuration does not simply indicate that tomato is more susceptible to surfactants than wheat. A species like pea covered with epicuticular crystalline waxes absorbed relatively easily 2,4-D derivatives (De Ruiter *et al.*, 1993) and a surfactant (Silcox & Holloway, 1986a).

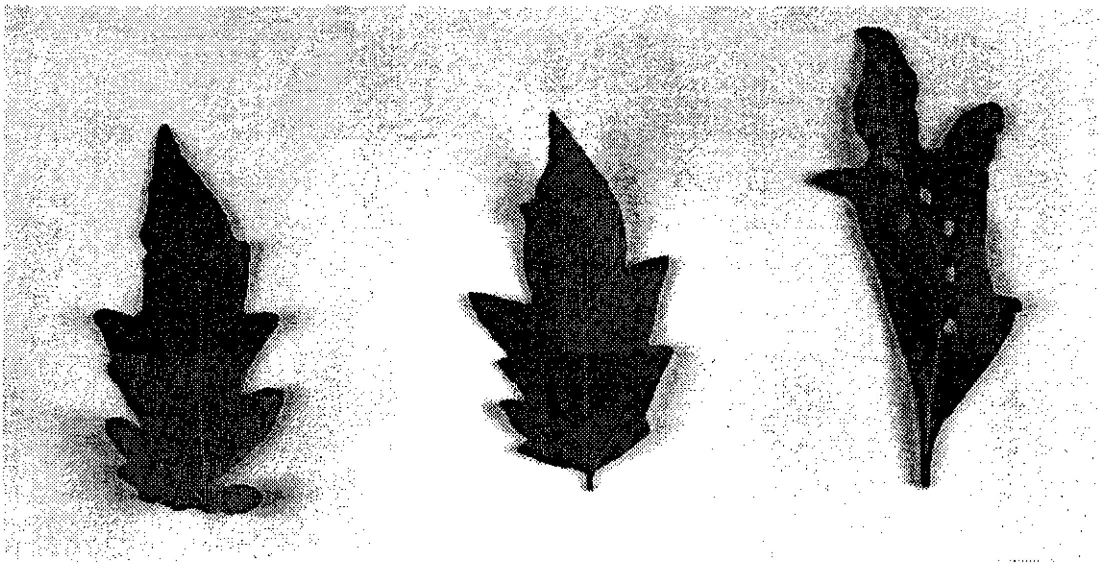

Photo 1. Effect of a polyalkoxy fatty alcohol, Dehydol LT 5, on tomato leaves after application of 1-µl drops containing surfactant at 0.005, 0.05 and 0.5 %, respectively.

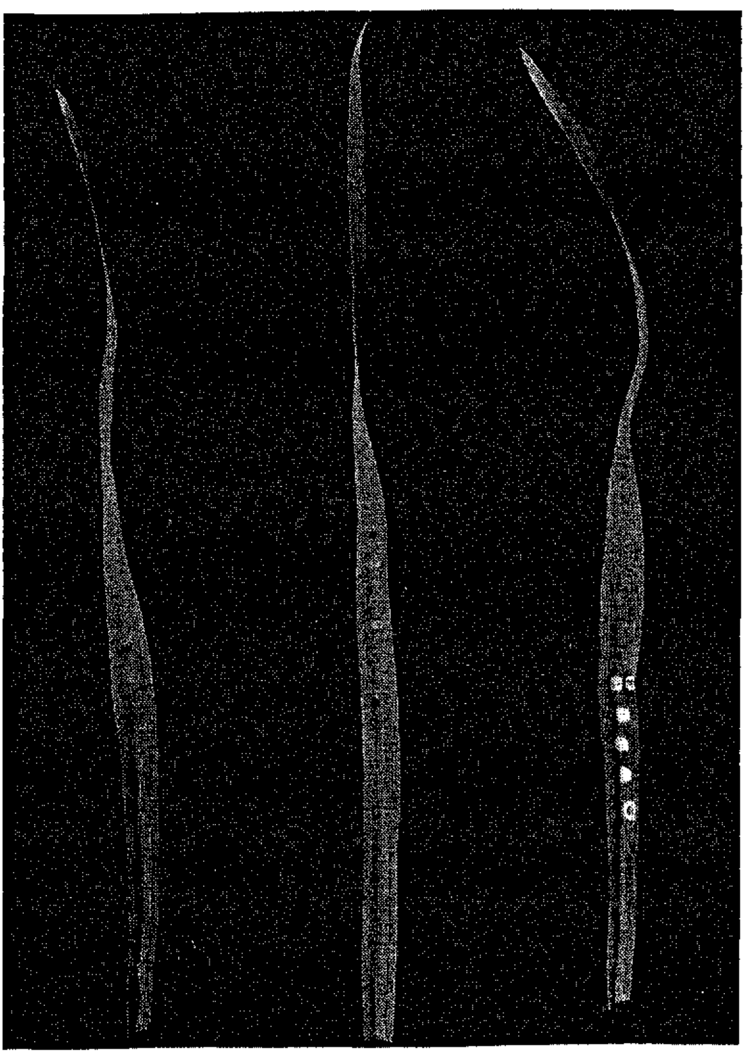

Photo 2. Effect of a polyalkoxy fatty alcohol, Dehydol LS 9.5, on wheat leaves after application of 1-µl drops containing surfactant at 0.005, 0.05 and 0.5 %, respectively.

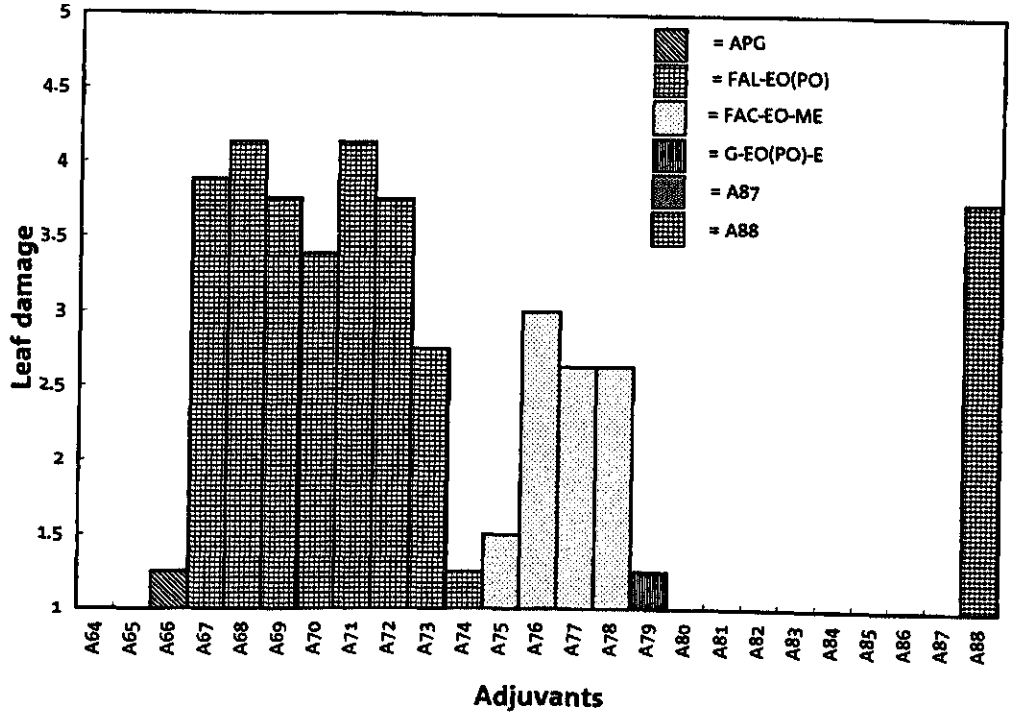

Figure 3. Phytotoxicity of the compounds on tomato, 3 days after drop-application and applied at 0.5 % (LSD = 0.3).

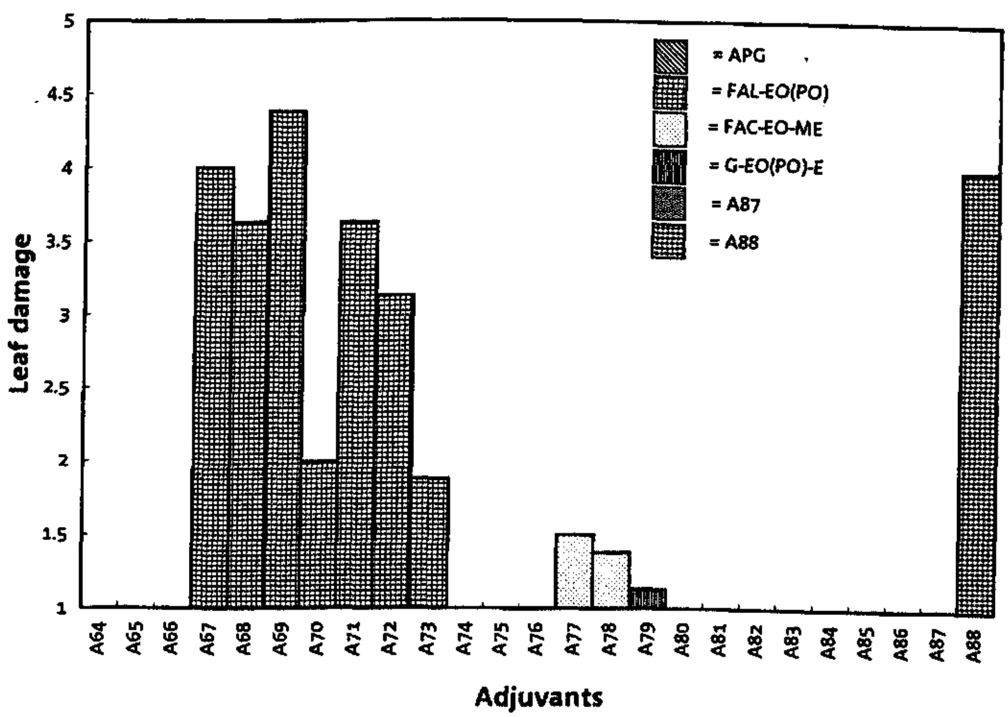

Figure 4. Phytotoxicity of the compounds on tomato, 3 days after spraying and applied at 0.5 % (LSD = 0.2).

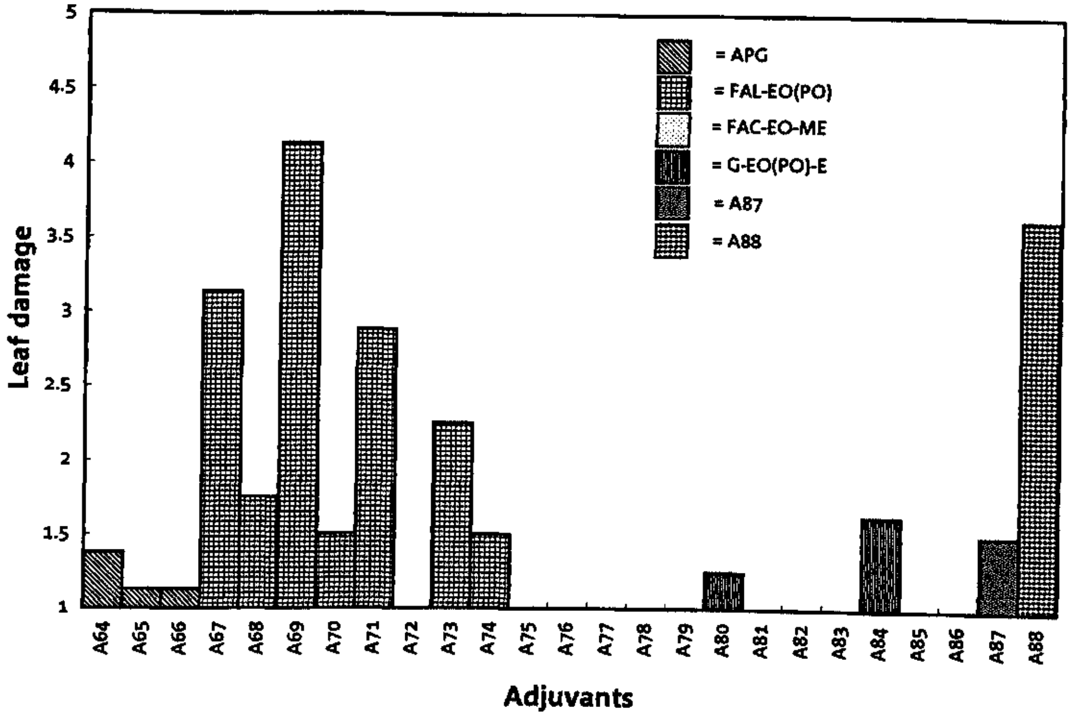

Figure 5. Phytotoxicity of the compounds on wheat, 3 days after drop-application and applied at 0.5 % (LSD = 0.3).

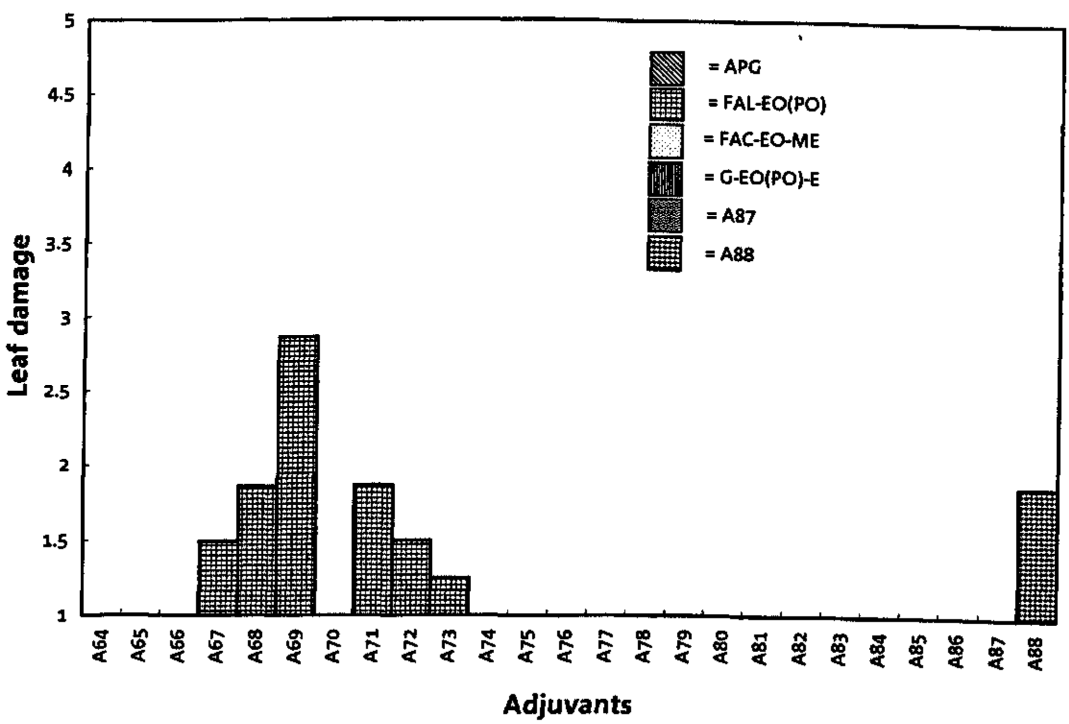

Figure 6. Phytotoxicity of the compounds on wheat, 3 days after spraying and applied at 0.5 % (LSD = 0.2).

Regarding the appearance of necrosis, three groups of adjuvants could be distinguished (Tables 5, 7 and 9): no phytotoxic effects on both species, phytotoxic effects on both species, and phytotoxic effects on one of the two species. The first group comprises: the alkyl polyglycosides (APG), and the esterified polyalkoxy glycerols [G-EO(PO)-E]. The second group comprises the polyalkoxy fatty alcohols [FAL-EO(PO)] and the polyoxyethylene (10) nonylphenol. The third group comprises the methylated polyalkoxy fatty acids (FAC-EO-ME), being phytotoxic on tomato.

The phytotoxicity of polyoxyethylene alcohols and that of the polyoxyethylene alkyl phenols are well known (Gaskin, 1995) but phytotoxicity data on the other classes are not well known in the public domain as indicated by our literature system and a literature search from 1995 up to now.

The different phytotoxicity levels observed within the class of the polyalkoxy fatty alcohols (Table 4) and the phytotoxicity observed with Dehydrophen 100, correlate with eye irritation data of similar compounds (Henkel, personal communication). The polyalkoxy fatty alcohols, and the methylated polyalkoxy fatty acids were more toxic on tomato (Tables 4-9, Figures 3-6) than on wheat. At this stage we can only speculate that the end-capping of the EO chain by methyl and/or the additional carbonyl group resulted in a lower level of phytotoxicity of the methylated polyalkoxy fatty acids on tomato and the absence of phytotoxicity on wheat. We just suggest that the carbonyl group makes the hydrophobe more polar, which may explain that the both C8-18 methylated polyalkoxy fatty acids are more phytotoxic on tomato than the C6-10 methylated polyalkoxy fatty acids (Table 8). The influence of the carbonyl group will be less pronounced with a longer alkyl chain. To test this hypothesis, alkoxylated alcohols and alkoxylated fatty acids (without end-capping) should be compared. Our study did not explain the very low phytotoxicity of the alkyl polyglycosides and the esterified polyalkoxy glycerols. When comparing all adjuvants (Table 1) it seems unlikely that the carbon content of he C-chain determined the differences in phytotoxicity because the contents are similar for different classes.

Table 4. Phytotoxicity of the compounds 3 days after treatment and applied at 0.005 %.

Class	Product name®	Code	Phytotoxicity[a,b] tomato 1-µl drops	tomato spray	wheat 1-µl drops	wheat spray
Polyalkoxy fatty Alcohol [FAL-EO(PO)]	Dehydol 980	A67	1.1	1	1	1
	Dehydol LS 5	A68	1	1	1	1
	Dehydol LS 9.5	A69	1.1	1	1	1
	Dehydol LT 2	A70	1	1	1	1
	Dehydol LT 5	A71	1	1	1	1
	Mergital BL 589	A72	1	1.1	1	1
	Eumulgin ET 5L	A73	1.1	1	1	1
	Eumulgin VP 3370	A74	1	1	1	1
Alkyl Polyglycoside [APG]	Agrimul PG 220	A64	1	1	1	1
	Agrimul PG 600	A65	1	1	1	1
	Agrimul PG 3399	A66	1	1	1	1
Methylated Polyalkoxy fatty acid [FAC-EO-ME]	Eumulgin ME 3516	A75	1	1	1	1
	Eumulgin ME 3517	A76	1.1	1	1	1
	Eumulgin ME 3401	A77	1	1	1	1
	Eumulgin ME 3402	A78	1	1	1	1
Esterified Polyalkoxy Glycerol [G-EO(PO)-E]	Cetiol HE	A79	1	1	1	1
	Eumulgin RT 40	A80	1	1	1	1
	Eumulgin CO 3371	A81	1	1	1	1
	Eumulgin CO 3522	A82	1	1	1	1
	Eumulgin CO 3523	A83	1	1	1	1
	Eumulgin CO 3524	A84	1	1	1	1
	Eumulgin CO 3525	A85	1	1	1	1
	Eumulgin CO 3393	A86	1	1	1	1
Polyglycerin polyhydroxystearat	KE3190	A87	1	1	1	1
Polyoxyethylene alkyl phenol	Dehydrophen 100	A88	1	1	1.3	1
	LSD (0.05)		0.3	0.2	0.3	0.2

Table 5. Phytotoxicity per product class, based on results obtained 3 days after treatment and compounds applied at 0.005 %.

Product class	Phytotoxicity[a,b] tomato 1-µl drops	tomato spray	wheat 1-µl drops	wheat spray
FAL-EO(PO)	1	1	1.1	1
APG	1	1	1	1
FAC-EO-ME	1	1	1	1
G-EO(PO)-E	1	1	1	1
LSD (0.05)	0.3	0.3	0.3	0.1

[a] Visual assessment using a scale of 1 = no effect to 5 = severe necrosis plus loss of leaf turgor.
[b] Mean values of two experiments with each four replicates.

Table 6. Phytotoxicity of the compounds 3 days after treatment and applied at 0.05 %.

Class	Product name®	Code	Phytotoxicity[a,b] tomato 1-µl drops	tomato spray	wheat 1-µl drops	wheat spray
Polyalkoxy fatty	Dehydol 980	A67	1.5	1	1	1
Alcohol	Dehydol LS 5	A68	1.6	1	1	1
[FAL-EO(PO)]	Dehydol LS 9.5	A69	2.1	1.3	1.9	1
	Dehydol LT 2	A70	1	1	1	1
	Dehydol LT 5	A71	1.3	1.1	1.5	1
	Mergital BL 589	A72	1.1	1	1	1
	Eumulgin ET 5L	A73	1	1	1	1
	Eumulgin VP 3370	A74	1	1	1	1
Alkyl	Agrimul PG 220	A64	1	1	1	1
Polyglycoside	Agrimul PG 600	A65	1	1	1	1
[APG]	Agrimul PG 3399	A66	1.1	1	1	1
Methylated	Eumulgin ME 3516	A75	1	1	1	1
Polyalkoxy	Eumulgin ME 3517	A76	1.1	1	1	1
fatty acid	Eumulgin ME 3401	A77	1	1	1	1
[FAC-EO-ME]	Eumulgin ME 3402	A78	1	1	1	1
Esterified	Cetiol HE	A79	1	1	1	1
Polyalkoxy	Eumulgin RT 40	A80	1	1	1	1
Glycerol	Eumulgin CO 3371	A81	1	1	1	1
[G-EO(PO)-E]	Eumulgin CO 3522	A82	1	1	1.1	1
	Eumulgin CO 3523	A83	1	1	1	1
	Eumulgin CO 3524	A84	1	1	1	1
	Eumulgin CO 3525	A85	1	1	1.3	1
	Eumulgin CO 3393	A86	1	1	1	1
Polyglycerin polyhydroxystearat	KE3190	A87	1	1	1	1
Polyoxyethylene alkyl phenol	Dehydrophen 100	A88	1.4	1.1	1.7	1
	LSD (0.05)		0.3	0.2	0.3	0.2

Table 7. Average phytotoxicity per product class, based on results 3 days after treatment and compounds applied at 0.05 %.

Product class	Phytotoxicity[a,b] tomato 1-µl drops	tomato spray	wheat 1-µl drops	wheat spray
FAL-EO(PO)	1.3	1	1.2	1
APG	1	1	1	1
FAC-EO-ME	1	1	1	1
G-EO(PO)-E	1	1	1.2	1
LSD (0.05)	0.3	0.3	0.3	0.1

[a] Visual assessment using a scale of 1 = no effect to 5 = severe necrosis plus loss of leaf turgor.
[b] Mean values of two experiments with each four replicates.

Table 8. Phytotoxicity of the compounds 3 days after treatment and applied at 0.5 %.

Class [abbreviation]	Product name®	Code	Phytotoxicity[a,b] tomato 1-µl drops	tomato spray	wheat 1-µl drops	wheat spray
Polyalkoxy fatty Alcohol [FAL-EO(PO)]	Dehydol 980	A67	3.9	4	3.1	1.5
	Dehydol LS 5	A68	4.1	3.6	1.8	1.9
	Dehydol LS 9.5	A69	3.8	4.4	4.1	2.9
	Dehydol LT 2	A70	3.4	2	1.5	1
	Dehydol LT 5	A71	4.1	3.6	2.9	1.9
	Mergital BL 589	A72	3.8	3.1	1	1.5
	Eumulgin ET 5L	A73	2.8	1.9	2.3	1.3
	Eumulgin VP 3370	A74	1.3	1	1.5	1
Alkyl Polyglycoside [APG]	Agrimul PG 220	A64	1	1	1.4	1
	Agrimul PG 600	A65	1	1	1.1	1
	Agrimul PG 3399	A66	1.3	1	1.1	1
Methylated Polyalkoxy fatty acid [FAC-EO-ME]	Eumulgin ME 3516	A75	1.5	1	1	1
	Eumulgin ME 3517	A76	3	1	1	1
	Eumulgin ME 3401	A77	2.6	1.5	1	1
	Eumulgin ME 3402	A78	2.6	1.4	1	1
Esterified Polyalkoxy Glycerol [G-EO(PO)-E]	Cetiol HE	A79	1.3	1.1	1	1
	Eumulgin RT 40	A80	1	1	1.3	1
	Eumulgin CO 3371	A81	1	1	1	1
	Eumulgin CO 3522	A82	1	1	1	1
	Eumulgin CO 3523	A83	1	1	1	1
	Eumulgin CO 3524	A84	1	1	1.6	1
	Eumulgin CO 3525	A85	1	1	1	1
	Eumulgin CO 3393	A86	1	1	1	1
Polyglycerin polyhydroxystearat	KE3190	A87				1
Polyoxyethylene alkyl phenol	Dehydrophen 100	A88	3.8	4	3.6	1.9
	LSD (0.05)		0.3	0.2	0.3	0.2

Table 9. Average phytotoxicity per product class, based on results 3 days after treatment and compounds applied at 0.5 %.

Product class	Phytotoxicity[a,b] tomato 1-µl drops	tomato spray	wheat 1-µl drops	wheat spray
FAL-EO(PO)	3.4	3	2.3	1.6
APG	1.1	1	1.2	1
FAC-EO-ME	2.4	1.2	1	1
G-EO(PO)-E	1	1	1.1	1
LSD (0.05)	0.3	0.3	0.3	0.1

[a] Visual assessment using a scale of 1 = no effect to 5 = severe necrosis plus loss of leaf turgor.

[b] Mean values of two experiments with each four replicates.

We can only speculate that the glycoside part in the APG class and the glycerol-based structure of the G-EO(PO)-E class hinder passage of the leaf cuticle and/or a strong interaction with cell membranes. The glycoside- and glycerol-based structures deviate strongly from the more linear structure of the polalkoxy alcohols and polyalkoxy fatty acids and we suggest that linearity favours diffusion across the leaf cuticle and interaction with cell membranes. A very low toxicity to plant cells was also recorded (Matsui *et al.*, 1992) for the sorbitol-based surfactant Tween 20 (polyoxyethylene (20) sorbitan monolaurate) and the hexitan-based surfactant Atplus 201 (De Ruiter & Meinen, 1996).

It is well known that high EO-content surfactants are less phytotoxic (Lownds & Bukovac, 1988; Matsui *et al.*, 1992; Gaskin, 1995). The more hydrophilic character of a high EO-content surfactant and its increased size may hinder diffusion of the surfactant across the lipophilic leaf cuticle and the subsequent interaction with the cell membrane. In this study the EO-content of the fatty alcolohols was realitively low. We expect the fatty alcohols with an EO-content higher than 20 will be much less phytotoxic.

In this study we also conducted a preliminary visual assessment of the turbidity of the adjuvant solutions at 0.5 %. In collaboration with Wageningen Agricultural University (Dept. Molecular Sciences, Dr. Arie de Keizer) we also measured the particle size of the adjuvant solutions (0.05 %) using dynamic light scattering. The last method was hindered by the heterodisperse character of the adjuvants and dependence on the history (preparation and storage) of the adjuvant solutions. In spite of these problems we found some relations between particle size and surfactant structure.

Turbidity of the polyalkoxy fatty alcohols: Dehydol LT 2 and Eumulgin VP 3370 gave turbid solutions and Eumulgin ET 5L gave an intermediate turbidity. EO-content and the partly unsaturated character of the alkylchain of the Eumulgin alcohol products may cause this outcome. The alkyl polyglycoside solution were clear solutions. Turbidity and the polyalkoxy fatty acids: only the Eumulgin ME 3402 gave a clear solution; the 3EO ester solutions were more turbid than the 6EO esters with Eumulgin ME 3401 giving the most turbidity. It looks as if EO-content and the C-content of the alkylchain determined the turbidity. The solutions of the glycerol-based product were turbid except Cetiol HE, Eumulgin RT 40 and Eumulgin CO 3525. Again EO-content and C-content of the alkyl chain seem to be relevant. For all compounds there was no clear relation between turbidity and phytotoxicity.

For the polyalkoxy fatty alcohols the particle size varied from 6.7 nm (Dehydol LS 9.5) to 224 nm (Dehydol LT 2). The particle size of the alkylpolyglycosides varied from 10.2 nm (Agrimul PG 600) to 68.4 nm (Agrimul PG 220). For the methylated polyalkoxy fatty acids the particle size varied from 7.7 nm (Eumulgin ME 3402) to 159.3 (Eumulgin ME 3516). For the glycerol based products the particle size varied from 6 nm (Eumulgin RT 40) to 140.5 nm (Eumulgin CO 3524). It was not unexpected to see that there was a positive correlation between turbidity and particle size.

The spray-application of surfactant solutions to tomato plants resulted in a visible reduction of growth (Photo 3). Therefore, the fresh weight of all plants (treated plus untreated) were measured (Tables 10 and 11). The data of individual treatments (Table 10) demonstrate that four of the polyalkoxy fatty alcohols (Dehydol 980, Dehydol LS 5, Dehydol LS 9.5 and Dehydol LT5) and the reference compound Dehydrophen 100 (all applied at 0.5 %) gave a lower fresh weight than all other treatments. Pooling of the data over the adjuvant classes (Table 11) demonstrated that all product classes reduced the fresh weight at each concentration applied. It is unlikely that a product class like the alkyl polyglycosides, not causing necrosis, will reduce the fresh weight when applied at 0.005 %. Therefore, we suggest that the spraying of demineralized water reduced the growth. We started a control experiment to verify this, but the data were not yet available during the preparation of this report. A theoretical explanation is that the products contained a growth-inhibiting substance. However the lack of a strong concentration-dependence (Table 11) does not support this explanation.

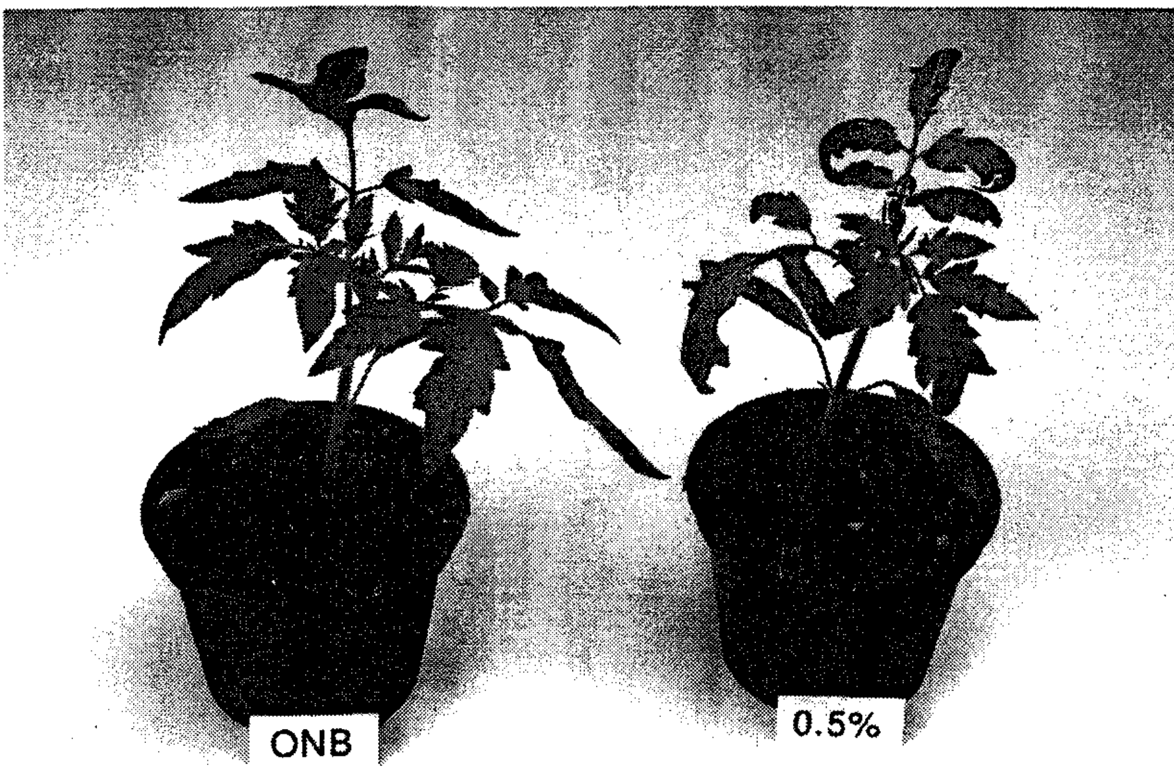

Photo 3. Effect of spray application on size of tomato plants: untreated control plant (left) and tomato plant sprayed with 0.5 % of a polyoxyethylene alkyl phenol, Dehydrophen 100 (right).

Table 10. Fresh weight of tomato plants 1 week after sprayed application of surfactants at 0.005, 0.05 and 0.5 % (LSD (0.05) = 0.58).

Class [abbreviation]	Product name®	Code	Fresh weight (g)[a,b] 0.005 %	0.05 %	0.5 %
Polyalkoxy fatty Alcohol [FAL-EO(PO)]	Dehydol 980	A67	2.34	2.91	1.64
	Dehydol LS 5	A68	3.06	2.58	1.72
	Dehydol LS 9.5	A69	2.85	2.76	1.74
	Dehydol LT 2	A70	2.80	2.73	2.72
	Dehydol LT 5	A71	2.91	3.08	2.10
	Mergital BL 589	A72	2.30	3.16	2.68
	Eumulgin ET 5L	A73	3.01	3.01	3.03
	Eumulgin VP 3370	A74	3.04	2.82	3.23
Alkyl Polyglycoside [APG]	Agrimul PG 220	A64	2.42	2.20	2.15
	Agrimul PG 600	A65	2.44	2.27	2.54
	Agrimul PG 3399	A66	2.08	2.41	2.40
Methylated Polyalkoxy fatty acid [FAC-EO-ME]	Eumulgin ME 3516	A75	3.14	3.29	3.18
	Eumulgin ME 3517	A76	3.38	3.63	3.08
	Eumulgin ME 3401	A77	3.07	2.76	2.91
	Eumulgin ME 3402	A78	3.10	3.12	3.04
Esterified Polyalkoxy Glycerol [G-EO(PO)-E]	Cetiol HE	A79	2.89	2.86	3.01
	Eumulgin RT 40	A80	2.92	3.06	3.00
	Eumulgin CO 3371	A81	3.27	3.33	3.02
	Eumulgin CO 3522	A82	3.16	2.95	2.81
	Eumulgin CO 3523	A83	3.15	2.87	3.11
	Eumulgin CO 3524	A84	3.19	3.14	3.16
	Eumulgin CO 3525	A85	3.13	3.17	3.20
	Eumulgin CO 3393	A86	3.23	3.14	3.27
Polyglycerin polyhydroxystearat	KE3190	A87	3.47	3.11	3.35
Polyoxyethylene alkyl phenol	Dehydrophen 100	A88	3.19	3.99	2.72

Table 11. Average fresh weight of tomato plants 1 week after sprayed application of surfactants at 0.005, 0.05 and 0.5 %, results per product class (LSD (0.05) = 0.38).

Product class	Fresh weight (g)[a,b] 0.005 %	0.05 %	0.5 %
FAL-EO(PO)	2.79	2.88	2.36
APG	2.32	2.29	2.36
FAC-EO-ME	3.17	3.20	3.05
G-EO(PO)-E	3.12	3.06	3.07

[a] Average fresh weight untreated tomato plants is 3.68 g.
[b] Mean values of two experiments with each four replicates.

4. Recommendations

To investigate why surfactant-induced necrosis depends on the surfactant class, the cuticular penetration and the toxicity to plants cells can be investigated. For practical reasons (simplicity and accuracy) we prefer to start with the plant cells. The outcome with plant cells in combination with the whole plant phytotoxity will indicate in how far the surfactant classes differ in their diffusion from the drop deposit to the cell membrane via the leaf cuticle and the primary cell wall.

A logical next step is to combine the Henkel products with active ingredients and to investigate the influence on foliar uptake and efficacy.

5. Conclusion

This report indicates that esterified polyalkoxy glycerols and the alkylpolyglycosides are not or hardly phytotoxic, which may be beneficial in pesticide formulations.

Our study did not point out clearly the influence of EO content and the size of the hydrophobic region on the phytotoxicity of the compounds within a class because these factors were not varied systematically. Besides, a class like the èsterified polyalkoxy glycerols demonstrated a very low phytotoxicity irrespective the degree of alkoxylation.

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