DEVELOPMENT, PHYSICOCHEMICAL PROPERTIES AND SPRAY BEHAVIORAL CHARACTERISTICS OF FENITROTHION AND AMINOCARB EMULSION FORMULATIONS

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INTRODUCTION

During the spring months, the New Brunswicks's forest managers found themselves in a very critical position, when the Province reacted to the recommendation of the Task Force headed by Dr. W.O. Spitzer, and deleted the use of Atlox 3409F emulsifier from the operational spray program against the spruce budworm in 1982. Consequently, there arose an emergency situation to develop an alternative emulsifier acceptable for operational use in 1983. A crash program, otherwise known as "The Action Plan", was therefore initiated by the Forest Pest Management Institute, involving several cooperating agencies (federal, provincial and pesticide manufacturing companies), aimed at generating all the required data for registering new aqueous emulsions of fenitrothion and aminocarb containing the alternative emulsifier. With the urgency of the program and the necessity of meeting the safety requirements of HEALTH AND WELFARE CANADA, preference was given to chemicals for which mammalian toxicology data were available, and/or to those which are already in wide use in agricultural pesticide formulations and in foods, drugs, cosmetics and consumer products. Table 1 lists the emulsifiers, diluent oils and polymeric additives that were tried in various combinations and proportions for good miscibility and emulsion characteristics.

Out of the list in Table 1, Triton®X-100 was chosen since there were mammalian toxicology data on this product. Since Triton®X-100 gave difficulties in mixing at cold temperatures under field conditions, preference was given to Triton®X-114, a closely related compound to Triton®X-100. However, since field studies were carried out with Triton®X-100, laboratory studies were conducted, for the sake of comparison, on both emulsifiers Triton®X-100 and Triton®X-114.

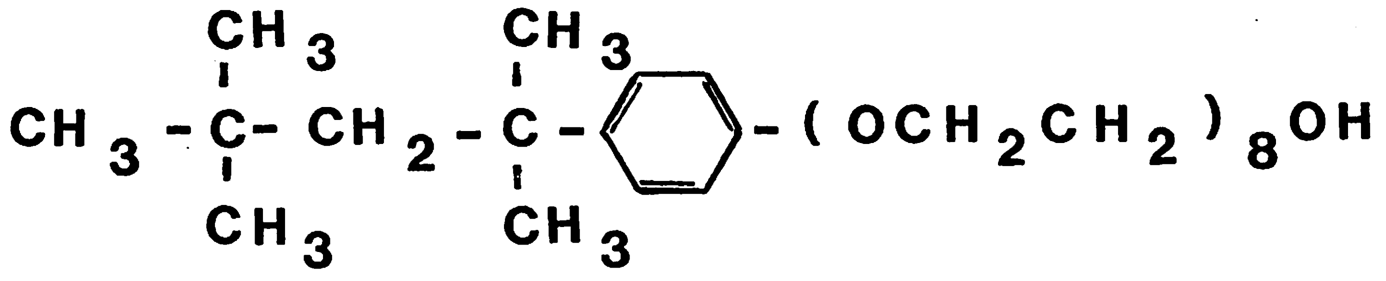


FIG. 1a. TRITON® X-114

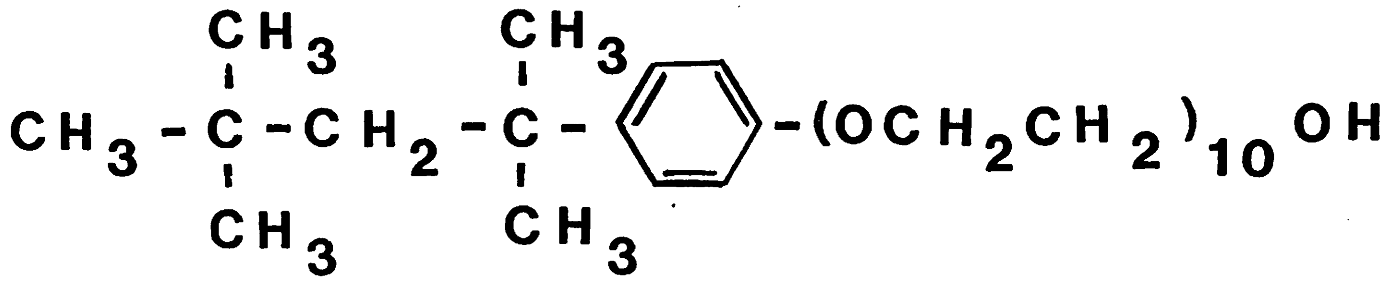


FIG. 1b. TRITON® X-100

TABLE 1

LISTS OF EMULSIFIERS, DILUENT OILS AND POLYMERIC ADDITIVES STUDIED WITH FENITROTHION TECHNICAL AND AMINOCARB FLOWABLE

Emulsifier	Cosolvents	Polymeric Additives
Tween® 80	ID 585	Nalco-Trol®
Tween® 60	Dowanol TPM	Polyvinyl alcohols
Triton® AG-460	Cyclo-Sol® 63	Acrylic polymers
Triton® X-45	Canola oil	Sodium silicates
Triton® X-100	Sunspray® 6N	Potassium silicates
Triton® X-114	Sunspray® 11N	
Triton® X-193	Glycerol	
Triton® B-1956	Propylene glycol	
Pluronic® L-31	Sorbo®	
Renex® 20		
Span® 20		
ATPLUS® 109		

In order to get a complete picture on formulation properties and spray droplet spectra, the two currently registered fenitrothion formulations, and the two currently proposed/ field tested aminocarb formulations (one of each is an emulsion containing ATLOX 3409F and the other is an oil based formulation containing ID 585) were also studied for comparative purposes.

METHODS

In order to develop a formulation acceptable for forestry spraying in Canada, the need was recognized to develop a series of methodologies and a battery of test procedures so that its suitability under operational field conditions can be maximized. The following rationale was used:

Rationale for developing a battery of test procedures for formulation technology

The use of pesticides under inappropriate formulation conditions causes many problems. First, the ingredients may separate during spray application, resulting in uneven deposition of the active ingredient. This would lead not only to inefficient pest control but also to unnecessary environmental impact in areas where the concentrated active ingredient had deposited. Second, the physicochemical properties of formulations may not be appropriate to enable easy storage, pumping out, and mixing capabilities under field application conditions, especilly under extreme cold weather conditions that are encountered in Canada. Formulation properties play a key role in efficient atomization by the available spray equipment (i.e.by the nozzle and aircraft types), to result in target-specific drop size range at the site of the biological interface in order to bring about maximum impaction efficiency of droplets on target surface. Formulation properties may not be appropriate for optimum retention characteristics of spray droplets on the target surface, i.e. the droplet should be retained just long enough to accomplish critical pest control and then should ideally rapidly dissipate (either by cuticular absorption and degradation, or by evaporation and sublimation) to minimize the residue problems leading to phytotoxicity of sensitive shoots and injury to beneficial insects.

It is therefore very important to develop a battery of test procedures to investigate the following;

① Selection of the most optimum ingredients and their proportions for good miscibility and emulsion characteristics at a wide temperature range.

② Stability of formulations with respect to phase separation at a wide temperature range; and re-emulsifiability upon shaking.

③ Compatibility of the active ingredient with inert ingredients over a defined period of time.

④ Mixing, storing and pumping capabilities under extreme cold weather conditions.

⑤. Spray atomization characteristics with different nozzle systems and application equipment.

⑥. Rate and degree of droplet evaporation.

⑦. Rate and degree of vapourization of the active ingredient from spray droplets

⑧. Droplet impaction characteristics on the intended target surface.

⑨. Droplet retention characteristics on the target in question.

⑩. Droplet dissipation characteristics and phytotoxicity.

Without the knowledge of these data, the success or failure of an aerial spray trial cannot be correlated with formulation properties, as this step is crucial to understand the role of formulation properties on efficacy, environmental impact and environmental residue characteristics of a pesticide chemical. Consequently methodologies were developed and the above aspects were studied. Results of each investigation are presented below under corresponding headlines;

①. Selection of Triton® X-100 and Triton® X-114, suitable cosolvents and their proportions, for good miscibility at a wide temperature range.

The temperature range appropriate for field application is generally from 5° C to 15° C, although occasionally colder temperatures, i.e. near freezing, could be experienced. Therefore miscibility and emulsification studies were conducted at 5°C to 15°C. However, the laboratory toxicology studies (both insect and mammalian toxicology) are usually carried out at 20°C to 25°C, and therefore it is important to investigate the suitability of formulations at 20°C to 25°C. In view of this, a wide temperature range of 5°C to 25°C was selected for formulation testing.

Table 2 lists the ingredients and their proportions selected on the basis of good miscibility and emulsion characteristics at the above temperature range.

TABLE 2. PERCENTAGE COMPOSITION OF INGREDIENTS

1. Formulation No. FT-114: Fenitrothion, Triton® X-114 and Water

	w/v	w/w	v/v %
Fenitrothion technical	14.5	13.9	11.0
Triton® X-114	14.5	13.9	13.8
Water	To a total vol. of 100 ml.	72.2	75.2
	100.0	100.0	100.0

2. Formulation No. FT-100: Fenitrothion, Triton® X-100 and Water

	w/v	w/w	v/v %
Fenitrothion technical	14.5	13.9	11.0
Triton® X-100	14.5	13.9	13.7
Water	To a total vol. of 100 ml.	72.2	75.3
	100.0	100.0	100.0

3. Formulation No. FCT-114: Fenitrothion, Cyclo-Sol® 63, Triton® X-114 and Water

	w/v	w/w	v/v %
Fenitrothion technical	14.5	14.3	11.0
Cyclo-Sol® 63	24.0	23.7	26.3
Triton® X-114	3.0	3.0	2.8
Water	To a total vol. of 100 ml.	59.0	59.9
	100.0	100.0	100.0

4. Formulation No. FCT-100: Fenitrothion, Cyclo-Sol® 63, Triton® X-100 and Water

	w/v	w/w	v/v %
Fenitrothion technical	14.5	14.3	11.0
Cyclo-Sol® 63	24.0	23.7	26.3
Triton® X-100	3.0	3.0	2.8
Water	To a total vol. of 100 ml.	59.0	59.9
	100.0	100.0	100.0

TABLE 2, Continued

5. Formulation No. FDA-3409: Fenitrothion, Dowanol TPM, ATLOX 3409F and Water

	w/v	w/w	v/v %
Fenitrothion technical	14.5	14.0	11.0
Dowanol TPM	1.5	1.45	1.5
ATLOX 3409F	1.5	1.45	1.5
Water	To a total vol. of 100 ml.	83.1	86.0
	100.0	100.0	100.0

6. Formulation No. FCID-585: Fenitrothion, Cyclo-Sol® 63 and ID 585

	w/v	w/w	v/v %
Fenitrothion technical	14.5	16.1	11.0
Cyclo-Sol® 63	32.0	35.3	35.0
ID 585	To a total vol. of 100 ml.	48.6	54.0
	100.0	100.0	100.0

7. Formulation No. AT-114: MATACIL® 180F, Triton® X-114 and Water

	w/v	w/w	v/v %
MATACIL® 180F	24.3	24.9	26.7
Triton® X-114	3.0	3.1	2.8
Water	To a total vol. of 100 ml.	72.0	70.5
	100.0	100.0	100.0

8. Formulation No. AT-100: MATACIL® 180F, Triton® X-100 and Water

	w/v	w/w	v/v %
MATACIL® 180F	24.3	24.9	26.7
Triton® X-100	3.0	3.1	2.8
Water	To a total vol. of 100 ml.	72.0	70.5
	100.0	100.0	100.0

TABLE 2, Continued:

9. Formulation No. AA-3409: MATACIL® 180F, ATLOX 3409F and Water

	w/v	w/w	v/v %
MATACIL® 180F	24.3	25.0	26.7
ATLOX 3409F	1.5	1.5	1.5
Water	To a total vol. of 100 ml.	73.5	71.8
	100.0	100.0	100.0

10. Formulation No. AID-585: MATACIL® 180F and ID 585

	w/v	w/w	v/v %
MATACIL® 180F	24.3	29.0	26.7
ID 585	To a total vol. of 100 ml.	71.0	73.3
	100.0	100.0	100.0

The above ratios and proportions are applicable to room temperature only (20° to 22° C) and will vary slightly if the ratios are to be calculated at colder temperatures. Table 3 shows density values of ingredients which can be used for calculating the accurate proportions at the desired temperature, although it should be borne in mind that the data in Table 3 are applicable only for the lot number used in the study and may differ slightly for other lot numbers.

Formulation appearance, type and foaming properties were also studied, and the findings are listed in Table 4.

TABLE 3

DENSITY VALUES FOR INGREDIENTS

Ingredients		Density (g/ml)				
No.	Description	5° C	10° C	15° C	20° C	25° C
1.	Fenitrothion technical	1.336	1.328	1.322	1.318	1.315
2.	Triton® X-114	1.065	1.059	1.054	1.050	1.047
3.	Triton® X-100	1.074	1.069	1.065	1.060	1.055
4.	Cyclo-Sol® 63	0.923	0.920	0.917	0.914	0.911
5.	Dowanol TPM	0.996	0.992	0.988	0.983	0.979
6.	ATLOX 3409F	1.042	1.037	1.031	1.026	1.022
7.	ID 585	0.823	0.819	0.816	0.812	0.809
8.	MATACIL® 180F	0.917	0.914	0.911	0.908	0.906
9.	Water	1.000	0.9997	0.9991	0.9982	0.9971

TABLE 4

APPEARANCE, FOAMING PROPERTIES AND FORMULATION TYPE

Formulation No.	Appearance	Colour	Type	% Solids (w/w)	Foaming Properties
FT-114	Creamy viscous liquid	Pale Yellow	Emulsion	None	Low-disappears in 30 min.
FT-100	Creamy light liquid	" "	"	"	Moderate-disappears in 1.5 hours
FCT-114	" " "	" "	"	"	Low-disappears in 15 min.
FCT-100	" " "	" "	"	"	" " " "
FDA-3409	" " "	White	"	1.13	High-stays for 6 hours
FCID-585	Clear oily liquid	Yellow	Oily solution	None	Not applicable
AT-114	Creamy light liquid	Beige	Emulsion/suspension	7.0	Low-disappears in 20 min.
AT-100	" " "	"	" "	7.0	Low-disappears in 30 min.
AA-3409	" " "	"	" "	8.13	Moderate-disappears in 1.5 hours
AID-585	Cloudy oily liquid	Yellow	Oily suspension	7.0	Not applicable

Mixing procedures

For easy mixing under field conditions and in large quantities, it is advisable to follow optimum mixing procedures. For this purpose, the ten formulations were grouped into three distinct categories A, B and C.

A). Formulations FT-114, FT-100, FCT-114, FCT-100, FDA 3409 and AA-3409

These six formulations are aqueous emulsions. To ensure thorough mixing, the non-aqueous ingredients must be added first and mixed well before adding water. After adding water the contents should be mixed thoroughly for about 20 to 30 min.

It is important to bear in mind that the two emulsifiers Triton® X-100 and Triton® X-114 must not be allowed to come into direct contact with water, otherwise gel formation will occur and cause serious mixing problems.

B). Formulations AT-114 and AT-100

These two aminocarb formulations are aqueous emulsions with suspended particles. To ensure ready mixing without coagulation, the emulsifier should be added to MATACIL® 180F, while the mixture is being mixed very gently during addition of the emulsifier. The shaking should be so gentle that the emulsifier should be just dispersed in the medium without coagulation (coagulation will occur rather readily with Triton® X-100 but not with Triton® X-114). Immediately after, the water should be added and the contents be thoroughly mixed for about 20 to 30 min.

C). Formulations FCID-585 and AID-585

These are non-aqueous formulations and are very simple to prepare. Ingredients can be added in any sequence and be thoroughly mixed by agitating for up to 20 to 30 min.

②. Stability of formulations (phase separation and/or viscosity changes) and re-emulsifiability

The term stability refers to the tendency of the formulation to resist separation into its ingredients. Actual separation of the component phases can occur if stability is low. This phenomenon is often observed when formulations are left standing with no stirring or agitation. With gentle stirring however, phase separation may not be observed visually but a reduction in viscosity can result due to changes in micelle formation and stability. These aspects were studied at a wide range of temperatures, the findings are presented in Table 5.

TABLE 5 . STABILITY OF MIXES

	Time (hr) Required for			
	Phase Separation With No Agitation		Reduction in Viscosity By Approx. 20% With Agitation*	
Formulation No.	5-15° C	20-22° C	5-15° C	20-22° C
FT-114	Exceptionally stable			
FT-100	2.0-2.5	1.5	12-18	6
FCT-114	3.0-4.0	2.0	24-36	10
FCT-100	3.0-4.0	2.0	24-36	10
FDA-3409	2.0-2.5	1.5	10-15	6
FCID-585	Not applicable (clear solution)			
AT-114	1.0-1.5	0.5	3- 5	3
AT-100	1.0-1.5	0.5	3- 5	3
AA-3409	1.5-2.0	0.75	6- 8	3
AID-585	2.0-3.0	1.0	10-15	5

* Constant stirring at 300 rpm

Stability with tracer dyes was studied in order to provide stability data to laboratory and field researchers who are involved in spray deposit assesment and droplet spectra analysis. Tracer dyes are highly polar and sometimes are ionic. Unlike the oil based formulations, the aqueous based emulsion formulations are highly susceptible to instability and phase separation, whenever extraneous ionic/polar compounds are added, even in microgram quantities. Therefore, it is very important to study the suitability of each dye tracer for a particular emulsion. Results of this aspect of the study are presented in Table 6 and 7.

Stability at variable hardness of water was also studied, since under field conditions, water is liable to vary in hardness. To study this aspect, variable amounts of magnesium and calcium salts were added to water to prepare water with variable degree of hardness. Stability was tested by preparing formulations with these types of water. Results are tabulated in Table 9.

The term re-emulsifiability refers to the tendency of the separated phases to revert to the emulsion state having the same stability as that of the freshly prepared one. This aspect was studied after gentle and vigorous agitation. Findings are listed in Table 10.

③ Compatibility of active ingredient

Very often, the inert ingredients in the formulation can interact chemically with the active ingredient reducing its pesticidal activity.

This aspect was investigated after a lapse of six weeks after preparing the formulations. The active ingredient was recovered almost completely (within the experimental error) in all formulations indicating a good compatibility between ingredients.

TABLE 6.

STABILITY WITH TRACER DYES AT 20° TO 22°C

Formulation No.	Time required (hr) for					
	phase separation with no agitation			reduction in viscosity by ~ 20%, with agitation at 300 rpm		
	Rhodamine B	Rhodamine WT	Erio Acid Red	Rhodamine B	Rhodamine WT	Erio Acid Red
FT-114	very stable	very stable	very stable	very stable	very stable	very stable
FT-100	0.75	1.0	1.5	3.0	5.0	5.0
FCT-114	1.5	1.75	2.0	7.0	9.0	9.0
FCT-100	1.5	1.75	2.0	7.0	9.0	9.0
FDA-3409	0.7	1.0	1.5	4.0	5.0	5.0
FCID-585	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
AT-114	0.33	0.5	0.5	1.5	2.0	3.0
AT-100	0.33	0.5	0.5	1.5	2.0	3.0
AA-3409	0.5	0.75	0.75	1.5	3.0	3.0
AID-585	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable

TABLE 7.

STABILITY WITH TRACER DYES AT 5° TO 15° C

Formulation No.	Time (hr) required for					
	phase separation with no agitation			reduction in viscosity by ~ 20%, with agitation at 300 rpm		
	Rhodamine B	Rhodamine WT	Erio Acid Red	Rhodamine B	Rhodamine WT	Erio Acid Red
FT-114	very stable	very stable	very stable	very stable	very stable	very stable
FT-100	~ 1.25	~ 1.75	~ 2.0	~ 4.0	~ 6.0	~ 6.0
FCT-114	~ 2.0	~ 2.5	~ 3.0	~ 8.0	~ 10.0	~ 10.0
FCT-100	~ 2.0	~ 2.5	~ 3.0	~ 8.0	~ 11.0	~ 12.0
FDA-3409	~ 1.0	~ 1.5	~ 2.0	~ 5.0	~ 6.0	~ 6.0
FCID-585	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
AT-114	~ 0.7	~ 1.0	~ 1.5	~ 2.0	~ 3.0	~ 3.5
AT-100	~ 0.7	~ 1.0	~ 1.5	~ 2.0	~ 3.0	~ 3.5
AA-3409	~ 0.7	~ 1.0	~ 1.5	~ 2.0	~ 3.0	~ 3.5
AID-585	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable

TABLE 8.

STABILITY AT WATER PH VALUES

OF 5 TO 8 AT 20° TO 22° C*

Formulation No.	Time (hr) required for phase separation with no agitation			
	PH=5	PH=6	PH=7	PH=8
FT-114	0.5	2.5	Exceptionally stable	Highly stable
FT-100	0.1	0.5	1.5	1.5
FCT-114	1.7	2.0	2.0	2.0
FCT-100	1.7	2.0	2.0	2.0
FDA-3409	0.7	1.5	1.5	1.5
FCID-585	Not applicable	Not applicable	Not applicable	Not applicable
AT-114	0.1	0.3	0.5	0.5
AT-100	0.1	0.3	0.5	0.5
AA-3409	0.1	0.5	0.75	0.75
AID-585	Not applicable	Not applicable	Not applicable	Not applicable

* At colder temperatures, the time periods increased to some extent but not dramatically.

TABLE 9.

STABILITY AT VARIABLE HARDNESS

OF WATER AT 20° TO 22° C*

Formulation No.	Time (hr) required for phase separation with no agitation		
	Soft water	Medium hard	Very hard water
FT-114	Very stable	1.6	0.5
FT-100	1.5	0.3	0.1
FCT-114	2.0	2.0	1.7
FCT-100	2.0	2.0	1.7
FDA-3409	1.5	1.0	0.7
FCID-585	Not applicable	Not applicable	Not applicable
AT-114	0.5	0.1	0.1
AT-100	0.5	0.1	0.1
AA-3409	0.75	0.33	0.1
AID-585	Not applicable	Not applicable	Not application

* At colder temperatures, the time periods increased to some extent but not drastically.

TABLE 10

RE-EMULSIFIABILITY UPON STORAGE AT 5° TO 15° C FOR UP TO FOUR DAYS

Formulation No.	Re-emulsifiability After Standing for 4 Days at 5° to 15° C With Gentle Mixing (300 rpm)	With Good Agitation (Vigorous shaking)	Resettling Time (hr) After Vigorous Shaking
FT-114	No need to shake	No need to shake	Exceptionally stable
FT-100	Fair	Excellent	8 to 10
FCT-114	Good	Excellent	16 to 20
FCT-100	Good	Excellent	16 to 20
FDA-3409	Good	Excellent	2.5 to 4.5
FCID-585	Not applicable	Not applicable	Not applicable
AT-114	Poor	Good	0.2 to 0.5
AT-100	Poor	Good	0.2 to 0.5
AA-3409	Fair	Good	0.33 to 0.5
AID-585	Poor	Fair	0.2 to 0.4

④ Mixing and pumping capabilities, viscosity, pour point and freezing point of ingredients

Viscosity, pour and freezing points of ingredients directly influence the mixing and pumping capabilities with the available equipment under field conditions. Tables 11 and 12 provide the required data.

Triton® X-100 is extremely viscous below 10°C and has a pour point of 7°C. ATLOX 3409F is very viscous below 7°C and has a pour point of 4°C. Since these properties would affect the pumping and mixing capabilities under extremely cold field temperatures (say 5°C and below), a laboratory metering pump was used to study these aspects; both Triton® X-100 and ATLOX 3409F were difficult to pump out at 5°C, and Triton® X-100 was completely solid at this temperature. Triton® X-114 did not pose any of these problems since

TABLE 11

VISCOSITY OF INGREDIENTS

Ingredient		Viscosity (cp)				
No.	Description	5° C	10° C	15° C	20° C	25° C
1.	Fenitrothion technical	126.0	82.5	53.4	40.0	27.7
2.	Triton® X-114	1470.0	974.0	600.0	380.0	204.0
3.	Triton® X-100	Solid	Extremely viscous	6880.0	1010.0	228.0
4.	Cyclo-Sol® 63	1.62	1.47	1.33	1.28	1.13
5.	Dowanol TPM	20.2	16.3	13.1	10.8	9.27
6.	ATLOX 3409F	Extremely viscous	5660.0	443.0	329.0	217.0
7.	ID 585	2.39	2.12	1.89	1.78	1.56
8.	MATACIL® 180F	157.0	111.0	80.0	62.0	45.8
9.	Water	1.52	1.31	1.14	1.05	0.894

TABLE 12

PROPERTIES OF INGREDIENTS

Ingredients		Appearance and Colour	Solubility in Water	Product Nature	Pour Point/ Freezing Point (° C)	Flash Point (° C)
No.	Description					
1.	Fenitrothion technical	Clear brownish-yellow liquid	Insoluble	Single product	Below 0° C	---
2.	Triton® X-114	Clear colourless liquid	Soluble	" "	Pour point -9° C	> 150° C
3.	Triton® X-100	Clear to mildly cloudy colourless liquid	"	" "	Pour point 7° C Freezes at 6° C	> 150° C
4.	Cyclo-Sol® 63	Clear thin colourless liquid	Insoluble	Mixture of aromatic hydrocarbons	Below 0° C	57° C
5.	Dowanol TPM	Clear thin colourless liquid	Soluble	Single Product	" "	110° C
6.	ATLOX 3409F	Cloudy amber-coloured liquid	"	Formulated product	Pour point 4° C Freezes 3° C	12.2° C
7.	ID 585	Clear creamy yellow thin liquid	Insoluble	Mixture of hyrdocarbons	Below 0° C	52° C
8.	MATACIL® 180F	Heavy creamy beige liquid	"	Formulated product	" "	93° C
9.	Water	Clear colourless liquid	---	Single Product	Freezes at 0° C	---

it has a considerably low pour point (-9°C), and was easier to pump out and mix with other ingredients.

With regard to mixing procedures for Triton® X-100 or Triton® X-114, an additional problem will arise if the emulsifiers were allowed to come into direct contact with water; these two chemicals tend to form a gel when added directly to water, contributing to difficulties for pumping out and mixing. The gel-formation tendency is much higher for Triton® X-100 than for Triton® X-114. This problem can be totally avoided if all the non-aqueous ingredients were thoroughly mixed before adding water.

5. Spray atomization characteristics

5a. With hydraulic and spinning disc nozzle systems in the Institute's spray chamber

In forestry spraying of pesticides, the efficiency of spray atomization and application largely depends upon the target we want to aim at. Unless we want to kill the spruce budworm larvae by direct droplet impingement (the probability of which is low considering the protected nature of the budworm microhabitat, whose shielding would filter off the larger droplets) or by fumigation by the pesticide vapour (the role of the vapour phase is yet to be investigated), the target of interest is generally the foliage. Foliar droplets and pesticide concentration can be assumed to approximately represent the insect dose, since most larvae are probably killed by feeding on the persistent toxic residues on the needles, and/or, to some extent, by cuticular absorption upon contact while crawling. This assumption, however, excludes the role of the vapour phase, if any.

To achieve maximum atomization and spray application efficiency, the optimum size range of droplets that would have maximum impaction efficiency on conifer needles should be known first. Droplets of the size of less than 15 - 20 µm in diameter have been known (Mason, 1971) to have a low impaction efficiency on targets of geometry similar to conifer needles, unless external forces are used to facilitate the impaction processes (Matthews and Lincoln 1982). These droplets have a high tendency to undergo off-target drift, if sprayed under certain unfavourable conditions(Lawson and Uk,1978). Large droplets on the other hand, are filtered off at the extreme periphery of the tree canopy and consequently have a low penetrability within the canopy (Joyce _et al_, 1977). For example, a 100 µm droplet would be too large to reach the budworm microhabitat region. Also large droplets do not give adequate coverage at the ULV application rate and hence contribute to low effectiveness of pesticides applied. Therefore, each target has a defined optimum range of droplet sizes for high impaction efficiency (Uk, 1977).

It's well known that the physical and chemical properties of ingredients of formulations contribute to the spray atomization efficiency of spray mixes (Yates and Akesson, 1973). A comparative study was therefore made on viscosity, density, surface tension, and droplet spreading characteristics on target surfaces. Viscosity was measured at 5°C to 25°C at 5°C intervals using Ostwald's viscometer. Density was measured at the same intervals of temperature using density bottles. Surface tension values were measured at the same temperatures using the capillary rise method. Values are listed in Tables 13 to 15.

For measuring the droplet spreading characteristics, it was necessary to add a dye tracer to make the droplets visible on target surfaces. A water-soluble dye, Erio Acid Red was added to emulsion formulations and an oil soluble dye Automate B Red was added to the oil-based ones. For measuring the degree of spreading of droplets of variable sizes (65 to 220 µm in diameter), droplets of uniform size were produced using the rotary device designed by Rayner and Haliburton (1955), and were captured on glass fibre of known thickness (5.6 ± 0.2 µm). The short and long diameters 'a' and 'b' of the ellipsoid formed on the fibre were measured at 22° ± 2°C in still air of relative humidity 52 ± 3%. From the volume V of the ellipsoid, the sperical diameter 'd' was calculated using equations shown below:

$$V_{drop} = V_{ellipse} - V_{fibre}$$

$$V_{drop} = (\pi/6)\,d^3 = (\pi/6)\,a^2 b - (\pi/4)\,5.6^2 b$$

TABLE 13

VISCOSITY VALUES OF FORMULATIONS

Formulation		Viscosity (cp)				
No.	Description	5° C	10° C	15° C	20° C	25° C
1.	FT-114	365	158	1449	990	276
2.	FT-100	11.8	11.5	12.0	14.8	16.4
3.	FCT-114	6.80	6.32	6.20	4.50	3.90
4.	FCT-100	9.25	7.42	6.26	5.69	4.72
5.	FDA-3409	2.89	2.53	2.13	1.80	1.49
6.	FCID-585	2.80	2.38	2.06	1.95	1.56
7.	AT-114	4.05	3.35	2.87	2.74	2.39
8.	AT-100	5.89	3.69	3.18	2.66	1.26
9.	AA-3409	2.94	2.58	2.12	1.80	1.54
10.	AID-585	5.36	4.24	3.48	3.23	2.80

TABLE 14

DENSITY VALUES OF FORMULATIONS

Formulation		Density (g/ml)				
No.	Description	5° C	10° C	15° C	20° C	25° C
1.	FT-114	1.046	1.045	1.044	1.042	1.040
2.	FT-100	1.055	1.051	1.050	1.048	1.046
3.	FCT-114	1.012	1.011	1.008	1.005	0.984
4.	FCT-100	1.016	1.013	1.011	1.009	1.040
5.	FDA-3409	1.012	1.011	1.010	1.009	1.008
6.	FCID-585	0.9233	0.9199	0.9158	0.9122	0.9082
7.	AT-114	0.9924	0.9899	0.9866	0.9853	0.9839
8.	AT-100	1.001	1.000	0.9970	0.9940	0.9916
9.	AA-3409	1.0133	1.0125	1.0116	1.0108	1.0096
10.	AID-585	0.8418	0.8384	0.8347	0.8319	0.8294

TABLE 15

SURFACE TENSION VALUES OF FORMULATIONS

Formulation		Surface Tension (dyne/cm)				
No.	Description	5° C	10° C	15° C	20° C	25° C
1.	FT-114	NA	NA	NA	NA	NA*
2.	FT-100	32.26	32.16	32.10	32.04	31.99
3.	FCT-114	32.24	32.22	32.10	32.03	31.35
4.	FCT-100	34.66	33.34	33.30	33.24	33.12
5.	FDA-3409	28.85	28.83	26.40	26.38	26.35
6.	FCID-585	27.87	27.14	26.70	27.22	26.79
7.	AT-114	23.01	22.76	22.42	22.33	21.92
8.	AT-100	32.53	31.86	30.40	31.48	30.06
9.	AA-3409	31.65	31.63	30.34	30.31	29.01
10.	AID-585	30.11	29.17	29.04	28.53	26.01

* Not available. Due to the high viscosity of FT-114, the capillary rise method is not suitable for this formulation.

TABLE 16

SPREAD FACTOR DATA OF FORMULATIONS

Formulation No.	Linear regression equation d = drop diam. D = stain diam.	$(R = \text{corr. coef.})^2$ (%)
FT-114	d = 6.75 + 0.268 D	99.1
FT-100	d = 1.50 + 0.309 D	99.5
FCT-114	d = 2.60 + 0.308 D	99.6
FCT-100	d = 0.461 + 0.367 D	99.1
FDA-3409	d = 0.0671 + 0.328 D	99.9
FCID-585	d = 0.104 + 0.222 D	99.9
AT-114	d = 3.85 + 0.314 D	99.6
AT-100	d = -0.102 + 0.325 D	99.9
AA-3409	d = 0.480 + 0.325 D	99.6
AID-585	d = 1.77 + 0.171 D	99.9

The generated droplets were also allowed to impact simultaneously on Kromekote® card, while falling freely under gravity. An interval of two hours was allowed before measuring the droplet stain sizes (D) on the card, so that spreading of highly viscous liquids would attain equilibrium. For size measurements of stain or droplet, a dissecting microscope was used at magnifications of 40X, 100X and 200X. Spreadability was assessed by a term defined as "spread factor" which is mathematically expressed as:

$$\text{Spread factor (SF)} = \frac{\text{Stain diameter on Kromekote}^{\text{®}}\text{ card}}{\text{Droplet diameter on glass fibre}}$$

The degree of droplet spreading was fitted into linear regression equations and were presented in Table 16.

Spray atomization was carried out in the spray chamber (Fig. 2.) using a pressure nozzle (a solid cone nozzle) and a spinning disc nozzle (Mini ULVA of Micronair Corporation). The objective of using two types of nozzles in the laboratory is to determine the influence of formulation properties on atomization efficiency, type of droplet spectra produced and impacted on target surfaces. The use of a hydraulic and/or a spinning disc nozzle for a particular formulation would provide knowledge on the type of droplet spectra that can be approximately expected for that formulation if similar nozzle systems were to be used under similar atomization conditions in the field (approximate examples would be the use of TBM aircrafts in N.B., fitted with hydraulic nozzles, and the use of the rotary cage atomizer "Micronair AU3000" with smaller aircrafts). The temperature of the spray chamber was 22° ± 2°C and, the relative humidity was 50 ± 3% throughout the study . For collection of spray droplets for measurements of droplet size spectra, a TV tower (sampling tower) of 3m high was mounted inside the spray chamber as shown in Fig. 2.. Kromekote cards were placed at 6 different heights of the sampling tower and the 7th card was placed beside the tower. A constant wind flow was generated, the direction being from left to right in the diagram, i.e. in such a manner the spray droplets falling

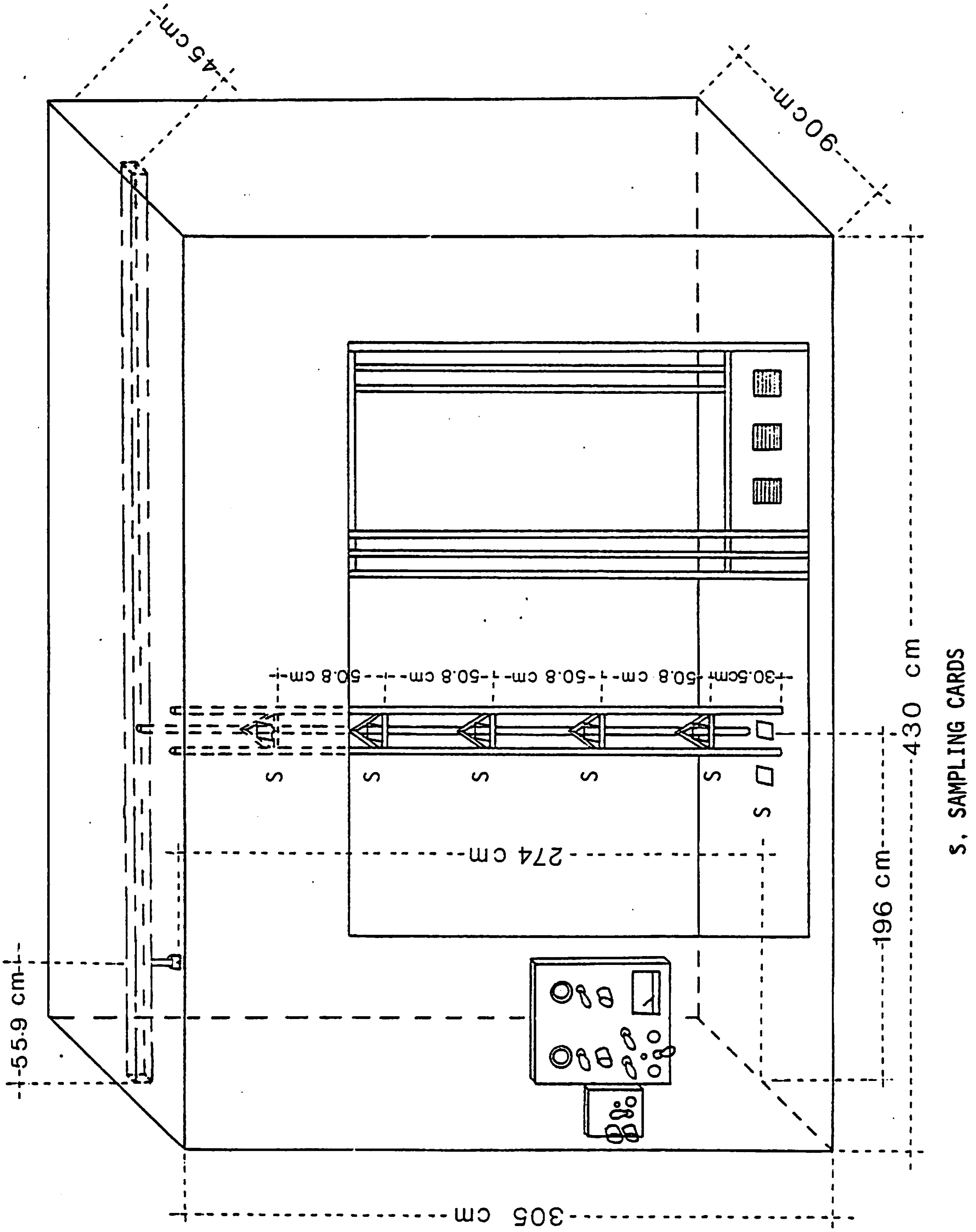


Fig.-2. Spray chamber

Table 17. Kromekote® Card Data Using Hydraulic/Spinning Disc Nozzles

Droplet Number/Volume Distribution According to Size Category

Formulation: FT-114

Stain diameter range (μm)	Spread factor	Droplet diameter range (μm)	Average droplet diameter (μm)	Hydraulic Nozzle Cumulative frequency (%)	Hydraulic Nozzle Cumulative droplet volume distribution (%)	Spinning Disc Nozzle Cumulative frequency (%)	Spinning Disc Nozzle Cumulative droplet volume distribution (%)
10-22	1.71	5.8-12.8	9.8	-	—	12.47	0.046
23-45	2.14	12.9-18.8	15.9	6.73	0.0216	17.56	0.124
46-67	2.58	18.9-24.7	21.9	15.32	0.0939	24.77	0.414
68-90	2.83	24.8-30.9	27.9	17.85	0.1380	33.60	1.150
91-113	2.99	31.0-37.0	34.1	23.41	0.3145	47.69	3.290
114-169	3.17	37.1-52.0	44.7	35.03	1.145	76.10	13.01
170-225	3.31	52.1-67.0	59.7	42.27	2.380	82.25	18.03
226-281	3.39	67.1-82.0	74.7	51.19	5.362	85.45	23.15
282-338	3.45	82.1-97.3	89.8	62.81	12.11	91.28	39.36
339-394	3.49	97.4-112.3	105.0	77.96	26.17	94.39	53.15
395-450	3.52	112.4-127.4	120.0	84.53	35.27	97.66	74.80
451-506	3.54	127.5-142.4	135.0	86.55	39.26	99.40	91.13
507-607	3.57	142.5-169.4	156.0	93.28	59.78	100.00	100.00
608-799	3.60	169.5-220.9	195.3	100.00	100.02	—	—

FIG.3. DROPLET SPECTRA OF FT-114

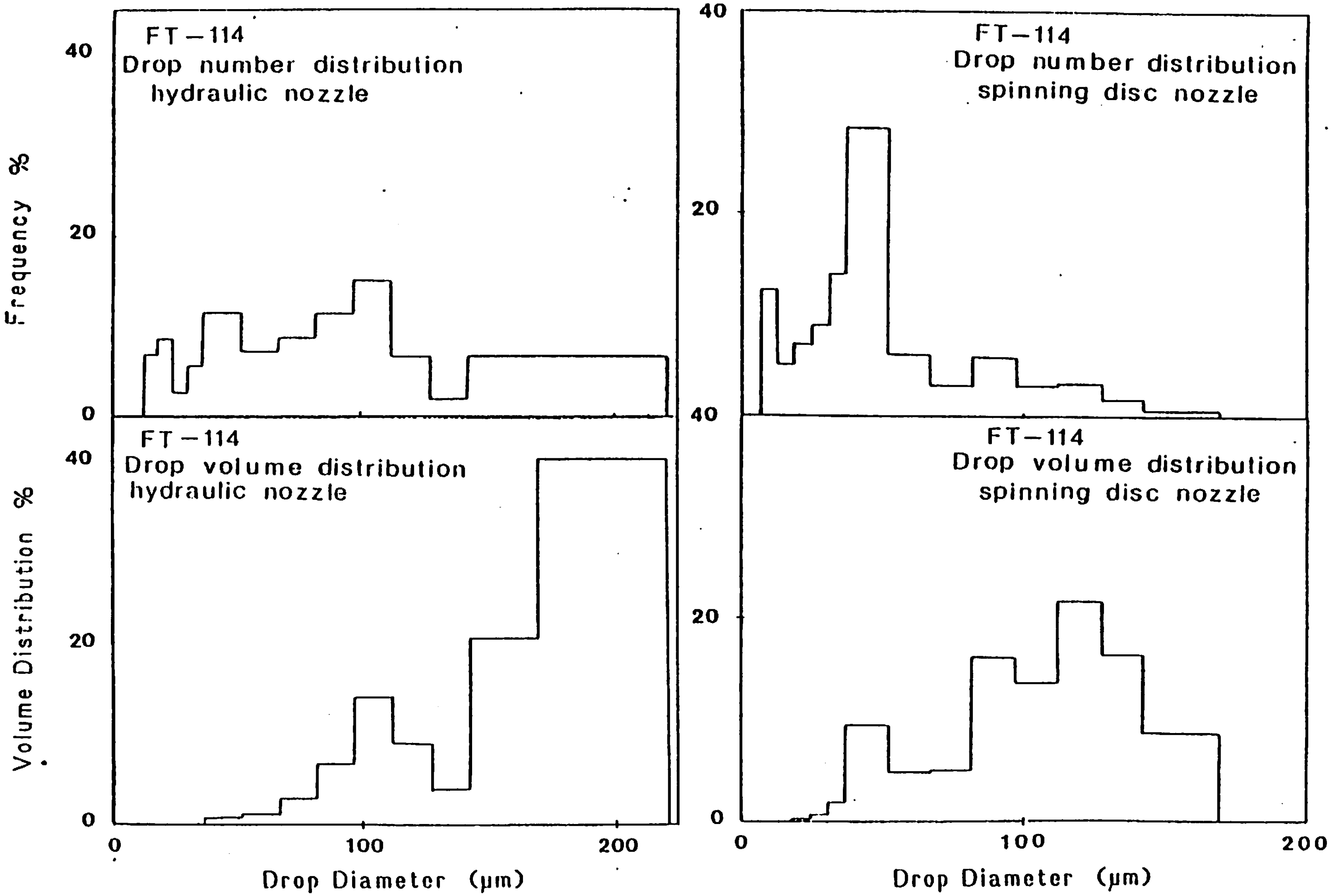


Table 18. Kromekote® Card Data Using Hydraulic/Spinning Disc Nozzles

Droplet Number/Volume Distribution According to Size Category

Formulation: FT-100

				Hydraulic Nozzle		Spinning Disc Nozzle	
Stain diameter range (µm)	Spread factor	Droplet diameter range (µm)	Average droplet diameter (µm)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)
10-22	2.28	4.4-8.3	5.1	4.66	0.0004	0.32	0.001
23-45	2.83	8.4-15.4	12.0	13.86	0.012	1.44	0.020
46-67	2.98	15.5-22.2	19.0	23.70	0.062	15.94	0.974
68-90	3.05	22.3-29.3	25.9	30.44	0.148	30.99	3.498
91-113	3.09	29.4-36.4	33.0	35.49	0.283	57.80	12.80
114-169	3.13	36.5-53.7	45.2	41.97	0.725	88.98	40.60
170-225	3.16	53.8-71.0	62.5	50.78	2.317	96.11	57.42
226-281	3.18	71.1-88.3	79.8	57.77	4.947	97.83	65.89
282-338	3.19	88.4-105.9	97.3	66.06	10.585	98.77	74.29
339-394	3.19	106.0-123.2	114.7	78.11	24.027	99.40	83.41
395-450	3.20	123.3-140.6	132.1	88.99	42.534	99.59	87.67
451-506	3.20	140.7-157.9	149.4	91.97	49.861	99.98	100.00
507-607	3.21	158.0-189.1	173.6	95.08	61.875	—	—
608-799	3.21	189.2-248.4	218.9	100.00	99.999	—	—

FIG. 4. DROPLET SPECTRA OF FT-100

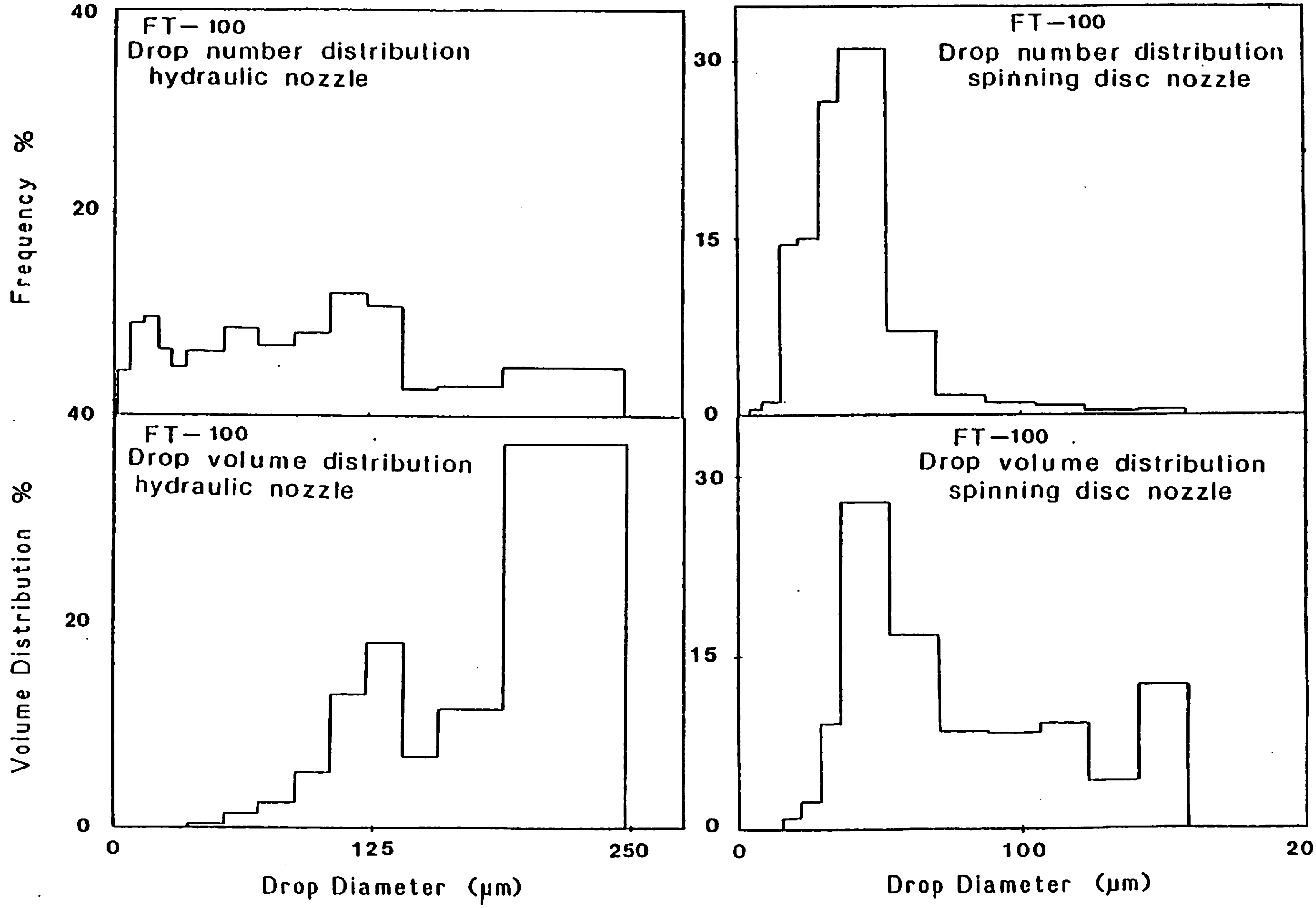


Table 19. Kromekote® Card Data Using Hydraulic/Spinning Disc Nozzles

Droplet Number/Volume Distribution According to Size Category

Formulation: FCT-114

				Hydraulic Nozzle		Spinning Disc Nozzle	
Stain diameter range (µm)	Spread factor	Droplet diameter range (µm)	Average droplet diameter (µm)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)
10-22	1.87	5.3 -9.4	6.1	1.88	0.0006	8.58	0.07
23-45	2.60	9.5-16.5	13.1	10.34	0.0277	22.91	1.16
46-67	2.82	16.6-23.2	20.0	17.55	0.1102	55.29	9.94
68-90	2.93	23.3-30.3	26.9	20.37	0.1890	68.54	18.71
91-113	3.00	30.4-37.4	34.0	25.07	0.4541	90.04	47.38
114-169	3.06	37.5-54.7	46.2	38.55	2.355	98.22	74.67
170-225	3.11	54.8-71.9	63.4	51.09	6.937	99.45	85.32
226-281	3.14	72.0-89.1	80.7	66.76	18.72	99.80	91.54
282-338	3.16	89.2-106.7	98.1	80.24	36.93	99.90	94.46
339-394	3.17	106.8-124.0	115.5	89.64	57.65	100.0	100.0
395-450	3.18	124.1-141.2	132.7	95.91	78.63	—	—
451-506	3.19	141.3-158.4	150.0	99.36	95.29	—	—
507-607	3.20	158.5-189.6	174.2	99.99	100.00	—	—

FIG. 5. DROPLET SPECTRA OF FCT-114

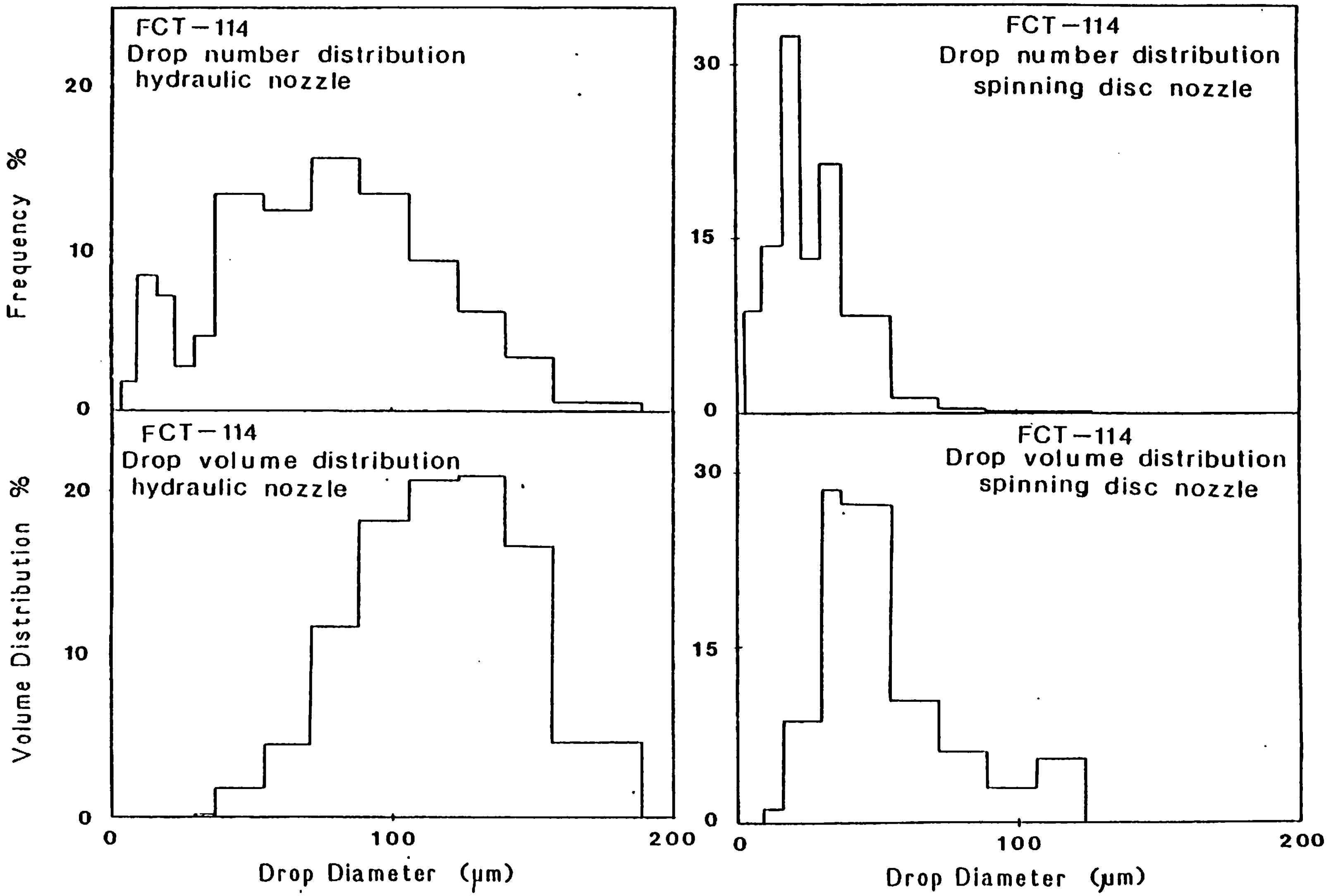


Table 20. Kromekote® Card Data Using Hydraulic/Spinning Disc Nozzles

Droplet Number/Volume Distribution According to Size Category

Formulation: FCT-100

				Hydraulic Nozzle		Spinning Disc Nozzle	
Stain diameter range (µm)	Spread factor	Droplet diameter range (µm)	Average droplet diameter (µm)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)
10-22	2.46	4.0-8.5	4.7	0.54	0.0001	20.59	0.03
23-45	2.63	8.6-17.0	12.9	4.90	0.0124	24.78	0.16
46-67	2.67	17.1-25.1	21.2	9.53	0.0700	49.75	3.48
68-90	2.68	25.2-33.5	29.5	15.43	0.2669	63.10	8.24
91-113	2.69	33.6-41.9	37.9	22.42	0.7637	84.13	24.20
114-169	2.70	42.0-62.5	52.4	34.14	2.963	96.51	49.01
170-225	2.71	62.6-83.0	72.9	57.85	14.97	98.61	60.41
226-281	2.71	83.1-103.6	93.5	81.19	39.87	99.22	67.40
282-338	2.71	103.7-124.5	114.2	93.54	63.91	99.42	71.78
339-394	2.72	124.6-145.1	135.0	97.26	75.86	99.67	80.31
395-450	2.72	145.2-165.6	155.5	97.99	79.43	99.83	88.34
451-506	2.72	165.7-186.2	176.1	98.44	82.68	99.99	100.0
507-607	2.72	186.3-223.2	204.9	99.98	100.01	–	–

FIG. 6. DROPLET SPECTRA OF FCT-100

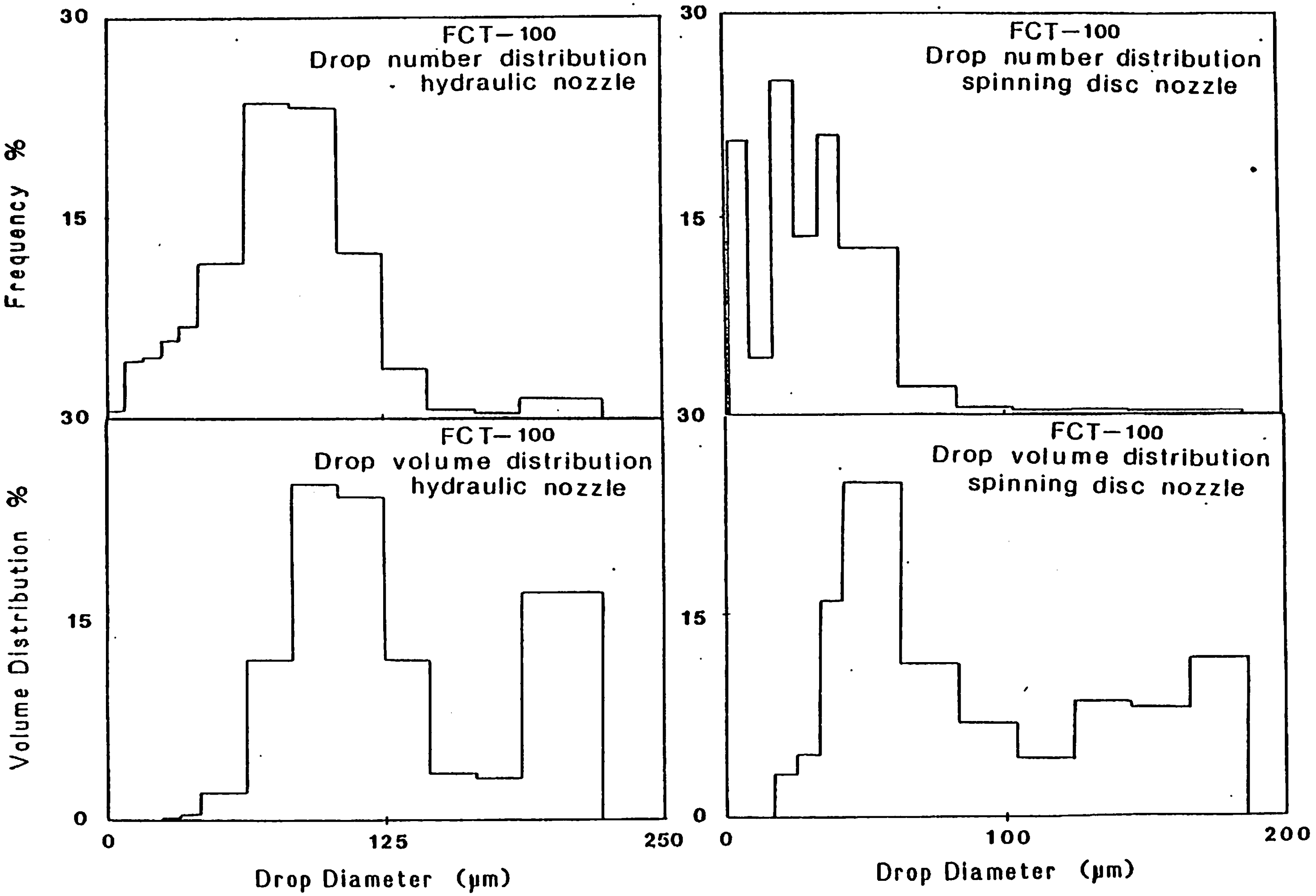


Table 21. Kromekote® Card Data Using Hydraulic/Spinning Disc Nozzles

Droplet Number/Volume Distribution According to Size Category

Formulation: FDA-3409

Stain diameter range (μm)	Spread factor	Droplet diameter range (μm)	Average droplet diameter (μm)	Hydraulic Nozzle		Spinning Disc Nozzle	
				Cumulative frequency (%)	Cumulative droplet volume distribution (%)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)
10-22	3.00	3.3-7.3	3.8	4.28	0.0002	1.57	0.001
23-45	3.03	7.4-14.8	11.2	18.64	0.0192	6.67	0.054
46-67	3.04	14.9-22.0	18.6	28.72	0.0799	29.80	1.139
68-90	3.04	22.1-29.6	26.0	31.99	0.1336	50.37	3.769
91-113	3.04	29.7-37.1	33.5	35.52	0.2580	68.96	8.877
114-169	3.04	37.2-55.5	46.5	44.34	1.087	85.24	20.81
170-225	3.05	55.6-73.9	64.8	54.16	3.596	92.71	35.68
226-281	3.05	74.0-92.2	83.2	66.00	9.988	95.54	47.57
282-338	3.05	92.3-110.9	101.7	78.85	22.66	97.98	66.32
339-394	3.05	111.0-129.3	120.3	86.91	35.80	99.13	80.91
395-450	3.05	129.4-147.7	138.6	88.67	40.20	99.74	92.71
451-506	3.05	147.8-166.0	157.0	92.45	53.91	99.99	100.0
507-607	3.05	166.1-199.2	182.8	99.50	94.23	—	—
608-799	3.05	199.3-262.1	230.8	100.00	100.00	—	—

FIG. 7. DROPLET SPECTRA OF FDA-3409

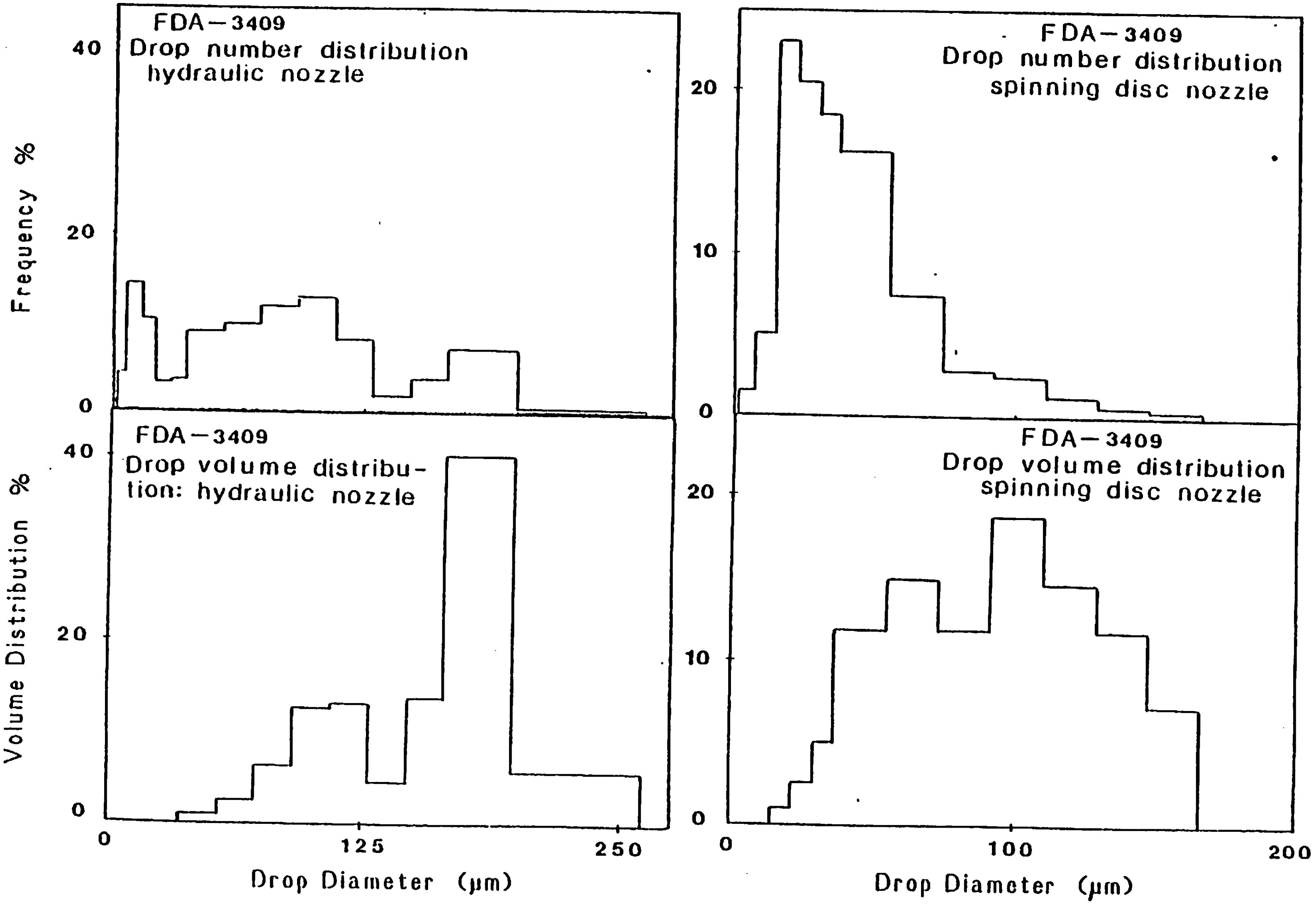


Table 22. Kromekote® Card Data Using Hydraulic/Spinning Disc Nozzles

Droplet Number/Volume Distribution According to Size Category

Formulation: FCID-585

				Hydraulic Nozzle		Spinning Disc Nozzle	
Stain diameter range (µm)	Spread factor	Droplet diameter range (µm)	Average droplet diameter (µm)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)
10-22	4.33	2.0-5.0	2.7	5.32	0.0001	0.20	0.00
23-45	4.44	5.1-10.0	7.7	10.84	0.0024	7.88	0.06
46-67	4.47	10.1-15.0	12.6	17.59	0.0151	24.59	0.67
68-90	4.48	15.1-20.0	17.6	21.27	0.0339	34.35	1.63
91-113	4.48	20.1-25.2	22.7	25.77	0.0832	45.42	3.97
114-169	4.49	25.3-37.6	31.5	39.06	0.4705	66.61	15.88
170-225	4.49	37.7-50.1	44.0	53.37	1.602	91.44	53.73
226-281	4.50	50.2-62.5	56.4	60.32	2.762	97.70	73.90
282-338	4.50	62.6-75.1	68.9	66.05	4.507	99.16	82.46
339-394	4.50	75.2-87.6	81.5	71.16	7.081	99.46	85.29
395-450	4.50	87.7-100.0	93.9	75.45	10.39	99.72	89.21
451-506	4.50	100.1-112.4	106.3	80.15	15.65	99.80	91.01
507-607	4.50	112.5-134.9	123.8	91.40	35.50	99.92	95.26
608-799	4.50	135.0-177.5	156.3	93.85	44.22	99.99	100.01
800-1125	4.50	177.6-250.0	213.8	99.98	100.00	—	—

FIG. 8. DROPLET SPECTRA OF FCID-585

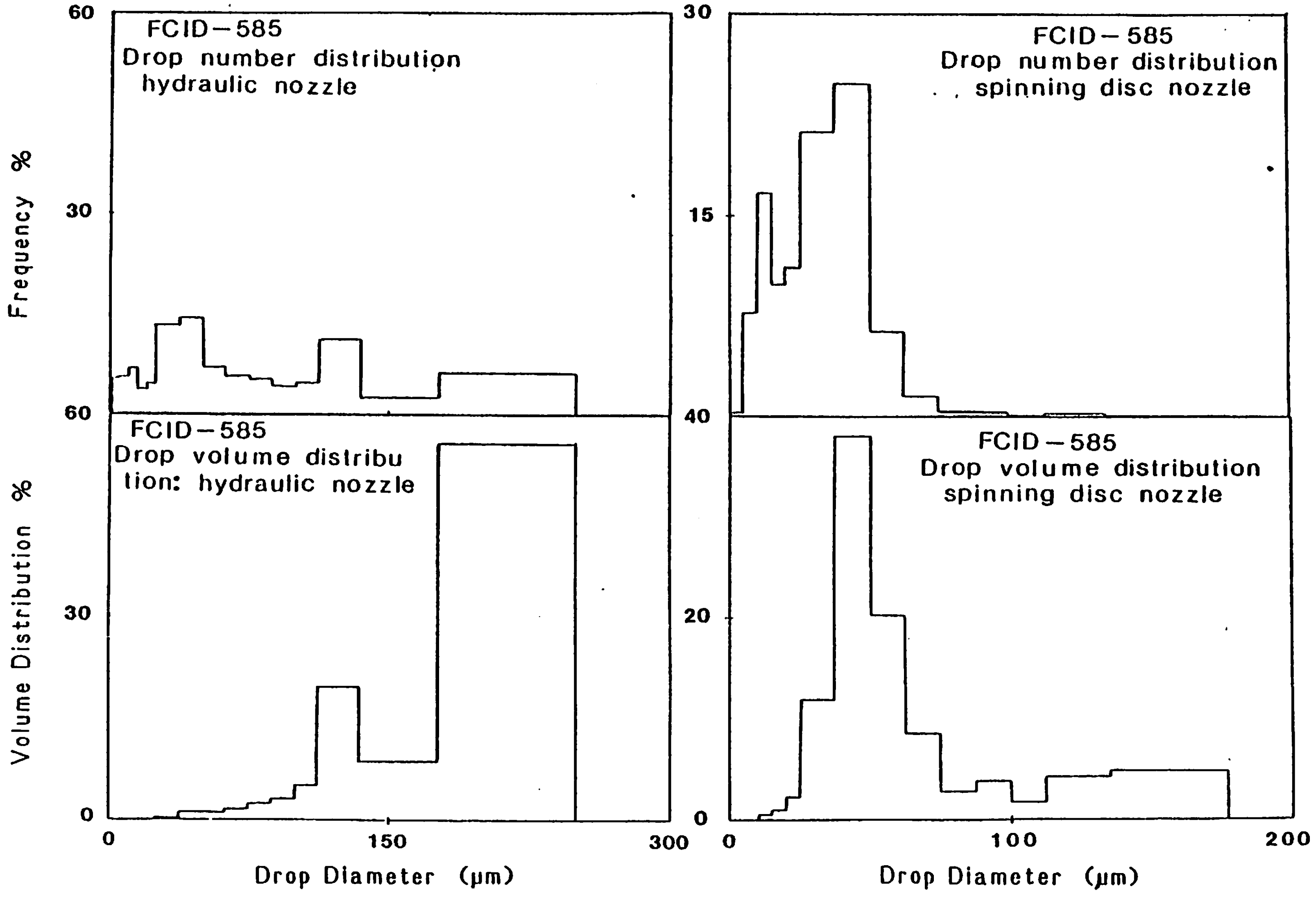


Table 23. Kromekote® Card Data Using Hydraulic/Spinning Disc Nozzles

Droplet Number/Volume Distribution According to Size Category

Formulation: AT-114

				Hydraulic Nozzle		Spinning Disc Nozzle	
Stain diameter range (µm)	Spread factor	Droplet diameter range (µm)	Average droplet diameter (µm)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)
10-22	1.54	4.2-10.8	7.5	18.98	0.0074	10.80	0.03
23-45	2.34	10.9-18.0	14.5	22.73	0.0193	14.43	0.10
46-67	2.62	18.1-24.9	21.6	29.82	0.0905	28.77	0.96
68-90	2.76	25.0-32.1	28.7	32.74	0.1590	47.10	3.53
91-113	2.84	32.2-39.3	35.9	37.02	0.3558	75.05	11.21
114-169	2.93	39.4-56.9	48.3	47.86	1.573	85.98	18.53
170-225	3.00	57.0-74.5	65.9	66.73	6.949	90.98	27.04
226-281	3.04	74.6-92.1	83.4	87.48	18.97	94.13	37.94
282-338	3.06	92.2-110.0	101.2	88.84	20.37	96.49	52.52
339-394	3.08	110.1-127.6	118.9	89.15	20.89	98.24	70.08
395-450	3.09	127.7-145.2	136.5	89.67	22.22	99.49	88.94
451-506	3.11	145.3-162.7	154.1	90.40	24.88	100.00	100.01
507-607	3.12	162.8-194.4	178.7	96.34	58.72	—	—
608-799	3.13	194.5-254.7	224.7	99.99	100.02	—	—

FIG. 9. DROPLET SPECTRA OF AT-114

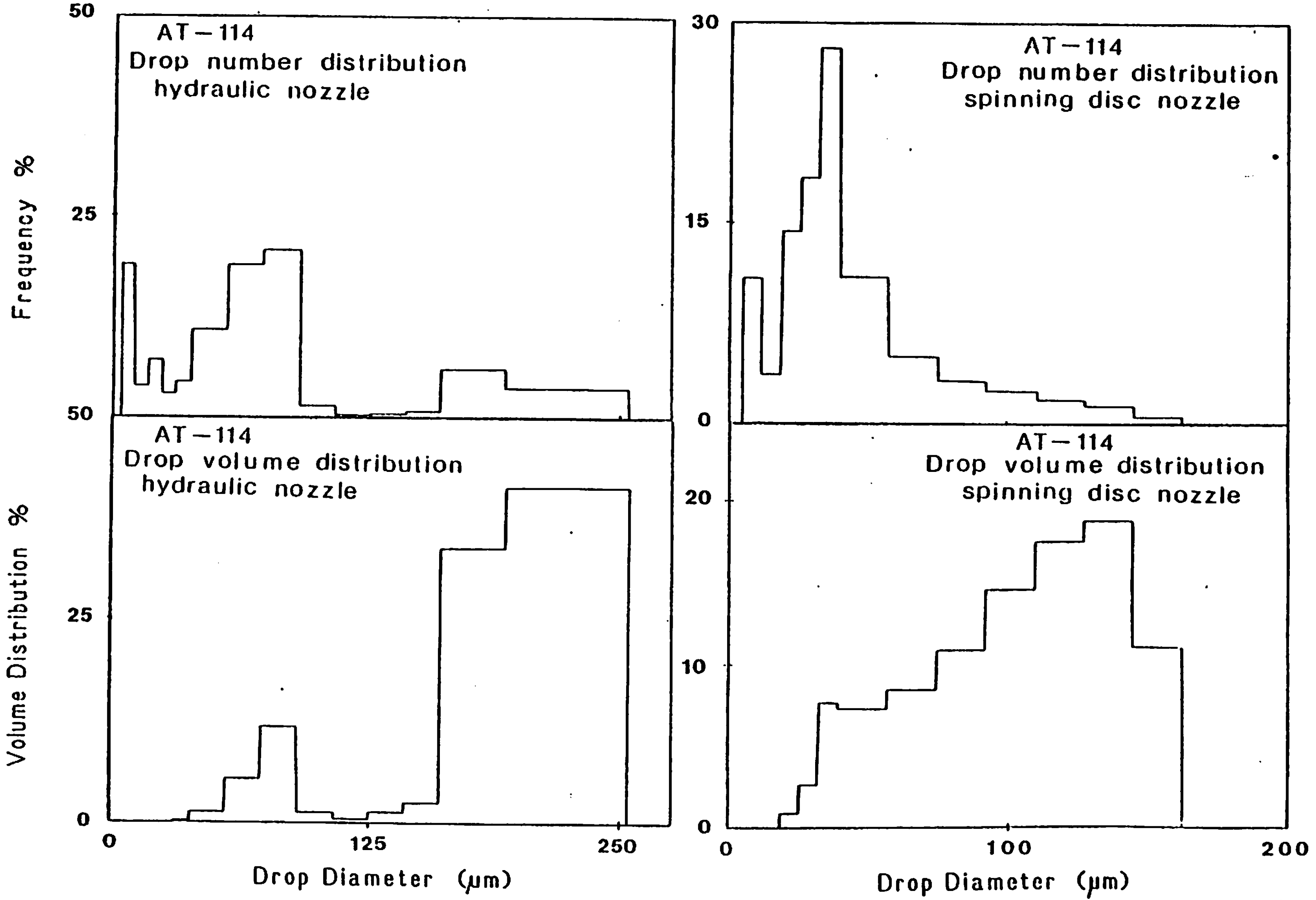


Table 24. Kromekote® Card Data Using Hydraulic/Spinning Disc Nozzles

Droplet Number/Volume Distribution According to Size Category

Formulation: AT-100

Stain diameter range (µm)	Spread factor	Droplet diameter range (µm)	Average droplet diameter (µm)	Hydraulic Nozzle: Cumulative frequency (%)	Hydraulic Nozzle: Cumulative droplet volume distribution (%)	Spinning Disc Nozzle: Cumulative frequency (%)	Spinning Disc Nozzle: Cumulative droplet volume distribution (%)
10-22	3.16	3.0-7.0	3.6	19.37	0.0027	1.24	0.001
23-45	3.11	7.1-14.5	10.9	23.24	0.0176	3.85	0.053
46-67	3.09	14.6-21.7	18.3	27.85	0.0867	15.28	1.10
68-90	3.09	21.8-29.1	25.6	31.17	0.2494	46.69	9.07
91-113	3.09	29.2-36.6	33.0	39.10	1.088	86.33	30.77
114-169	3.08	36.7-54.8	45.9	59.21	6.781	94.33	42.49
170-225	3.08	54.9-73.0	64.1	70.46	15.46	97.16	53.80
226-281	3.08	73.1-91.2	82.3	83.01	35.93	98.44	64.61
282-338	3.08	91.3-109.7	100.6	94.82	71.21	99.35	78.75
339-394	3.08	109.8-127.9	119.0	99.43	93.99	99.79	89.97
395-450	3.08	128.0-146.1	137.2	99.80	96.77	99.90	94.27
451-506	3.08	146.2-164.5	155.4	99.80	96.77	100.00	99.99
507-607	3.08	164.6-197.1	180.9	99.98	100.00	—	—

FIG. 10. DROPLET SPECTRA OF AT-100

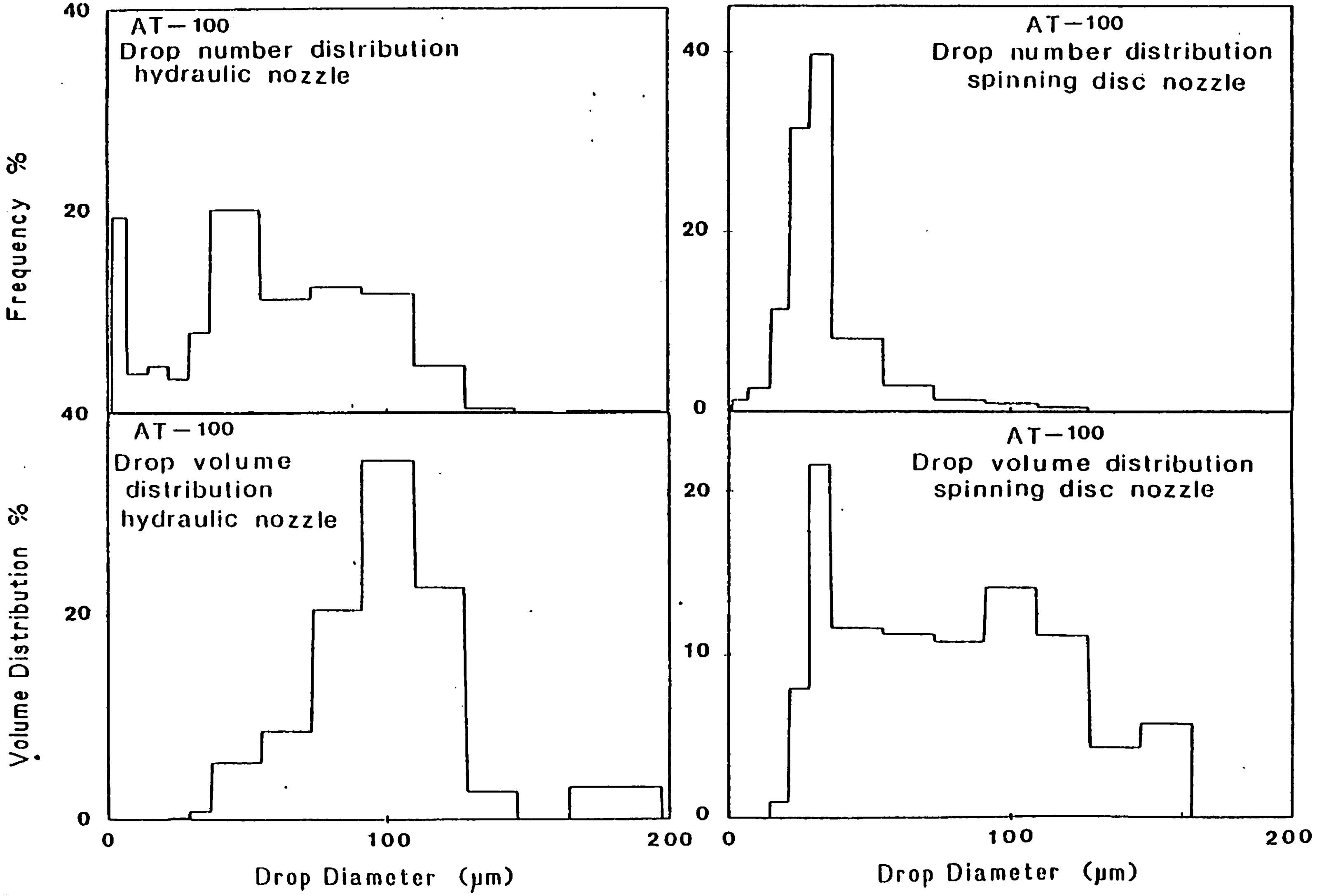


Table 25. Kromekote® Card Data Using Hydraulic/Spinning Disc Nozzle

Droplet Number/ Volume Distribution According to Size Category

Formulation: AA-3409

Stain diameter range (μm)	Spread factor	Droplet diameter range (μm)	Average droplet diameter (μm)	Hydraulic Nozzle		Spinning Disc Nozzle	
				Cumulative frequency (%)	Cumulative droplet volume distribution (%)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)
10-22	2.73	3.7-7.6	4.2	44.97	0.0021	31.10	0.07
23-45	2.95	7.7-15.1	11.5	47.93	0.0049	65.83	1.56
46-67	3.00	15.2-22.3	18.8	49.31	0.0106	91.17	6.29
68-90	3.02	22.4-29.7	26.2	50.10	0.0193	93.09	7.24
91-113	3.03	29.8-37.2	33.6	51.28	0.0472	94.69	8.95
114-169	3.05	37.3-55.4	46.5	55.22	0.2927	96.64	14.37
170-225	3.05	55.5-73.6	64.7	57.39	0.6563	97.67	22.24
226-281	3.06	73.7-91.8	82.9	64.29	3.094	98.86	41.16
282-338	3.06	91.9-110.3	101.2	75.14	10.08	99.28	53.23
339-394	3.06	110.4-128.5	119.6	85.20	20.75	99.72	74.55
395-450	3.07	128.6-146.7	137.8	88.75	26.50	99.82	81.07
451-506	3.07	146.8-164.9	156.0	90.13	31.62	100.00	100.0
507-607	3.07	165.0-197.8	181.5	91.51	36.74	—	—
608-799	3.07	197.9-260.2	229.1	99.99	100.01	—	—

FIG. 11. DROPLET SPECTRA OF AA-3409

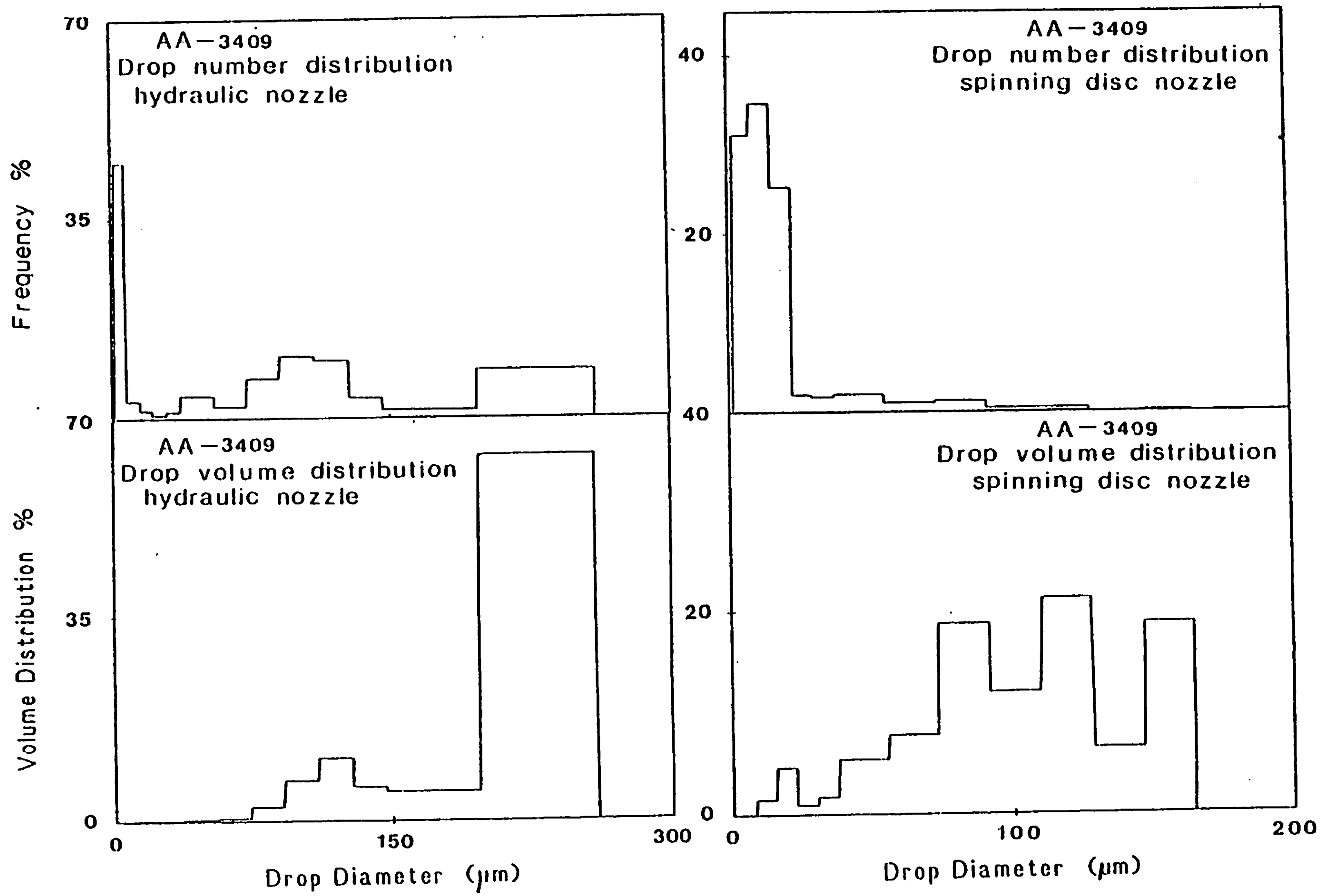


Table 26. Kromekote® Card Data Using Hydraulic/Spinning Disc Nozzles
Droplet Number/Volume Distribution According to Size Category
Formulation: AID-585

				Hydraulic Nozzle		Spinning Disc Nozzle	
Stain diameter range (μm)	Spread factor	Droplet diameter range (μm)	Average droplet diameter (μm)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)
10-22	3.08	3.2-5.5	3.8	0.12	0.0000	3.00	0.003
23-45	4.48	5.6-9.5	7.6	0.98	0.0005	8.59	0.043
46-67	4.94	9.6-13.2	11.4	3.21	0.0051	20.74	0.343
68-90	5.17	13.3-17.2	15.3	6.69	0.0221	33.19	1.073
91-113	5.31	17.3-21.1	19.2	12.35	0.0771	44.32	2.373
114-169	5.45	21.2-30.7	26.0	25.05	0.3824	59.26	6.683
170-225	5.56	30.8-40.2	35.5	36.92	1.114	84.15	25.07
226-281	5.62	40.3-49.8	45.1	49.60	2.712	93.67	39.45
282-338	5.66	49.9-59.6	54.8	56.28	4.219	97.09	48.71
339-394	5.69	59.7-69.1	64.4	60.05	5.604	98.19	53.59
395-450	5.71	69.2-78.7	74.0	63.59	7.575	98.35	54.55
451-506	5.72	78.8-88.3	83.6	70.39	13.03	98.97	60.47
507-607	5.74	88.4-105.6	97.0	76.45	20.62	99.16	63.24
608-799	5.76	105.7-138.4	122.1	94.66	66.07	99.71	79.81
800-1125	5.79	138.5-194.1	166.4	100.03	100.01	99.98	100.00

FIG. 12..DROPLET SPECTRA OF AID-585

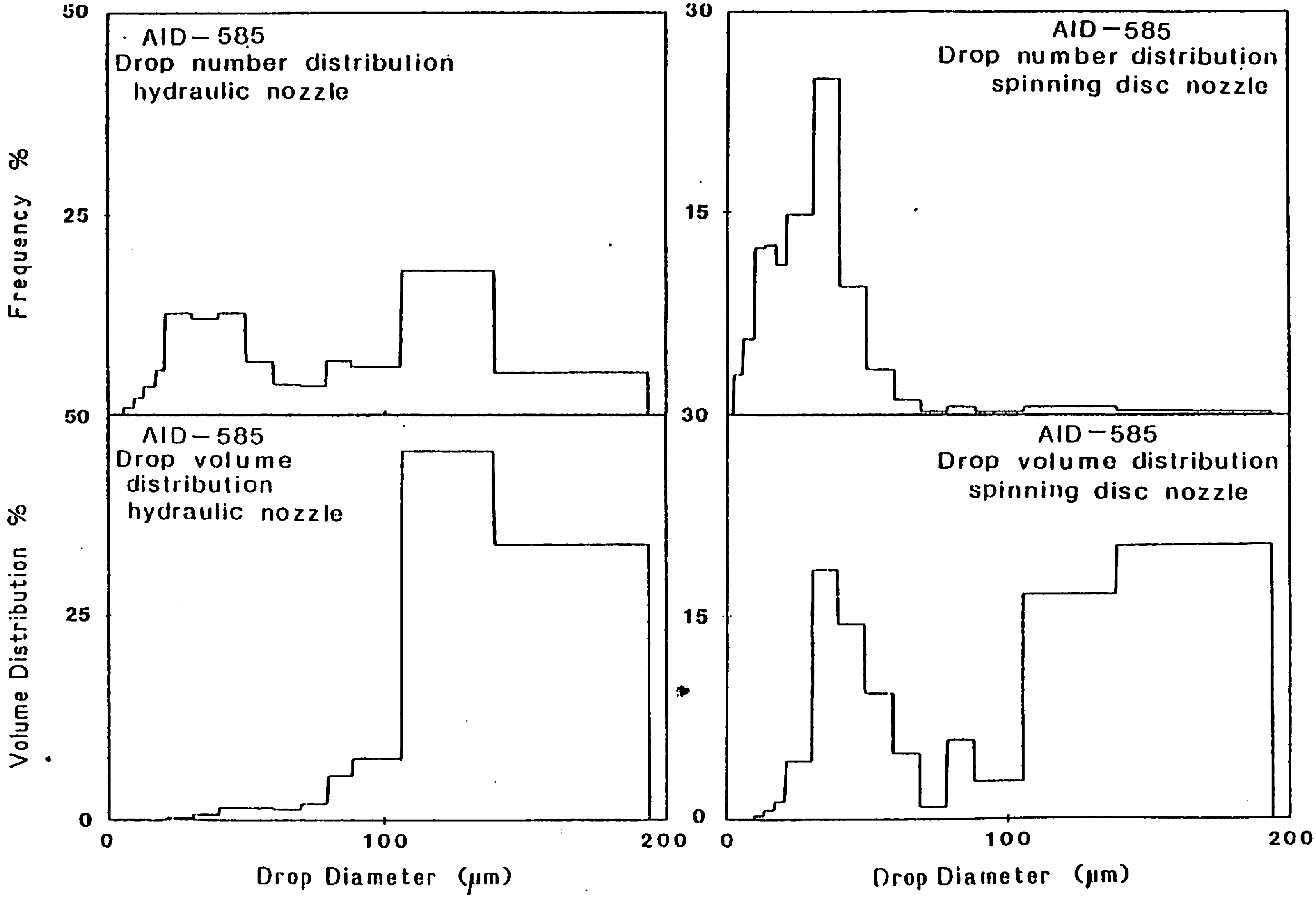


TABLE 27. SUMMARY DATA ON DROPLET SPECTRA OF FORMULATIONS ON KROMEKOTE® CARD: HYDRAULIC NOZZLE

Formulation No.	Drops per cm^2	$D_{min.}$ (µm)	$D_{max.}$ (µm)	Number mode (µm)	Volume mode (µm)	Number median diameter (µm)	Volume median diameter (µm)	Volume deposit (ml/ha)
FT-114	21	16	220	25-50& 80-110	150-220	69	143	1385
FT-100	28	5	250	100-140	190-250	63	148	1954
FCT-114	23	6	190	50-100	90-140	60	110	834
FCT-100	26	5	220	60-100	80-125& 185-220	66	101	1052
FDA-3409	21	4	260	10-22& 75-100	160-220	58	141	1190
FCID-585	18	3	250	25-50& 115-135	180-250	42	159	982
AT-114	17	8	255	55-90	165-255	49	175	900
AT-100	35	4	195	4-10& 35-55	80-110	44	89	606
AA-3409	15	4	260	4-10& 95-125	200-260	26	199	1297
AID-585	16	4	195	25-50& 110-135	110-190	46	116	758

TABLE 28. SUMMARY DATA ON DROPLET SPECTRA OF FORMULATIONS ON KROMEKOTE® CARD: SPINNING DISC NOZZLE

Formulation No.	Drops per cm^2	$D_{min.}$ (μm)	$D_{max.}$ (μm)	Number mode (μm)	Volume mode (μm)	Number median diameter (μm)	Volume median diameter (μm)	Volume deposit (ml/ha)
FT-114	31	10	156	35-50	100-140	35	101	426
FT-100	78	5	150	30-50	35-55	31	54	425
FCT-114	66	6	120	15-35	30-55	21	35	102
FCT-100	52	5	180	10-40	40-60	23	53	196
FDA-3409	58	4	160	15-45	90-110	26	83	417
FCID-585	72	3	160	20-45	40-55	25	42	210
AT-114	60	7	165	20-40	100-160	30	99	519
AT-100	109	4	160	20-40	30-35& 90-105	26	58	378
AA-3409	51	4	165	4-22	75-90& 110-130& 145-165	9	95	95
AID-585	49	4	194	20-40	30-50& 105-195	21	58	155

from the nozzle would travel to the sampling tower and impact on the sampling cards. Spray was generated for a fixed number of seconds and the atomizer switched off. The laminar wind flow was continued for another fixed number of minutes before the sample cards were removed. Droplets containing the added dye tracer impacted on cards forming droplet stains. Their number per unit area and sizes were measured using a dissecting microscope at magnification of 40X and 100X. The resulting data were grouped according to diameter classes and the cumulative droplet number and volume distribution in various size categories (Tables 17 to 26) was each calculated using a correction factor (spread factor, SF) for converting stain sizes into droplet sizes. This type of data treatment was carried out for both types of nozzles and the results are represented graphically in figures 3 to 12. From these results, the number median diameter, volume median diameter, maximum diameter, minimum diameter, drops per cm^2 area of Kromekote® card and volume of formulation deposited on unit area of Kromekote® card were all calculated and presented in Tables 27 and 28.

5b. With aircraft containing Micronair nozzles when spray was applied under field conditions

Spray droplet spectra were obtained under field conditions only for five out of the ten formulations listed in this report. These are FT-100, FCT-100, AT-100, AA-3409 and AID-585. The objective of the study was to investigate the role of formulation properties on spray droplet size spectra as collected on Kromekote® card placed in the field at the ground level in a clearing in the neighbourhood of sample trees. A 50 ha plot was selected for each formulation. Formulations FT-100, FCT-100 and AT-100 were sprayed in June 1982 near Charlo in N.B., whereas AA-3409 and AID-585 were sprayed in June 1981 near Bathurst N.B.. Details of the two studies are given below:

Balsam fir trees, Abies balsamea (L.) (Mill), of nearly uniform size and shape (ca. 14.0m in height and 16.5 cm in DBH) were chosen as sample trees, and a clearing of up to a radius of ca. 5m was made around each tree to enhance exposure to the spray cloud. Kromekote® cards were placed in the openings approximately 0.5 hr before spray application and were collected at 1.0 hr after spraying. They were examined under a magnification of 40X and

100X using a dissecting microscope, and the spray droplet stains were counted and sized. The data were grouped into specific diameter classes, and the droplet number and volume distribution in these size ranges were calculated using the spread factor for converting stain sizes into aerodynamic drop sizes. Data are represented graphically in figures 13 to 17. The cumulative droplet number and volume distribution were calculated and presented in Tables 29 to 33. Tables 34 and 35 lists the details on spray application, maximum and minimum droplet diameters, NMD, VMD and spray volume deposit per ha of the spray plot.

6. Rate and degree of droplet evaporation

High volume application techniques in which the droplets are directed onto a crop at a close range by hydraulic or pneumatic pressure are much less susceptible to evaporation in transit, than those very low or ultra-low volume techniques which utilize very fine sprays, the droplets of which are carried to the target primarily by the prevailing wind and its accompanying eddies, as well as being subject to evaporation in flight (Johnstone, 1978).

The rate of evaporation of small droplets of non-aqueous formulations, moving with an airstream is primarily a function of ambient air temperature but for aqueous emulsion formulations, the "saturation deficit", is an additional factor which regulates evaporation (Seymour, 1969, Johnstone, 1978). The evaporation of water and/or the volatile components of the formulations from the droplet surface is the cause of a decrease in droplet size which affects to a great deal the pattern of droplet deposition on target surfaces. It is therefore important to study the rate and degree of evaporation of spray droplets of variable sizes.

For measuring the evaporation rates of droplets of size range of ca. 50 to 200 um in diameter, droplets were produced using the rotary device designed by Rayner and Haliburton (1955) and were captured on glass fibre of known thickness (5.6 ± 0.2 µm). The spherical diameter of the droplet was estimated (see under "spread factor" for details) at various time intervals, 0,1,2,4,6,10,15,20,30 and 60 min., at a temperature of $22^\circ \pm 2^\circ$C, when the droplet is at rest in still air of relative humidity of 50 ± 3%.

Table 29. Kromekote® Card Data Using Aircraft with Micronair AU3000

Droplet Number/Volume Distribution According to Size Category

Formulation: FT-100

Stain diameter range (µm)	Spread factor	Droplet diameter range (µm)	Average droplet diameter (µm)	1st Application: Cumulative frequency (%)	1st Application: Cumulative droplet volume distribution (%)	2nd Application: Cumulative frequency (%)	2nd Application: Cumulative droplet volume distribution (%)
6-10	2.00	3.2-4.8	4.0	-	-	1.46	0.0033
11-20	2.28	4.9-7.7	6.3	0.04	0.0002	2.38	0.0115
21-35	2.83	7.8-12.3	10.2	2.55	0.0681	2.59	0.0195
36-45	2.90	12.4-15.4	14.0	21.29	1.402	3.68	0.1275
46-55	2.98	15.5-18.5	17.0	31.75	2.756	10.99	1.440
56-65	3.02	18.6-21.6	20.2	40.26	4.568	11.85	1.695
66-90	3.05	21.7-29.3	25.6	69.38	17.21	70.94	37.30
91-110	3.09	29.4-35.5	32.6	82.63	29.03	90.96	62.10
111-130	3.11	35.6-41.7	38.7	88.48	37.83	97.94	76.67
131-155	3.13	41.8-49.4	45.7	93.81	50.99	98.99	80.28
156-175	3.15	49.5-55.6	52.6	95.80	58.49	99.45	82.70
176-220	3.16	55.7-69.5	62.7	98.15	73.45	99.57	83.71
221-265	3.18	69.6-83.4	76.6	99.38	87.79	99.65	84.95
266-310	3.19	83.5-97.3	90.5	100.02	100.00	99.77	88.01
311-413	3.20	97.4-129.0	-	-	-	100.00	100.00

FIG. 13. DROPLET SPECTRA OF FT-100
AIRCRAFT APPLICATION WITH MICRONAIR AU 3000

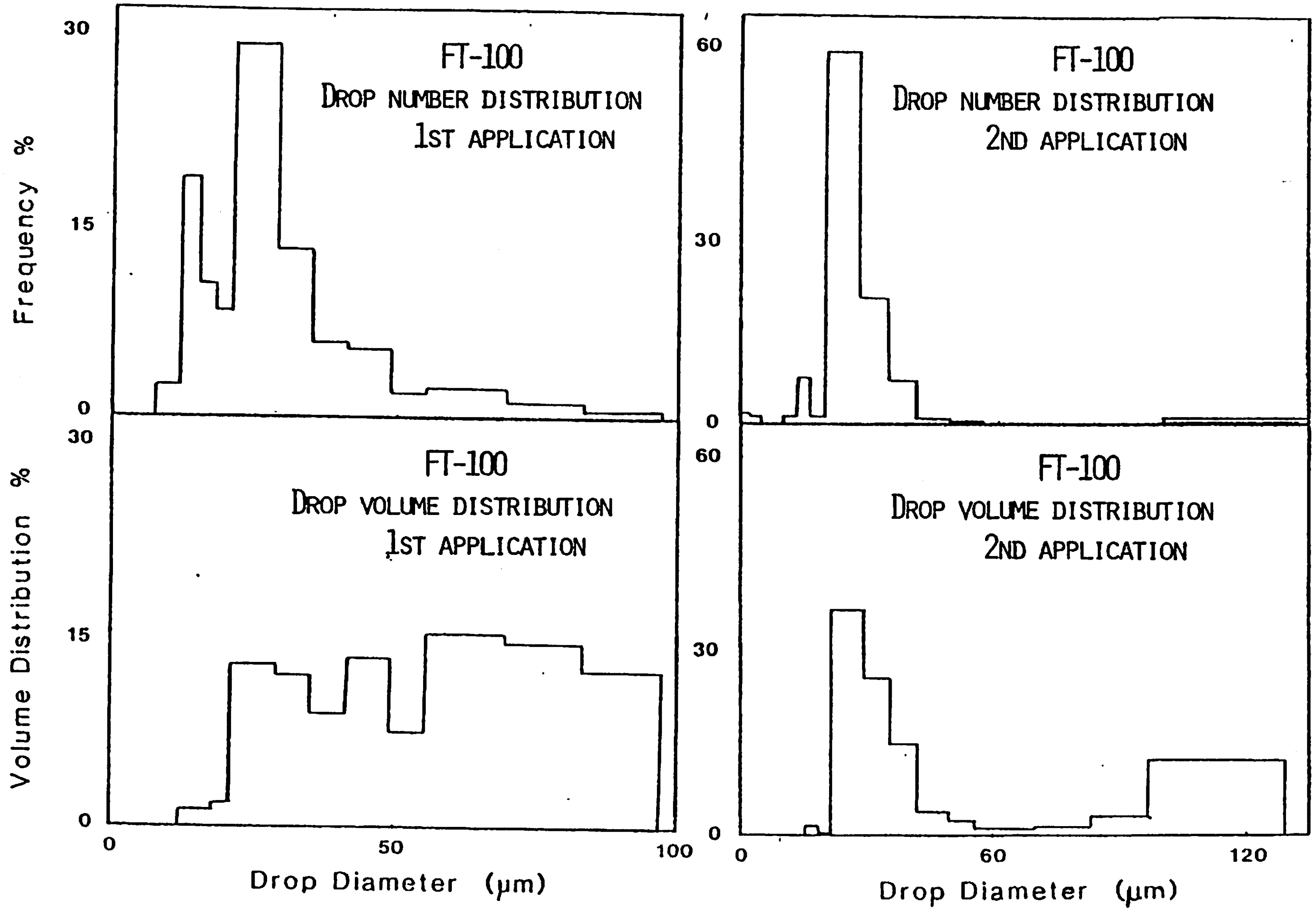


Table 30. Kromekote® Card Data Using Aircraft with Micronair AU3000

Droplet Number/Volume Distribution According to Size Category

Formulation: FCT-100

Stain diameter range (μm)	Spread factor	Droplet diameter range (μm)	Average droplet diameter (μm)	1st Application		2nd Application	
				Cumulative frequency (%)	Cumulative droplet volume distribution (%)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)
6-10	2.34	2.7-4.4	3.4	—	—	0.03	0.0000
11-20	2.50	4.5-7.8	6.2	0.38	0.0000	0.20	0.0001
21-35	2.60	7.9-13.3	10.7	1.56	0.0142	1.82	0.0057
36-45	2.64	13.4-17.0	15.3	12.44	0.3936	21.08	0.1973
46-55	2.66	17.1-20.7	19.0	18.43	0.7906	30.00	0.3663
56-65	2.67	20.8-24.3	22.7	26.06	1.649	39.81	0.6821
66-90	2.68	24.4-33.5	29.1	47.16	6.677	45.93	1.099
91-110	2.69	33.6-40.8	37.3	63.80	15.07	54.60	2.347
111-130	2.69	40.9-48.2	44.7	74.94	24.69	58.37	3.278
131-155	2.70	48.3-57.4	52.9	86.12	40.74	65.61	6.250
156-175	2.70	57.5-64.7	61.2	90.72	50.94	68.69	8.200
176-220	2.71	64.8-81.2	73.1	96.85	74.14	78.17	18.45
221-265	2.71	81.3-97.7	89.6	99.11	89.91	86.72	35.49
266-310	2.71	97.8-114.2	106.2	99.98	100.00	94.72	61.96
311-437	2.74	114.3-159.5	137.5	—	—	100.00	100.00

FIG. 14. DROPLET SPECTRA OF FCT-100
AIRCRAFT APPLICATION WITH MICRONAIR AU 3000

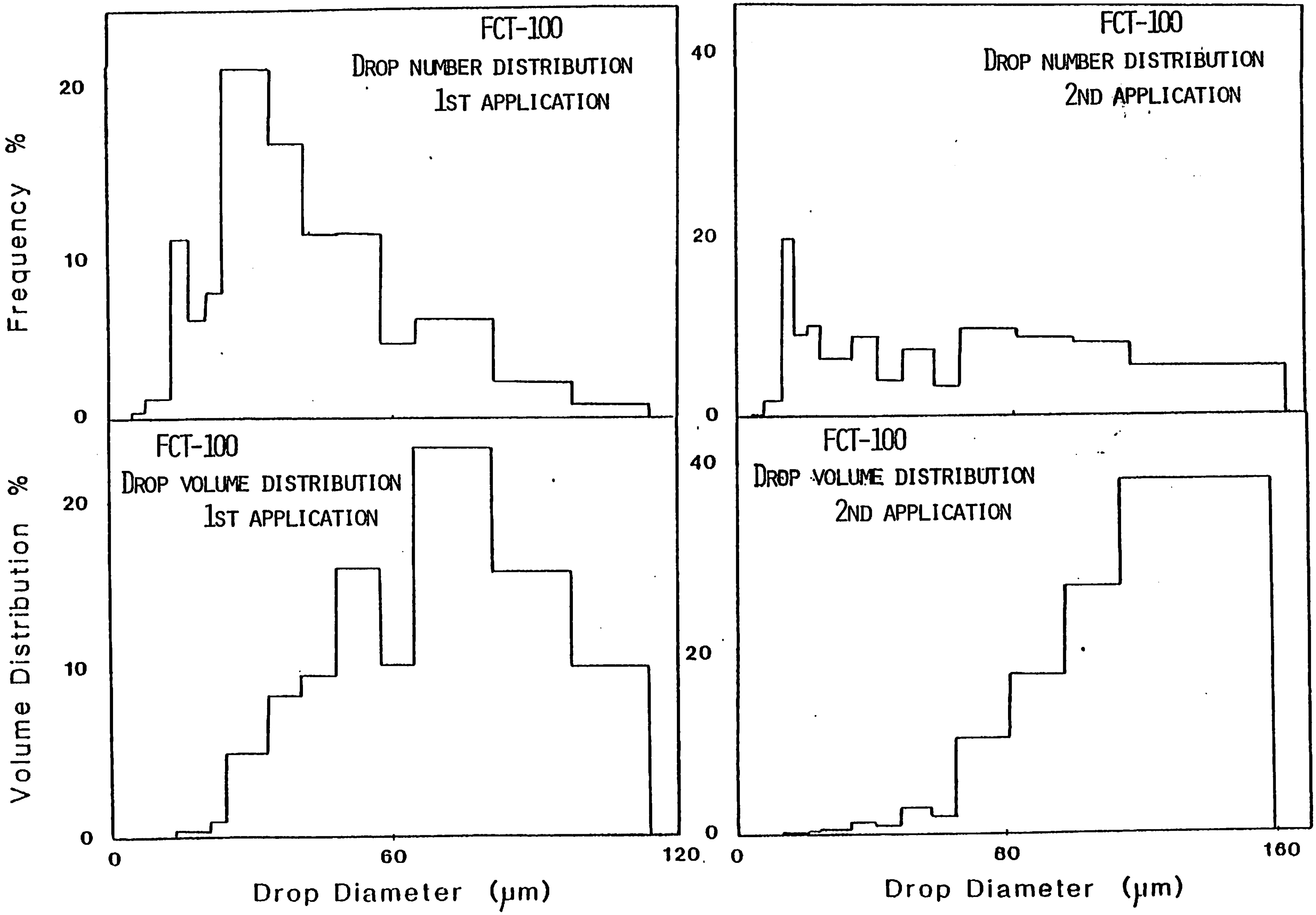


Table 31. Kromekote® Card Data Using Aircraft with Micronair AU3000

Droplet Number/Volume Distribution According to Size Category

Formulation: AT-100

Stain diameter range (μm)	Spread factor	Droplet diameter range (μm)	Average droplet diameter (μm)	1st Application: Cumulative frequency (%)	1st Application: Cumulative droplet volume distribution (%)	2nd Application: Cumulative frequency (%)	2nd Application: Cumulative droplet volume distribution (%)
6-10	3.21	1.9-3.2	2.5	0.92	0.0009	-	-
11-20	3.15	3.3-6.4	4.9	6.24	0.0419	-	-
21-35	3.12	6.5-11.3	9.0	23.03	0.827	0.20	0.0056
36-45	3.10	11.4-14.5	13.1	58.65	5.92	12.40	1.057
46-55	3.10	14.6-17.8	16.3	75.95	10.73	23.18	2.87
56-65	3.09	17.9-21.0	19.6	87.93	16.48	30.26	4.92
66-90	3.09	21.1 -29.2	25.3	93.35	22.08	75.77	33.26
91-110	3.09	29.3-35.7	32.6	96.63	29.32	89.68	51.83
111-130	3.08	35.8-42.2	39.1	96.83	30.10	95.08	64.28
131-155	3.08	42.3-50.3	46.4	96.93	30.76	97.47	73.48
156-175	3.08	50.4-56.8	53.7	97.34	34.84	98.91	82.13
176-220	3.08	56.9-71.4	64.3	98.77	59.19	99.54	88.63
221-265	3.08	71.5-86.0	78.9	99.90	94.63	99.81	93.69
266-310	3.08	86.1-100.7	93.5	100.00	100.01	100.01	100.01

FIG. 15. DROPLET SPECTRA OF AT-100
AIRCRAFT APPLICATION WITH MICRONAIR AU 3000

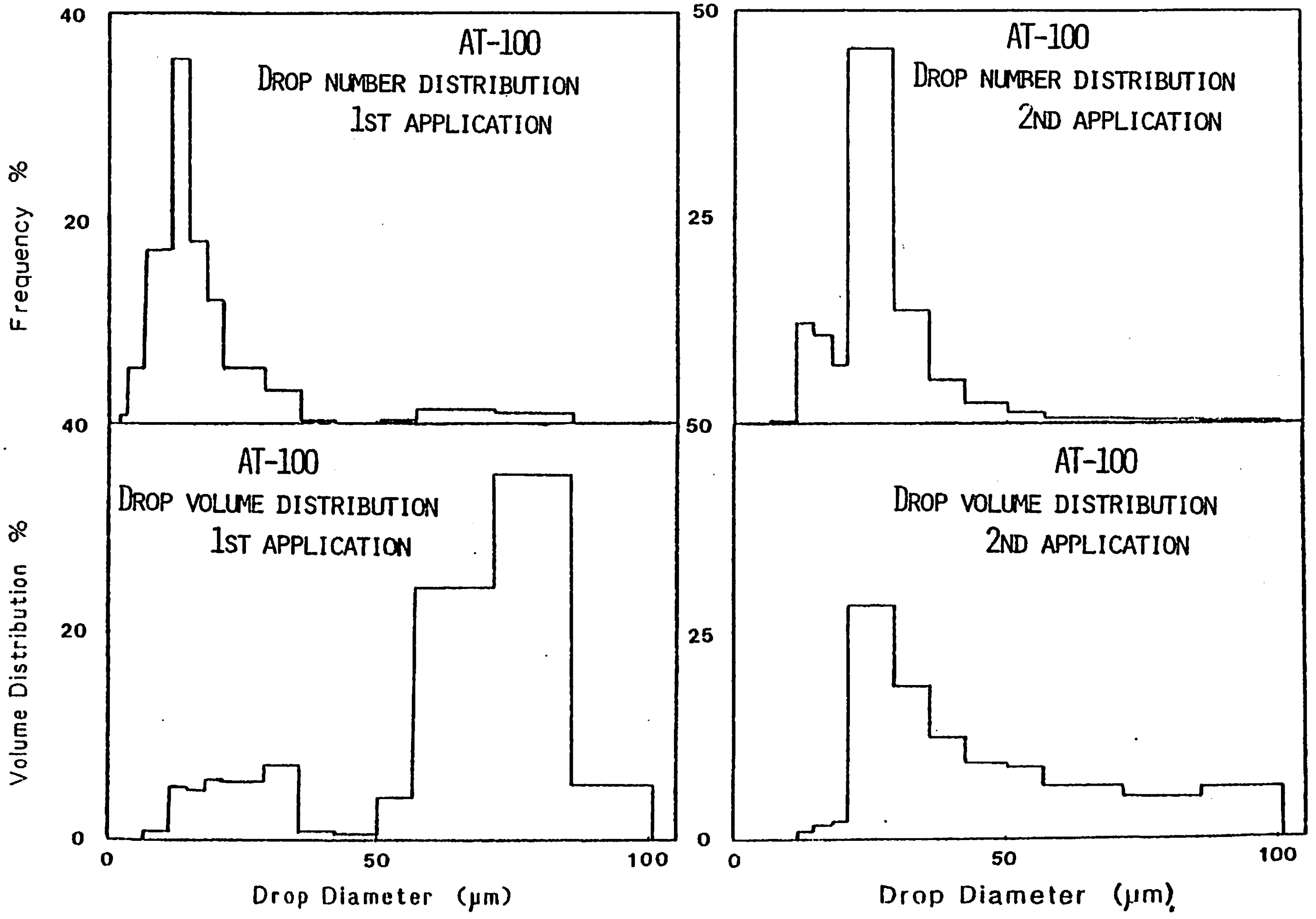


TABLE 32. KROMEKOTE® CARD DATA USING AIRCRAFT WITH MICRONAIR AU3000

DROPLET NUMBER/VOLUME DISTRIBUTION ACCORDING TO SIZE CATEGORY

FORMULATION: AA-3409

Stain diameter range (um)	Spread factor	Droplet diameter range (um)	Average droplet diameter (um)	1st application		Second application	
				Cumulative frequency (%)	Cumulative droplet volume distribution (%)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)
20- 45	2.95	7-15	11	1.0	0.03	0.0	0.0
46- 70	3.00	16-20	18	22.0	2.96	32.0	5.0
71- 90	3.02	21-29	25	40.0	10.48	52.0	13.0
91-115	3.03	30-36	33	70.0	36.04	86.0	51.0
116-135	3.05	37-42	40	87.0	62.12	92.0	61.0
136-160	3.05	43-51	47	99.0	91.96	98.0	78.0
161-180	3.05	52-58	55	99.3	93.31	99.0	87.0
181-225	3.05	59-73	66	100.3	100.00	100.0	102.0

FIG. 16. DROPLET SPECTRA OF AA-3409
AIRCRAFT APPLICATION WITH MICRONAIR AU 3000

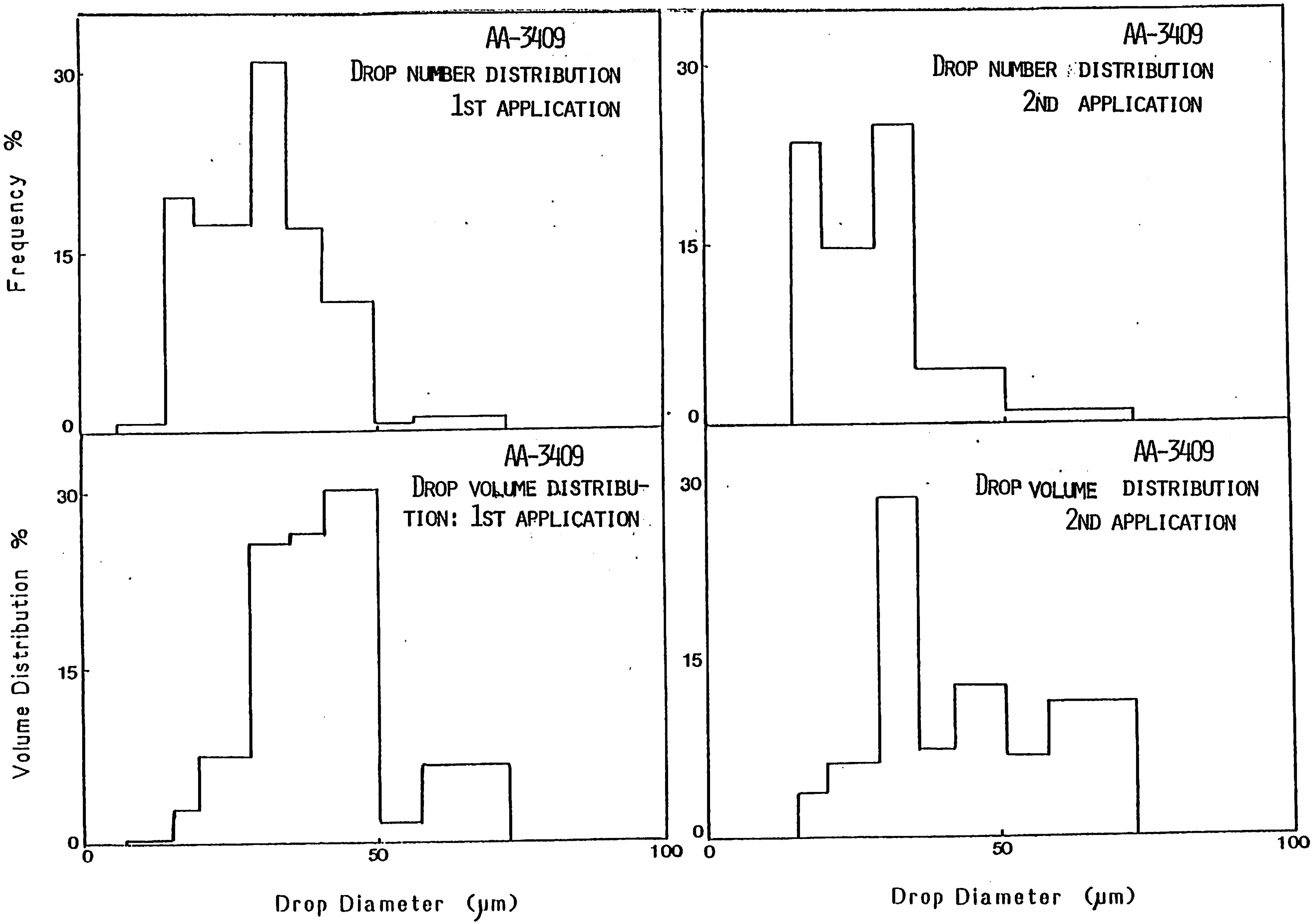


TABLE 33. KROMEKOTE® CARD DATA USING AIRCRAFT WITH MICRONAIR AU3000

DROPLET NUMBER/VOLUME DISTRIBUTION ACCORDING TO SIZE CATEGORY

FORMULATION: AID-585

Stain diameter range (um)	Spread factor	Droplet diameter range (um)	Average droplet diameter (um)	1st application		Second application	
				Cumulative frequency (%)	Cumulative droplet volume distribution (%)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)
20–40	4.8	4–8	6	-	-	2.3	0.00
41–64	4.9	9-12	10	-	-	11.6	0.42
65–79	5.0	13-15	14	-	-	22.9	1.46
80-100	5.0	16-20	18	4.8	0.41	35.2	3.76
101-125	5.4	21-23	22	9.1	1.04	51.2	9.40
126-150	5.4	24-26	26	19.9	3.40	66.2	18.20
151-190	5.4	27-33	30	32.2	8.10	76.9	27.80
191-235	5.5	34-42	38	64.8	33.43	88.3	48.70
236-285	5.6	43-49	46	87.3	64.37	95.6	72.50
286-345	5.7	50-58	54	97.5	87.00	99.3	91.70
346-485	5.7	59-85	72	100.0	100.00	100.0	100.10

FIG. 17. DROPLET SPECTRA OF AID-585
AIRCRAFT APPLICATION WITH MICRONAIR AU 3000

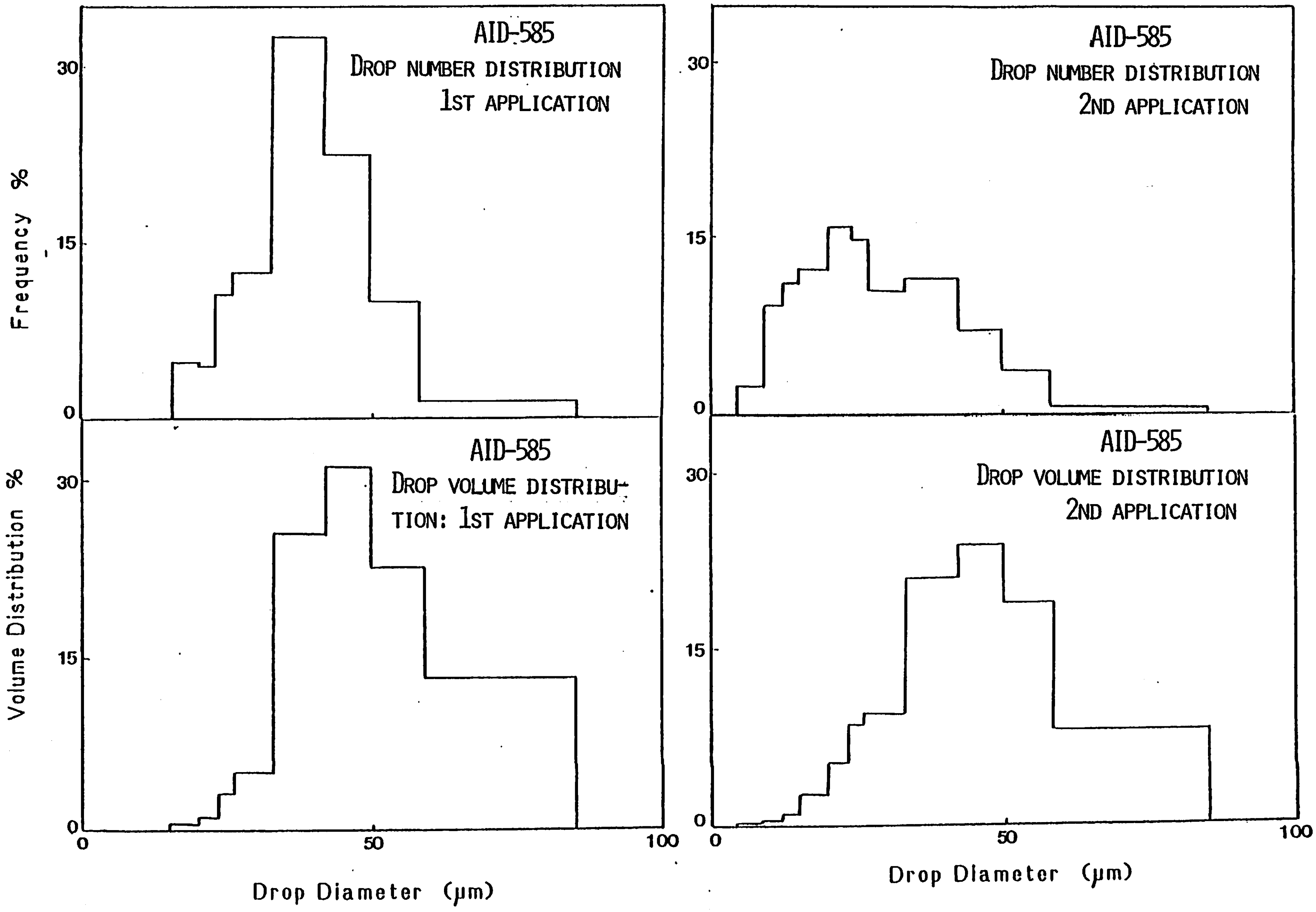


TABLE 34. SUMMARY DATA ON DROPLET SPECTRA OF FORMULATIONS ON KROMEKOTE® CARD: FIELD DATA USING AIRCRAFT WITH MICRONAIR AU3000

1ST APPLICATION

Formulation No.	Drops per cm^2	D_{min} (um)	D_{max} (um)	Number mode (um)	Volume mode (um)	Number median diameter (um)	Volume median diameter (um)	Volume deposit (ml/ha)	% deposited
FT- 100	4.4	6	114	20-30	---	21	46	9.0	0.61
FCT- 100	3.9	6	114	25-40	65-90	30	60	21.0	1.44
AT- 100	3.3	3	101	10-20	10-35& 60-85	12	61	2.7	0.18
AA-3409	6.0	7	73	30-40	30-50	28	36	13.0	0.90
AID- 585	13.0	16	85	35-45	35-55	35	41	49	3.26

1. Dosage rate for each of FT-100 and FCT-100 was 210g AI/ha per application, and for each of AT-100, AA-3409 and AID-585, 70g AI/ha per application.

2. Volume rate for each of all five formulations was 1.46 L/ha per application.

TABLE 35. SUMMARY DATA ON DROPLET SPECTRA OF FORMULATIONS ON KROMEKOTE® CARD: FIELD DATA USING AIRCRAFT WITH MICRONAIR AU3000

2ND APPLICATION

Formulation No.	Drops per cm^2	D_{min} (µm)	D_{max} (µm)	Number mode (µm)	Volume mode (µm)	Number median diameter (µm)	Volume median diameter (µm)	Volume deposit (ml/ha)	% deposited
FT- 100	41	4	130	20-30	20- 35& 100-130	24	31	60	4.12
FCT- 100	5.3	4	138	---	110-160	34	99	100	6.83
AT- 100	73	9	101	20-30	20- 35	20	32	98	6.71
AA-3409	0.5	7	73	15-35	30- 60	23	33	1.0	0.07
AID- 585	3	4	85	10-40	35- 60	21	39	5.0	0.34

1. Dosage rate for each of FT-100 and FCT-100 was 210g AI/ha per application and for each of AT-100, AA-3409 and AID-585, 70g AI/ha per application.

2. Volume rate for each of all five formulations was 1.46 L/ha per application.

The degree of evaporation was expressed as a percentage of droplet volume remaining after 60 minutes. Since there was no further evaporation, the volume at 60 minutes also represented the limiting volume of the droplet (Tables 36 to 39). Fig. 18 represents the rate and degree of evaporation of droplets of variable sizes for two of the ten formulations as examples (No's FCID-585 and AID-585).

⑦ Rate and degree of vaporization of the active ingredient from the spray droplets

Pesticides are known to have appreciable tendency to volatilize into the ambient air from droplet surfaces. The degree to which this can occur depends primarily on the vapour pressure, surface area of the air-liquid interface and the air-liquid partition ratios. In the case of emulsion formulations, the water solubility of pesticides in presence of the emulsifier is an important factor affecting the vaporization. Two processes are known to occur simultaneously resulting in pesticide loss into atmosphere from aqueous systems, volatilization (or vaporization) and codistillation (Acree et al 1963; Liss and Slater 1974; MacKay and Leinonen 1975).

A simple experiment was carried out to study the relative rates of vaporization of fenitrothion from thin films of formulations spread on Petri dishes. Three formulations, FT-114, FDA-3409 and FCID-585 were tried. An air-flow of defined velocity was allowed to pass over the surfaces of these films for one hr. The preliminary results suggest that the loss of fenitrothion was the least with FT-114, higher with FDA-3409 and the highest with FCID-585. It appears that Triton® X-114 reduces the rate of loss of AI from the emulsion as compared to ATLOX 3409F; or the reason could simply be due to higher concentration of the emulsifier in FT-114 than that of ATLOX 3409F in FDA-3409. High concentrations of emulsifiers are known to reduce the rate of loss of water from spray droplets (Sundaram 1982, unpublished data)

These results are only preliminary but suggest that detailed investigations are required before any definite conclusion can be drawn.

TABLE 36. RATE AND DEGREE OF DROPLET EVAPORATION OF NEW FENITROTHION FORMULATIONS

Formulation No.	Initial droplet diameter (μm)	Droplet diameter at 1.0 min (μm)	Droplet diameter at 30 min (μm)	Droplet diameter at 60 min (μm)	Residual drop volume at 60 min (%)
FT-114	205	144	144	144	34.6
	176	123	123	123	34.1
	153	111	111	111	38.2
	131	97	97	97	40.6
	97	70	70	70	37.6
	85	63	63	63	40.7
			Mean ± SD =37.6 ± 2.8		
FT-100	153	100	100	100	27.9
	142	97	97	97	31.9
	131	89	89	89	31.4
	119	77	77	77	27.1
			Mean ± SD = 29.6 ± 2.4		
FCT-114	216	137	137	137	25.5
	165	107	107	107	27.3
	157	100	100	100	25.8
	153	97	97	97	25.5
	131	85	85	85	27.3
	119	77	77	77	27.1
			Mean ± SD = 26.4 ± 0.9		

TABLE 37 . RATE AND DEGREE OF DROPLET EVAPORATION OF NEW AND REGISTERED FENITROTHION FORMULATIONS

Formulation No.	Initial droplet diameter (μm)	Droplet diameter at 1.0 min (μm)	Droplet diameter at 30 min (μm)	Droplet diameter at 60 min (μm)	Residual drop volume at 60 min (%)
FCT-100	210	142	142	142	30.9
	198	134	134	134	31.0
	179	123	123	123	32.4
	168	111	111	111	28.8
	153	104	104	104	31.4
	145	97	97	97	29.9
			Mean ± SD = 30.7 ± 1.2		
FDA-3409	169	96	96	96	18.3
	157	89	89	89	18.2
	105	61	61	61	19.6
	96	55	55	55	18.8
	80	45	45	45	17.8
			Mean ± SD = 18.5 ± 0.7		
FCID-585	160	133	96	96	21.5
	123	96	76	76	23.6
	108	92	64	64	20.8
	83	55	51	51	23.2
	68	55	41	41	21.9
			Mean ± SD = 22.2 ± 1.2		

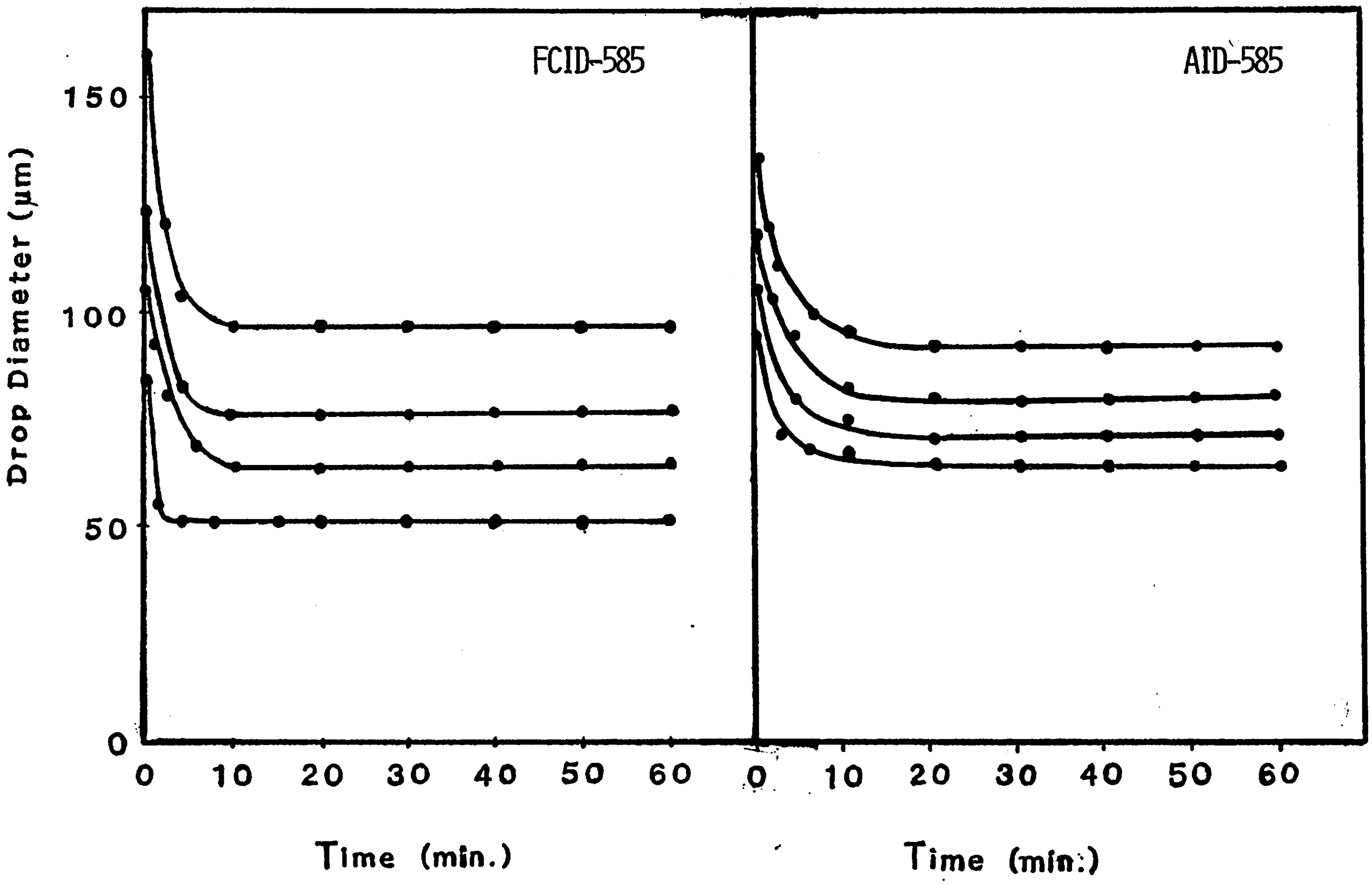
TABLE 38. RATE AND DEGREE OF DROPLET EVAPORATION OF NEW AMINOCARB FORMULATIONS

Formulation No.	Initial droplet diameter (μm)	Droplet diameter at 1.0 min (μm)	Droplet diameter at 30 min (μm)	Droplet diameter at 60 min (μm)	Residual drop volume at 60 min (%)
AT-114	131	87	87	87	29.3
	123	81	81	81	28.6
	108	74	74	74	32.2
	86	58	58	58	30.7
	74	51	51	51	32.7
			Mean ± SD = 30.7 ± 1.8		
AT-100	153	97	97	97	25.5
	119	81	77	77	27.1
	111	76	76	76	32.1
	89	58	58	58	27.7
	74	48	48	48	27.3
			Mean ± SD = 27.9 ± 2.5		
AA-3409	166	108	108	108	27.5
	145	96	96	96	29.0
	133	86	86	86	27.0
	123	82	82	82	29.6
	83	55	55	55	29.1
	71	45	45	45	25.5
			Mean ± SD = 28.0 ± 1.6		
AID-585	136	120	92	92	30.9
	133	111	89	89	30.0
	120	105	80	80	29.6
	108	92	71	71	28.4
	96	80	64	64	29.7
			Mean ± SD = 29.7 ± 0.9		

TABLE 39. LIMITING RESIDUAL VOLUME AND NON-AQUEOUS AND NON-VOLATILE COMPONENTS OF FORMULATIONS

Formulation No.	Formulation Description	Mean limiting volume of droplets at 60 min (%)	Non-aqueous components (v/v%)	Non-volatile components (v/v%)
1	FT-114	37.6	24.8	24.8
2	FT-100	29.6	24.7	24.7
3	FCT-114	26.4	40.1	13.8
4	FCT-100	30.7	40.1	13.8
5	FDA-3409	18.5	14.0	12,5
6	FCID-585	22.2	100.0	11.0
7	AT-114	30.7	29.5	29.5
8	AT-100	27.9	29.5	29.5
9	AA-3409	28.0	28.2	28.2
10	AID-585	29.7	100.0	26.7

FIG, 18, RATE AND DEGREE OF DROPLET EVAPORATION OF FCID-585 AND AID-585



⑧ Droplet impaction characteristics on conifer needles using potted seedlings in the spray chamber.

This study was carried out and the data reduction is in progress. The preliminary results indicate good impaction characteristics of droplets of FT-114 and FCT-114 formulations on balsam fir needles. The relative impaction efficiencies of droplets of the ten formulations can be evaluated following data reduction and statistical treatment.

⑨ Droplet retention characteristics on target surface.

This study was carried out on balsam fir needles. Droplets of all formulations, except those of FDA-3409, FCID-585 and AID-585 were retained very well on the surface of the needles. With FDA-3409, the droplets were absorbed readily into the needle surface but a droplet stain (because of the tracer dye added to the formulations) was visible enabling droplet counting. On the other hand, with the two oil-based formulations, FCID-585 and AID-585, the droplets dissolved instantly into the waxy cuticle of the needle and were absorbed completely. As a result, the droplets became invisible within a few seconds in spite of the tracer dye added. These preliminary results indicate that with formulations of Triton® emulsifiers, there is a possibility of additional exposure from crawling contact, a phenomenon not possible with the rest of the formulations studied. These findings suggest a possible enhancement of insect toxicity with Triton® emulsifiers. However detailed studies are necessary before any definite conclusion can be drawn from these data.

⑩. Droplet dissipation characteristics in balsam fir needles.

This study was carried out and the data reduction is in progress. The preliminary results indicate good dissipation characteristics of droplets of all formulations. However, droplets of Triton® formulations stayed in tact on foliage somewhat longer than those of the ATLOX-based or oil-based ones, although there was no indication of injury to the sensitive buds or to the mature needles. Droplets disappeared from the needle surface within a few days after spray application, indicating optimum persistence characteristics. The results suggest the possibility of a slightly greater foliar half-life with Triton® formulations than with ATLOX-based or oil-based formulations.

These preliminary results point out the need for further detailed studies on the dissipation characteristics of the Triton® formulations.

RESULTS AND DISCUSSION

Results of each investigation are discussed below under each of the ten headlines described in " METHODS ".

① Selection of the most optimum ingredients and their proportions

Based on good miscibility and emulsion characteristics a minimum ratio of 1:1 was found to be necessary for the fenitrothion-emulsifier ratio (abbreviated as fen:emul ratio), in FT-100 formulation . Therefore this ratio was recommended for the field studies. For Triton® X-114 however, its greater lipophilicity than Triton® X-100, required a ratio much less than 1:1. In fact, a ratio of 2:1 for fen:emul was found to be sufficient to give good emulsion properties. However, the formulation FT-114 was prepared in the same proportion as FT-100 because the field studies and the mammalian acute toxicity studies were both carried out for FT-100 at the fen:emul 1:1 level, and therefore for the laboratory studies, formulation FT-114 was also maintained at the same 1:1 fen:emul level.

For the FCT-114 and FCT-100 formulations, a wide range of Cyclo-Sol® 63 proportions, i.e. 15 to 24 w/w % were found to give good emulsion characteristics, although a minimum amount of 3% Triton® emulsifiers were found to be necessary for all mixtures. For the field studies the maximum level of 24 % was recommended because at this level the evaporation properties of droplets were minimal.

For FDA-3409, the minimum concentration necessary for good miscibility and emulsion properties was found to be 2.0% w/w for each of Dowanol TPM and ATLOX 3409F. However this formulation was prepared at the 1.5 w/w % level because this is the concentration which was used in New Brunswick field formulations.

With MATACIL® 180F, Triton® X-100 does not provide as good an emulsion as with Triton® X-114 or with ATLOX 3409F. This is because of the lower lipophilicity of Triton® X-100 than the other two emulsifiers, and the presence of a heavy oil in MATACIL® 180F requires an emulsifier that can have a moderate solubility in oils. However, one point worth noting is that MATACIL® 180F contains a solid pesticide suspended in a non-aqueous medium and preparation of either an emulsion or an oil-based formulation would result in a medium containing suspended particles of pesticides. It is therefore essential not to store this formulation once mixed. It should be sprayed soon after mixing.

While selecting emulsifiers for formulating fenitrothion and aminocarb, it was observed that Triton® X-114 and ATLOX 3409F both provided much better emulsions than with Triton® X-100. This is not only due to the lower lipophilicity of Triton® X-100 but also due to its inappropriate hydrophile-lipophile balance number, referred to as the HLB number. While formulating water-insoluble pesticides, it must be remembered that the emulsifier system must cause the pesticide to disperse spontaneously into small, stable droplets when mixed with water. To accomplish this, the surfactant system must have a most favorable solubility relationship: a proper balance between oil and water solubility or in other words, a favorable hydrophile-lipophile balance in solubility (HLB number). The HLB system is based on the structure of a surfactant molecule, and for Triton® X-100, the HLB number is 13.5, whereas for Triton® x-114 and ATLOX 3409F they are 12.4 and 12.0 respectively. Since the latter two compounds have approximately the same HLB number they are both equally suitable for formulating the pesticides chosen in this study.

In addition to the HLB number, another property of surfactants, called micellization or the ability to form micelles, gives the medium many special properties including the ability to dissolve some water-insoluble substances. A surfactant solution at a concentration somewhat above the critical micelle concentration (CMC) is a very complex system containing a large number of aggregates of surfactant monomers in dynamic equilibrium. This property is mainly responsible for good solubility and emulsion characteristics of formulations. If the CMC value is low for a surfactant, it would have a relatively high solubilizing ability and if it is high, its solubilizing effect would be poor at an equal concentration. The CMC values at 25°C for Triton® X-100 and Triton® X-114 are 9.0×10^{-4} (Meguro and Shoji 1979) and 2.3×10^{-4} (McNicoll et al 1979) moles per litre, which explains clearly why Triton® X-114 has a higher solubilizing effect on fenitrothion and aminocarb.

② Stability and re-emulsifiability of formulations.

For stability considerations, an emulsion is defined as a dispersion of one immiscible liquid (discontinuous or dispersed phase) in a second, continuous phase. The system is said to lack stability if the dispersed phase is no longer homogeneously dispersed in the continuous phase. As the dispersed phase separates out in an emulsion, it will first " cream " . A cream is that region which contains a higher proportion of the dispersed phase than the average amount in the system. If oil droplets separate out as an intact layer when the dispersed phase coalesce sufficiently, the emulsion is said to have " oiled out " resulting in phase separation. Factors influencing emulsion stability are : proportions of ingredients, viscosity of the dispersed and continuous phases,interfacial tension, polarity and chemical constituents, pH of the aqueous phase, solubility of ingredients in the continuous phase, particle size and size distribution of solid components, electroviscous effect, ionic strength of the continuous phase, attractive forces between the chemical constituents, temperature, light, pressure and others.(Van Valkenburg 1973).

In the present study, the time for stability considerations was determined when phase separation has occurred to a level of 25% and above. For determining stability while stirring gently, the top portion of the mixture was periodically tested for viscosity reduction and the time noted when the values differed by 20%. Results indicate that FT-114 is a highly stable formulation. The extremely high viscosity of this formulation is indicative of a very high degree of micellization in this formulation resulting in high stability (Table 5). Formulations of MATACIL® 180F were generally less stable than those of fenitrothion. This is obviously due to solid components present in MATACIL® 180F.

The addition of water soluble dyes appears to have affected the stability of emulsions considerably. Similarly the addition of acidic (or low pH) and hard (or high ionic strength) water seems to have reduced the stability, as evidenced by the lower time required for phase separation. In all these cases the phenomenon observed is termed as the " electrolyte effect ". The addition of certain electrolytes are known to cause a sharp reduction in the degree of micellization and some compounds may totally eliminate the formation of micelles (Van Valkenburg 1973). The role of electrical forces between the surfactant molecules and the added electrolytes has been extensively studied, explaining the electrolyte effect (Anacker 1979). Tables 6 to 9 presents data related to this phenomenon.

The ability to re-emulsification following storage appears to be high for fenitrothion formulations. For the aminocarb formulations however, re-emulsifiability is rather poor because of the agglomeration of the aminocarb microparticles during the time of storage (Table 10).

With emulsions of flowable concentrates of solid pesticides (e.g. aminocarb in MATACIL® 180F), two properties, dispersibility and suspensibilty, play a key role in stability. Both are dependent on, among many factors, particle size distribution of solid components and chemical nature of ingredients (Polon 1973). With MATACIL® 180F the initial dispersibility was spontaneous with all three emulsifiers, a property necessary for preparing good emulsions. However, suspensibility was satisfactory only for a short period of time, ca. 12 hr (Sundaram 1982, unpublished data). Suspensibility determines the ability of the particulate phase to remain in suspension for an adequate period of time to allow homogeneity of the tank mix until the completion of spray operation.

Physical stability during storage is an important property that determines the ability to re-disperse and re-suspend upon shaking. During storage, the individual microparticles can stick together and agglomerate to form larger aggregates , resulting in poor re-dispersibilty and re-suspensibility (Polon 1973). Agglomeration was found to occur with all aminocarb formulations. It occurred to the maximum degree in the oil-based formulation AID-585 and re-suspensibility posed considerable difficulty. This was obviously due to the absence of aqueous phase which facilitates micelle formation and hydrogen bonding leading to higher stability during storage.

In view of these findings, it is prudent not to store spray mixes when once prepared. Otherwise sedimentation of aminocarb will occur resulting in poor emulsions upon mixing. This consequently would lead to uneven deposition of the active ingredient during spraying. With fenitrothion however, re-emulsification is efficient since it is a liquid pesticide. Vigorous mixing is sufficient for preparing a good emulsion of the stored formulations.

③ Compatibility of the active ingredient in the formulations.

Results of this investigation are not listed here since the findings are simple and straightforward : following storage at temperatures ranging from 0°C to 5°C, no loss was observed in the active ingredient in any of the ten formulations within 6 weeks after preparation. This indicates good compatibilty of the ingredients in the mixes.

④ Mixing, pumping and storing capabilities of formulations

As evident from Tables 11 and 12, Triton® X-100 is the most viscous material and will pose problems in pumping, mixing and storing at temperatures of 0°C to 10°C. Both Triton® X-114 and ATLOX 3409F will require a high powered pump for mixing purposes. Both MATACIL® 180F and fenitrothion technical can be pumped by moderately powerful pumps, but at temperatures below 5°C , they would also require high powered pumps for speedy mixing.

MATACIL® 180F is a suspension of microparticles of aminocarb and other solid ingredients. Its suspensibility appears to be satisfactory during storage for a few months. However its long-term suspensibility remains yet to be investigated. Therefore, it would be prudent not to store this concentrate after one spray season.

5. Spray atomization characteristics of formulations as collected on Kromekote® cards

5a. Using hydraulic and spinning disc nozzles in the Institute's spray chamber

Results of droplet spectra obtained with hydraulic and spinning disc nozzles following collection on Kromekote® cards, are presented in Tables 17 to 26 and in Figs. 3 to 12. Even though the Kromekote® card is known not to collect the entire spectrum of droplets produced during atomization, they were still used in order to compare the relative atomization efficiencies of formulations. Secondly, it is customary to use Kromekote® cards in the field for droplet assessment, and since the objective of the study is to compare the droplet spectra of sprays under laboratory and field conditions, the use of Kromekote® cards is fully appropriate. Tables 27 and 28 present a comparative summary of all the parameters for the two nozzles.

To evaluate the efficiency of optimum atomizability of spray formulations, a scale was used, based on the target of interest in the present study i.e. conifer needles, for choosing the most optimum droplet size range, as collected on Kromekote® cards. Droplets less than 20 um in diameter were assumed to be of less interest since they are known to have poor impaction efficiencies on the target of interest (Mason 1971). Similarly droplets greater than 150 um were assumed to be of less interest since they contribute to inefficient plot coverage in ULV applications. Tables 40 and 41 list the percentages of droplets and spray volume distribution outside the range of interest i.e. 20 to 150 um.

From the Tables and Figures listed above, the influence of formulation on spray atomizability is quite evident with both nozzles. With the hydraulic nozzle, most formulations produced coarse droplet spectra with no distinct modes, except those containing Cyclo-Sol® 63/ Triton® emulsifiers (FCT-114 and FCT-100). The simultaneous presence of these two ingredients in an emulsion appears to provide the optimum viscosity and and surface tension values that are necessary to cause optimum atomization of spray mixes,Formulations with variable physicochemical properties were

TABLE 40. KROMEKOTE® CARD DATA USING HYDRAULIC NOZZLE

DROPLET NUMBER/VOLUME DISTRIBUTION OUTSIDE THE 20 - 150 um RANGE

Formulation Description	Drops per cm^2	Volume deposit (ml/ha)	No. of drops* < 20 µm (%)	Vol. of drops* < 20 µm (%)	No of drops@ >150 µm (%)	Vol. of drops@ >150 µm (%)	Effective drops per cm^2	Effective vol. deposit (ml/ha)
FT-114	21	1385	8	0.03	10	50	17	693
FT-100	28	1954	20	0.05	10	53	20	918
FCT-114	23	834	15	0.09	3	14	19	717
FCT-100	26	1052	7	0.06	2.5	22	24	821
FDA-3409	21	1190	27	0.07	11	59	13	488
FCID-585	18	982	21	0.03	8	40	13	589
AT-114	17	900	25	0.07	10	77	11	207
AT-100	35	606	28	0.09	0.2	3	25	588
AA-3409	15	1297	48	0.01	10	72	6.3	363
AID-585	16	758	12	0.08	3	20	14	600

* Droplets and volume deposits in the size range < 20 um do not impact efficiently on targets.

@ Droplets and volume deposits in the size range > 150 um contribute to inefficient target coverage.

TABLE 41. KROMEKOTE® CARD DATA USING SPINNING DISC NOZZLE

DROPLET NUMBER/VOLUME DISTRIBUTION OUTSIDE THE 20 - 150 UM RANGE

Formulation Description	Drops per cm^2	Volume deposit (ml/ha)	No. of drops* $<$ 20 µm (%)	Vol. of drops* $<$ 20 µm (%)	No. of drops@ $>$150 µm (%)	Vol. of drops@ $>$150 µm (%)	Effective drops per cm^2	Effective vol.deposit (ml/ha)
FT-114	31	426	20	0.10	0.3	5	25	405
FT-100	78	425	14	0.85	0.2	6	67	400
FCT-114	66	102	38	6.5	0.0	0.0	41	102
FCT-100	52	196	36	2.0	0.25	16	33	165
FDA-3409	58	417	27	0.95	0.25	6.5	42	390
FCID-585	72	210	34	1.6	0.06	2.5	48	205
AT-114	60	519	20	0.4	0.25	5.5	48	490
AT-100	109	378	15	1.0	0.07	4.0	93	363
AA-3409	51	95	86	5.2	0.07	12	7	84
AID-585	49	155	44	2.4	0.2	14	27	133

* Droplets and volume deposits in the size range $<$ 20 um do not impact efficiently on targets.

@ Droplets and volume deposits in the size range $>$ 150 um contribute to inefficient target coverage.

known to produce distinctly different drop spectra (Yeo 1959; Holly 1956; Courshee 1960; Dombrowski et al 1960; Ford and Furmidge 1969; Dombrowski and Neale 1974). Furthermore, aqueous formulations with suspended solid particles have been shown to influence the atomizability considerably (Holly 1956). The present observation with aminocarb emulsion containing ATLOX 3409F appears to be in agreement with that of Holly (1956). It provided distinctly low NMD and a high VMD, a phenomenon not observed with the rest of the formulations (Table 27). This is also evident in Table 40 where formulation AA-3409 is shown to provide the highest amounts of droplets $<$20 um, contributing to a very low value for "effective" drops/cm^2.

With respect to drops/cm^2 obtained with hydraulic nozzle, formulations containing the Triton® X-100 emulsifier appear to give higher values than the remaining formulations. This trend is reflected even in " effective" drops/cm^2 in Table 40. This is probably due to the combined effect of viscosity, density, surface tension and droplet evaporation of these formulations. The total volume of deposit per unit area (ml/ha) of formulations indicate that AT-100 provides the lowest value in spite of the highest number of drops/cm^2 (Table 27). This is due to the high percentage of small droplets produced (Table 24 and Fig. 10). This is evident in the " effective" volume deposit/ha which is not the lowest for AT-100 (Table 40). Formulation AA-3409 on the contrary provides a high value for the total deposit (ml/ha) but a very low " effective deposit " (Table 40). This is obviously due to the combined effect of a high proportion of small droplets and a wide drop size spectrum observed (Table 25 and Fig. 11).

With the spinning disc nozzle, most formulations produced narrow drop spectra (Tables 17 to 26 and Figs. 3 to 12). Rotary nozzles are known to produce narrow droplet spectra (Bals 1978; Farmery 1978). Formulations FT-114, FDA-3409 and AT-114 provide a higher proportion of large droplets than the remaining ones. This is evident in Figs. 3, 7 and 9. Formulation AA-3409 provides a high percentage of small droplets (Fig.11) similar to the one observed earlier with hydraulic nozzle. This behaviour of AA-3409 with both nozzles is probably due to the presence of solid particles in the emulsion, combined with a low concentration of the emulsifier. As a result, micellization and emulsion characteristics appear to be affected significantly.

With respect to the total drops/cm^2 (droplet density) FT-114 provided the lowest value. This is obviously due to the very high viscosity of this formulation. Highly viscous solutions are known to affect the rotational speed of the spinning disc nozzles and this in turn affects the droplet spectrum and droplet density (Sundaram 1981, unpublished data). An increase in viscosity is also known to physically dampen the natural wave formation which generally delays the disintegration of ligaments, resulting in larger droplet sizes (Yates and Akesson 1973). This is demonstrated in the higher values for NMD, VMD and D_{min} for FT-114 formulation than for the rest (Table 28). However, the " effective" droplet density is not the lowest. The reason for this is the narrow drop size spectrum observed. Formulation AA-3409 on the other hand, provides a high number for total drops/cm^2 but its " effective " drops/cm^2 is the lowest (Table 41). It is worth noting that with both nozzles AA-3409 provided the lowest value for "effective" droplet density and volume deposit. This appears to be due to insufficient quantities of the emulsifier.

5b. With aircraft fitted with Micronair AU3000 nozzles, following field application

Spray droplet spectra obtained under field conditions for five out of the ten formulations are presented in Tables 29 to 33 and in Figs. 13 to 17. Unlike the laboratory studies, the field studies are seldom performed under identical experimental and weather conditions , and consequently high variations in droplet density and size spectrum are likely to occur. In fact, a knowledge of these parameters under variable conditions would provide a base-line data to indicate the degree of variations as relatable to spray application conditions and meteorological factors. With all formulations, marked variations were observed in the droplet spectra and droplet density between 1st and 2nd applications (Figs. 13 to 17). However, the NMD and VMD values were quite similar

(Tables 34 and 35). Formulations FT-100 and AT-100 show pronounced differences in droplet densities between the 1st and 2nd applications (Tables 34 and 35). The reason for this lies in the mixing difficulties experienced during the 1st application. While mixing the ingredients, extreme cold weather conditions were encountered; and since the non-aqueous ingredients were not thoroughly mixed before adding water, gel formation occurred with Triton® X-100. As a result, most of the emulsifier remained undissolved in the mixing tank. Since the spray mix contained mostly water, the spray droplets evaporated considerably in air without reaching the sample cards at the ground level. During the 2nd application the mixing problem was solved by thorough mixing of the non-aqueous ingredients before adding water. The presence of high concentration of the emulsifier in the spray mix minimized droplet evaporation, resulting in high droplet density on the sample card. Formulation FCT-100 does not show similar differences in droplet density values between the two applications because this formulation did not pose problems in mixing, and consequently, droplet evaporation was similar both times, which resulted in approximately the same droplet density. However, the reason for the low drops/cm^2 observed both times is not clear. This cannot be explained on the basis of high evaporation rate because Tables 36 to 38 do not show significant differences in the rate and degree of droplet evaporation for the three formulations FT-100, FCT-100 and AT-100. The reason, on the other hand, appears to lie in the spray atomization characteristics of the three formulations. Since the field data cannot be used to compare the atomization characteristics of the three formulations (because of variations in experimental conditions), the laboratory data obtained using the spinning disc nozzle, can be used for this purpose since all formulations were sprayed under identical conditions.

From Figs. 4, 6 and 10 , and Table 41, it is evident that FT-100 and AT-100 do not show high proportions of droplets less than 20 um in diameter. The total droplet density of FT-100 is 78, but only 14 of these were < 20 um. AT-100 has a total droplet density of 60 and only 20 were < 20 um. However, out of the total number of 52 for FCT-100, 38 were < 20 um. This shows that FCT-100 has a greater tendency to produce smaller droplets than FT-100 or AT-100. These small droplets, under field conditions, must have remained airborne with a low probability of reaching and impacting on the sample cards at the ground level. This is evident in Fig. 14 where the high proportion of small droplets was not demonstrated. This is not because they were not produced, but because they did not impact on the sample cards. The reason for FCT-100 producing a large number of small droplets appears to be due to Cyclo-Sol® 63. Formulations containing light petroleum oils were known to produce a high proportion of small droplets when rotary nozzles were used for spray atomization (Sundaram 1981, unpublished data). The present results with FCT-114 and FCID-585 also support this observation, since they both produced large amounts of small droplets (Table 41).

A comparison of spray droplet spectra and other parameters obtained under laboratory and field conditions, indicate that values from hydraulic nozzle are not comparable to the field data but those from spinning disc nozzle were quite similar. This is obviously due to the similar nature of the two rotary nozzles. However, the droplet density and volume deposit values were consistently lower in the field studies. This is clearly related to the differences in application conditions and weather factors.

Since the main objective of the present study is to research and develop an emulsifier alternative to ATLOX 3409F, formulations containing Triton® emulsifiers are the most important to understand the physicochemical properties. In this context, FT-114 and FCT-114 are the relevant ones since Triton® X-100 is not suitable for use under cold weather conditions in the field. In the present study FT-114 has shown to be too viscous, and consequently produces a good proportion of large drops. This can be reduced by decreasing the amounts of the emulsifier. Consequently formulations containing less amounts of emulsifier were prepared to study the physico-chemical properties. Similarly with FCT-114, the presence of high amounts of Cyclo-Sol® 63 was shown to cause a high proportion of small droplets and therefore this formulation should be studied with lower amounts of Cyclo-Sol® 63. The following presents results obtained with FT-114 and FCT-114 containing varied amounts of the relevant ingredients.

5c. Spray atomization characteristics of fenitrothion emulsions with varied amounts of Triton® X-114 or Cyclo-Sol® 63, using hydraulic and spinning disc nozzles (including stability considerations)

i). FT-114 formulations:

Formulations of fenitrothion containing 6, 7, 8, 10, and 14% (v/v) of Triton® X-114 were prepared for studying physicochemical properties. Table 42 lists percentage compositions of the 7% and 10% (v/v) mixtures, referred to as FT-114/7% and FT-114/10% respectively. Stability data were obtained for the 6, 7, 10 and 14% mixtures (Table 43). Stability was found to be satisfactory at cold temperatures but was high at room temperatures. Viscosity (η), density (d), surface tension (γ) and spread factor (SF) values for the 6, 7, 8, 10, and 14% mixtures indicate a progressive sharp increase in η, a gradual increase in 'd' but a slight decrease in γ with increasing emulsifier concentration (Tables 44 to 46).

Spray atomization characteristics were studied for the 7 and 10% mixes only, with hydraulic and spinning disc nozzles (Tables 48 and 49, and Figs. 19 and 20). Results indicate a definite improvement in droplet number and volume distribution curves, as compared to those of FT-114/14% (Fig. 3). FT-114/7% produced a higher proportion of smaller droplets than FT-114/10%. However, they both showed narrow, desirable drop spectra. This improvement over the earlier 14% formulation can only be attributed to the lower viscosity values of FT-144/7% and FT-114/10% (Table 44). Table 52 presents droplet density, volume deposit, NMD, VMD, D_{max} and D_{min} values for these formulations. When compared to the droplet density of FT-114/14% (Table 27), these formulations provide a progressive increse in drops/cm^2 (Table 52) as the viscosity decreased or as the emulsifier concentration decreased gradually. The NMD, VMD, D_{max} and D_{min} were also generally lower except for the single case of FT-114/10%, the NMD was slightly higher (Tables 27 and 52). These improvements are due to a reduction in viscosity values of FT-114/7% and FT-114/10%.

TABLE 42. PERCENTAGE COMPOSITION OF INGREDIENTS

11. Formulation No. FT-114/7% : Fenitrothion, Triton® X-114 and water

	w/v	w/w	v/v %
Fenitrothion technical	14.5	14.0	11.0
Triton® X-114	7.35	7.1	7.0
Water	To a total vol. of 100 ml.	78.9	82.0
	100.0	100.0	100.0

12. Formulation No. FT-114/10% : Fenitrothion, Triton® X-114 and water

	w/v	w/w	v/v %
Fenitrothion technical	14.5	14.0	11.0
Triton® X-114	10.5	10.1	10.0
Water	To a total vol. of 100 ml.	75.9	79.0
	100.0	100,0	100.0

13. Formulation No. FCT-114/15% : Fenitrothion, Cyclo-Sol® 63, Triton® X-114, water.

	w/v	w/w	v/v %
Fenitrothion technical	14.5	14.25	11.0
Cyclo-Sol® 63	13.7	13.45	15.0
Triton® X-114	2.86	2.80	3.0
Water	To a total vol. of 100 ml.	69.5	71.0
	100.0	100.0	100.0

14. Formulation No. FCT-114/20% : Fenitrothion, Cyclo-Sol® 63, Triton® X-114, water

	w/v	w/w	v/v %
Fenitrothion technical	14.5	14.3	11.0
Cyclo-Sol® 63	18.3	18.0	20.0
Triton® X-114	2.86	2.8	3.0
Water	To a total vol. of 100 ml.	64.9	66.0
	100.0	100.0	100.0

TABLE 43. STABILITY OF FORMULATIONS

No.	Formulation Description	Time required (hr) for phase separation with no agitation		reduction in viscosity by 20%, with agitation at 300 rpm	
		$5^\circ - 15^\circ C$	$20^\circ - 22^\circ C$	$5^\circ - 15^\circ C$	$20^\circ - 22^\circ C$
		FT-114 Formulations			
1.	FT-114/6%	4 - 6	$\sim$13	16 - 20	$\sim$25
2.	FT-114/7%	6 - 8	$\sim$ 15	24 - 48	$\sim$ 30
3.	FT-114/10%	16 - 20	$\sim$ 26	36 - 54	$\sim$ 50
4.	FT-114/14%	Exceptionally stable			
		FCT-114 Formulations			
5.	FCT- 114/10%	1.5 - 2.5	1.5	18 - 24	$\sim$18
6.	FCT-114/15%	2.0 - 4.0	2.0	24 - 36	$\sim$20
7.	FCT-114/20%	2.0 - 4.0	2.0	24 - 36	$\sim$20
8.	FCT-114/24%	2.0 - 4.0	2.0	24 - 36	$\sim$20

TABLE 44. VISCOSITY VALUES OF FORMULATIONS

Formulation No.	Description	Viscosity (cp) 5° C	10° C	15° C	20° C	25° C
		FT-114 Formulations				
1.	FT-114/ 6%	8.03	6.85	5.49	11.06	6.50
2.	FT-114/ 7%	25.6	15.7	24.6	47.8	22.2
3.	FT-114/ 8%	70.6	20.8	105	112	46.2
4.	FT-114/10%	119	35	944	403	205
5.	FT-114/14%	340	150	1398	940	270
		FCT-114 Formulations				
6.	FCT-114/15%	3.09	2.45	2.06	1.95	1.62
7.	FCT-114/20%	4.47	3.78	3.12	2.90	2.46
8.	FCT-114/24%	6.80	6.32	6.20	4.50	3.90

TABLE 45. DENSITY VALUES OF FORMULATIONS

Formulation No.	Description	Density (g/ml) 5° C	10° C	15° C	20° C	25° C
		FT-114 Formulations				
1.	FT-114/ 6%	1.039	1.038	1.037	1.036	1.035
2.	FT-114/ 7%	1.044	1.043	1.042	1.040	1.038
3.	FT-114/ 8%	1.044	1.042	1.041	1.040	1.037
4.	FT-114/10%	1.045	1.044	1.042	1.040	1.038
5.	FT-114/14%	1.046	1.045	1.044	1.042	1.040
		FCT-114 Formulations				
6.	FCT-114/15%	1.024	1.023	1.022	1.020	1.018
7.	FCT-114/20%	1.016	1.015	1.013	1.011	1.009
8.	FCT-114/24%	1.012	1.011	1.008	1.005	0.984

TABLE 46. SURFACE TENSION VALUES OF FORMULATIONS

Formulation No.	Description	Surface Tension (dynes/cm) 5° C	10° C	15° C	20° C	25° C
		FT-114 Formulations				
1.	FT-114/ 6%	39.8	35.4	31.7	24.3	22.2
2.	FT-114/ 7%	35.6	33.9	31.4	24.8	22.7
3.	FT-114/ 8%	33.6	32.9	31.0	23.6	22.7
4.	FT-114/10%	29.5	27.7	NA*	NA	NA
5.	FT-114/14%	NA	NA	NA	NA	NA
		FCT-114 Formulations				
6.	FCT-114/15%	31.1	31.5	29.7	28.8	28.3
7.	FCT-114/20%	32.2	31.9	30.6	29.7	29.4
8.	FCT-114/24%	32.24	32.22	32.10	32.03	31.35

* Not available. Due to the high viscosity of FT-114, the capillary rise method is not suitable for this formulation.

TABLE 47. SPREAD FACTOR DATA OF FORMULATIONS

Formulation No.	Description	Linear Regression Equation d=drop diameter. D=stain diameter	$(R=\text{corr.coef})^2$ %
		FT-114 Formulations	
1.	FT-114/ 7%	d= 8.19 + 0.285 D	98.2
2.	FT-114/10%	d= 4.00 + 0.282 D	99.6
3.	FT-114/14%	d= 6.75 + 0.268 D	99.1
		FCT-114 Formulations	
4.	FCT-114/15%	d= 0.409 + 0.367 D	99.9
5.	FCT-114/20%	d= 2.83 + 0.306 D	99.8
6.	FCT-114/24%	d= 2.60 + 0.308 D	99.6

TABLE 48. KROMEKOTE® CARD DATA USING HYDRAULIC/SPINNING DISC NOZZLES
DROPLET NUMBER/VOLUME DISTRIBUTION ACCORDING TO SIZE CATEGORY
FORMULATION FT-114/7%

Stain diameter range (μm)	Spread factor	Droplet diameter range (μm)	Average droplet diameter (μm)	Hydraulic Nozzle		Spinning Disc Nozzle	
				Cumulative frequency (%)	Cumulative droplet volume distribution (%)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)
10- 22	2.02	6.0- 14.4	10.0	1.88	0.0029	4.45	0.048
23- 45	2.14	14.6- 21.0	17.9	10.34	0.0767	8.42	0.294
46- 67	2.33	21.1- 27.3	24.3	17.55	0.2339	24.91	2.847
68- 90	2.57	27.4- 33.8	30.7	20.37	0.3580	38.81	7.186
91- 113	2.74	33.9- 40.4	37.3	25.07	0.7289	61.54	19.92
114- 169	2.92	40.5- 56.4	48.5	38.55	3.06	87.39	51.74
170- 225	3.06	56.5- 72.3	64.5	51.09	8.180	97.46	80.90
226- 281	3.15	72.4- 88.3	80.4	66.76	20.56	99.43	91.96
282- 338	3.21	88.4-104.5	96.5	80.24	38.97	99.75	95.10
339- 394	3.25	104.6-120.5	112.7	89.64	59.43	99.87	96.92
395- 450	3.29	120.6-136.4	128.6	95.91	79.70	99.99	99.62
451- 506	3.31	136.5-152.4	144.6	99.36	95.54	100.00	100.00
507- 607	3.34	152.5-181.2	166.9	99.99	99.97	------	------

FIG. 19. DROPLET SPECTRA OF FT-114/7%

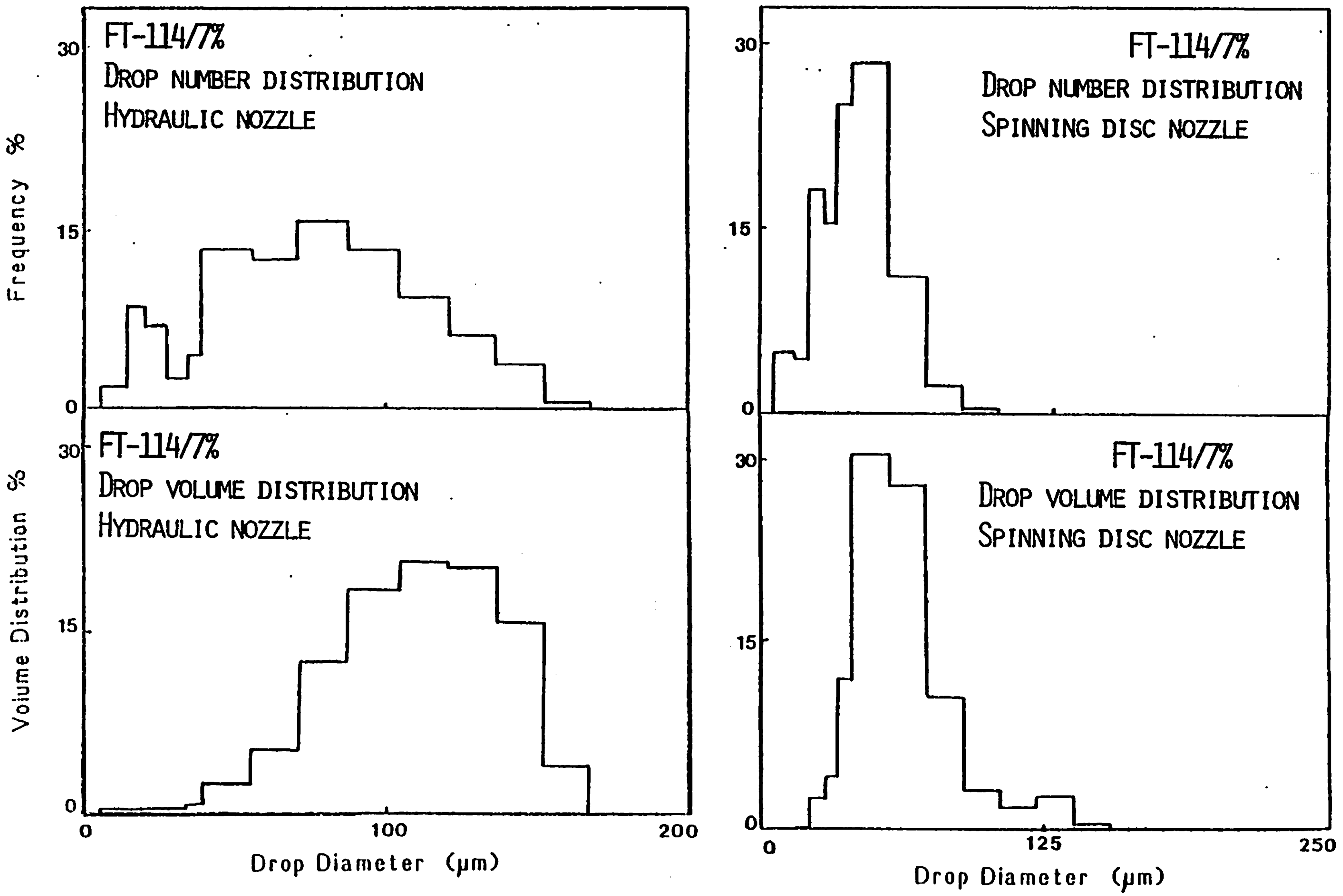


TABLE 49. KROMEKOTE® CARD DATA USING HYDRAULIC/SPINNING DISC NOZZLES DROPLET NUMBER/VOLUME DISTRIBUTION ACCORDING TO SIZE CATEGORY

FORMULATION FT-114/10%

Stain diameter range (µm)	Spread factor	Droplet diameter range (µm)	Average droplet diameter (µm)	Hydraulic Nozzle		Spinning Disc Nozzle	
				Cumulative frequency (%)	Cumulative droplet volume distribution (%)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)
10- 22	2.02	4.3- 10.2	7.2	2.00	0.0009	0.67	0.0012
23- 45	2.50	10.3- 16.7	13.6	5.36	0.1133	2.68	0.0274
46- 67	2.83	16.8- 22.9	19.9	10.04	0.1621	8.03	0.2473
68- 90	3.01	23.0- 29.4	26.3	14.67	0.2724	24.76	1.829
91- 113	3.11	29.5- 35.9	32.8	19.19	0.4813	42.05	5.000
114- 169	3.22	36.0- 51.7	43.9	23.47	0.9575	68.63	16.68
170- 225	3.31	51.8- 67.5	59.7	34.93	4.167	82.40	31.92
226- 281	3.36	67.6- 83.2	75.5	52.53	14.14	91.85	53.08
282- 338	3.39	83.3- 99.3	91.4	72.23	33.96	96.34	70.89
339- 394	3.41	99.4- 115.1	107.4	85.04	54.85	98.72	86.19
395- 450	3.43	115.2- 130.9	123.2	93.57	75.79	99.71	95.83
451- 506	3.44	131.0- 146.7	138.9	98.26	92.32	99.96	99.33
507- 607	3.46	146.8- 175.2	161.1	99.80	97.78	99.99	99.98
608- 799	3.48	175.3- 229.3	202.4	100.01	100.02	------	------

FIG. 20. DROPLET SPECTRA OF FT-114/10%

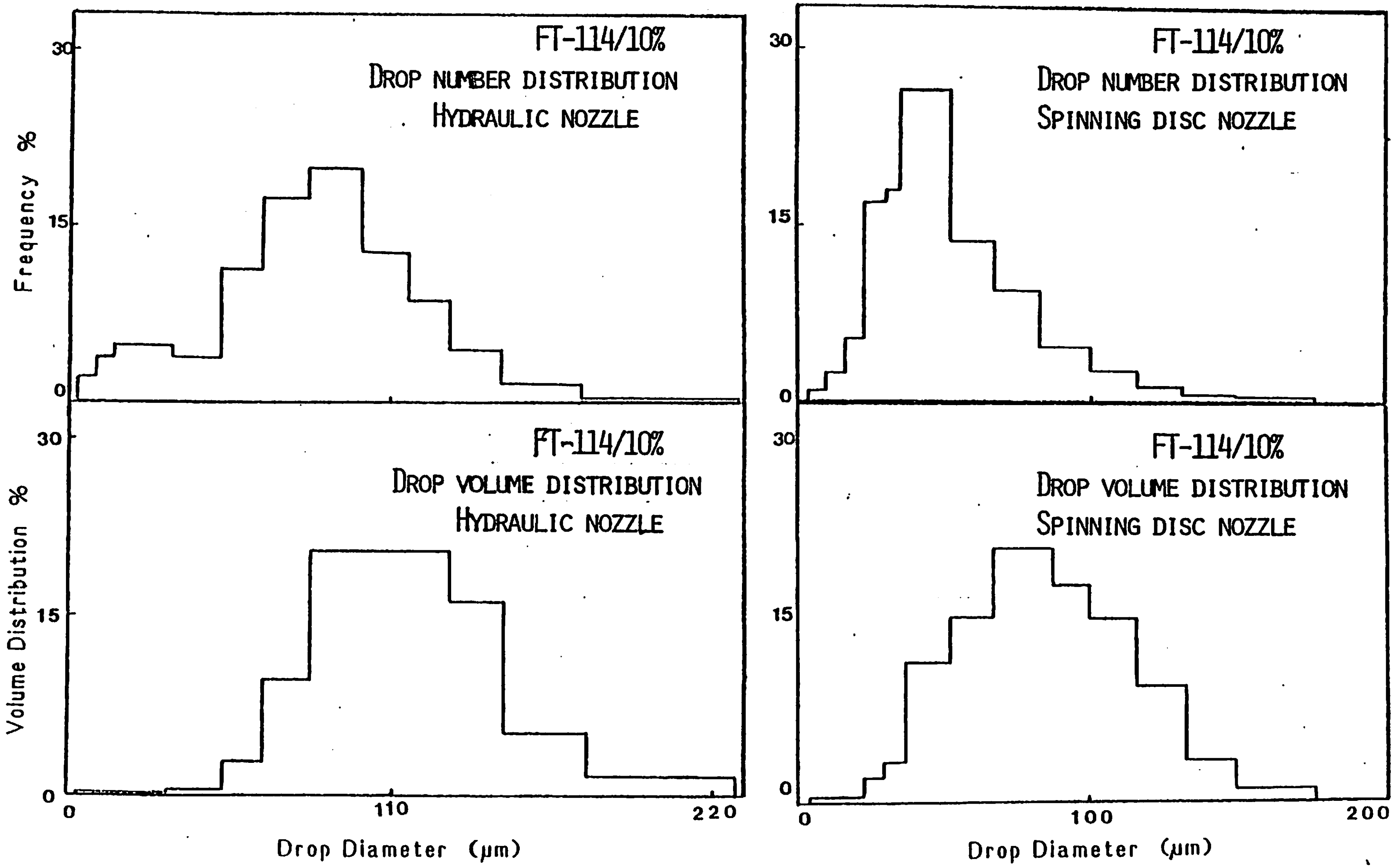


TABLE 50. KROMEKOTE® CARD DATA USING HYDRAULIC/SPINNING DISC NOZZLES

DROPLET NUMBER/VOLUME DISTRIBUTION ACCORDING TO SIZE CATEGORY

FORMULATION FCT-114/15%

Stain diameter range (µm)	Spread factor	Droplet diameter range (µm)	Average droplet diameter (µm)	Hydraulic Nozzle		Spinning Disc Nozzle	
				Cumulative frequency (%)	Cumulative droplet volume distribution (%)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)
5- 10	2.50	2.5- 4.0	3.5	1.66	0.0000	1.14	0.0003
11- 22	2.67	4.1- 8.5	6.0	2.75	0.0002	3.32	0.0032
23- 45	2.62	8.6- 16.9	13.0	4.74	0.0030	8.08	0.0686
46- 67	2.69	17.0- 25.0	21.2	6.98	0.0162	18.34	0.6633
68- 90	2.72	25.1- 33.4	29.1	10.06	0.0641	34.52	3.131
91- 113	2.68	33.5- 41.9	37.8	16.26	0.2810	58.97	11.52
114- 169	2.72	42.0- 62.4	52.1	27.24	1.265	84.16	33.69
170- 225	2.71	62.5- 83.0	73.0	37.62	3.840	94.02	57.67
226- 281	2.70	83.1- 103.5	93.9	54.22	12.63	97.83	77.44
282- 338	2.72	103.6- 124.4	114.1	71.75	29.19	99.69	94.57
339- 394	2.71	124.5- 145.0	135.1	83.77	48.04	99.93	98.25
395- 450	2.73	145.1- 165.5	155.0	92.15	67.92	99.98	99.26
451- 506	2.72	165.6- 186.1	176.1	98.56	90.19	100.00	100.00
507- 607	2.72	186.2- 223.1	205.0	99.69	96.40	—	—
608- 799	2.72	223.2- 293.6	259.1	100.02	100.00	—	—

Fig. 21. Droplet Spectra Of FCT-114/15%

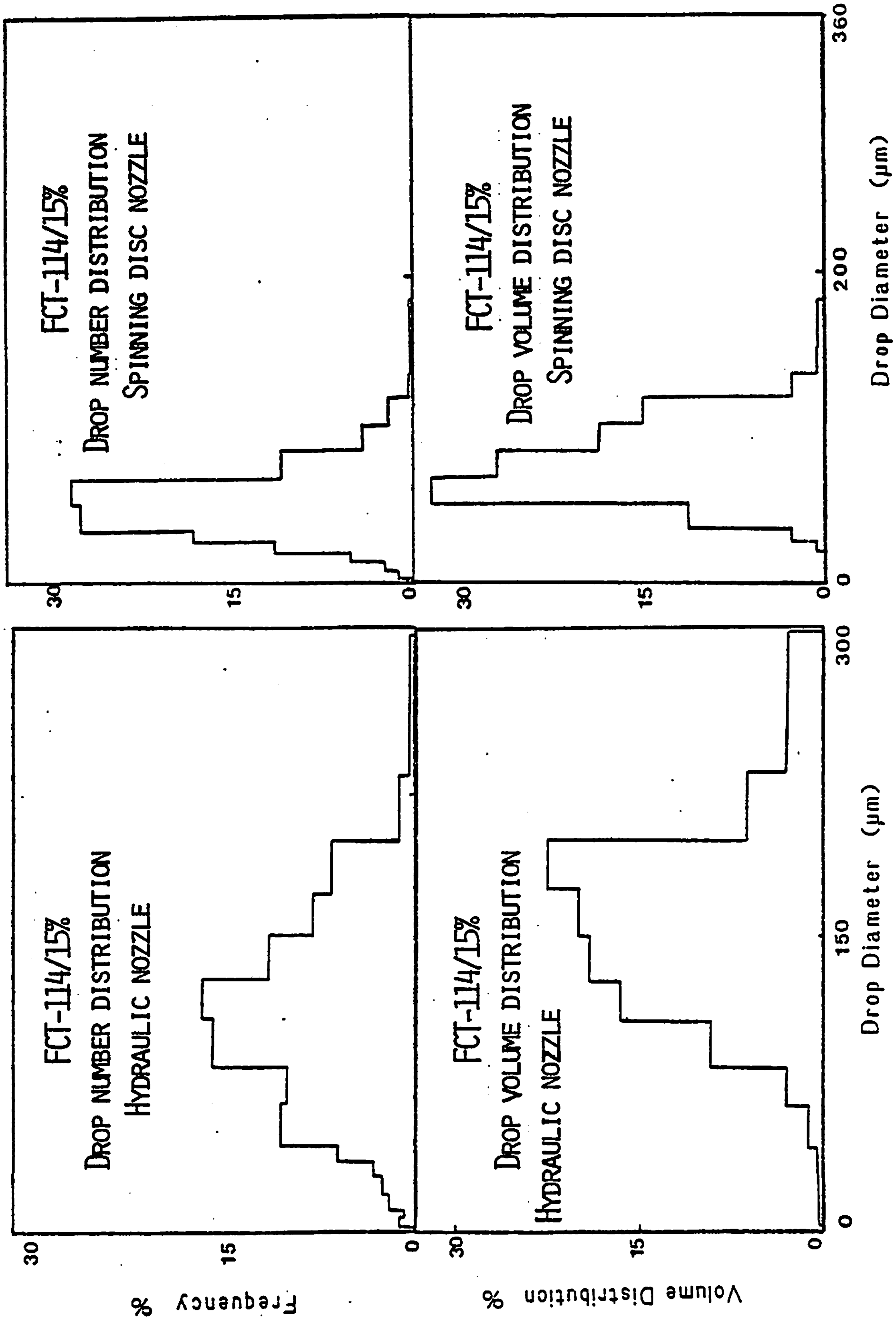


TABLE 51. KROMEKOTE® CARD DATA USING HYDRAULIC/SPINNING DISC NOZZLES
DROPLET NUMBER/VOLUME DISTRIBUTION ACCORDING TO SIZE CATEGORY
FORMULATION FCT-114/20%

Stain diameter range (µm)	Spread factor	Droplet diameter range (µm)	Average droplet diameter (µm)	Hydraulic Nozzle		Spinning Disc Nozzle	
				Cumulative frequency (%)	Cumulative droplet volume distribution (%)	Cumulative frequency (%)	Cumulative droplet volume distribution (%)
10- 22	2.07	5.9- 9.6	7.7	7.20	0.0030	0.32	0.001
23- 45	2.57	9.7- 16.6	13.2	8.44	0.0056	1.83	0.016
46- 67	2.81	16.7- 23.3	20.1	12.65	0.0369	5.18	0.131
68- 90	2.92	23.4- 30.4	27.0	15.98	0.0967	12.96	0.776
91- 113	3.00	30.5- 37.4	34.1	21.86	0.3083	29.27	3.484
114- 169	3.07	37.5- 54.5	46.1	34.14	1.407	55.40	14.27
170- 225	3.12	54.6- 71.7	63.3	52.69	5.688	83.69	44.42
226- 281	3.15	71.8- 88.8	80.4	66.37	12.18	96.12	71.60
282- 338	3.17	88.9- 106.3	97.7	76.86	21.09	97.87	78.45
339- 394	3.19	106.4- 123.4	115.0	85.72	33.37	98.91	85.12
395- 450	3.20	123.5- 140.5	132.1	90.44	43.30	99.50	90.84
451- 506	3.21	140.6- 157.7	149.3	93.22	51.72	99.76	94.65
507- 607	3.21	157.8- 188.6	173.3	97.67	72.81	99.99	99.61
608- 799	3.23	188.7- 247.3	218.1	99.37	88.85	100.00	100.01
800- 965	3.24	247.4- 298.0	269.0	100.00	100.00	—	—

FIG. 22. DROPLET SPECTRA OF FCT-114/20%

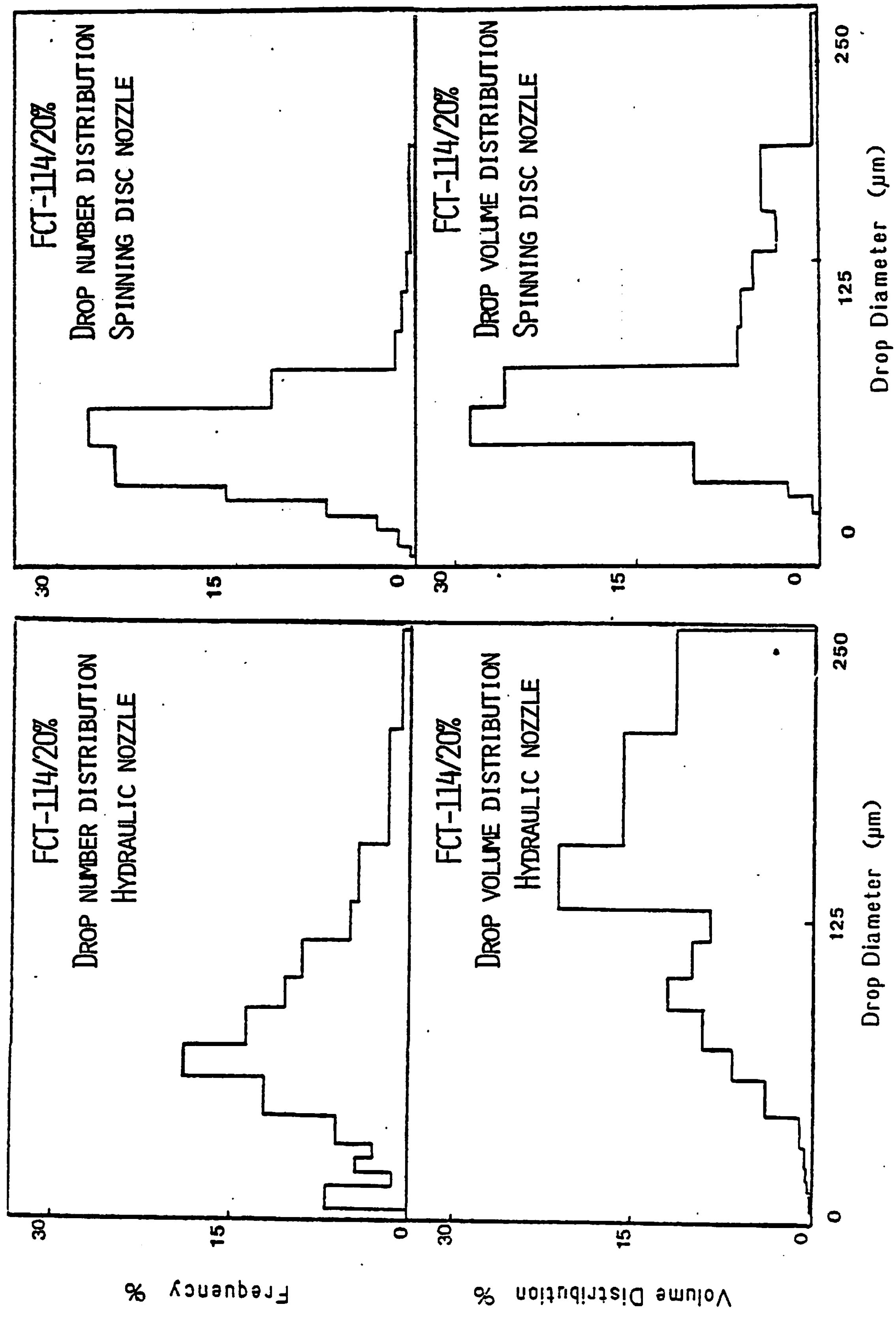


TABLE 52 . SUMMARY DATA ON DROPLET SPECTRA OF FENITROTHION FORMULATIONS ON KROMEKOTE® CARD

Formulation No.	Drops per cm^2	D_{min} (um)	D_{max} (um)	Number mode (um)	Volume mode (um)	Number median diameter (um)	Volume median diameter (um)	Volume deposit (ml/ha).
Hydraulic Nozzle								
FT-114/ 7%	51	10.0	167	40-100	100-167	60	120	248
FT-114/10%	29	7.2	202	70-100	80-130	74	102	1163
FCT-114/15%	15	3.5	259	80-125	110-190	82	134	1259
FCT-114/20%	20	7.7	269	60-100	130-180	64	140	1143
Spinning Disc Nozzle								
FT-114/ 7%	64	10.0	145	35- 55	40- 70	33	46	307
FT-114/10%	67	7.2	161	30- 55	60- 85	33	71	719
FCT-114/15%	46	3.5	176	35- 60	50- 80	33	64	385
FCT-114/20%	44	7.7	218	40- 65	55- 85	40	66	549

TABLE 53. RATE AND DEGREE OF DROPLET EVAPORATION OF FT-114 FORMULATIONS

Formulation No.	Initial droplet diameter (um)	Droplet diameter at 1.0 min. (um)	Droplet diameter at 30 min. (um)	Droplet diameter at 60 min. (um)	Residual drop volume at 60 min. (%)
FT-114/7%	241	145	145	145	21.8
	209	129	129	129	23.5
	178	105	105	105	20.5
	160	96	96	96	21.6
	136	80	80	80	20.4
	111	68	68	68	23.0
				Mean ± SD = 21.8 ± 1.3	
FT-114/10%	234	145	145	145	23.8
	209	129	129	129	23.5
	185	117	117	117	25.3
	169	105	105	105	24.0
	160	96	96	96	21.6
	145	89	89	89	23.1
	96	58	58	58	22.1
				Mean ± SD = 23.3 ± 1.2	
FT-114/14%	205	144	144	144	34.6
	176	123	123	123	34.1
	153	111	111	111	38.2
	131	97	97	97	40.6
	97	70	70	70	37.6
	85	63	63	63	40.7
				Mean ± SD = 37.6 ± 2.8	

TABLE 54. RATE AND DEGREE OF DROPLET EVAPORATION OF FCT-114 FORMULATIONS

Formulation No.	Initial droplet diameter (um)	Droplet diameter at 1.0 min. (um)	Droplet diameter at 30 min. (um)	Droplet diameter at 60 min. (um)	Residual drop volume at 60 min. (%)
FCT-114/15%	230	148	139	139	22.1
	202	133	120	120	21.0
	160	105	96	96	21.6
	136	96	83	83	22.7
	129	96	80	80	23.9
	117	68	68	68	19.6
					Mean ± SD = 21.8 ± 1.5
FCT-114/20%	226	160	136	136	21.8
	185	120	108	108	19.9
	178	129	105	105	20.5
	160	108	96	96	21.6
	136	89	80	80	20.4
	111	68	68	68	23.0
					Mean ± SD = 21.2 ± 1.1
FCT-114/24%	216	137	137	137	25.5
	165	107	107	107	27.3
	157	100	100	100	25.8
	153	97	97	97	25.5
	131	85	85	85	27.3
	119	77	77	77	27.1
					Mean ± SD = 26.4 ± 0.9

TABLE 55. LIMITING RESIDUAL VOLUME OF NON-AQUEOUS AND NON-VOLATILE COMPONENTS OF FORMULATIONS

Formulation		Mean limiting volume of droplets at 60 min. (%)	Non-aqueous components (v/v%)	Non-volatile components (v/v%)
No.	Description			
		FT-114 Formulations		
1	FT-114/7%	21.8	18.0	18.0
2	FT-114/10%	23.3	21.0	21.0
3	FT-114/14%	37.6	25.0	25.0
		FCT-114 Formulations		
4	FCT-114/15%	21.8	29.0	14.0
5	FCT-114/20%	21.2	34.0	14.0
6	FCT-114/24%	26.4	38.0	14.0

Fenitrothion appears to form a thixotropic and viscoelastic formulation with Triton® X-114 at the 14% level. However, as the concentration of the emulsifier decreased, the thixotropy appears to decrease sharply, and as a result the viscosity is reduced drastically. The present results indicate that FT-114/7% and FT-144/10% are probably more suitable than FT-114/14% for aerial application over conifer forests. Table 56 lists droplets and volume of deposits outside the 20 - 150 um range. It can be seen that with both nozzles the two formulations provide approximately 10% of the droplets only, in the outside range, indicating that FT-114/7% and FT-114/10% are suitable for use with both types of nozzles.

ii). FCT-114 formulations.

These formulations contain fenitrothion, Cyclo-Sol® 63 and Triton® X-114 and water, with variable amounts of Cyclo-Sol® 63. Table 42 lists percentage compositions in w/v, w/w and v/v ratios. Two formulations were found suitable; one with 15% of the oil and the other with 20%. These were comparatively studied for their atomizability, stability and other physicochemical properties, with the 24% formulation (Tables 43 to 56). Stability studies show that FCT-114/15% and FCT-114/20% both are less stable than FT-114 formulations (Table 43). However the stability is sufficiently long to allow homogeneity of the tank mix until the completion of the spray operation. Viscosity measurements indicate a gradual decrease as the concentration of Cyclo-Sol® 63 decreases. However the decrease is only slight as opposed to the sharp decrease observed with FT-114 formulation. The surface tension values also appear to decrease, unlike the FT-114 formulations where a gradual increase was observed as the concentration of emulsifier increased (Table 46).

Spray atomization characteristics were studied with hydraulic and spinning disc nozzles. Results indicate a definite improvement in both cases. With hydraulic nozzle, the 24% formulation produced 15% of the total droplets in the size range <20 um, whereas the 20% and 15% formulations produced only 10% and 5% of the droplets in this size range. There was a progressive decrease of small droplets as the concentration of Cyclo-Sol® 63 decreased gradually (Tables 40

TABLE 56. KROMEKOTE® CARD DATA USING HYDRAULIC/SPINNING DISC NOZZLES

DROPLET NUMBER/VOLUME DISTRIBUTION OUTSIDE THE 20 - 150 UM RANGE

Formulation Description	Drops per cm^2	Volume deposit (ml/ha)	No.of drops* < 20 um (%)	Vol.of drops* < 20 um (%)	No.of drops@ > 150 um (%)	Vol.of drops@ > 150 um (%)	Effective drops per cm^2	Effective vol.deposit (ml/ha)
Hydraulic nozzle								
FT-114/7%	51	248	10.0	0.075	1.5	5.0	45	236
FT-114/10%	29	1163	9.5	0.155	1.5	5.0	26	1100
FCT-114/15%	15	1259	5.8	0.010	15.0	50	12	630
FCT-114/20%	20	1143	10.0	0.025	10.0	51	16	560
Spinning disc nozzle								
FT-114/7%	64	307	8.0	0.260	0.00	0.0	59	306
FT-114/10%	67	719	7.5	0.235	0.00	0.0	62	717
FCT-114/15%	46	385	15.0	0.400	0.01	1.0	39	380
FCT-114/20%	44	549	4.0	0.120	0.35	7.0	42	546

* Droplets and volume deposits in the size range < 20 um do not impact efficiently on targets.

@ Droplets and volume deposits in the size range > 150 um contribute to inefficient target coverage.

and 56, and Figs. 5, 21 and 22). The trend looks even better with the spinning disc nozzle. The FCT-114/24% formulation produced 38% of the total droplets in the range < 20 um, whereas FCT-114/15% and FCT-114/20% produced only less than 15% in this size range (Tables 41 and 56, and Figs. 5, 21 and 22). It is evident that low amounts of Cyclo-Sol® 63 improved the drop spectra, NMD, VMD and D_{min} . Table 28 shows NMD and VMD values of 21 and 35 respectively for FCT-114/24% , whereas formulations FCT-114/15% and FCT-114/ 20% both show higher values. For the 15% formulation they are 33 and 64 um respectively. For the 20% formulation the values are somewhat higher, 40 and 66 respectively. The slight increse in the NMD and VMD values indicate a better droplet spectrum, indicating a better impaction pattern of droplets. This is evident in the volume deposit for these formulations as compared to the 24% formulation (Tables 28 and 56).

⑥ Rate and degree of droplet evaporation

The vapour pressure of the liquid carrier of formulations (for emulsions, it is mainly water and any volatile cosolvent, but for the oil-based spray mixes it is the diluent) has a direct effect upon the rate of droplet evaporation and consequently determines the size of a given droplet with respect to time.

Tables 36 to 38, 53 and 54 present data on the rate and degree of droplet evaporation of 14 formulations at laboratory temperatures and relative humidity. Although these would not represent field conditions, the study would provide data on comparative evaporation rates of formulations. The data indicate that, in most cases, the droplets evaporated very rapidly (within a minute) forming a residual droplet of constant volume for a period of up to one hr (Tables 36 to 38, 53 and 54). Under field conditions, the rate of evaporation is likely to be slower, but with the ULV applications and with the height of spray used in the forestry spraying, the droplets, being small, would linger in air for a long time before impaction. During this time, the droplets are likely to undergo maximum evaporation forming a constant volume (referred to here as the limiting volume or V_{lim}). It is because of this, the degree of evaporation rather than the rate, was considered to be more important.

The limiting volume percent (V_{lim}) of a droplet is found to be independent of droplet sizes (Tables 36 to 38, 53 and 54). However, it is expected to be equal to the non-aqueous and/or non-volatile components in the formulation mixture. Tables 39 and 55 present these data along with the mean V_{lim}. It can be seen that the V_{lim} values are not always equal to the non-volatiles. For the thixotropic formulation FT-114/14% , the V_{lim} is much greater than the percentage of non-volatiles. For the FT-100 and FDA-3409 emulsions, V_{lim} is only slightly higher, and for those containing suspended particulates (AT-114, AT-100 and AA-3409) the V_{lim} values are approximately the same as the % non-volatiles. The reason for such variations in the V_{lim} of different emulsions lie in the degree of micellization, hydration and hydrogen bonding, all of which contribute to the stability of emulsions. FT-114/14% is the most stable emulsion having a high degree of micellization, and consequently in the droplet some water is bound to remain. FT-100 and FDA-3409 have only a moderate stability with a low degree of micellization. This results in a greater loss of water from the droplet than in FT-114/14%. However, the aminocarb emulsions appear to be the least stable, having a very low degree of micellization and as a result, a complete loss of water occurs. The stability of formulations FT-114/7% and FT-114/10% is lower than the 14% formulation, and consequently their V_{lim} values are only slightly higher than the % non-volatiles (Table 55).

Emulsions containing Cyclo-Sol® 63 appear to be highly complex: their V_{lim} values are neither equal to the % non-aqueous additives nor to the non-volatiles (Tables 39 and 55). The values are in between the two percentages. The reason for this lies in the complexity of the emulsion type. The thermodynamic behaviour of these emulsions are yet to be understood.

From Tables 27, 28, 39, 52 and 55, it is apparent that no direct relationship exists between the residual volume% of formulations and either the droplet densities or the droplet spectra. This indicates that the use of non-volatile ingredients such as Sunspray® oils as diluents is probably not the answer for improving spray efficiency. The crux of the problem appears to be the atomizability of formulations.

The residual volume of a droplet is dependent on its initial volume at source, which in turn is governed by physicochemical properties including viscosity and surface tension. Therefore, the spray droplet spectrum of of a formulation results from a combined effect of many variables. Development of a model system, incorporating the important variables could throw some light in arriving at a solution.

⑦ Rate and degree of vaporization of pesticides from spray droplets

Pesticides are subject to considerable loss by volatilization when they are thinly spread over large areas exposed to moving air, and the rate and degree to which this occurs is influenced largely by the prevailing wind, but to some extent, by the physicochemical nature of the additives in the formulation (Hartley 1969). The influence of formulation on the rate and degree of loss is difficult to assess under field conditions since photochemical degradation is likely to occur simultaneously. Such assessment is however possible in the laboratory under controlled conditions.

Results from the experiments performed in our laboratory (described earlier on page 62) on Petri dishes can be extended to the situation of pesticide loss from fine droplets (large surface area/ mass ratio) of the ULV sprays that are carried to the target primarily by the prevailing wind and its accompanying eddies. The preliminary results of the laboratory studies support the role of formulation on the rate of pesticide loss, but these were carried out before the construction of the spray chamber in the Institute. Future studies can be conducted in the spray chamber mimicking the actual forestry situation of spray application and deposition. These studies would be more appropriate to evaluate the pesticide loss from spray droplets.

⑧ ⑨ and ⑩ Spray droplet impaction, retention and dissipation characteristics.

It has been frequently demonstrated that the toxicity of pesticides can be enhanced markedly by the addition of surface-active agents (Becher and Becher 1969). Any attempt taken to improve pesticide spray effectiveness has to be based on the following:

a). The spray droplet must get on the target of interest (here it is foliage). This process involves droplet impaction.
b). Once there, it must remain (droplet retention).
c). Not only must it remain, but the target insect must come into contact with the droplet (either by dermal absorption or by oral ingestion).

With respect to droplet impaction, it has been shown that unless the kinetic energy of the droplet is less than the energy barrier of the droplet/leaf interface, the droplet will be reflected. For example, a water droplet of 100 um in diameter falling at its terminal velocity of ca. 25 cm/sec, will have a kinetic energy of ca. 1.5 x 10^{-4} erg, while its surface energy (with a surface tension value of ca. 72 dyne/cm) is ca. 2.2 x 10^{-2} erg. Since the kinetic energy is much smaller than the surface energy, the droplet will generally adhere to the foliage and will not be reflected. However, for a 200 um droplet of water, the terminal velocity is about 75 cm/sec, its kinetic energy is ca. 1.1 x 10^{-2} erg, whereas its surface energy will be 8.8 x 10^{-2} erg. Here the kinetic energy is approaching the surface enegy, although it is still lower. For a 250 um droplet on the other hand, the terminal velocity is ca. 125 cm/sec and its kinetic energy ($\sim$6.0 x 10^{-2} erg) is only about half of its surface energy ($\sim$13.5 x 10^{-2} erg), and droplet reflection is quite probable, especially if the droplet is not pure water (minute amounts of impurities can lower the surface energy). The addition of surface-active agents can lower the surface tension of water from 72 to, say, 36 dynes per cm, reducing the surface energy to ca. half of its original value (Table 46 on page 85), This increases the probability of droplet reflection but, the energy barrier of the droplet/foliage interface is also lowered due to chemical forces, facilitating droplet impaction.

Once the droplet is deposited on the foliage, now the gravitational force of the droplet will tend to make the droplet run off the leaf, but this is opposed again by the adhesive forces between the droplet and the leaf. The addition of surface-active agents increases the chemical forces of adhesion and in our present study, droplet retention was found to be very good with all emulsions containing

Triton® emulsifiers.

With respect to droplet dissipation, three processes are possible:

i). Penetration into the leaf tissue, followed by rapid degradation, via plant/chemical interaction:

This possibly occurs with the oil-based formulations and with FDA-3409, since they are rapidly absorbed into the waxy cuticle, however the rate of degradation appears to be slow, so that insect control is possible (Sundaram, unpublished data). If degradation occurs too rapidly, the pesticide is likely to have reduced potency.

ii).Evaporation into the atmosphere:

This has been shown to occur, but its rate is primarily dependent on the ambient air temperature, relative humidity and the air movement around the leaf surface. In order to reduce the rate of loss, suitable adjuvants can be added to the formulation. The simple experiment performed in our laboratory (described on page 62), threw some light in this aspect.

iii). The droplet may be blown off by strong winds or be washed off by rain:

The probability of being blown by winds is appreciable for the encapsulated droplets. However, in the present study no encapsulation occurred and droplets remained very well on foliage, in spite of violent shaking of the sprayed branches. With respect to the rain-wash, the probabilty exists if it rains soon after spraying. However, it has been claimed that the rain droplets, being large, have a low penetrability into regions where small droplets would deposit.

In the present study, droplets of Triton® formulations of fenitrothion remained in tact on foliage for a few days during which gradual penetration occurred, with a complete dissipation of the droplet. Since fenitrothion is a liquid, its penetration into the leaf cuticle possibly occurs along with the rest of the ingredients of the droplet. However, with MATACIL® 180F, which contains suspended microparticles of aminocarb, the process of dissipation of the active ingredient is likely to be complex. The behaviour of a droplet of a true solution containing pesticide molecules in the size range < 1 nm in diameter, would be in rapid equilibrium with the liquid carrier, and foliar penetration of AI can occur along with the liquid phase of the carrier. Aqueous emulsions on the other hand, contain micelle-pesticide entities of the order of 1 to 1000 nm in diameter (Olivier 1965), and droplet penetration into the leaf membrane involves electrical forces (Mysels 1969). Even then, the AI penetration is possible along with the liquid carrier. With MATACIL® 180F however, the milled particles of aminocarb are mostly larger than 1000 nm and are suspended in the liquid carrier, and foliar penetration of the AI becomes more complex. This might be an interesting area to investigate since the insect/AI interactions can be enhanced by suitable choice of the additives.

Pesticides should be formulated not only for convenient dispersal but also to offer them to the target organism in a way that maximizes biological activity. Until now, methods of formulating a pesticide are often dictated by cost criteria rather than by its biological effectiveness (Matthews 1979). The recent awareness of the environmental effects of pesticide uses, caused the need to look into efficient ways of formulation and spray application. A formulator should therefore examine the phenomena of interaction of the chemical with the environment, transfer and absorption of the chemical into the target organism, and prevention of loss from the treated area. These phenomena reveal that certain physicochemical properties of a formulation can maximize its biological effectiveness. To attain these properties, selection of optimum solvents and additives is a prerequisite, in order to increase droplet deposition and retention on the target matrix, to overcome absorption barriers and to promote conservation of the chemical during the critical period of pest control.

SUMMARY

Aqueous emulsions of fenitrothion and aminocarb were prepared using three types of emulsifiers, Triton® X-114, Triton® X-100 and ATLOX 3409F. Their suitability for aerial spraying over conifer forests was investigated using a battery of test procedures. Stability studies were based on the physical separation of component phases. These indicated that fenitrothion/Triton® X-114/water mixtures were

more stable than other emulsions studied. Stability was acceptable for a concentration range of 7, 10 and 14% (v/v) of the emulsifier. Emulsions with good stability were prepared from fenitrothion/Cyclo-Sol®63/Triton®X-114/water, with a concentration range of 15, 20 and 24% of the cosolvent. Stability of the currently registered fenitrothion/Dowanol TPM (1.5% v/v)/ATLOX 3409F (1.5% v/v)/water emulsion was low. For acceptable stability, the formulation requires a greater concentration of the emulsifier and/or cosolvent. Stability was low for the fenitrothion/Triton®X-100/water mixture and for the three aminocarb emulsions, MATACIL® 180F/Triton® X-114/water, MATACIL® 180F/Triton® X-100/water and MATACIL® 180F/ATLOX 3409F/water.

Formulations were generally more stable at colder temperatures (5°C to 15°C) than at 15°C to 25°C. Emulsion stability of most formulations were affected by water acidity and hardness. Small amounts of water soluble dyes affected the stability of most emulsions, except for the Erio Acid Red with the fenitrothion/Triton® X-114/water mixtures. Studies on the re-emulsifiability, following storage for four days at 5°C to 15°C, indicated that fenitrothion emulsions can be readily re-emulsified upon agitation. However, in the MATACIL® 180F emulsions, agglomeration of the suspended solid components occurred during storage and introduced difficulties in the re-emulsification process .

Measurements of physicochemical properties revealed a marked reduction in surface tension with most emulsions. This lowered the surface energy of the spray droplets, enhancing droplet impaction and retention. The emulsion fenitrothion/Triton® X-114/water showed thixotropic and viscoelastic properties at the 14% level of the emulsifier, and was highly viscous. Spray atomization characteristics were studied using hydraulic and spinning disc nozzles. Droplets were collected on Kromekote® cards and their size spectra were evaluated. A study of the frequency and spray volume distribution in various size categories indicated the influence of formulation properties on droplet spectra. Among the fenitrothion/Triton® X-114/water mixtures studied, those containing 7 and 10% (v/v) emulsifier provided narrower and more desirable droplet spectra than the 14% mixture. This was attributed to the high viscosity of the mixture. Among the fenitrothion/Cyclo-Sol® 63/Triton® X-114/ water emulsions studied, the 15 and 20% (v/v) mixtures atomized better than the 24%, and provided more suitable droplet spectra. The presence of large amounts of Cyclo-Sol® 63 in the emulsion provided a high proportion of small droplets when spinning disc nozzle was used, and this was evident in all the three formulations containing this cosolvent. The oil-based MATACIL® 180F formulation, containing another light petroleum solvent ID 585 also provided a high proportion of small droplets. This was obviously due to the low viscosity and a high degree of evaporation of spray droplets of these formulations. The MATACIL® 180F/ATLOX 3409F/ water emulsion also produced large number of small droplets, but this is due to the low concentration of the emulsifier added, causing a low degree of micellization and low stability of the emulsion. For acceptable stability and droplet spectra, the emulsifier concentration should be increased for this emulsion.

Studies on droplet evaporation showed that the limiting residual volume percent of droplets is independent of droplet sizes. Spray droplets of all emulsions showed good impaction and retention characteristics. However, droplets of emulsions containing Triton® X-114 and Triton® X-100 persisted on balsam fir needles slightly longer than those of the ATLOX 3409F emulsifier, suggesting a possible enhancement of bioavailability to the target insect. The shorter period of droplet persistence of the ATLOX 3409F emulsions is probably due to a lower concentration of the emulsifier in the formulations.

The conclusion of the present investigation is that the following five emulsions:

i) Fenitrothion 11% /Triton® X-114 7% /water
ii) Fenitrithion 11% /Triton® X-114 10% /water
iii) Fenitrothion 11% /Cyclo-Sol® 63 15% /Triton® X-114 3% /water
iv) Fenitrothion 11% /Cyclo-Sol® 63 20% /Triton® X-114 3% / water
V) MATACIL® 180F 26.7% /Triton® X-114 3% / water

provide the required characteristics of a suitable formulation for forestry use, based on stability considerations, physicochemical properties, atomizability, and spray droplet evaporation, impaction, retention and dissipation. Since emulsion formulations are generally susceptible to changes in physical characteristics during storage, it is prudent to spray the formulations, once mixed.

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