植物葉の濡れの評価

誌名	日本農薬学会誌
ISSN	03851559
著者	渡部, 忠一 山口, 勇
巻/号	16巻3号
掲載ページ	p. 491-498
発行年月	1991年8月

J. Pesticide Sci. **16**, 491–498 (1991)

Original Article

Evaluation of Wettability of Plant Leaf Surfaces*

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(Received February 7, 1991)

A leaf immersion method to evaluate leaf surface wettability was investigated. Retention figures of immersion solutions containing a dye (Direct Fast Scarlet 4BS) 1.0% and surfactant(s) 0.2% on leaf surfaces were classified into six types (A–E and O) and the specific retentions (Up-2) on leaf surfaces were obtained at immersion lengths of more than 10 cm for Gramineae and 5 cm for soybean, cowpea and others with a solution making a continuous thin film (A-1 retention). Up-2 and whole-leaf retentions were measured for 23 crops from eight families. The former fell in a narrow range of *ca.* 0.6–1.1 $\mu l/cm^2$ for all the leaves but the latter was divided into two groups; almost the same retention (Cucurbitaceae, Brassicaceae and Malvaceae) and fairly varied retention (Gramineae, Legminosae and Solanaceae). It was possible to evaluate wettability on specific retention figures with the leaf immersion method we have developed.

INTRODUCTION

When a pesticide is applied to crops and weeds, its bioavailability depends on the retention of its active ingredient on the target plant surfaces. In the case of aqueous spray, retention on plant surfaces, especially on leaves and stems, primarily depends on the wettability of sprayed solution, and the wettability is affected by the kind of formulation and physicochemical properties of the spray solution, application method and its operation conditions, plant species and its stage, circumstance of growth, cultivation conditions and others.[1-9] Retention of an aqueous solution on solid surfaces is governed by parameters such as the surface tension and the contact angles of a droplet formed.[4,6,9-11] The contact angles of a droplet greatly change with the chemical constitution and structure of a solid surface.[12-15] And it is known that the wettability of plant surfaces with liquids is different from spreading properties of a droplet.[4,16,17] In spite of several distinguished studies,[6,17-23] methods for quantitative evaluation of wettability of leaf surfaces have not been well established; wettability of leaf surfaces relating to the retention (quantity and distribution) of pesticidal solutions applied is not fully elucidated on a basis of correlation between leaf surfaces and solutions.

This article describes a leaf immersion method for evaluating leaf wettability on a static and quantitative basis and characteristics of complete wetting on leaves of 23 plants.

MATERIALS AND METHODS

1. *Dye-Surfactant(s) Solution System*

For leaf immersion, aqueous solutions containing a dye (Direct Fast Scarlet 4BS, Colour Index; Direct Red 23, 29160, Mitsubishi Kasei Corp.) by 1.0% and surfactant(s) by 0.2% (based on weight per volume) were adjusted to pH 7.0 and put into polypropylene vessels. The solutions used are shown in Table 1.

2. *Plant Leaves*

Seeds of rice (cv. Aichiasahi), kidney bean (cv. Edogawa), cowpea (cv. Kurodanesanjaku) and soybean (cv. Mitsuguro) were sown and

* Studies on Wetting Phenomena on Plant Leaf Surfaces (Part 1)

Table 1 Physicochemical properties of immersion solutions containing Direct Fast Scarlet 4BS 1.0% and surfactant(s) 0.2%.

No.	Surfactant (w/v%)	Surface tension[a] (mN m^{-1})	Specific gravity[b] (d_4^{21})	Kinematic viscosity[c] (cSt)
1	PEG[d] (MW1000)	63.5	1.0022	1.0670
2	PEG (MW1500)	60.5	1.0024	1.0645
3	Lignosulfonate (Na[e])	53.5	1.0026	1.0545
4	PEG (MW3600)−PPG[f] (MW1800)−PEG (MW3600) block polymer	48.5	1.0022	1.0789
5	POE[g] (n=28[h]) tris(α-phenylethyl)phenyl ether	45.0	1.0022	1.0712
6	POE (n=18) tris(α-phenylethyl)phenyl ether	42.0	1.0024	1.0648
7	PEG (MW600)−PPG (MW1800)−PEG (MW600) block polymer	39.5	1.0023	1.0622
8	POE (n=15) oleyl ether	38.0	1.0020	1.0704
9	POE (n=15) nonyl[i] phenyl ether	37.0	1.0022	1.0585
10	POE (n=12) oleyl ether	36.5	1.0024	1.0606
11	POE (n=12) lauryl ether	35.0	1.0017	1.0601
12	Lauryl sulfate (Na)	33.5	1.0021	1.0742
13	POE (n=10) nonylphenyl ether	32.5	1.0023	1.0631
14	POE (n=10) lauryl ether	32.0	1.0020	1.0738
15	POE (n=8) nonylphenyl ether	31.5	1.0021	1.0764
16	POE (n=15) bis(nonyl)phenyl ether	31.0	1.0018	1.0755
17	Dodecyl[j] benzene sulfonate (Na)	30.5	1.0024	1.0772
18	POE (n=3) tridecyl[k] ether phosphate (Na)	29.5	1.0022	1.0914
19	Di-2-ethylhexyl sulfosuccinate (Na)	28.0	1.0019	1.0905
20	Silwet L-77[l]	21.5	1.0018	1.0506

[a] with du Nöuy's tensiometer at 21°C, [b] with Gay-Lussac's gravity bottle at 21°C, [c] with Cannon-Fenske's opaque viscometer at 21°C, [d] polyethyleneglycol, [e] sodium salt, [f] polypropyleneglycol, [g] polyoxyethylene, [h] average mol. No. of ethylene oxide condensated, [i] branched type, [j] branched type, [k] linear type, [l] supplied by Nippon Unicar Co., and surfactants No. 1–11, 13–16 and 18 were prepared by Toho Chemical Ind. Co. and the others by Tokyo Kasei Kogyo Co.

grown in commercial soils "Kumiai engei-youikubyobaido" and "Kumiai ryujobaido D" in an air-conditioned greenhouse (*ca.* 28°C in the daytime, *ca.* 20°C at night, r.h. *ca.* 70%, watered twice a day, supplementarily illuminated) to the 8–9 true leaf stage (5–6th leaves were used), 4–5 (2–3), 5–6 (2–3) and 4–5 (2–3), respectively. Also used were completely expanded leaves on newly developed branches of weeping forsythia and other plants grown in the same conditions. Five leaves were employed for one measurement plot.

3. Leaf Immersion and Determination of Dye Retention on Leaf Surfaces

Leaves excised 14 cm below leaf tips for rice and at laminar joints of leaves longer than 9 cm for other plants were hung vertically with clasps and immersed gently in solutions by lifting the vessels. After 1 min of immersion, the leaves were taken out of the solutions and dried by letting the solutions down for *ca.* 20 min. Retention figures of the solutions on adaxial and abaxial leaf surfaces were measured during drying, and the leaves were cut into pieces 0.5 cm wide rectangularly to longitudinal leaf axes from immersion front lines. The dye on leaf pieces (on adaxial and abaxial surfaces together) was washed with distilled water to be determined with a spectrophotometer (Model Shimadzu UV-265) at 504 nm. The surface area of each piece was measured with a automatic area meter (Model AAM-8, Hayashi Denko Co.).

4. Determination of the Adsorbed Dye onto Leaf Surfaces

One hundred and fifty milliliters of the solution containing the dye and surfactants at a given concentration was prepared in a 200-ml conical flask and slowly stirred. Leaves to be measured were kept in the solution for an indicated period, then taken out. The quantity of the dye adsorbed was calculated by the difference in absorbance at 504 nm before and after immersion. All the measurements were done at 20–23°C.

RESULTS

1. Retention Figures of Solutions on Leaf Surfaces

Retention figures of solutions on leaf surfaces after immersion varied significantly depending on plant species and the surface tension of the solutions. They were classified into six types (11 subtypes) (Table 2). O means no retention of the solutions in all retention conditions. C-2 is a retention on surface protuberancies such as trichome, hair, papilla, idioblast and the likes except on vein. D-1, E-1 and E-2 are special manners of retention observed on limited areas of leaf surfaces. Actual retention can be described by a combination of these retention figures.

2. Distribution of the Retained Dye on Leaf Surfaces

In the case of a continuous thin film of solution over an entire leaf surface (A-1), the retained solution tended to remain more at the leaf tip in a process of draining off and seemed to make a gradient from an area close to the immersion front line to the leaf tip in several min after immersion. On the contrary, the other figures were formed in a shorter period without making a gradient, since they were formed isolated on leaf surfaces. As the solution No. 13 (32.5 mN m^{-1}) gave a A-1 figure on most of the leaves tested, the following measurements were conducted to clarify the distribution of the retained dye on leaf surfaces. The dye of the solution No. 13 applied on adaxial and abaxial leaf surfaces of some plants was quantitatively recovered by water washing.

2.1 Immersion length and distribution of the dye on leaf surfaces

Leaves were immersed into solutions in two ways; the leaf tip up and down. The longitudinal distribution of the dye from the immersion front line on the leaf surface is shown in Fig. 1. The distribution curves can be regarded to comprise of the initial, constant and gradient regions, which are separated from the immersion front line, *ca.* 1 cm for all the leaves, and *ca.* 7 cm for rice (leaf tips down) and *ca.* 3–4 cm for rice (leaf tips up) and the others. It was considered that the initial region could result from an end position effect by starting of flowing down of solutions, the gradient from

Table 2 Classification of observed retention figures of immersion solutions on leaf surfaces.

Type A	(as a thin film of immersion solution)
	(1) A-1; a continuous thin film all over a leaf surface
	(2) A-2; a fragment of thin film or flattened lacked sphere on a leaf surface except on veins.
Type B	(as a lacked sphere of immersion solution)
	(1) B-1; a lacked sphere or the like on a leaf surface except on veins.
	(2) B-2; a lacked sphere or the like on vein.
	(3) B-3; a lacked sphere or the like as a bridge between on veins.
Type C	(as a thin film of immersion solution only on surface protuberancies)
	(1) C-1; a thin film of immersion solution only on veins.
	(2) C-2[a]; a retention of immersion solution on surface emergences except on veins.
Type D	(as infiltration of immersion solution through surface openings into a leaf inside)
	(1) D-1; infiltration through stomata and/or hydropores.
Type E	(as climbing-up of immersion solution on a leaf surface above immersion front line)
	(1) E-1; climbing up over interveinal surface.
	(2) E-2; climbing up on veins
Type O[b]	(as no retention of immersion solution in any form at all on a leaf surface)

[a] as predicted, not observed, [b] additionally established for no retention.

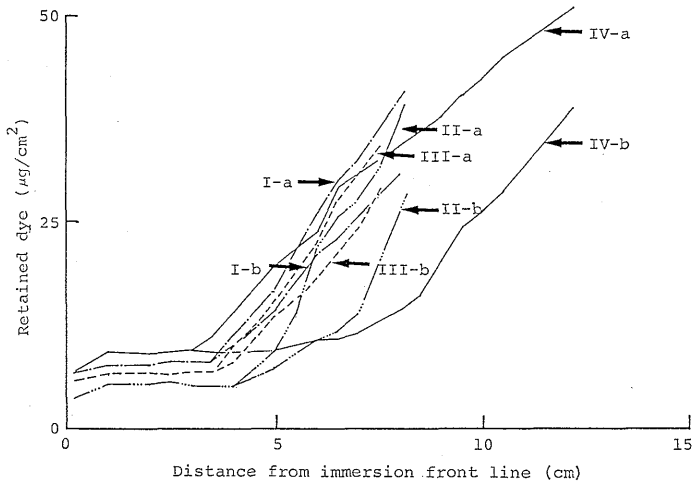

Fig. 1 Distribution of retained dye within immersed area of leaf surface.
Leaves: (I) soybean, (II) cowpea, (III) weeping forsythia, (IV) rice, way of leaf immersion: leaf tips up (a) and down (b).

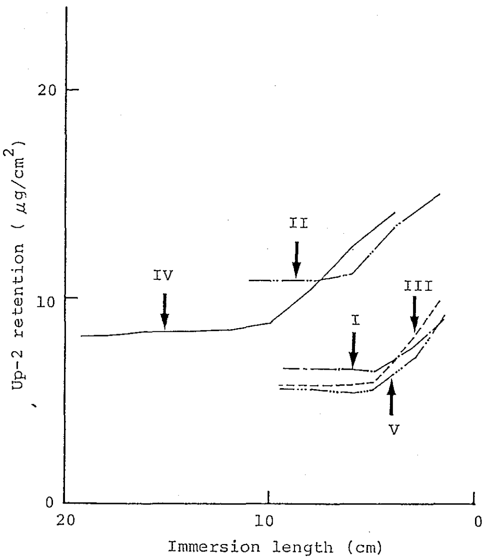

Fig. 2 Relationship between Up-2 retention and immersion length.
Leaves: (I) soybean, (II) cowpea, (III) weeping forsythia, (IV) rice, (V) kidney bean. Way of leaf immersion: leaf tips down.

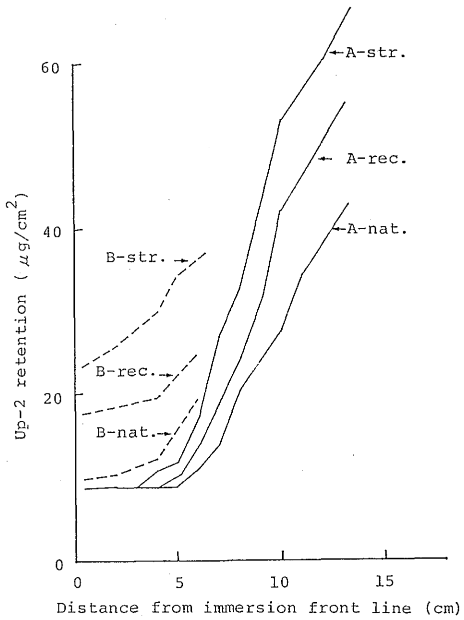

Fig. 3 Relationship between Up-2 retention and leaf-end shapes of rice.
End shape: (str.) straight line, (rec.) rectangular shape, (nat.) natural leaf tips. Immersion length: (A) 14 cm, (B) 7 cm.

a waiting solution at the leaf tip to drain off and the constant from a specific result of interactions between leaf surfaces and solutions. To reconfirm how the constant region appeared, retention of the dye in the area within 1 to 3 cm below the immersion front line (hereafter, Up-2 retention and area) with various immersion lengths were measured (Fig.

2). The critical immersion lengths for the constant region when leaves were immersed with the tips down were obtained; *ca.* 10 cm for rice and *ca.* 5 cm for the others. Up-2 retention differed a great deal between two immersion ways. As the difference could be due to leaf-end shape, retention on rice leaves with various artificial end shapes made by cutting were examined to clarify the effect of leaf-end shape on Up-2 retention (Fig. 3). The result showed that the appearance of the constant region was greatly influenced by leaf-end shape and immersion length. In the following measurements to determine the specific retention as Up-2 on leaf surfaces, immersion length was chosen 14 cm for rice and 9 cm for the others, and immersion was done with leaf tips down. The constant retention was thought to be specific in an area free from the influence of a waiting solution to drain off.

2.2 *Adsorption of the dye onto leaf surfaces during immersion*

How much of the retained dye was adsorbed was investigated with the modified solution No. 13, because the retained dye originally included the adsorbed one as a preferential adsorption of the solute onto leaf surfaces during immersion. The effect of surfactant concentration on the adsorption of the dye onto soybean leaves was examined (Fig. 4) at an immersion period of 5 min and at a concentration of the dye as low as 0.0015% for direct determination by spectrophotometry. The adsorption of the dye was extensively reduced by the co-existence of a surfactant.

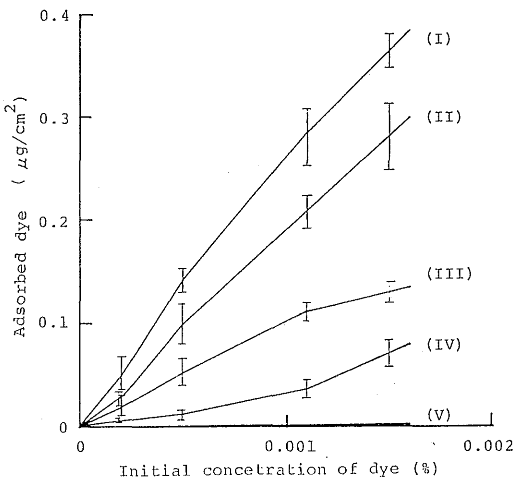

Fig. 4 Effect of surfactant on dye adsorption onto leaf surfaces of soybean.

Surfactant: POE ($n=10$) nonylphenylether, (I) 0%, (II) 0.003%, (III) 0.0075%, (IV) 0.015%, (V) 0.03%. Immersion period: 5 min.

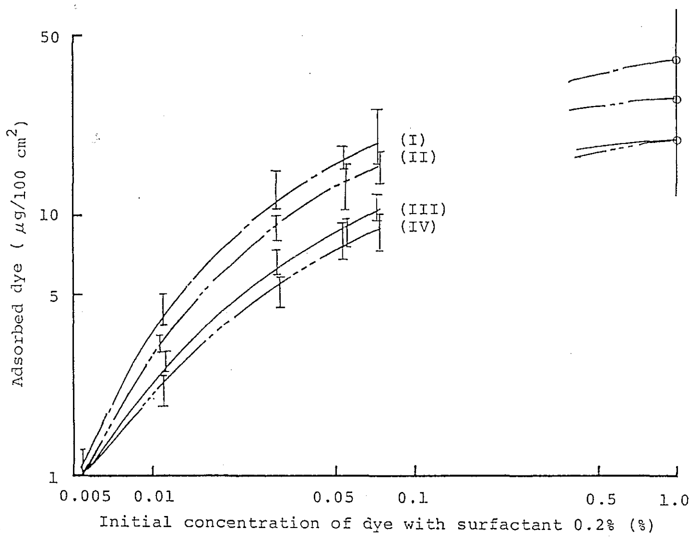

Fig. 5 Dye adsorption onto leaf surfaces in immersion solution with surfactant 0.2%.

Surfactant: POE ($n=10$) nonylphenylether. Leaves: (I) soybean, (II) kidney bean, (III) rice, (IV) cowpea, immersion period: 1 min.

Table 3 Retained volume as A-1 of immersion solution on crop leaf surfaces.

Plants	Tested leaf position/growth stage	Retention (μl/cm²)	
		Specific[a]	Whole leaf[b]
1: Gramineae			
Oryza sativa L. (cv. Aichiasahi)	5–6/8–9	0.86±0.09	1.18±0.17
Triticum aestirum L. (cv. Norin 26)	2–3/4–5	0.60±0.07	1.30±0.21
Holdeum vulgare L. (cv. Nijo)	2–3/4–5	0.64±0.06	1.13±0.11
Avena sativa L.	3–4/5–6	1.10±0.09	1.57±0.20
Secale cereale L.	3–4/5–6	0.83±0.07	1.30±0.22
Panicum miliaceum L.	3/4–5	1.06±0.05	1.50±0.16
2: Legminosae			
Phaseolus vulgaris L. (cv. Edogawa)	2/4–5	0.91±0.07	1.31±0.19
Vigna sinensis Endl. (cv. Kurodanesanjaku)	2/3–4	0.66±0.01	1.00±0.21
Vicia faba L. (cv. Wase)	2/3–4	0.95±0.08	1.68±0.10
Glycine max Merril (cv. Mitsuguro)	2–3/4–5	0.83±0.10	1.96±0.18
3: Solanaceae			
Capsicum annuum L. (cv. Zuiho)	2–3/5–6	0.71±0.06	1.38±0.21
Solanum melongena L. (cv. Tsubakuronaganasu)	2/3–4	0.88±0.16	1.58±0.18
Nicotiana glutinosa L.	2/3–4	1.15±0.15	2.46±0.28
4: Brassicaceae			
Brassica pekinensis Rupr. (cv. Nozaki No. 2)	2/3–4	0.76±0.08	2.41±0.22
Brassica napus L. *var. oleifera* DC. (cv. Natane-C)	2/4–5	0.96±0.07	2.12±0.14
Brassica oleracea var. capitata L. (cv. Hikari kanran)	2–3/4–6	0.85±0.11	2.20±0.24
5: Convolvulaceae			
Ipomea batatas Poiret (cv. Big-one)	3–5/6–8	0.75±0.09	1.14±0.15
6: Malvaceae			
Abelmoschus esculentus (L.) Moench	1–2/3–4	0.75±0.06	1.26±0.15
Gossypium spp. (cv. Tall cotton)	1–2/3–4	0.85±0.05	1.45±0.22
7: Citrus			
Citrus natsudaidai Hayata	4–5/8–9	0.70±0.06	1.65±0.16
8: Cucurbitaceae			
Benincasa hispida Cogn. (cv. Daimarutogan)	1/3–4	0.84±0.11	2.47±0.31
Lagenaria siceraria Standley (cv. Daimaruyugao)	1/3–4	0.80±0.15	2.30±0.24
Lagenaria siceraria Standley (cv. Sennarihyotan)	1/2–3	0.88±0.13	2.78±0.22

[a] specific retention, [b] whole-leaf retention.

This result indicated that the adsorption was influenced by both concentrations of the dye and surfactants. For this reason, the adsorbed dye had to be detected in the actual immersion solutions of 1.0% dye and 0.2% surfactant(s). Since 1.0% is too high to be detected directly, the concentration of the surfactant was fixed at 0.2%, while the dye concentration was changed from 0.0055% to 0.075%, the maximum limit for direct detection, and the result obtained was extrapolated to dye 1.0% (Fig. 5). Preferential adsorption of the dye was estimated to be 0.43 μg/cm² for soybean, 0.29 μg/cm² for kidney bean and 0.21 μg/cm² for rice and cowpea. The extents to which these quantities contributed to the specific retentions were estimated to be 7.1%, 3.4%, 2.8% and 4.7%, respectively, referring to the result from Fig. 2. These figures, which imply an overestimation in introducing the retained volume of solution by multipling 100 by the retained dye, do not seem to give rise to substantial errors in wettability evaluation by the retained volume of solution, though involvement of other surfactants to preferential adsorption of the dye remains to be investigated.

3. Retention of Solution on Leaves of 23 Plants

The specific and whole-leaf retentions of the solution No. 13 were measured on leaves of 23 plants from eight families (Table 3). The retention on leaves of Cucurbitaceae, Brassicaceae and Malvaceae was almost constant but fairly varied in Gramineae, Legminosae and Solanaceae within each family. The specific retention tended to fall in a narrower range of *ca.* 0.6–1.1 $\mu l/cm^2$ for all the leaves but the whole-leaf retention varied to a wider extent depending on families among which leaf tip shapes fluctuated greatly.

DISCUSSION

Wettability of leaf surface was investigated by a leaf immersion method on a concept defined as an ability of leaf surface to form a persistent liquid/solid interface.[4,11,16] Difference and similarity in specific retention among families were considered to result mainly from leaf-surface structures. The specific retention figures of solutions appeared at longer than critical immersion lengths seem to be substantially more important for evaluation of leaf-surface wettability than the retained volumes, because the former can decide the latter in any manner of application. The retention figures were classified into six types (11 subtypes) in this study but other classification can be also possible.[16] Since retention figures of a droplet on a solid surface are known to be governed by surface tension and contact angles (advancing and receding)[4,6,9-11] and these contact angles vary sensitively with chemical constitution and roughness of solid surface,[12-15] the specific retention figure on a leaf surface measured by our method is considered to be an intrinsic and quantitative expression of the integrated result of interactions between a solution and a leaf surface, which (especially micro leaf surface structures) can be variable according to parameters such as plant species, growth stage, nutritional condition, location in a leaf, position in a plant, maturation, vegetation, agricultural meteorology (temperature, humidity, light, wind, snowfall, rainfall *etc.*) and others.[10,11,14,18,19,23] The results obtained by the leaf immersion method could be applicable indirectly to actual applications of pesticidal solutions, because retention of the solution on a vertical surface relates to that on variously inclined surfaces.[6] Thus, the leaf immersion method we developed can be a useful technique to evaluate wettability of leaf surfaces on a static and quantitative basis. Moreover, hydrodynamic study of measuring processes in terms of viscosity and evaporation of solutions could present information of another aspects of leaf surface wettability.[16,17,24]

ACKNOWLEDGMENTS

The authors wish to express their thanks to Drs. Hiroyasu Watanabe and Kunihiko Matsumori of Ehime Univ. and Dr. Katsuyoshi Yoneyama of Meiji Univ. for their helpful suggestions. Their thanks are also due to Toho Chemical Ind. Co. and Mitsubishi Kasei Corp. for kindly providing some surfactants and a dye, respectively.

REFERENCES

1) G. E. Blackman, R. S. Bruce & K. Holly: *J. Exp. Bot.* **9**, 175, (1958)
2) C. G. L. Furmidge: *J. Sci. Food Agric.* **10**, 267 (1959)
3) A. S. Craft & C. L. Foy: *Residue Rev.* **1**, 112 (1962)
4) T. Suzuki: "Noyakuseizaigaku", Nankodo Inc., Tokyo, pp. 327–366, 1965 (in Japanese)
5) H. M. Hull: *Residue Rev.* **31**, 161 (1970)
6) D. R. Johnstone: "Pesticide Formulation," ed. by W. V. Valkenburg, Marcel Dekker Inc., New York, pp. 343–386, 1973
7) K. Holly: "Herbicides," vol. 1, ed. by L. J. Audus, Academic Press Inc., London, pp. 246–267, 1976
8) H. M. Hull, D. G. Davies & G. E. Stolzenberg: "Adjuvants for Herbicides," ed. by R. H. Hodgson, Weed Sci. Soc. America, Illinois, pp. 42–47, 1982
9) T. F. Tadros: *Aspects Appl. Biol.* **14**, 1 (1987)

10) C. G. L. Furmidge: *J. Sci. Food Agric.* **13**, 127 (1962)
11) C. G. L. Furmidge: *J. Sci. Food Agric.* **15**, 542 (1964)
12) R. N. Wenzel: *Ind. Eng. Chem.* **28**, 988 (1936)
13) A. B. D. Cassie & S. Baxter: *Trans. Faraday Soc.* **40**, 546 (1944)
14) P. J. Holloway: *Pestic. Sci.* **1**, 156 (1970)
15) D. E. Bayer & L. M. Lumb: "Pesticide Formulation," ed. by W. V. Valkenburg, Marcel Dekker Inc., New York, pp. 394–402, 1973
16) A. C. Evans & H. Martin: *J. Pomol. Hortic. Sci.* **13**, 261 (1935)
17) R. M. Woodman: *J. Pomol. Hortic. Sci.* **4**, 38 (1924)
18) C. G. L. Furmidge: *J. Sci. Food Agric.* **10**, 247 (1959)
19) C. G. L. Furmidge: *J. Sci. Food Agric.* **16**, 134 (1965)
20) D. I. Conibear & C. G. L. Furmidge: *J. Sci. Food Agric.* **16**, 144 (1965)
21) R. M. Amsden & C. P. Lewins: *World Rev. Pest Control.* **5**, 187 (1966)
22) G. Kadota & S. Matsunaka: *J. Pesticide Sci.* **11**, 597 (1986)
23) E. A. Baker: "The Plant Cuticle," ed. by D. F. Cutler, K. L. Alvin & C. E. Price, Academic Press Inc., London, pp. 139–179, 1982
24) R. S. Standley & J. A. Radley: *Proc. 3rd Int. Congr. on Surface Activity* (*Cologne*) **2**, 464 (1960)

要　約

植物葉の濡れの評価*

渡部忠一，山口　勇

植物葉の濡れ状態を定量的に評価するため，葉浸漬法を検討した．Direct Fast Scarlet 4BS 1.0% と界面活性剤 0.2% を含有する浸漬液（表面張力：21.5～63.5 mN m^{-1}）の葉表面の付着形状を 6 タイプ（A-E, O）に分類した．連続的薄膜付着（A-1）を形成する浸漬液を用いて，葉表面の付着量分布を測定すると，浸漬深がイネ葉で 10 cm，ダイズ・ササゲ等の葉で 5 cm 以上で付着量（μl/cm^2）一定の領域（Up-2 領域）が出現し，この領域に葉表面に個有の付着が生じ，また，葉先端に生ずる浸漬液の滞留は葉先端の形状に影響され，付着量分布の一要因になるものと考えられた．8 科 23 種の作物葉の Up-2 領域と全葉の付着量を測定すると，Up-2 付着量は約 0.6～1.1 μl/cm^2 の狭い範囲に集中したが，全葉付着量では，科に特徴的な付着量を示すもの（ウリ・アブラナおよびアオイ科）を科内で変動するもの（イネ・マメおよびナス科）などが認められた．本葉浸漬法によって葉表面の個有の濡れ状態を溶液と葉表面の相互作用の結果として評価することが可能である．

* 植物葉の濡れ現象に関する研究（第 1 報）