ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

Effects of processing shear intensity upon droplet size and emulsion stability of oil- in-water emulsion formulation of insecticide Lambda Cyhalothrin

Dr. Amrish Agrawal *, Dr. D.K. Hazra , Mrs. Smriti Kala , Dr. P.K. Patanjali , Dr. S.K. Raza
Institute of Pesticide Formulation Technology Sector-20, Udyog Vihar, Opposite – Ambience Mall Gurgaon – 122 016, Haryana, India.

Manuscript Info

Manuscript History:

Received: 15 September 2014
Final Accepted: 26 October 2014
Published Online: November 2014

Key words:
Processing, Emulsion, shear, droplet, turbidity, stability

Corresponding Author

Dr. Amrish Agrawal

Abstract

The conventional Emulsifiable Concentrate (EC) formulation of insecticide Lambda Cyhalothrin is being used worldwide for controlling various agricultural insects and mosquitoes. It contains large quantities of petroleum distillate organic solvents and thus has disadvantages of flammability, environmental contamination by evaporation of solvents and penetration into the skin of farmers and spray application workers causing higher dermal toxicity. Water based oil-in-water emulsion (EW) formulation of Lambda Cyhalothrin may be a safer and better alternative to EC formulation. In the present studies, the composition and process for preparing EW formulation were optimized. The process of shear mixing is generally applied for preparing emulsion formulations, but data is not available about the process variables, specially the effects of changes in shear intensity upon the droplet size and emulsion stability, therefore, studies were conducted to examine the effects of changes in processing shear intensity upon droplet size and emulsion stability. The increase in processing shear intensity from 500 rpm to 4000 rpm (at increments of 500 rpm), gradually decreased droplet size from 9.3 microns to 2.22 microns. The emulsion stability increased with increase in processing shear intensity & decrease in droplet size and it was maximum i.e., 99.67 % in the sample prepared at highest shear rate of 4000 rpm. The emulsions prepared with high shear rate and having small droplet size were found stable in mild acidic, alkaline and saline dilution mediums and after accelerated temperature storage. The optimized composition and applying high processing shear intensity were found very effective for preparing stable formulation.

Introduction

Insecticide Lambda Cyhalothrin [Cyano-3-phenoxybenzyl-(2-chloro-3, 3, 3-trifluoro-1-propenyl)-2, 2-dimethylcyclo propane carboxylate] is a contact and stomach insecticide of synthetic pyrethroid group and is being widely used at global level to control mosquitoes and agricultural insects like aphids, jassids, thrips, lepidoptera larvae and insect borne plant viruses. Emulsifiable Concentrate (EC) formulation is the commonly used formulation of Lambda cyhalothrin. The EC formulations contain large quantities of petroleum distillate organic solvents and thus has disadvantages of flammability, risk of phytotoxicity to crops, inhalation and penetration into the skin of farmers and spray application workers causing higher dermal toxicity and itching problems.. After application, the organic solvents evaporate and contaminate the environment. The EC formulation is therefore less safer to the user and environment.

The oil-in-water emulsion formulations of pesticides (EW) are user & environment friendly new generation formulations being developed for pest control applications. The EW formulations are concentrated oil in water emulsions of pesticides, which are further diluted with water before spray applications.. The EW formulations are water based formulations and contain none or minimum organic solvents, therefore, they overcome the shortcomings of conventional EC formulations. The EW formulations are now gaining popularity due to their various advantages like good dispersion in the spray tank, good bio-efficacy, cost effectiveness and minimum use of organic solvents (Knowles, 2008).

EW formulation of Insecticide Lambda Cyhalothrin may be a better and safer alternative to its existing EC formulation. In present studies, the composition and process were optimized for preparing EW formulation of Insecticide Lambda Cyhalothrin

Samples of Lambda Cyhalothrin EW formulation were prepared using different formulation additives (emulsifiers, viscosity modifiers, anti-freezing agents, defoamers etc.) for optimization of composition of the formulation . The process of shear mixing is generally used by the industries and also mentioned in the literature for producing emulsion formulations (Ramdas, 1996) but data is not available about the process variables, specially the effects of changes in shear intensity upon the droplet size and stability of emulsion.

The droplet size and emulsion stability have significant role in application of pesticide emulsion formulations. An emulsion containing tiny droplets gives better spreading and penetration on the target surface and produces better bio-efficacy. At the time of application, the formulation is diluted with water and then sprayed. In diluted form, the emulsion should be stable so that the spray tank mixing requirement is minimized and homogeneity is maintained in the diluted emulsion, this ensures uniform distribution of active ingredient on target area (Mulqueen, 1998).

In the present study, the effect of changes in processing shear intensity upon the emulsion droplet size and further the effect of droplet size upon stability of emulsion have been investigated. In agricultural applications, the farmers dilute the formulation with readily available irrigation water for making spray solution. The irrigation water may be hard, mild acidic, alkaline or saline. The effect of mild acidic, alkaline and saline dilution water and also the effect of accelerated temperature storage upon the emulsion stability with respect to processing shear intensity and droplet size have been studied.

2. MATERIALS AND METHODS

2.1 Materials

Insecticide Lambda cyhalothrin (technical grade) and solvent CIX were obtained from Tagros Chemicals Ltd., Chennai, India. Emulsifiers, xanthan gum and silicon emulsion defoamer were obtained from Rhodia surfactants, Mumbai, India and propane 1, 2- di-ol was obtained from Qualigens Ltd., Mumbai, India.

2.2 Methods

2.2.1 Preparation of different batches of Lambda cyhalothrin EW formulation

The oil phase containing Lambda cyhalothrin (Tedchnical grade) dissolved in minimum amount of solvent C-IX was emulsified into the aqueous phase under shear mixing using a Laboratory variable shear mixer (Model- Silverson L5M-Digital fitted with fine disperser head). Different samples were prepared in the laboratory using various commercially available standard pesticide formulation additives such as non-ionic emulsifiers (nonyl phenol ethoxylate, Caster oil ethoxylate, fatty alcohol ethoxylates, Ethoxylated tristeryl phenol), an-ionic emulsifiers (Calcium dodecyl benzene sulphonate, Lauryl alcohol sulfate, Ethoxylated tristeryl phenol phosphate, Ethoxylated tristeryl phenol phosphate amine salt) anti freezing agent (Propane 1,2-di-ol) viscosity modifier (xanthan gum) , defoamers (silicon emulsion) etc.. Various batches were prepared to optimize the right composition. The composition providing good white emulsion was finalized. With the final optimized composition, eight batches (200 gm. batch size) were prepared at processing shear intensities of 500, 1000, 1500, 2000, 2500, 3000, 3500 and 4000rpm to check its effect upon droplet size and emulsion stability.

2.2.2 Physico-chemical analysis

The physic-chemical parameters mentioned in WHO & FAO manual for pesticide formulations (WHO &FAO, 2010) were analysed by method no. 463/TC/M for active ingredient, method no. 75.3 for pH, method no. 39.3 for stability at 0^0 C and metod no. 46.3 for stability at elevate temperature of CIPC Handbook (CIPAC, 2007)

2.2.3 Droplet size analysis

The droplet size of emulsions were analyzed by Laser light scattering based Particle Size Analyzer (Model- Malvern Master Sizer 2000). Water was used as dispersant. The analysis was conducted without sonication to avoid mechanical breakdown of emulsion droplets.

2.2.4 Emulsion stability studies

The emulsions generally destabilize in the form of sedimentation (settling down of droplets) or creaming (rising of droplets), resulting in reduction of thickness of emulsion thereby reduction in the turbidity. The percentage of turbidity retained may be used for quantitative estimation of emulsion stability (Reddy & Fogler, 1981; Song et al, 2000,). Turbidity analysis was used for checking the emulsion stability of different samples. EW sample (0.2 ml) of each batch was poured into 99.8 ml standard hard water (342 ppm) in a 100ml stoppered glass cylinder and given one inversion of 180^0. The emulsion was then immediately transferred to sample vial of digital turbidity meter (Model-Jain 2115) and the reading is recorded. The sample was kept undisturbed and the turbidity reading is recorded after 1 hour. and 24 hours. The emulsion stability was calculated as the percentage part of turbidity retained after 1 hour. and 24 hours by using following formula :\

Emulsion stability (%) = Initial turbidity (NTU) x 100 / Final Turbidity (NTU)

2.2.5 Effect of processing shear intensity and droplet size upon emulsion stability in mild acidic, alkaline and saline dilution mediums

The samples were diluted with mild acidic (pH=5, adjusted by 1N Hydrochloric acid addition), alkaline (pH=9, adjusted by 1N- Sodium hydroxide solution addition) and saline water (2% sodium chloride solution)r and emulsion stability was analyzed by the turbidity procedure.

2.2.5 Effect of processing shear intensity and droplet size upon emulsion stability after accelerated temperature storage (ATS)

The storage stability of pesticide formulations is checked by Accelerated temperature storage. To check the effect of storage upon emulsion stability with respect to processing shear intensity, the samples were subjected to accelerated temperature storage (ATS) by keeping the samples in sealed glass tubes in an oven maintained at 54^0C for 14 days. After ATS, the emulsion stability of the samples diluted in standard hard water (342 ppm hardness) was analyzed by turbidity method.

3. RESULTS & DISCUSSION

3.1. Finalized composition of Lambda cyhalothrin EW formulation

Out of various samples prepared for compatibility screening of different formulation additives (inert ingredients), the samples prepared with composition given in Table 1 provided a good white emulsion formulation qualifying physico-chemical analysis tests (analysis results are given in table 2) . Therefore, this composition was finalized for studying the effect of processing shear intensity upon droplet size and emulsion stability The role of each ingredient in the formulation is given in parenthesis in the table 1.

Table 1: Finalized composition of Lambda cyhalothrin EW formulation

Ingredient	% w/w
Lambda cyhalothrin, Technical grade, a.i= 95% (Insecticide)	10.6
Solvent C-IX (Minimum amount to dissolve solid insecticide)	5.9
Ethoxylated tristeryl phenol (Non ionic emulsifier)	2.5
Ethoxylated tristeryl phenol phosphate (Anionic emulsifier)	2.5
Propane 1,2-di-ol (Anti freezing agent)	5.0
Xanthan gum (Viscosity enhancer for gravitational stabilization)	0.16
Silicon emulsion defoamer (for foaming reduction during processing and application)	0.5
Distilled Water (bulk medium)	q.s
Total	100

Table2: Physico-chemical analysis results of sample of finalized composition

Quality parameter	Analysis Result
Active ingredient	10.02%
pH of 1% aqueous dispersion	6.9
Persistent foam	< 2 ml
Stability at 0^0C (7 days)	No phase separation, creaming or sedimentation. Active ingredient – No degradation

ATS Stability (54^{0}C,14 days)	No phase separation, creaming or sedimentation. Active ingredient - No degradation

3.2. Effect of processing shear intensity upon droplet size

The droplet size of samples prepared at different processing shear intensities is given in the table 3.

Table 3: Effect of processing shear intensity upon droplet size

Processing Shear Intensity (rpm)	500	1000	1500	2000	2500	3000	3500	4000
Droplet Size (Microns) [Mean Diameter]	9.30	5.28	5.11	4.40	3.24	2.78	2.45	2.22

From the results, it may be seen that with the increase in processing shear intensity, there was a gradual decrease in droplet size. From 500rpm to 3000rpm, there was sharp reduction in droplet size from 9.30 microns to 2.78 microns. Above 3000rpm, the further reduction of droplet size was less. Above 4000 rpm, no further reduction of droplet size was observed.

The results indicate that the change in processing shear rate remarkably affected the emulsion droplet size. During the preparation of emulsion, the internal oil phase is broken into droplets by agitation. The mild agitation results in the formation of bigger droplets while the strong agitation results in the formation of fine droplets. From 500rpm to 3000rpm, there was sharp reduction in droplet size from 9.30μm to 2.78μm. Above 3000rpm, the further reduction of droplet size was very less, possibly due to reaching of turbulence to a maximum, beyond which the further breakdown of droplets is very less. Similar trend of oil droplet size reduction is reported for petroleum emulsions (Issaka et al, 2010)¨, for these emulsions, the droplet size was qualitatively analyzed by optical microscopy.

3.3. Effect of processing shear intensity and droplet size upon emulsion stability in standard hard water dilution

The effect of processing shear intensity and droplet size upon emulsion stability of different samples diluted with standard hard water (342 ppm) is given in the table4.

Table 4: Effect of processing shear intensity and droplet size upon emulsion stability in standard hard water dilution

Processing shear intensity (rpm)	**Emulsion Droplet Size (Microns)**	**Turbidity-Initial (NTU)**	**Turbidity After 1 hour (NTU)**	**Emulsion Stability After 1 hour (%)**	**Turbidity After 24 hours (NTU)**	**Emulsion Stability After 24 hrs. (%)**
500	9.30	296	256	86.49	63	21.28
1000	5.28	346	314	90.75	79	22.83
1500	5.11	349	322	92.26	85	24.35
2000	4.40	414	394	95.17	127	30.68
2500	3.24	512	488	95.31	247	48.24

3000	2.78	676	648	95.85	393	58.14
3500	2.45	825	801	97.09	544	65.94
4000	2.22	1200	1196	99.67	904	75.33

The results indicate that the sample prepared at lowest shear rate of 500 rpm (having droplet size 9.3 microns) had minimum emulsion stability (86.49 % after 1 hr). The emulsion stability gradually increased with increase in shear rate and decrease in the droplet size. The emulsion stability was maximum (99.67% after 1 hr) of smallest droplet size sample. The emulsion stability after 24 hrs. also shown the similar trends. The increase of processing shear intensity reduced the droplet size and thereby increased stability of emulsion.

Usually the main emulsion destabilization mechanisms are flocculation (adhesion of droplets), coalescence (merging of droplets) and Oswald ripening (transport of materials from small to big droplets). Any of these or combination of these mechanisms result in emulsion destabilization in the form of sedimentation (settling down of droplets) or creaming (rising of droplets) depending upon density of dispersed phase. The emulsifiers protect the emulsion from destabilization by reducing the interfacial tension and creating a repulsive film around the droplets of inner oil phase. The emulsifier film protects agglomeration of droplets by electrostatic repulsion (formation of electrical double layer on the oil droplet surfaces) by ionic emulsifier and stearic repulsion by non-ionic emulsifiers. Ionic and non-ionic emulsifiers are ampophile molecules and active on the surface of oil droplets. In case of bigger droplets, the surface area is less and only very less percentage of emulsifier molecules get adsorbed on the surface of oil droplets and the rest remain free and inactive in the bulk phase, thereby the repulsive action between inner phase oil droplets is less resulting in destabilization of the emulsion. The smaller droplets have more surface area, thus the adsorption of emulsifier molecules on surface of oil droplets is increased and the repulsive action between oil droplets is more effective resulting in more stable emulsion.

It is obvious from the results that sufficient reduction of droplet size enhances the emulsion stability significantly. In Triacylglycerol emulsions, the interfacial tension was found to be inversely proportional to droplet size and emulsions containing smaller droplets were found stable. (Chung et al, 1991)..

3.4. Effect of processing shear intensity and droplet size upon emulsion stability in mild acidic, alkaline and saline dilution water

The effect of processing shear intensity and droplet size upon emulsion stability of different samples diluted with mild acidic (pH=5) water are given in the table 5.

Table 5: Effect of processing shear intensity and droplet size upon emulsion stability in mild acidic (pH=5) dilution water

Processing shear intensity (rpm)	Emulsion Droplet Size (Microns)	Turbidity-Initial (NTU)	Turbidity After 1 hour (NTU)	Emulsion Stability After 1 hour (%)	Turbidity After 24 hours (NTU)	Emulsion Stability After 24 hrs. (%)
500	9.30	238	215	90.34	57	23.95
1000	5.28	378	350	92.59	99	26.19
1500	5.11	402	380	94.53	112	27.86
2000	4.40	424	404	95.28	154	36.32
2500	3.24	497	480	96.58	235	47.28

3000	2.78	660	640	96.96	365	55.30
3500	2.45	801	780	97.38	461	57.55
4000	2.22	1050	1029	98.00	688	65.52

The effect of processing shear intensity and droplet size upon emulsion stability of different samples diluted with mild alkaline (pH=9) water are given in the table 6.

Table 6: **Effect of processing shear intensity and droplet size upon emulsion stability in mild alkaline (pH=9) dilution water**

Processing shear intensity (rpm)	**Emulsion Droplet Size (Microns)**	**Turbidity-Initial (NTU)**	**Turbidity After 1 hour (NTU)**	**Emulsion Stability After 1 hour (%)**	**Turbidity After 24 hours (NTU*)**	**Emulsion Stability After 24 hours (%)**
500	9.30	298	263	88.25	61	20.47
1000	5.28	448	418	99.30	95	21.21
1500	5.11	460	430	93.48	100	21.74
2000	4.40	502	475	94.62	137	27.29
2500	3.24	571	542	94.92	230	40.28
3000	2.78	636	605	95.12	300	47.17
3500	2.45	815	790	96.93	460	56.44
4000	2.22	965	950	98.45	670	69.43

The results of effect of processing shear intensity and droplet size upon emulsion stability in saline dilution water (2% NaCl solution) are given in the table 7.

Table 7: **Effect of processing shear intensity and droplet size upon emulsion stability in saline water dilution**

Processing shear intensity (rpm)	**Emulsion Droplet Size (Microns)**	**Turbidity-Initial (NTU)**	**Turbidity After 1 hour (NTU)**	**Emulsion Stability After 1 hour (%)**	**Turbidity After 24 hours (NTU)**	**Emulsion Stability After 24 hours (%)**
500	9.30	216	175	81.02	44	20.37

1000	5.28	315	260	82.54	106	33.65
1500	5.11	437	370	84.67	141	32.26
2000	4.40	505	425	84.16	189	37.42
2500	3.24	564	529	93.79	252	44.68
3000	2.78	666	625	93.84	376	56.45
3500	2.45	888	851	95.83	522	58.78
4000	2.22	949	932	98.20	621	65.43

From the results given in tables 5, 6 & 7, it can be seen that in the case of samples diluted in mild acidic, alkaline and saline water, the trend of increase in emulsion stability with decrease in droplet size continued. In case of the sample prepared at lowest shear rate of 500rpm and having highest droplet size, the emulsion stabilities after one hour were 90.34%, 88.25% and 81.02% in acidic, alkaline and saline dilution mediums respectively. The emulsion stability gradually increased with decrease in droplet size. In the sample prepared at highest shear rate of 4000rpm having smallest droplet size of 2.22 microns, the emulsion stability values were maximum i.e., 98%, 98.45% and 98.2% in acidic, alkaline and saline dilution mediums respectively. The similar trends were observed in the emulsion stability after 24 hours.

If the results of emulsion stability after 24 hours in hard water are compared with emulsion stability in mild acidic, alkaline and saline dilution water (table 4, 5, 6 and 7), it is observed that the smallest droplet size sample had 75.33% stability in standard hard water, but the same sample had 65.52%, 69.43%, 65.43 % stability in acidic, alkaline and saline dilution medium respectively. It indicates that mild acidic, alkaline and saline dilution medium reduced the emulsion stability and this effect was more prominent after 24 hours than after 1 hour in the samples kept in diluted condition.

The ions present in acidic, alkaline and saline medium interact with the repulsive film formed over the surface of droplets of inner oil phase, the film gets weakened and the repulsion between oil droplets is reduced resulting in reduction of emulsion stability.

Reported results for edible oil- in- water emulsion containing splittable surfactant Triton-SP-100, denote that the acidic pH increased interfacial tension and destabilized the emulsion (Chen et al, 2000). The Methyl myristate emulsions containing silica and polyvinyl pyridine microgel particles as emulsifier were destabilized by addition of sodium chloride due to ionization and detachment of surfactant layer from surface of oil droplets (Binks et al, 2006). In the present study also, the stability of Lambda cyhalothrin emulsion reduced in acidic, alkaline and saline dilution medium but the trend of increase in stability with decrease in droplet size continued.

3.5. Effect of processing shear intensity and droplet size upon emulsion stability after accelerated temperature storage (ATS)

The results of effect of processing shear intensity and droplet size upon emulsion stability after accelerated temperature storage (ATS) are given in table 8.

Table 8: Effect of processing shear intensity and droplet size upon emulsion stability after accelerated temperature storage (ATS)

Processing shear intensity (rpm)	Emulsion Droplet Size (Microns)	Turbidity-Initial (NTU)	Turbidity After 1 hour (NTU)	Emulsion Stability After 1 hour (%)	Turbidity After 24 hours (NTU)	Emulsion Stability After 24 hours (%)
500	9.30	273	233	85.35	60	21.98

1000	5.28	362	331	91.44	87	24.03
1500	5.11	382	357	93.46	105	27.48
2000	4.40	400	377	94.25	125	31.25
2500	3.24	447	435	97.31	211	47.20
3000	2.78	453	444	98.01	251	55.41
3500	2.45	564	550	97.52	378	67.02
4000	2.22	589	578	98.13	488	82.85

The same trend of increase in emulsion stability with increase of shear rate continued in the samples after accelerated temperature storage also. It is interesting to note that the sample prepared at highest shear rate of 4000 rpm, having smallest droplet size of 2.22 microns showed higher emulsion stability of 82.85% (after 24 hrs.) compared to 75.33% (after 24 hrs.) stability in case of same fresh sample The stabilization of small droplet size emulsion after ATS might be due to strengthening of repulsive film formed on the surface of oil droplets.

4. CONCLUSIONS

After screening various inert ingredients, a composition containing non-ionic and an-ionic emulsifiers Ethoxylated tristeryl phenol and Ethoxylated tristeryl phenol phosphate, propane 1,2- di-ol as anti freezing agent, xanthan gum as viscosity modifier and silicon emulsion as defoamer was optimized, it provided a good quality oil-in water formulation of insecticide Lambda cyhalothrin. The results indicate that in the preparation of EW formulation, the processing shear intensity had remarkable effect upon droplet size and stability of emulsion. The increase in processing shear intensity gradually decreased emulsion droplet size and thereby increased emulsion stability.

The acidic, alkaline and saline dilution medium reduced emulsion stability, but the trend of increase in emulsion stability with decrease in droplet size persisted in these mediums also. The small droplet size emulsions have good emulsion stability after accelerated temperature storage also.

An optimized composition and applying high shear intensity during processing produces a stable EW formulation of Lambda cyhalothrin having very fine droplets and excellent emulsion stability.

REFERENCES

Binks, B.P., Murakami, R., Armes, S.P., Fujii, S., (2006) Effect of pH and salt concentration on oil-in-water emulsion stabilized solely by nanocomposite microgel particles, Langmuir **22**(5): 2050-2057

Chen C.M., Lu C.H., Chan C.H., Yang Y.M., Maa J.R., (2000) Influence of pH on the stability of oil-in-water emulsions stabilized by a splittable surfactant, Colloids and Surfaces A: Physicochemical and Engineering Aspects **170** (2-3): 173-179

Chung, H., Kim, T.W., Kwon, I.C. & Jeong, S.Y., (1991)Stability in the oil-in-water type triacylglycerol emulsions, Biotechnology and Bioprocess Engineering. **6**(4): 284-288

CIPAC Handbook (2007) . Physico-chemical methods for technical and formulated pesticides. Collaborative International Pesticide Analytical Council, Harpenden, Herts, United Kingdom

Issaka, S.A., Nour, A.H., Yunus, R.M., (2010) Decolourization and characterization of petroleum emulsions, J. Applied Science, **10**(3): 215-220

Knowles, A., (2008) Recent developments of safer formulations of agrochemicals. Environmentalist **28**: 35-44

Mulqueen, P.J., (1998) Recent developments on safer of agrochemicals in Chemistry and technology of agrochemicals formulations ed. by D.A. Knowles, Kluwer Academic Publishers, London : 121-157

Ramdas, P.K., (1996) Advances in pesticide formulations under Indian context in Agrochemicals and sustainable agriculture, ed. by N. K Roy , APC Publications, New Delhi: 23-28

Reddy S.R., Fogler H.S., (1981) Emulsion stability: determination from turbidity. Journal of Colloid and Interface Science, **79**(1): 101-104

Song Myung-Geun, Jho Sung-Ho, Kim Jong, Kim Jong-Duk,. (2000) Rapid evaluation of Water-in-Oil (w/o) emulsion stability by turbidity ratio measurements. Journal of Colloid and Interface Science, **230**(1): 213-215

WHO & FAO (2010) Manual on development and use of WHO and FAO specifications for pesticides, World Health Organization & Food and Agriculture Organization, Rome :119-181