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Original Article

Solvents and Insecticidal Efficacy of the Aerosol Containing Tetramethrin and *d*-Phenothrin*

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Effects of solvents on the insecticidal efficacy of spray formulation against houseflies, mosquitos and cockroaches were determined. Among the solvents examined, kerosene with its boiling point of 200°C to 250°C was relatively more effective than others. The gas chromatographic analysis showed the main components of the effective kerosene were paraffins such as dodecane, tridecane and tetradecane. The detailed comparison of the insecticidal efficacy was conducted by employing various paraffins, and tetradecane was found most effective for knockdown efficacy against all the insects. Each paraffin showed different killing efficacy against different insects: Tetradecane showed the strongest killing effect against mosquitos and cockroaches whereas octane to dodecane showed the strongest killing effect against houseflies. The difference in knockdown and killing efficacy against houseflies was considered to be caused by the different behavior of the particles of each paraffin in the air after sprayed.

INTRODUCTION

Aerosol is a rather new formulation of insecticide. It was first developed by Goodhue *et al.*[1] for practical use during the Second World War, and it has been improved and used widely in many fields ever since.

When an insecticidal aerosol is formulated, attention must be paid to not only its safety but also its efficiency to obtain the maximum insecticidal efficacy of the active ingredients. Generally, an insecticidal aerosol formulation must have both rapid knockdown efficacy and strong killing efficacy against insect pests. When these points are taken into account, studies are focused on how the particles behave in the air before they reach to insects and how they penetrate into the target site through the cuticle.

Many researches conducted on the spray formulation of insecticides made it clear that solvents employed in an insecticidal formulation had a lot to do with its insecticidal efficacy.

David[2] reported that an insecticidal formulation containing odorless kerosene (boiling point: 200–260°C) as a solvent was more effective than the one containing petroleum ether (boiling point: 30–40°C) against *Aedes aegypti*.

Kanellopoulos[3] reviewed that some kind of oil containing a large amount of paraffinic hydrocarbons with a relatively small amount of aromatic and naphthenic constituents could be a very effective solvent for insecticide spray. Tsetlin *et al.*[4] reported that the use of kerosene much enhanced the activity of insecticides in aerosol formulations while kerosene had its own insecticidal activity 100 times less than those of the studied insecticides. Dixon *et al.*[5] reported that the knockdown efficacy of solutions containing pyrethrins in different solvents varied widely. Wickham *et al.*[6] reported that there was a big difference in the insecticidal activity against cockroaches between kerosene-based formulations and water-

* Factors Which Affect the Insecticidal Efficacy of Aerosol Formulation (Part 1)

based ones. They also described that this difference was observed in aerosol flyspray, too. Hayashi[7] reported that there was a difference in the insecticidal efficacy of aerosol formulations containing allethrin as an active ingredient using various distillates of kerosene. He also described that the knockdown efficacy was rapidest when solvents were kerosene distillates with the distillation range of 226–234°C and 228–246.5°C, and that the main components of the distillates were *n*-tridecane and *n*-tetradecane.

This is to report the study of the effect of solvents on the insecticidal efficacy of spray formulations when the active ingredients were tetramethrin and *d*-phenothrin, and the detailed determination of the most effective paraffin against some insect pests.

MATERIALS AND METHODS

1. *Chemicals*

Tetramethrin; technical grade of *N*-(3,4,5,6-tetrahydrophthalimidomethyl (1*RS*)-*cis*, *trans*-chrysanthemate (Neo-pynamin®, Sumitomo Chemical Co., Ltd.).

d-Phenothrin; technical grade of 3-phenoxybenzyl (1*R*)-*cis*, *trans*-chrysanthemate (Sumithrin®, Sumitomo Chemical Co., Ltd.).

Solvents; listed in Tables 1 and 2 together with their physical properties.

2. *Preparations of Formulations*

0.05% (w/v) of tetramethrin and 0.025% (w/v) of *d*-phenothrin were dissolved in each solvent to prepare an oil-liquid formulation.

Aerosol formulations were prepared according to the following recipe using various kinds of *n*-paraffins as a solvent. The valving system employed was; actuator ϕ 0.3 mm, stem ϕ 0.3 mm, vapor-phase tap ϕ 0.3 mm and housing ϕ 1.5 mm.

Tetramethrin		0.4% (w/w)
d-Phenothrin		0.1
n-Paraffin	(up to)	60.0
Propane/butane*		40.0
Total		100.0

* Pressure; 4.8 kg/cm²/20°C (gauge)

Table 1 Physical properties of solvents.

Solvent name	Common name	Boiling point (°C)	Specific gravity (15–20°C)
Ondina 17 (Shell)	Kerosene	350 (50%)	0.868
Neochiozol (Cyuokasei)	″	224–268	0.769
Isopar M (Esso)	″	207–257	0.781
Isopar H (Esso)	″	174–189	0.757
Isopar E (Esso)	″	115–142	0.723
Fog solvent (Nisseki)	″	202–272	0.847
O-solvent M (Nisseki)	″	219–247	0.760
Diesel oil (Esso)	″	205–252	0.822
Solvesso 150 (Esso)	Alkylbenzene	188–210	0.895
Methyl cellosolve (reagent)	—	122–126	0.974
Chlorothene NU (Dow)	Methylchloroform	72– 88	1.325
Isopropanol (reagent)	—	81– 83	0.790

Remarks: Physical properties were quoted from the pamphlet of each solvent.

Table 2 Physical properties of *n*-paraffins.

n-Paraffin	Melting point (°C)	Boiling point (°C)	Specific gravity (at 20°C)	Vapor pressure (mmHg at 20°C)
n-Octane	−56.8	125.7	0.703	10.5
n-Decane	−29.7	174.1	0.730	9.00×10^{-1}
n-Dodecane	− 9.6	216.3	0.749	7.30×10^{-2}
n-Tetradecane	5.9	253.4	0.763	5.45×10^{-3}
n-Hexadecane	18.2	286.5	0.773	3.45×10^{-4}

3. Insects

Houseflies (*Musca domestica*, CSMA susceptible strain); 3 to 5 day-old male and female adults

Mosquitos (*Culex pipiens pallens*, susceptible strain); 2 to 3 day-old female adults

Cockroaches (*Blattella germanica*, susceptible strain); 20 to 30 day-old male and female adults

Insects were reared at the Takarazuka Research Center of Sumitomo Chemical Co., Ltd. at 26±1°C and 60±10% of relative humidity.

4. Methods of Application

The Peet Grady spray method; According to the test method of Chemical Specialties Manufacturers Association (CSMA),[8] 12 ml of oil-liquid was sprayed per Peet Grady chamber.

The cockroach spray method; According to the test method of CSMA,[8] 1.5 ml of oil-liquid was sprayed per CSMA chamber.

Aerosol test method for flying insects; According to the test method of CSMA,[8] 650±100 mg of an aerosol was sprayed per Peet Grady chamber.

Direct spray method for cockroach; According to the method of Okuno *et al.*,[9] 400±100 mg of an aerosol was directly sprayed per glass cylinder.

Topical application method; Acetone solutions of the test solvents at various concentrations were applied topically onto dorsum prothorax of each insect at the rate of 0.5 μl on houseflies and 0.3 μl on mosquitos, respectively.

For the synergistic study, a *n*-paraffin solution of tetramethrin was applied topically at the rate of 0.1 to 1.0 μl onto dorsum prothorax of houseflies.

5. Methods of Analysis

Semi-quantitative analysis of kerosene; Kerosene was analyzed quantitatively using a gas chromatograph equipped with a flame ionization detector under the following conditions; glass column: 1.5 m, 3 mm i.d. packed with 5% Thermon 1000 on chromosorb W (AW, DMCS) 80–100 mesh; carrier gas: nitrogen at approximately 60 ml/min; injection temperature: 300°C; column temperature: from 50 to 235°C at the rate of 10°C/min.

Particle size measurement; The particle size of aerosol spray was measured using Malvern Particle Sizer Model 2200.[10] The aerosol was sprayed 30 cm apart from the laser beam.

RESULTS AND DISCUSSION

1. Insecticidal Efficacy of Oil-liquid Spray Using Various Kinds of Solvents

The insecticidal efficacy of oil-liquid spray using various kinds of solvents against flying insects by the Peet Grady method is shown in Table 3. A big difference in the knockdown efficacy was observed both against houseflies and mosquitos but was not such a big difference in the killing activity among the solvents except Ondina 17 and Isopar E. Petroleum distillates with relatively high boiling point such as 200 to 250°C generally showed strong efficacy.

Table 4 shows insecticidal efficacy of oil-liquid spray using various kinds of solvents against cockroaches by the cockroach spray method. The difference in the efficacy among the solvents was bigger than that against flying insects by the Peet Grady method. However, the solvents which had shown strong efficacy against flying insects showed the same strong efficacy against cockroaches. These results indicate that a petroleum distillate at certain boiling point range is most effective.

2. Semi-quantitative Analysis of Kerosenes

Figure 1 shows the semi-quantitative analytical results of various kinds of kerosenes by gas chromatography. It was seen that the kerosenes which showed good efficacy had their main peaks in the region of decane to hexadecane, especially dodecane to tetradecane, and their boiling point ranged from 200 to 250°C. Diesel oil which did not show good efficacy against cockroaches had a wide range of paraffins, although apparent boiling point was around 200 to 250°C. This result suggests that the difference in the efficacy among kerosene depends on its components; *i.e.* the kind of paraffins which constitutes kerosene.

Table 3 Insecticidal efficacy of oil-liquid formulations containing 0.05% of tetramethrin and 0.025% of *d*-phenothrin using various kinds of solvents against flying insects by the Peet Grady method.

Solvent	Housefly		Mosquito	
	KT_{50} (min)	Kill (%)	KT_{50} (min)	Kill (%)
Ondina 17	5.3	62	3.2	93
Neochiozol	1.9	90	1.8	93
Isopar M	2.4	87	1.4	100
Isopar H	2.4	100	2.3	99
Isopar E	6.0	91	9.5	87
Nisseki fog solvent	1.9	98	2.1	100
Nisseki O-solvent M	1.3	91	1.1	97
Diesel oil	2.5	95	2.7	95
Solvesso 150	2.0	100	1.5	95
Methyl cellosolve	5.0	97	7.4	95
Chlorothene NU	5.3	93	6.7	98
Isopropanol	5.2	97	8.2	96

Table 4 Insecticidal efficacy of oil-liquid formulations containing 0.05% of tetramethrin and 0.025% of *d*-phenothrin using various kinds of solvents against cockroaches by the cockroach spray method.

Solvent	% knockdown at min			% kill at 48 hr
	5	10	20	
Ondina 17	0	2	3	7
Neochiozol	73	82	87	68
Isopar M	15	22	25	13
Isopar H	8	8	10	7
Isopar E	0	0	0	0
Nisseki fog solvent	27	45	47	47
Nisseki O-solvent M	68	83	87	57
Diesel oil	2	5	10	32
Solvesso 150	15	27	40	45
Methyl cellosolve	0	0	0	8
Chlorothene NU	0	0	0	13
Isopropanol	0	0	0	0

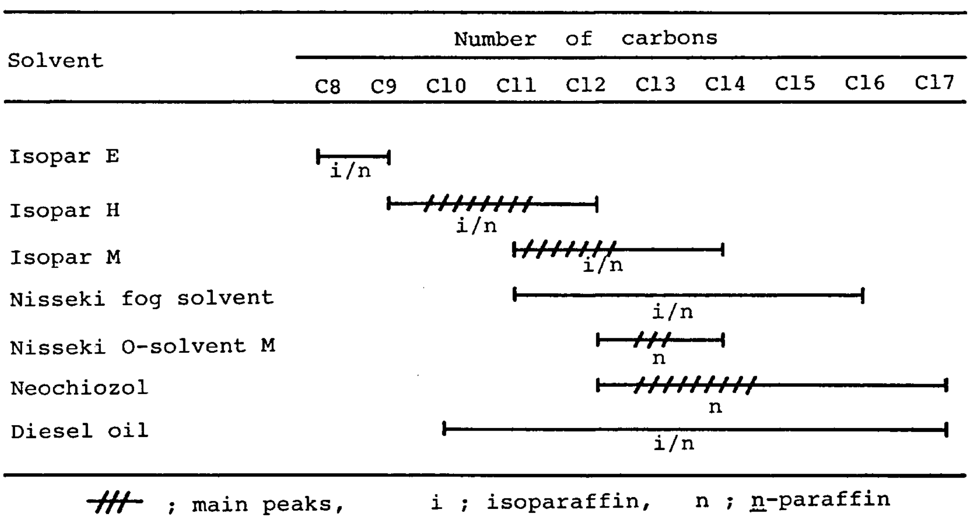

Fig. 1 Quantitative analysis of various kinds of kerosene by using gas chromatography.

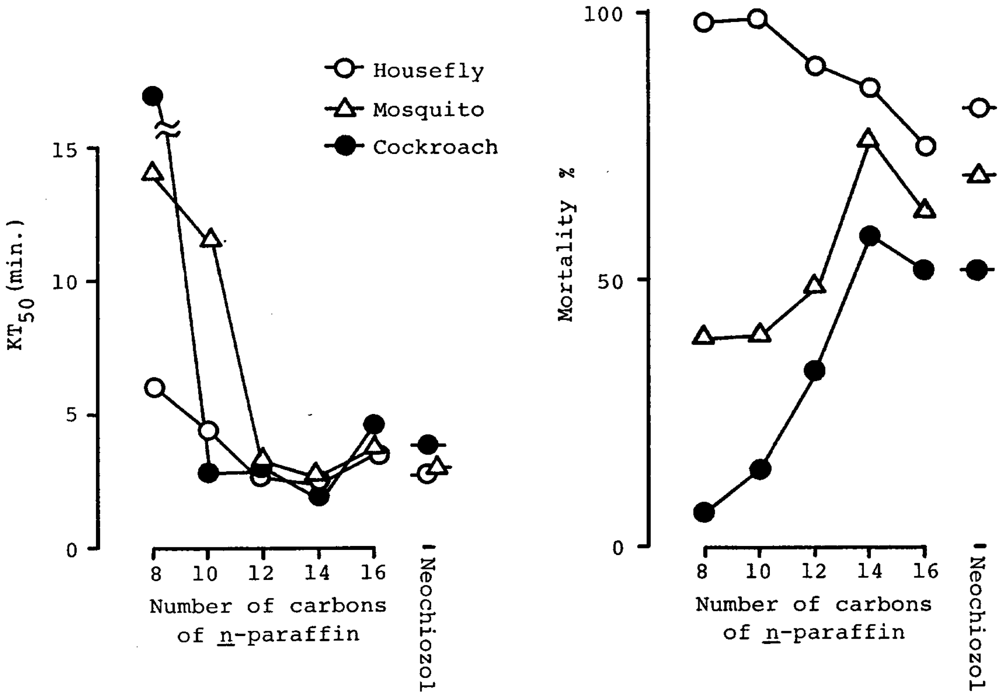

Fig. 2 Insecticidal efficacy of oil-liquid formulations containing 0.05% of tetramethrin and 0.025% of *d*-phenothrin using *n*-paraffin as a solvent by the Peet Grady spray method and the cockroach spray method.

3. *Insecticidal Efficacy of Oil-liquid Spray and Aerosol Spray Using Various Kinds of n-Paraffins as a Solvent*

Figure 2 shows the insecticidal efficacy of oil-liquid spray using a *n*-paraffin as a solvent by the Peet Grady method and the cockroach spray method. Figure 3 shows the insecticidal efficacy of aerosol spray using the same solvent by the aerosol test method for flying insects and the direct spray method for cockroaches. *n*-Dodecane to *n*-hexadecane showed the best knockdown efficacy against all three insects tested. *n*-Tetradecane showed the best killing efficacy against mosquitos and cockroaches, while *n*-octane to *n*-dodecane showed the best killing efficacy against houseflies. It is quite reasonable that the efficacy of the formulation containing Neochiozol is almost equivalent to that of *n*-dodecane to *n*-hexadecane since they are the main components of Neochiozol.

These results show that the difference in the efficacy among kerosene depends on the kind of paraffins which constitute it.

The lines in Figs. 2 and 3 suggest that the *n*-paraffins with their carbons exceeding 16 would show less efficacy than *n*-hexadecane. The *n*-paraffins whose carbons exceed 16 are not liquid at room temperature, which must be also taken into account.

Therefore, *n*-tetradecane is concluded an optimum *n*-paraffin for obtaining good knockdown efficacy against insects and good killing efficacy against insects except houseflies. This coincides well with the result found by Hayashi[7] when he examined the insecticidal efficacy of aerosol formulations containing allethrin as an active ingredient using various distillates of kerosene.

4. *Topical Application Test*

An interesting finding was that a solvent optimal in killing houseflies was not optimal in knockdown, which was further confirmed by a topical application test.

Table 5 shows the LD_{50} values of solvents against houseflies and mosquitos by the topical application method. There was a big difference in the toxicity of solvents against both insects. Table 6 shows the LD_{50} values of *n*-paraffins against houseflies and mosquitos by the topical application method. The toxicity of *n*-paraffins depended on the number of carbons they contained. The most effective *n*-paraffin against houseflies was *n*-dodecane and

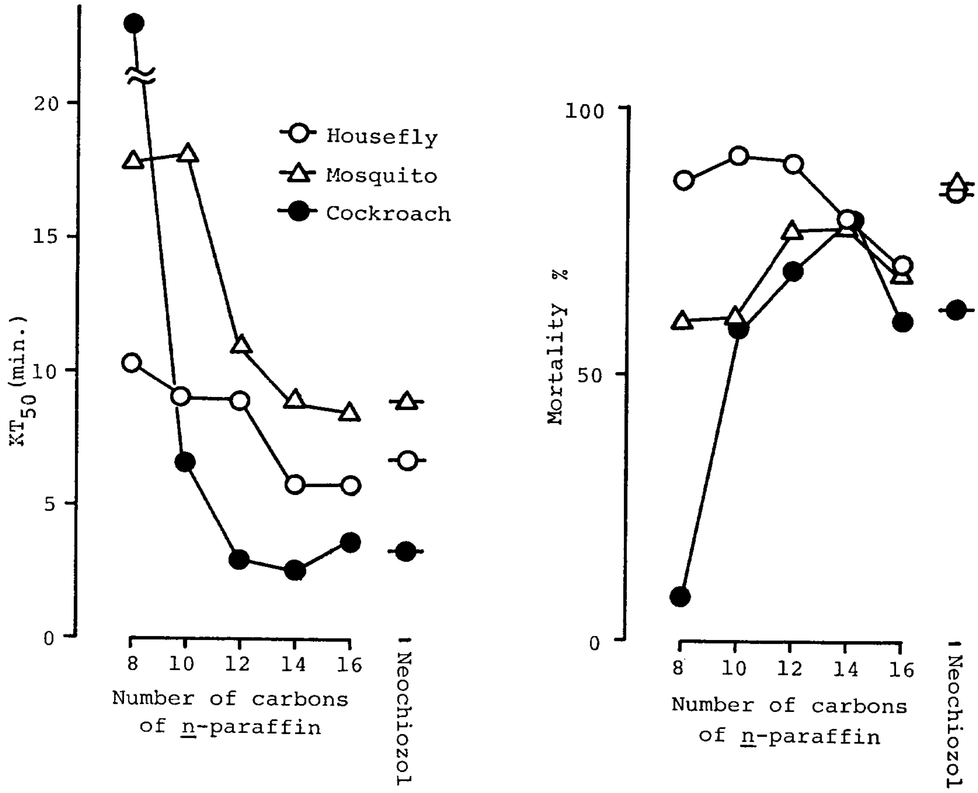

Fig. 3 Insecticidal efficacy of aerosol formulations containing 0.4% of tetramethrin and 0.1% of *d*-phenothrin using *n*-paraffin as a solvent by the aerosol test method for flying insects and the direct spray method for cockroaches.

Table 5 Insecticidal efficacy of various kinds of solvents against insects by the topical application method.

Solvent	LD_{50} (μg/♀)	
	Housefly	Mosquito
Ondina 17	>433	81
Neochiozol	253	48
Isopar M	255	60
Isopar H	237	59
Isopar E	>362	97
Nisseki fog solvent	158	34
Nisseki O-solvent M	269	41
Diesel oil	>411	27
Solvesso 150	71	37
Methyl cellosolve	>320	>292
Chlorothene NU	>663	>398
Isopropanol	>395	>237

that against mosquitos, *n*-tetradecane. This result of the topical application test coincided well with that of the killing efficacy test by the spray method.

Table 7 shows the insecticidal efficacy of

Table 6 Insecticidal efficacy of *n*-paraffins against insects by the topical application method.

n-Paraffin	LD_{50} (μg/♀)	
	Housefly	Mosquito
n-Octane	>352 (25%)[a]	55
n-Decane	207	57
n-Dodecane	189	47
n-Tetradecane	>383 (28%)	38
n-Hexadecane	>387 (8%)	43

[a] Figures in parentheses mean mortality % when the maximum amount of the solvent was topically applied.

oil-liquid containing tetramethrin against houseflies by the topical application method. When 0.2 μl of *n*-paraffins containing tetramethrin was topically applied, the mortality of houseflies for the sample using *n*-dodecane was higher than that for *n*-octane followed by *n*-hexadecane. When the mortality was corrected for the solvent control, the order of the efficacy did not change. This result indicates

Table 7 Insecticidal efficacy of oil-liquid formulations containing tetramethrin using a different kind of *n*-paraffin as a solvent against houseflies by the topical application method.

μg of tetramethrin in solvent	Mortality %						
	n-Octane		*n*-Dodecane		*n*-Hexadecane		Acetone
	0.2 μl[a]	0.3 μl	0.1 μl	0.2 μl	0.2 μl	1.0 μl	0.3 μl
0.8	76%	88%	100%	—	76%	88%	40%
0.4	52	52	88	96%	36	48	12
0.2	20	52	32	72	0	52	8
0.1	12	24	12	44	0	24	0
0.05	12	20	4	12	0	16	0
0.025	—	16	0	—	—	16	0
Solvent control	8	8	4	20	0	0	0

[a] Applied amount of the solvent on an insect (♀).

that the difference in the efficacy of oil-liquid containing tetramethrin using various kinds of *n*-paraffin does not depend on the toxicity of tetramethrin nor the solvent independently, but on some synergistic action between them, which is assumed to be some facilitating action of the solvent on tetramethrin to penetrate into the target site of an insect body through the cuticle. Also it is evident in Table 7 that the killing efficacy got stronger when the amount of the solvent applied per insect increased.

The results suggest that if the same amount of tetramethrin in the same amount of solvent is caught by houseflies, the knockdown efficacy can be rapidest when *n*-dodecane is used. The difference between this hypothesis and the actual result of the spray test seems to be caused by the behavior of sprayed particles in the air.

Another possible explanation can be that there is a difference in solvent's efficacy in killing and knockdown. However, if the target site of insecticides for both knockdown and killing effects in insect body is the same central nervous system, as Burt *et al.*[11] mentioned, this explanation does not seem reasonable.

5. *Behavior of Particles*

The particle size distribution of the aerosol formulation containing various *n*-paraffins as a solvent is shown in Fig. 4. There was not a big difference in the particle size distribution among aerosols when sprayed 30 cm apart

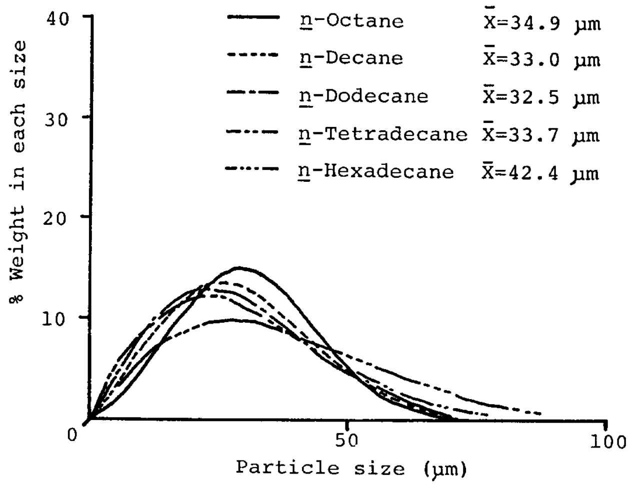

Fig. 4 Particle size distribution of five different aerosols using *n*-paraffin as a solvent measured 30 cm from actuator.

from the actuator. However, when a solvent was a very volatile one such as *n*-octane, the volume of particles would decrease rapidly in the air due to the evaporation and thus the concentration in the air would last for a long period. On the contrary, when a non-volatile solvent like *n*-hexadecane was employed, the sprayed particles retained their volume for a long period and thus they would precipitate rapidly. According to our estimation, the complete evaporation time of a 20 μm particle of *n*-octane is 0.4 sec and that of *n*-hexadecane, 3 to 4 hr. (This estimation was based on the comparison of the vapor pressure of each solvent and water using the data of Hinds.[12])

The inertia of a particle must also be taken into consideration. If a particle is very small, it can not stick and stay on an insect.

Spillman[13] reported that these two factors affected the catch efficiency of sprayed particles to flying insects.

Therefore, when the effect of solvents on the knockdown efficacy of an aerosol formulation is discussed, both the behavior of particles in the air before they reach an insect and the penetration speed of active ingredients through the cuticle after they reach should be taken into account.

It is supposed that relatively coarse particles may be more effective in knockdown efficacy than very fine particles, because the former can attack insects more rapidly than the latter owing to the difference in their inertia.

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要　　約

テトラメスリンと*d*-フェノスリンを含むエアゾール製剤の溶剤と殺虫効力*

津田重典，奥野吉俊

ハエ，蚊，ゴキブリに対する噴霧剤の効力に及ぼす溶剤の影響を調べた．供試した溶剤中，200から250°Cの沸点をもつケロシンが，比較的良好な効力を示した．ガスクロマトグラフィーを用いた分析から，これらの良好な効力を示すケロシンの主成分は，ドデカンからテトラデカンのパラフィンであることがわかった．各種のパラフィン類を用いた殺虫効力の比較から，供試した3種の害虫に対し最も良好なノックダウン効果を示すものはテトラデカンであることがわかった．致死効力面で最良の効果を示すパラフィンは害虫種により異なった．すなわち，蚊やゴキブリに対しては，テトラデカンが良く，ハエに対してはドデカンが最良であった．ハエに対し，ノックダウン効力と致死効力で最適な溶剤が異なる理由のひとつとしては，これらのパラフィンが噴霧されたのちの，粒子の空中での挙動差が考えられた．

* エアゾール製剤の殺虫効力に影響を及ぼす要因（第1報）